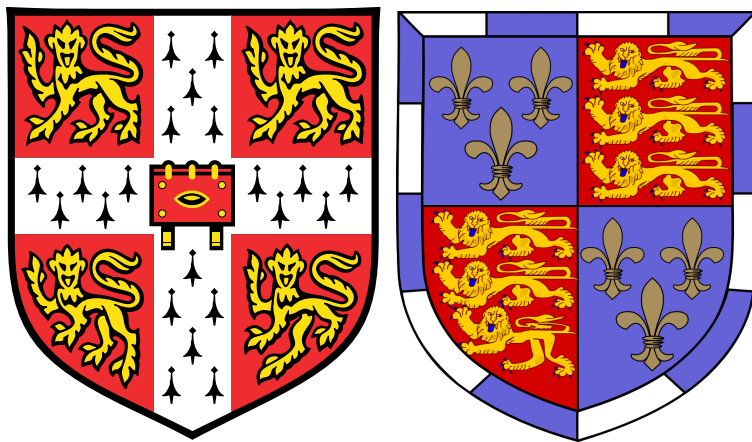


# A heavy stable isotope approach to tracing mantle source and process



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This thesis is submitted for the degree of  
*Doctor of Philosophy*

St John's College  
August 2022



## **Declaration**

This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the Preface and specified in the text. I further state that no substantial part of my thesis has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. It does not exceed the prescribed word limit for the relevant Degree Committee.

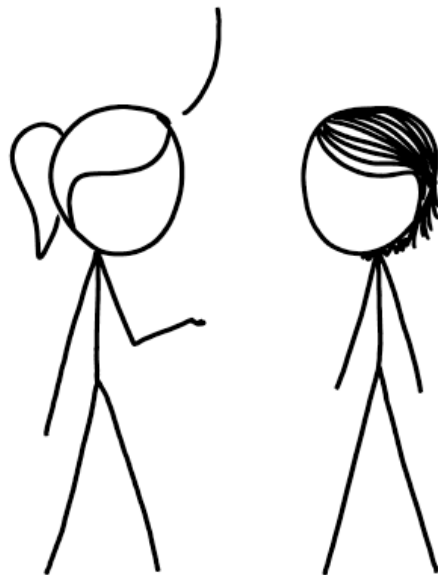
Caroline Soderman

August 2022



I LIVE NEXT TO A WALL OF ROCK 20 MILES THICK. THERE'S NO WAY AROUND OR OVER IT. I'M TRAPPED ON THIS SIDE FOREVER.

I STUDY THE STUFF ON THE OTHER SIDE.



MANTLE GEOLOGY SEEMS LIKE  
THE MOST FRUSTRATING FIELD.

*'Speak your truth clearly and quietly, and listen to others...Enjoy your achievements as well as your plans. Keep interested in your career, however humble. It is a real possession in the changing fortunes of time.'*

Max Ehrmann, *Desiderata*

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...

Many people have made the past four years so enjoyable, even with a global pandemic getting in the way.

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*'The Neptune Is On Fire' by Sarah Humbert*

## Publications arising from this thesis

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## Co-author publications using work presented in this thesis

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Ruttor S., Nebel O., Williams H. M., Beier C., Richter M., Nebel-Jacobsen Y., Romer R. H. W., Turner S. P. and **Soderman C. R.** (2022), ‘Iron isotope evidence in ocean island basalts for plume- and plate-controlled melting, São Miguel, Azores’, *Geochimica et Cosmochimica Acta*.

## Abstract

The geochemistry of global mantle melts suggests that both mid-ocean ridge basalts (MORB) and ocean island basalts (OIB) sample lithological heterogeneities originating in both the upper and lower mantle, with recycled crustal material accounting for a significant part of this variability. Recently, heavy stable isotopes have been suggested as a new tool to complement existing tracers of mantle heterogeneity and lithology (e.g., major and trace elements, radiogenic isotopes), because mineral- and redox-specific equilibrium stable isotope fractionation effects can link the stable isotope ratios of melts to their source mineralogy and melting degree. In this thesis, I present a unique ‘bottom-up’ approach to understanding how mantle lithology, such as recycled crust (pyroxenite), could be reflected in the stable isotope composition of the erupted melts, and the insights that heavy stable isotope data from basalts could provide into mantle source and process.

Throughout this thesis, I investigate five stable isotope systems (Mg-Ca-Fe-V-Cr) that have shown promise in models or natural samples as tracers of mantle lithology. I develop a quantitative model, combining thermodynamically self-consistent mantle melting and equilibrium isotope fractionation models, to explore the behaviour of the stable isotope ratios of these elements during melting of three mantle lithologies (peridotite, and silica-excess and silica-deficient pyroxenites). I also present new Fe isotope data for Samoan shield and Azores volcanoes, and for a suite of samples from 90 million years of evolution of the Galápagos mantle plume system. These OIB allow me to study the role of recycled mantle components in generating Fe isotope variability in melts, to compare to my mantle melting and isotope fractionation model.

I find that single-stage melting of a MORB-like eclogitic pyroxenite cannot generate the high  $\delta^{57}\text{Fe}$  seen in some OIB, notably Pitcairn, the Azores and rejuvenated Samoan lavas. Instead, the generation of high  $\delta^{57}\text{Fe}$  melts in OIB requires: (1) processes that make subducted eclogite isotopically heavier than its pristine precursor MORB (e.g., hydrothermal alteration, metamorphism, sediment input); (2) lithospheric processing, such as remobilisation of previously frozen small-degree melts, or a contribution from lithospheric material metasomatised by silicate melts; and/or (3) melting conditions that limit the dilution of melts with high  $\delta^{57}\text{Fe}$  by ambient lower  $\delta^{57}\text{Fe}$  materials. Therefore, it cannot be assumed that a pyroxenite lithology derived from recycled crustal material is the sole producer of high  $\delta^{57}\text{Fe}$  melts in OIB, as has sometimes been assumed in the literature. Instead, the observation of high  $\delta^{57}\text{Fe}$  OIB melts cannot be ascribed to a unique source or process. This ambiguity reflects the multitude of processes operating from the generation of recycled lithologies through to their mantle melting: from MORB generation, its low temperature alteration, through mantle heterogeneity development and lithospheric processing, to eruption at ocean islands.

I also find that, given current analytical precision, the five stable isotope systems examined here are not predicted to be sensitive to mantle potential temperature variations through equilibrium isotope fractionation processes, for the melting of peridotite. By contrast, source lithological het-

erogeneity is predicted to be detectable in some cases in the stable isotope ratios of erupted basalts, although generally only at proportions of  $>10\%$  MORB-like pyroxenite in the mantle source, given current analytical precision. However, even when considering analytical uncertainty on natural sample measurements, the range in stable isotope compositions seen across the global MORB and OIB datasets suggests that kinetic isotope fractionation, or processes modifying the isotopic composition of recycled crustal material such that it is distinct from MORB, may be required to explain all the natural data.

Finally, I combine the insight into and modelling of Fe stable isotope behaviour presented throughout the thesis to highlight the potential of heavy stable isotopes to constrain mantle dynamics, in the Galápagos plume system. I show that although the proportion of pyroxenite-derived melt has increased through time as the plume has cooled by  $400\text{ }^{\circ}\text{C}$  over its lifetime, these results are consistent with a cooling plume containing a small and approximately constant proportion of pyroxenite. This result is consistent with geodynamic models of entrainment of dense material, such as from a lower mantle low velocity superstructure underlying the plume. The small proportion of pyroxenite throughout plume evolution also suggests that geochemical signatures of primordial mantle may be diluted approximately uniformly by recycled components throughout plume evolution and therefore could be identified in early plume localities.

From my combined mantle melting and isotope fractionation model, and comparison to natural datasets, I conclude that the five stable isotope systems considered in this thesis have potential to be powerful tracers of the source lithology of erupted basalts, complementary to other geochemical tools. However, continued improvements in analytical precision in conjunction with experimental and theoretical predictions of isotopic fractionation between mantle minerals and melts are required before these heavy stable isotopes can be unambiguously used to understand source heterogeneity in erupted basalts.

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# 1 Introduction

A key window into Earth's mantle is through the petrology and geochemistry of its melts, which include both mid-ocean ridge basalts (MORB) and ocean island basalts (OIB). Numerous isotopic, major and trace element studies of these basalts suggest that the Earth's mantle is geochemically heterogeneous on scales from hundreds of kilometres, across entire mantle plume and ridge systems, to less than a kilometre or metres, as recorded by melt inclusions (e.g., Allègre et al., 1984; Zindler and Hart, 1986; Dupuy et al., 1988; Weaver, 1991; Hofmann, 1997; Schiano et al., 1997; Agranier et al., 2005; Janney et al., 2005; Stracke et al., 2005; Prytulak and Elliott, 2007; Maclennan, 2008; Waters et al., 2011; Shorttle, 2015; Gill et al., 2016; Liu and Liang, 2017a; Mundl et al., 2017; Jiang et al., 2021). Understanding the origin of the present state of mantle heterogeneity, and the interactions between Earth's crust and mantle is important for developing a basic understanding of Earth's compositional evolution. Therefore, key questions for mantle geochemists and geodynamicists are: what is the origin of this geochemical heterogeneity; how and where is geochemical heterogeneity stored, maintained and mixed in the mantle; how can the geochemistry of erupted rocks and the mantle sources that they sample be linked?

Existing studies linking geochemical heterogeneity to mantle lithology, combined with geophysical observations, have led to a consensus that large-scale geochemical cycling between silicate reservoirs (oceanic and continental crust and lithosphere, associated sediments and the asthenospheric mantle) is a fundamental process in generating geochemical diversity in the mantle, with recycled crustal reservoirs stored in both the upper and lower mantle. These recycled materials may be present as distinct mantle components that are sampled by basalts, and may each be represented by unique radiogenic isotopic signatures (e.g., White, 1985; Zindler and Hart, 1986; Stracke et al., 2005), providing a source of the mantle's geochemical diversity.

Although radiogenic isotopes have been the traditional tracer of mantle heterogeneity, heavy stable isotopes have become a more widely-used tool to investigate mantle heterogeneity in recent decades, because mineral- and redox-specific equilibrium stable isotope fractionation effects can link the stable isotope ratios of melts to their source mineralogy. In particular, iron (Fe) stable isotopes in erupted basalts have become a widely applied tool for studying variations in mantle lithology. This application of Fe stable isotopes follows work suggesting that equilibrium inter-mineral Fe isotope fractionations may result in recycled or metasomatically re-enriched material, and the melts derived from these materials, having distinct isotope compositions from ambient peridotite melts (Williams and Bizimis, 2014; Macris et al., 2015). There is now extensive MORB and OIB Fe (and other stable isotope) data, with variability ascribed to combinations of partial

melting, crystal fractionation, metasomatism and source heterogeneity. This thesis will address some of the questions raised as the basalt stable isotope dataset has grown, specifically:

- Does bulk source isotopic composition (as a result of the processes forming a mantle component) or mineralogical-driven fractionation dominate in determining the stable isotope composition of basalts?
- Can mantle lithological heterogeneity account for Fe (and other) stable isotope variability in basalts? Do explanations for Fe stable isotope variability in basalts require the lithological variability inferred from other geochemical observations?
- Does MORB have a stable isotope composition distinct from that of OIB? What could their isotopic compositions tell us about their mantle sources, and the processes involved in their generation?
- Do the endmember mantle reservoirs identified by radiogenic isotopes have a distinct stable isotope signature, and how might that relate to their origin?

## **1.1 Tracers of lithological heterogeneity in the mantle**

Mantle heterogeneity was first identified in radiogenic isotopic variations (Gast et al., 1964; Hedge, 1966), with initial models suggesting two or three distinct reservoirs to explain the Sr-Nd-Pb isotope variability in MORB and OIB (White and Hofmann, 1982; Zindler et al., 1982). However, only a few years later, new geochemical data showed that the wide isotopic variability measured in basalts can be derived from five different groups of long-lived radiogenic isotopic compositions in the mantle, each distinguished by a unique correlation between isotope ratios, or certain isotope compositions (White, 1985; Zindler and Hart, 1986). Most basalts converge on an isotopically intermediate composition, referred to as the prevalent mantle (PREMA)/focal zone (FOZO)/common component ‘C’ (Zindler and Hart, 1986; Hart et al., 1992; Hanan and Graham, 1996; Stracke et al., 2005), with four further distinct groups of basalts in multi-isotope space. These four groups, or reservoirs, were first identified by their type ocean island locality (e.g., Society, Kerguelen; White, 1985), but were renamed as depleted mantle (DMM), enriched mantle (EM1 and EM2) and HIMU by Zindler and Hart (1986), a nomenclature which is still used today (e.g., Stracke et al., 2005; Stracke, 2012). These isotopic reservoirs represent ‘species’ or components in the mantle, with individual basalt suites forming arrays between the intermediate FOZO reservoir and the DMM, EM and HIMU reservoirs. The terms are now mostly used to describe the endmember isotopic composition within each group of isotopically similar localities. Zindler and Hart (1986) suggested that these five endmember components (including FOZO) are distinct, unique components which mix together to form the variety of multi-isotopic arrays seen in global basalt data. However, the original interpretation by White (1985) was subtly but importantly different, whereby each iden-

tified mantle component is itself an ‘internally heterogeneous reservoir’ and may be formed of a number of isotopically and chemically similar, but not necessarily identical, reservoirs. Given increasing amounts of multi-isotope data, where individual island chains within each group form distinct, although similar, correlations that trend towards each endmember component (and with a largely continuous array seen amongst EM trends; Willbold and Stracke, 2010), the interpretation by White (1985) seems more likely than that of Zindler and Hart (1986) (Stracke, 2012; White, 2015). Radiogenic isotopes have also been used to argue for enriched (and depleted) components in the mid-ocean ridge basalt source (e.g., Hirschmann and Stolper, 1996; Salters and Dick, 2002; Liu et al., 2008; Byerly and Lassiter, 2014). In addition to these components, noble gas and short-lived radiogenic isotopic systematics (e.g.,  $^3\text{He}/^4\text{He}$ ,  $^{182}\text{W}/^{184}\text{W}$ ,  $^{20}\text{Ne}/^{22}\text{Ne}$  anomalies; Craig and Lupton, 1976; Trierloff et al., 2002; Honda and Woodhead, 2005; Kurz et al., 2009; Jackson et al., 2017; Mundl et al., 2017; Mundl-Petermeier et al., 2020) and transition element ratios (e.g., Fe/Mn, Humayun et al., 2004; Qin and Humayun, 2008) have been used to support the presence of a small amount of a primordial, lower mantle or core-derived component entrained in some OIB.

Linking the heterogeneity in long-lived radiogenic isotopes to mantle lithology has been achieved through combining radiogenic and stable isotopes (e.g., Day et al., 2009, 2010), major element compositions of basalts (e.g., Klein and Langmuir, 1987; Langmuir et al., 1992; Jackson and Dasgupta, 2008; Dasgupta et al., 2010; Shorttle and MacLennan, 2011; Jackson et al., 2012; Lambart et al., 2013; Yang et al., 2019; Mallik et al., 2021) – including first row transition element ratios (Le Roux et al., 2010; Davis et al., 2013) and experimental studies of melt compositions (Hirschmann and Stolper, 1996; Hirschmann et al., 2003; Pertermann and Hirschmann, 2003a; Kogiso et al., 2004; Pertermann et al., 2004) – and trace elements in olivine (e.g., Sobolev et al., 2005, 2007; De Hoog et al., 2010; Herzberg, 2011; Weiss et al., 2016; Neave et al., 2018; Gazel et al., 2018). These techniques have led to the widely accepted view that recycled oceanic crust generates a significant amount of the variation seen in OIB geochemistry, along with small contributions from sediments and continental crust (e.g., Armstrong, 1968; Cohen and O’Nions, 1982; Hofmann and White, 1982; Weaver, 1991; Chauvel et al., 1992; Kogiso et al., 2003; Willbold and Stracke, 2006; Sobolev et al., 2007; Jackson and Dasgupta, 2008; Willbold and Stracke, 2010; Shorttle and MacLennan, 2011; see also Stracke, 2012). The recycled basaltic component is thought to be present as discrete eclogite or, more commonly, pyroxenite (olivine-poor, pyroxene-rich) lithologies, the latter possibly formed by solid-state or melt reaction of eclogite with ambient peridotite (Sobolev et al., 2007; Herzberg, 2011; Mallik and Dasgupta, 2012; Rosenthal et al., 2014; Lambart, 2017). However, the success of using major elements to identify pyroxenite in OIB sources may depend on the type of enriched component invoked (Lambart et al., 2013); and due to uncertainties over the melting conditions and role of crustal processes (magma recharge events, mixing, diffusional re-equilibration; Matzen et al., 2017; Hole, 2018; Gleeson and Gibson, 2019) it is unclear whether source compositional differences unambiguously control the trace element concentrations in olivine phenocrysts.

Non-traditional stable isotope systems, such as Fe, may provide an important, alternative method for identifying lithological heterogeneity (of both enriched and depleted components) in the mantle source of basalts, to complement radiogenic isotopes and major element calculations. Unlike incompatible trace elements and radiogenic isotopes of incompatible elements, both of which are likely to be disproportionately affected by contributions from enriched mantle components, the Fe abundances of melts derived from pyroxenitic and peridotitic source mineralogies are similar. Therefore, neither pyroxenite nor peridotite lithologies should dominate the Fe isotopic composition of erupted melts, and the Fe isotopic composition of the lavas should reflect the relative contributions from these different lithologies (Williams and Bizimis, 2014). Since Fe isotopes are time-independent, and their equilibrium partitioning is a function of mineral chemistry as outlined below, they are the natural extension of major element calculations. This stable isotope system may therefore provide a unique opportunity to explore the petrological and mineralogical characteristics of mantle heterogeneity, and could help distinguish common source lithologies and processes in the mantle (Williams and Bizimis, 2014; Konter et al., 2016; Nebel et al., 2018, 2019; Gleeson et al., 2020; Sun et al., 2020; Wang et al., 2021; Ruttor et al., 2022; Shi et al., 2022).

## 1.2 Background to equilibrium stable isotope fractionation

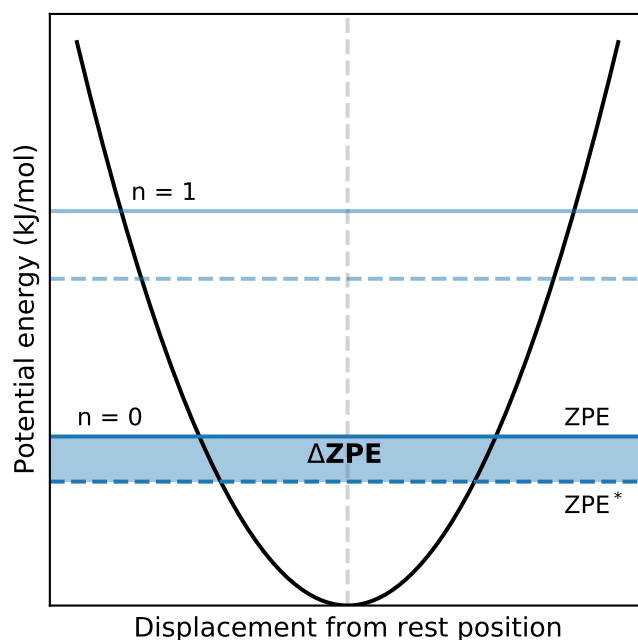
In the field of high-temperature stable isotope geochemistry, the isotopes of the ‘heavy’ elements – i.e., multi-isotope systems from Mg upwards in atomic mass on the periodic table (Ibañez-Mejia and Tissot, 2021) – are often referred to as ‘non-traditional’. These are isotope systems that, until the development of the multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), historically had unresolvable (or unmeasurable) isotopic variability. However, although the high-precision measurement of the isotopic behaviour of these heavy stable isotope systems for high temperature applications has only been possible in the past couple of decades, the theory behind mass-dependent, equilibrium stable isotope fractionation was first published by Urey (1947) and Bigeleisen and Mayer (1947).

Equilibrium mass-dependent stable isotope fractionation is a quantum mechanical effect. The isotope fractionation is driven by the differences in zero point energy (the vibrational energy of a molecule at absolute zero) that arise from the substitution of different atomic masses (i.e., different isotopes) into a molecule. The vibrational energy,  $E$ , of a molecule is given by:

$$E = (n + 1/2)h\nu \quad (1.1)$$

where  $\nu$ , the vibrational frequency (for a diatomic molecule, approximated as a frictionless spring following Hooke’s Law) is calculated as:

$$\nu = (1/2\pi)\sqrt{k/\mu} \quad (1.2)$$



**Figure 1.1: Schematic of zero point energy reduction ( $\Delta ZPE$ ) associated with substitution of a heavy isotope into a molecule.** For a molecule at ground state ( $n=0$ , equation 1.1), substituting a heavy isotope reduces the vibrational frequency, hence potential energy ( $ZPE^*$ ) relative to a molecule containing a lighter isotope. Based on figure from Ibañez-Mejia and Tissot (2021).

and  $n$  is the vibrational energy level,  $h$  is Planck's constant,  $k$  is the force constant for the 'spring', and  $\mu$  is the reduced mass of the molecule. For the simplified diatomic case,  $\mu$  is calculated as

$$\mu = \frac{1}{\frac{1}{m_1} + \frac{1}{m_2}} \quad (1.3)$$

with  $m_1$  and  $m_2$  the masses of the two bodies in the system.

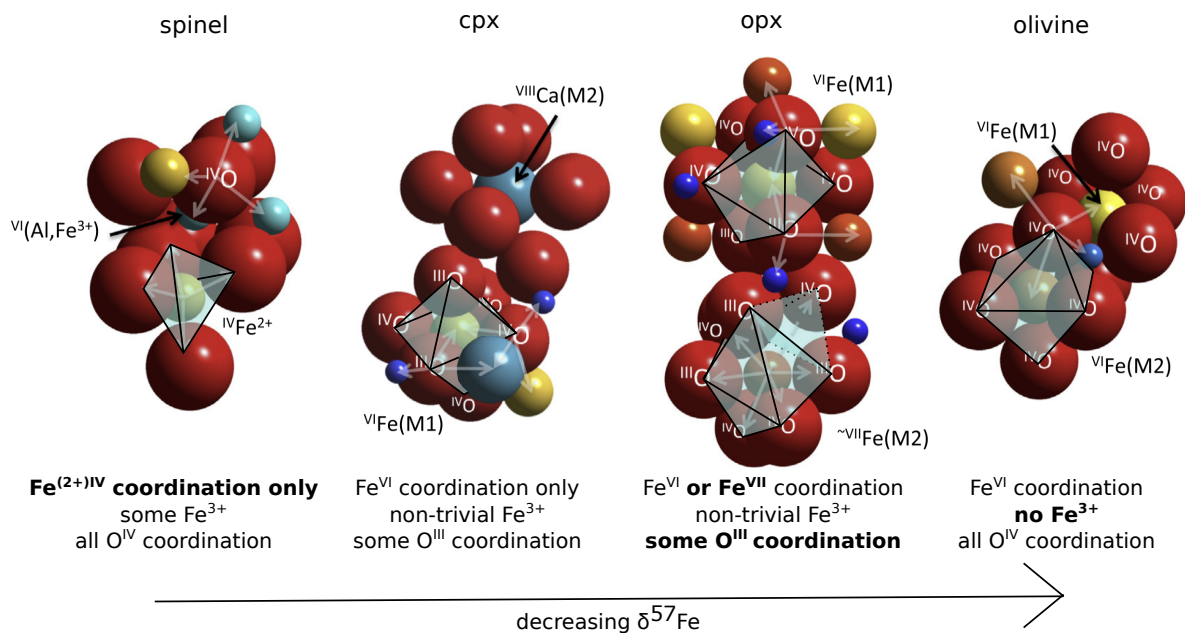
The substitution of a heavy isotope into a molecule (i.e., increasing either  $m_1$  or  $m_2$  in equation 1.3) increases the reduced mass,  $\mu$ , therefore decreasing the vibrational frequency (equation 1.2) and the vibrational energy (equation 1.1) of the molecule relative to a molecule containing a lighter isotope. Therefore, the zero point energy (energy at  $n=0$  in equation 1.1, the ground vibrational state) of a molecule containing a heavy isotope ( $ZPE^*$ ) is less than the zero point energy of a molecule containing a light isotope (Fig. 1.1).

This energy reduction ( $\Delta ZPE$ , Fig. 1.1) means that a molecule containing the heavy isotope is more energetically favourable than a molecule containing the light isotope – all substances will be stabilised by heavy isotope substitution by this mechanism. Equilibrium stable isotope fractionation between any two phases is then controlled by how much zero point energy reduction can be gained by substituting a heavy isotope into one phase relative to the other. Generally, phases with a large force constant,  $k$ , in equation 1.2 have the most energy reduction to gain by substituting a heavy isotope into their structure. Therefore, phases containing strong bonds with the element under consideration will have more of the heavy isotope incorporated into their structure, and

have a heavier equilibrium stable isotope composition (Schauble, 2004; Young et al., 2009). For equilibrium isotope fractionation, it is also expected that the magnitude of isotopic fractionation varies proportionally to  $1/T^2$  (Bigeisen and Mayer, 1947; Schauble, 2004). For this reason, it is generally not expected that high temperature magmatic processes should generate large isotopic fractionations.

### 1.2.1 Using equilibrium stable Fe isotope fractionation as a tracer of mantle mineralogy

Based on the qualitative rules predicted by stable isotope fractionation theory (Schauble, 2004; Young et al., 2009, 2015), numerous works have looked at the potential for non-traditional stable isotopes, in particular Fe, to trace specific mineralogy in the mantle. With relevance to mantle minerals and melts, the main factors controlling the force constant,  $k$ , in a phase are coordination number, bond length, and valence state of the element under consideration (Fig. 1.2; Macris et al., 2015; Sossi and O'Neill, 2017; Blanchard and Dauphas, 2021). The theory outlined above predicts that minerals with strong Fe–O bonds – due to low coordination number, such as in spinel; or some  $\text{Fe}^{3+}$  content, such as pyroxene – will have a heavier Fe isotope composition than olivine, which contains only  $\text{Fe}^{2+}$ , and 6-fold Fe coordination. This thesis will focus on Fe stable isotopes, but I explore other isotope systems in chapter 4. Throughout this thesis, I will use the  $\delta$  notation for



**Figure 1.2: Schematic bonding environment of Fe in common mantle minerals**, modified from Macris et al. (2015).

isotope composition, where

$$\delta^{57/54}\text{Fe} = \left( \frac{(^{57}\text{Fe}/^{54}\text{Fe})_{\text{sample}}}{(^{57}\text{Fe}/^{54}\text{Fe})_{\text{IRMM-014}}} - 1 \right) \times 1000. \quad (1.4)$$

$\delta^{57/54}\text{Fe}$  is commonly written as  $\delta^{57}\text{Fe}$ , as will be adopted throughout this thesis. A heavy Fe isotope composition refers to the preferential partitioning of  $^{57}\text{Fe}$  relative to  $^{54}\text{Fe}$ , hence a high  $\delta^{57}\text{Fe}$ . For consistency, I use  $\delta^{57}\text{Fe}$  for all measured data, but note that for mass-dependent fractionation  $\delta^{57}\text{Fe} \approx 1.5 \times \delta^{56}\text{Fe}$ , with  $\delta^{56}\text{Fe}$  (representing  $\delta^{56/54}\text{Fe}$ ) sometimes used in existing literature. IRMM-014 is an international metallic iron standard with an isotopic composition equal to the chondritic value (Weyer et al., 2005; Craddock and Dauphas, 2010). High-precision analyses of Fe isotopes in standards such as IRMM-014, as well as other reference materials by MC-ICP-MS, have been reproducible between different laboratories throughout the past two decades, despite differences in Fe separation or mass spectrometer methods (e.g., Craddock and Dauphas, 2010; Millet et al., 2012; He et al., 2015; Zhu et al., 2018a).

Prior to 2004, the Fe isotopic composition of igneous rocks was considered homogenous, because all igneous rocks showed uniform isotopic composition given the analytical precision available at the time (Beard and Johnson, 2004b). However, since the early 2000s and the routine measurement of Fe isotopes using MC-ICP-MS, numerous studies have investigated high-temperature inter-mineral Fe isotope variability in relation to the predictions made above, using experimental approaches, measurements of the isotope compositions of natural samples, and the calculation or measurement of force constants and/or vibrational properties. The valence state of Fe in spinels was shown to affect isotope composition by Polyakov and Mineev (2000), and both Shahar et al. (2008) and Sossi and O'Neill (2017) have experimentally shown that, as expected, magnetite (with 4-fold coordinated Fe) is isotopically heavier at equilibrium than fayalite (with 6-fold coordinated Fe). Isotope measurements of spinel-olivine pairs from natural samples also show the expected equilibrium isotopic behaviour (Macris et al., 2015), with the main isotope fractionation control attributed to Fe coordination number, and the natural sample measurements are supported by spinel force constants measured using nuclear resonant elastic X-ray scattering (NRIXS; Roskosz et al., 2015). A complicating factor for understanding the natural Fe isotope dataset is that in many natural lithospheric samples, the relative isotopic compositions of coexisting minerals (particularly olivine, pyroxene and spinel) do not show clear equilibrium fractionation trends (Zhu et al., 2002; Beard and Johnson, 2004a; Williams et al., 2005; Zhao et al., 2010, 2012, 2015; Macris et al., 2015), which is likely due to non-equilibrium metasomatic effects.

Natural clinopyroxenes have also been shown to have heavier isotope compositions than coexisting olivine (Williams et al., 2005; Williams and Bizimis, 2014). This result agrees with predictions from Fig. 1.2, where there is a small amount of  $\text{Fe}^{3+}$  in pyroxene, hence stronger Fe–O bonds than in olivine. This equilibrium fractionation effect suggests that an olivine-dominated peridotite will be isotopically lighter than a more pyroxene-rich (pyroxenite) recycled component, and was first

used to suggest that Fe isotopes in basalts may be able to trace recycled crustal components in their mantle source (Williams and Bizimis, 2014).

### 1.2.2 Kinetic isotope fractionation

Unlike equilibrium fractionation, the magnitude of kinetic, or disequilibrium, isotope fractionation – associated with processes such as evaporation, chemical or thermal (Soret) diffusion, or chemical reactions – can be large, even at high temperatures (Richter et al., 2009a). Kinetic isotope fractionation is discussed at points throughout this thesis, so is briefly outlined here.

The term ‘kinetic’ fractionation, although used broadly, covers two types of process (Watkins and Antonelli, 2021). The first is diffusion-driven, whereby light isotopes diffuse faster than heavy isotopes of the same element, as demonstrated for diffusion between molten basalt and rhyolite by Richter et al. (2003). This difference in speed, hence diffusivity, occurs because light isotopes have greater velocity than heavy isotopes for a given kinetic energy. The isotope fractionation induced by this process will depend on the the elemental concentrations in each reservoir and the diffusion coefficients of each isotope,  $D$ , described by:

$$\frac{D_H}{D_L} = \left( \frac{m_L}{m_H} \right)^\beta \quad (1.5)$$

where  $m$  refers to the mass of each isotope, either heavy (H) or light (L), and  $\beta$  is an empirical parameter usually  $< 0.5$  for geological materials (Richter et al., 2003). Kinetic Fe isotope fractionation associated with diffusion has been identified during crystal growth (including associated with Fe-Mg zoning in olivine), and fractionation (e.g., Dauphas et al., 2010; Teng et al., 2011; Sio et al., 2013; Oeser et al., 2015; Watkins et al., 2017; McCoy-West et al., 2018), and during melt transport and metasomatism (e.g., Richter et al., 2003; Weyer and Ionov, 2007; Zhao et al., 2015; Kang et al., 2020), and thermal (Soret) diffusion. In this latter case for silicate melts, the cold end of a reservoir is enriched in heavy isotopes relative to the hotter end (Huang et al., 2009; Richter et al., 2009b). These diffusion-driven processes are usually referred to as ‘kinetic’ isotope fractionation in the literature discussed throughout this thesis.

The second category of kinetic isotope fractionations are associated with chemical reactions and, like equilibrium isotope fractionation, are a quantum mechanical phenomenon. As chemical reactions involve bond breaking, the magnitude of reaction-driven kinetic isotope fractionation is generally expected to be smaller than diffusion-driven fractionation (Watkins and Antonelli, 2021). The reaction-driven kinetic isotope fractionation is driven by the assumption of quasi-equilibrium between the reactants and a transition state (rather than between reactants and products directly, as in equilibrium isotope fractionation). The transition state of a reaction will generally be more weakly bound than the reactants, so will have a smaller  $\Delta ZPE$  (see Fig. 1.1) than the reactants, resulting in less preference for heavy isotopes in the transition state, and hence reaction products,

than in the reactants (less  $\Delta ZPE$  energy reduction to be gained by heavy isotope substitution). These reaction-driven kinetic isotope fractionations are less well-studied than the larger diffusion-driven fractionations, although have been recorded in crystal growth at low temperatures (Watkins et al., 2017), and are not directly considered in this thesis.

## 1.3 High temperature stable Fe isotope behaviour on Earth

From the assumption of a ‘mean mafic Earth’ with  $\delta^{57}\text{Fe} = 0.10\text{‰}$  and that mafic igneous rocks can be used as an Fe isotope baseline (Beard et al., 2003; Beard and Johnson, 2004b; Poitrasson et al., 2004), seminal works by Williams et al. (2005) and Weyer et al. (2005) showed that peridotites have a lower  $\delta^{57}\text{Fe}$  than basalts, and opened up a new field of Fe stable isotope geochemistry in the mantle, where Fe isotopes can be used to trace high temperature planetary scale processes.

The origin of isotopically light peridotites relative to basalts has generally been attributed to partial melting. Partial melts (basalts) are expected to have a higher  $\delta^{57}\text{Fe}$  than their source (peridotite) because of (a) the relative incompatibility of isotopically heavy  $\text{Fe}^{3+}$  compared to isotopically light  $\text{Fe}^{2+}$  (Canil et al., 1994; Mallmann and O’Neill, 2009; Davis et al., 2013), and (b) the 5-fold coordination of Fe in silicate melts (Wilke et al., 2004) relative to 6-fold coordination in most mantle minerals. Building on this prediction, modelling by Dauphas et al. (2009); Sossi and O’Neill (2017) showed that the isotopic composition of mantle melts should scale inversely with melt fraction, with small fraction melts having the heaviest Fe isotope composition. This partial melting fractionation is in addition to mineralogical effects as predicted by equilibrium fractionation theory outlined above.

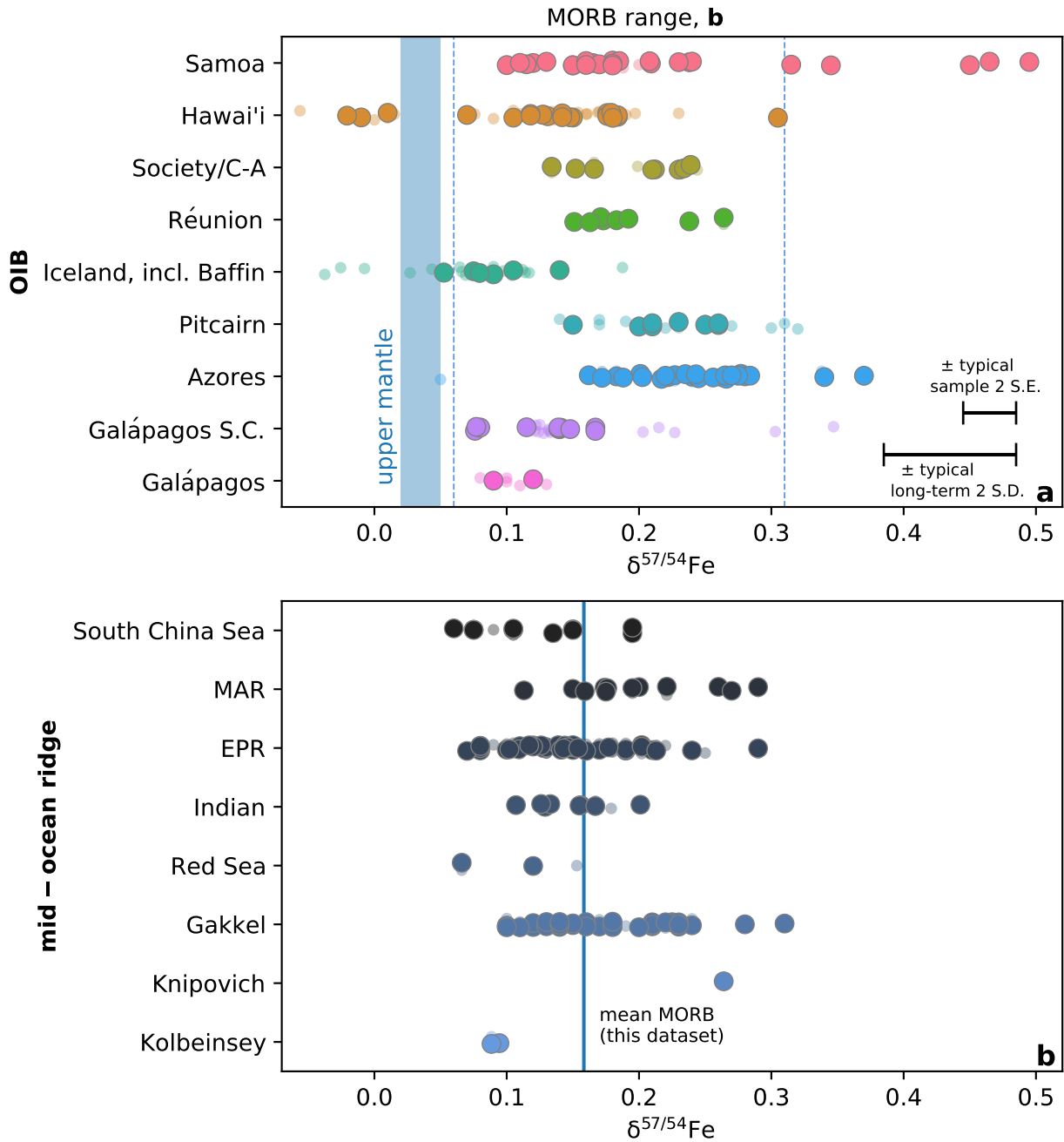
The natural dataset has grown rapidly over the past decade, and now, broadly, confirms the partial melting behaviour observed and predicted in earlier works (Williams et al., 2005; Weyer et al., 2005; Schoenberg and von Blanckenburg, 2006; Weyer and Ionov, 2007; Dauphas et al., 2009; Craddock et al., 2013; Williams and Bizimis, 2014), with partial melting products of the mantle isotopically heavier than peridotite. Estimates of the upper mantle or bulk silicate earth (BSE) isotope composition generally come from peridotite or ultramafic xenoliths, although samples affected by metasomatism associated with melt percolation (Weyer and Ionov, 2007; Poitrasson et al., 2013; Zhao et al., 2012, 2015; Kang et al., 2020) must be excluded. Two recent literature compilations have proposed upper mantle isotopic compositions of  $\delta^{57}\text{Fe} = 0.02\text{‰}$  (from unaltered lherzolite xenoliths; Johnson et al., 2020) and  $0.05\text{‰}$  (Sossi et al., 2016).

However, variation attributed to partial melting is only one aspect of the global basalt Fe isotope dataset. Large variations in isotope composition relative to BSE are seen in MORB and OIB (Fig. 1.3), as well as in subduction-related arc lavas, which are not considered in this thesis. Compilations of MORB data show that the isotopic composition of MORB is generally homogenous, with an average  $\delta^{57}\text{Fe}$  of  $\sim 0.15\text{‰}$ , however, there is variability in the data with some enriched MORB

recording heavier isotopic compositions (Fig. 1.3; Nebel et al., 2013; Sossi et al., 2016). The offset of MORB values relative to BSE is largely explained by partial melting (Sossi et al., 2016), but fractional crystallisation is also important in altering the Fe isotope composition of basalts (Teng et al., 2008; Schuessler et al., 2009; Sossi et al., 2012; Weyer and Seitz, 2012; McCoy-West et al., 2018; Nebel et al., 2018; Chen et al., 2019b; Richter et al., 2021). The generation of MORB isotope values will be discussed more throughout this thesis. Recent Fe isotope data from MORB has highlighted the potential for metasomatism and source heterogeneity to generate diversity in Fe isotope compositions in basalts from ridge settings (Nebel et al., 2018; Sun et al., 2020; Richter et al., 2021; Zhong et al., 2021b).

The observation that OIBs may, overall, record even more variable  $\delta^{57}\text{Fe}$  than MORB was first made by Teng et al. (2013), although previous measurements of Fe isotopes in OIB had been made, largely on international basalt standards from Hawai'i, as well as samples from Iceland and Society/the Cook-Austral islands (Schoenberg and von Blanckenburg, 2006; Weyer and Ionov, 2007; Teng et al., 2008; Schuessler et al., 2009; Craddock and Dauphas, 2010). Subsequently, extremely high  $\delta^{57}\text{Fe}$  ( $> 0.4\text{‰}$ ) was recorded in rejuvenated Samoan lavas and partly attributed to the presence of pyroxenite in the mantle source (Konter et al., 2016), following the conclusions of Williams and Bizimis (2014) that mantle pyroxenites may have a higher  $\delta^{57}\text{Fe}$  than peridotite. Since then, the global Fe isotope data for OIB has grown rapidly, to include Pitcairn (Nebel et al., 2019; Shi et al., 2022), Réunion (Peters et al., 2019), Galápagos (plume-related ridge basalts; Gleeson et al., 2020), Iceland (plume head lavas from Baffin Island; McCoy-West et al., 2018) and more Samoan (Wang et al., 2021) and Hawaiian data (Ruttor et al., 2022). This isotopic diversity of OIB relative to MORB may reflect the ability of mantle plumes to sample deeper into the mantle than MORB, and tap into more geochemically heterogeneous regions of the mantle, including recycled crust. Kinetic fractionation effects may also contribute to Fe isotopic variation in OIB melt sources, with thermodiffusion (Soret diffusion) in material diffusing from the outer core into the lowermost mantle recently proposed to generate high  $\delta^{57}\text{Fe}$  in entrained plume material (Leshner et al., 2020).

From the existing Fe isotope dataset and understanding of stable isotope behaviour in the mantle, a number of issues regarding the use of Fe, and other stable isotopes, as tracers of mantle sources and processes have arisen. For example, the origin of the isotopically heaviest basalts from Samoa (Konter et al., 2016) has been attributed to combinations of partial melting, an offset of the isotopic composition of the mantle source relative to peridotite due to the presence of pyroxenite, and fractional crystallisation. However, the magnitudes of isotopic fractionations required for these processes to generate the observed data are all large, and the constraints on expected fractionations from these processes are poor. Additionally, Fe isotope studies have generally used a 'top-down' approach to investigating the mantle with Fe isotopes: they calculate the required isotopic composition of a mantle endmember based on natural data, without rigorously considering how the isotopic composition of that component may be generated (e.g., Nebel et al., 2019). Therefore, it



**Figure 1.3: Compilation of current literature Fe isotope data for (a) OIB and (b) MORB, including from this thesis.** The large, outlined circles show samples with  $7.2 < \text{MgO (wt\%)} < 16$ , to rule out some variability due to fractional crystallisation, but remaining data is shown as pale, smaller circles. Data sources: **Samoa** (Konter et al., 2016; Wang et al., 2021; **Soderman et al., 2021 [chapter 3]**); Hawai'i (Teng et al., 2008, 2013; Ruttur et al., 2022); Society (Teng et al., 2013); Réunion (Weyer and Ionov, 2007; Peters et al., 2019); Iceland (Schuessler et al., 2009; McCoy-West et al., 2018); Pitcairn (Nebel et al., 2019; Shi et al., 2022); Azores (**Soderman et al., 2021 [chapter 3]**); Galápagos Spreading Centre (Gleeson et al., 2020); **Galápagos (Soderman et al., in review) [chapter 5]**; MORB (Weyer and Ionov, 2007; Nebel et al., 2013; Teng et al., 2013; Chen et al., 2019b; Sun et al., 2020; Richter et al., 2021; Zhong et al., 2021b). Upper mantle estimates from Johnson et al. (2020) and Sossi et al. (2016). Typical uncertainties from recent literature are shown in panel a.

is unclear whether known mantle processes can generate the heaviest isotopic values in the OIB dataset.

## 1.4 Thesis aims and outline

This thesis takes a unique ‘bottom-up’ approach to understanding the generation of isotopic heterogeneity in erupted basalts, in contrast to the ‘top-down’ approach usually taken in the literature. I combine new stable Fe isotope data for OIB with a thermodynamically self-consistent model of mantle melting and equilibrium isotopic fractionation, to create a robust framework for understanding the mantle processes which may generate stable isotope heterogeneity in the erupted basalts.

### 1.4.1 Chapter 2

This methods chapter is separated into two parts. First, I outline the laboratory techniques used to collect the stable Fe isotope data presented in this thesis. Second, I present the background of the combined mantle melting and equilibrium Fe isotope fractionation model that is used and developed throughout this thesis.

### 1.4.2 Chapter 3

This chapter presents work published as Soderman et al. (2021). I use new Fe isotope data for the Samoan and Azores plumes, combined with my Fe isotope fractionation model for peridotite and pyroxenite lithologies, to show that the heavy Fe isotope signatures recorded in many OIBs are likely the result of non-unique processes in the mantle source. Mantle heterogeneity can play a role in generating the high  $\delta^{57}\text{Fe}$  in some OIB, but is unable to create the full range of natural data unless disequilibrium processes are involved.

*Co-author contributions: In this manuscript, co-authors Saskia Ruttor, Oliver Nebel, Simon Turner, Christoph Beier, Marc-Alban Millet, Elisabeth Widom, and Helen Williams undertook sample collection/distribution and isotope data collection for Azores samples. Munir Humayun contributed Fe/Mn data, and Matthew Jackson provided the Samoan samples for Fe isotopic analysis, selected in collaboration with Helen Williams. Simon Matthews generated the initial versions of the THERMOCALC results and isotope fractionation model for peridotite. All co-authors above, as well as Helen Williams and Oliver Shorttle, contributed to editing the manuscript prior to its publication.*

### 1.4.3 Chapter 4

This chapter presents work published as Soderman et al. (2022). Building on the modelling approach taken in chapter 3, which raises questions about the range of Fe isotopic heterogeneities that can be generated by equilibrium mantle processes, I extend my mantle melting and isotope fractionation model to include an additional pyroxenite lithology, and to include four other stable isotope systems that have shown potential as tracers of mantle heterogeneity (Mg-Ca-V-Cr). I create a toolkit that highlights areas of most potential for identifying temperature and lithological heterogeneity in the mantle with these stable isotope systems, and assess the model results relative to global MORB and OIB data.

*Co-author contributions: In this manuscript, co-authors Oliver Shorttle, Simon Matthews and Helen Williams contributed to the development of ideas and editing prior to final publication.*

### 1.4.4 Chapter 5

This chapter presents work in review in Science Advances. I use the potential for Fe isotopes to trace lithological heterogeneity highlighted in the earlier chapters to examine the lithology of the Galápagos plume throughout its 90 million year history. I find that the Galápagos plume has contained a small amount of pyroxenite throughout its lifetime, consistent with geodynamic models of the entrainment of dense recycled crust into a plume. The Galápagos plume also overlies a low seismic velocity superstructure in the lower mantle, which may be a source of recycled crust, and I examine the constraints that my results place on the composition of the lower mantle material entrained by the plume. This chapter highlights the potential for Fe isotopes to trace mantle source and process.

*Co-author contributions: In this manuscript, co-authors Esteban Gazel and Dennis Geist provided the Galápagos plume-related samples from collaborations initiated by Helen Williams, with sample selection performed by Helen Williams and me. Helen Williams and Oliver Shorttle contributed to data interpretation. Oliver Shorttle provided initial feedback on this manuscript prior to its submission, with additional comments from Helen Williams and Simon Matthews.*



## 2 Methods

### 2.1 Iron isotope measurements

Iron isotope data was collected for this thesis during two main analytical periods, in November 2018 – August 2019, and November 2021 – February 2022. No new sample data was collected from August 2019 – October 2021, due to COVID-19-related laboratory closures, and issues with column chemistry as described in section 2.1.3.

#### 2.1.1 Standard column chemistry procedure

Iron isotope analyses were carried out on dissolutions of  $\sim 20$  mg of whole-rock powders following established procedures for quantitative Fe yields (Williams et al., 2005, 2009); Table 2.1. Powders were dissolved in a  $\sim 10:1$  mixture of  $\text{HF}:\text{HNO}_3$  on a hotplate at  $120^\circ\text{C}$  for 48 hours, evaporated to dryness and re-dissolved twice in 6 M HCl to remove fluorides and to ensure the Fe was quantitatively oxidised. Each dissolution was brought up in 2 ml 6 M HCl, and centrifuged to check for complete dissolution. Samples were then loaded onto pre-cleaned AG1-X4 anion exchange resin in Biorad columns (1 ml resin volume, with 1 ml acid reservoir) for Fe separation (Table 2.1). The column chemistry relies on the anion chloro-complex  $(\text{FeCl}_4)^-$  formed by ferric Fe in high molarity (e.g., 6 M) HCl, whereas most other major elements have no such anion complex (Strelow, 1980; Dauphas et al., 2017). Therefore, the Fe in the loaded sample is adsorbed onto anion exchange resin as its chloro-complex, whereas other major elements can be washed off the resin (Johnson et al., 2020).

**Table 2.1: Iron column chemistry procedure** for data collected for this thesis, following Williams et al. (2005, 2009).

| Purpose              | Procedure                                                                        |
|----------------------|----------------------------------------------------------------------------------|
| Load resin           | 1 ml AG1-X4, in trace HCl                                                        |
| Clean resin          | 8 ml trace HCl, 8 ml 6 M HCl<br>repeat 2.5 times total, to finish with trace HCl |
| Pre-condition        | 1 ml 6 M HCl                                                                     |
| Load sample          | in 0.5 ml 6 M HCl                                                                |
| Elute matrix (waste) | 4 ml 6 M HCl                                                                     |
| Elute Fe (collect)   | 7 ml 2 M HCl                                                                     |

The purified Fe solution was dried and refluxed twice in 4:1 – 1:1  $\text{HNO}_3\text{:H}_2\text{O}_2$  to remove any organic residue from the column chemistry. Samples were dissolved in 0.2 ml 4 M  $\text{HNO}_3$ , then diluted with 18.2  $\Omega$  MilliQ water, to produce 8 ml of sample dissolved in 0.1 M  $\text{HNO}_3$  for isotopic analysis.

With each session of samples run through column chemistry, at least two USGS international reference basalts (from BHVO-2, BIR-1a, BCR-2) were processed to check the column chemistry procedure, and a blank was processed to assess the background Fe contribution from the column chemistry process.

### 2.1.2 Mass spectrometry

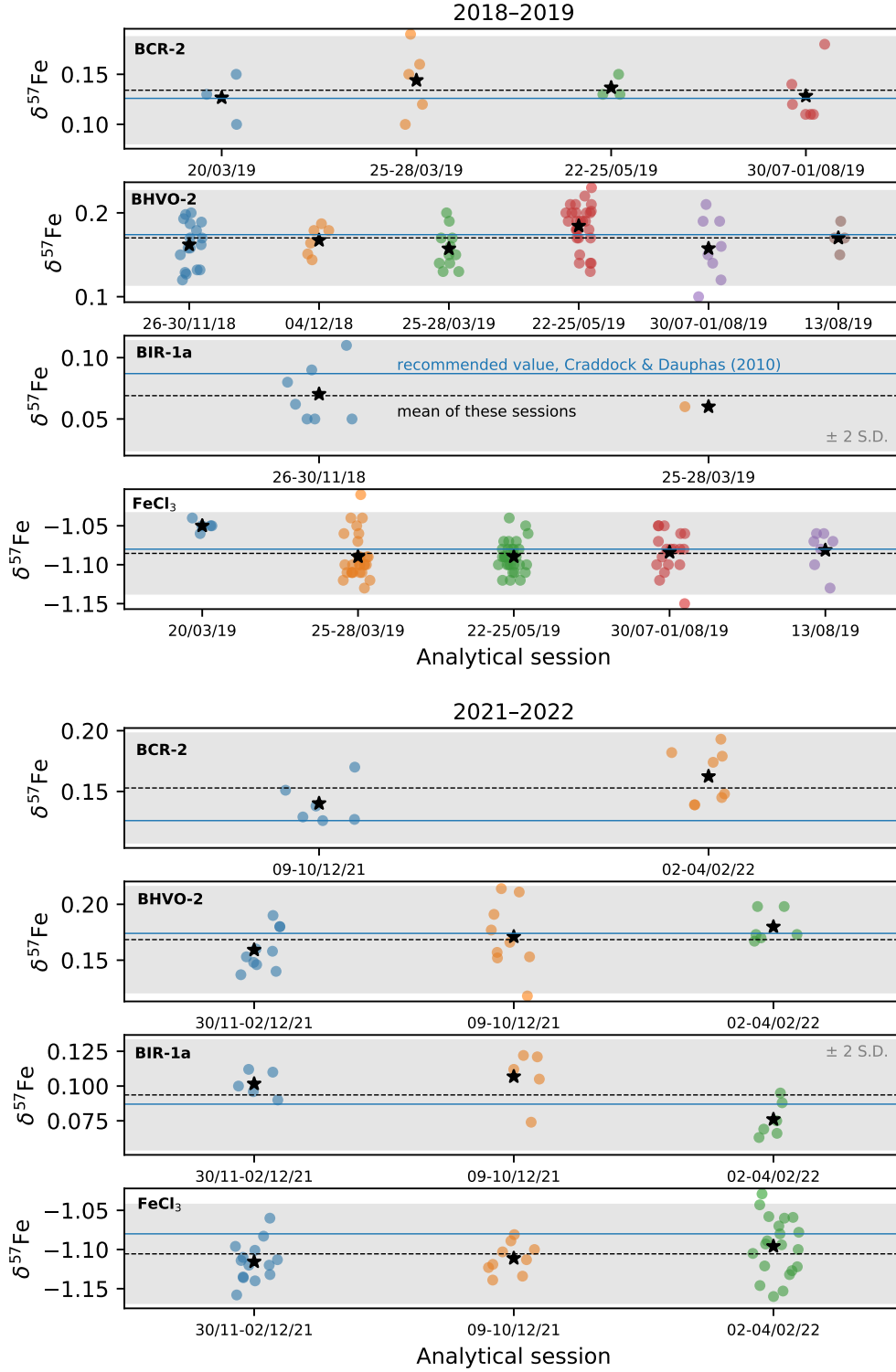
Sample solutions were analysed for Fe isotopes on a ThermoNeptune Plus MC-ICP-MS at 6–8 ppm Fe. Samples were introduced using a quartz cyclonic spray chamber, in wet plasma and medium resolution mode. Instrumental mass bias was corrected for by sample standard bracketing to the IRMM-014 standard. Sample and standard beam intensities (typically 5–7 V/ppm, measured on the centre cup ( $^{56}\text{Fe}$ ) with a  $10^{10} \Omega$  amplifier) were matched to within 5 %. Mass resolution above 7000 was achieved for all successful analysis sessions. The cup configurations used are given in Table 2.2, with  $^{53}\text{Cr}$  and  $^{60}\text{Ni}$  measured to correct for potential interferences on  $^{54}\text{Fe}$  and  $^{58}\text{Fe}$  respectively.

**Table 2.2: Amplifier configuration for Fe isotope analysis on MC-ICP-MS.**

| Cup       | L3               | L1               | C                | H1               | H2               | H4               |
|-----------|------------------|------------------|------------------|------------------|------------------|------------------|
| Isotope   | $^{53}\text{Cr}$ | $^{54}\text{Fe}$ | $^{56}\text{Fe}$ | $^{57}\text{Fe}$ | $^{58}\text{Fe}$ | $^{60}\text{Ni}$ |
| Amplifier | $10^{11} \Omega$ | $10^{11} \Omega$ | $10^{10} \Omega$ | $10^{11} \Omega$ | $10^{11} \Omega$ | $10^{11} \Omega$ |

The concentration of Fe in column-processed blanks was generally found to be  $< 10$  ng, negligible compared to the 700–800  $\mu\text{g}$  of Fe processed through column chemistry for the samples.

Mass dependence, reproducibility and accuracy were monitored by analysis of an in-house  $\text{FeCl}_3$  salt standard, and column-processed reference materials (BHVO-2, BIR-1a, BCR-2). The isotopic composition of these standards measured through time, over the two main analytical periods, is shown in Fig. 2.1, and is in agreement with published values (Craddock and Dauphas, 2010; Williams and Bizimis, 2014; Williams et al., 2018, 2021). In  $\delta^{56}\text{Fe}$ – $\delta^{57}\text{Fe}$  space, the standard data define a linear trend, with a slope of 1.48–1.49 (Fig. 2.2), demonstrating mass-dependent fractionation and a lack of analytical artefacts arising from isobaric interferences during analysis.



**Figure 2.1: Measured Fe isotope compositions of international reference materials, 2018–2019 (top) and 2021–2022 (bottom).** The black star shows the mean  $\delta^{57}\text{Fe}$  for each measurement session, with the black dashed line showing the mean of all the measurements and grey band representing  $\pm 2 \text{ S.D.}$  The blue solid line shows the recommended values from Craddock and Dauphas (2010) for the basaltic reference materials BCR-2, BHVO-2, BIR-1a, and an average of long-term measurements for the in-house  $\text{FeCl}_3$  standard from this thesis for the 2018–2019 measurements, given that previous measurements of this standard had only been performed prior to the mass spectrometer’s move from Durham University.

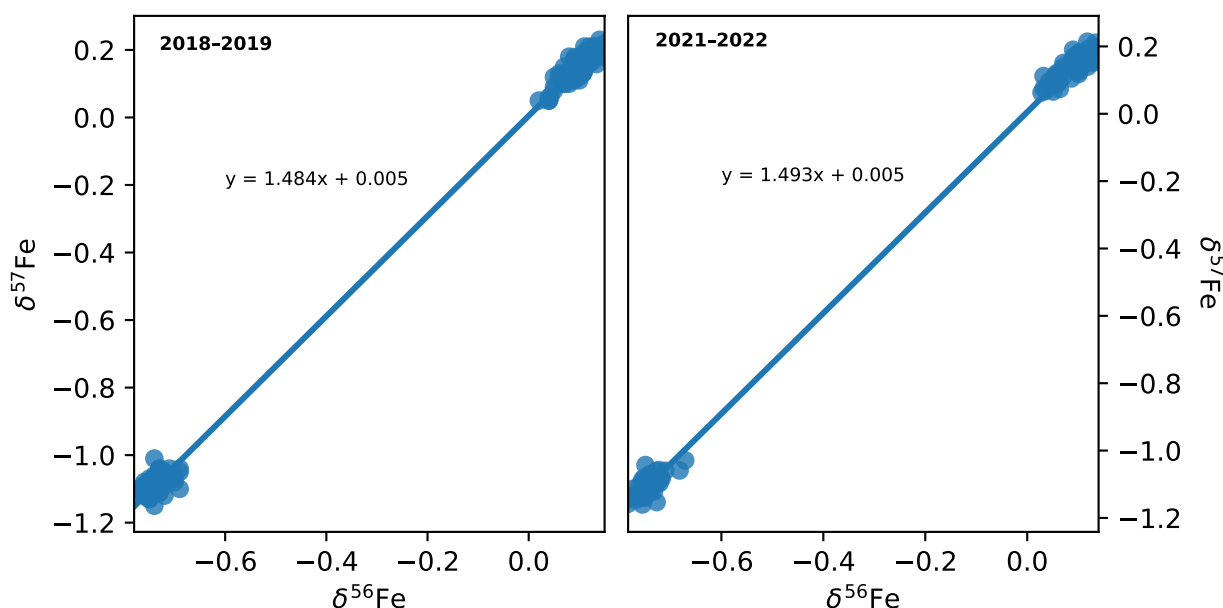


Figure 2.2: Mass fractionation of reference materials in three isotope space.

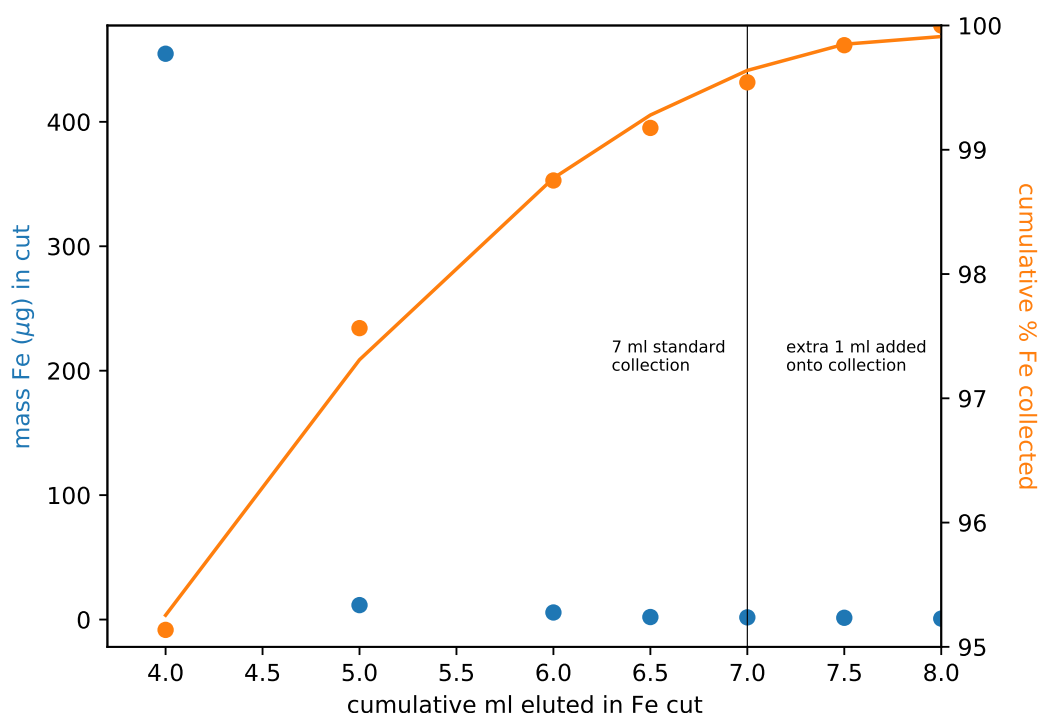
### 2.1.3 Column recalibration, after COVID-19 shutdown

Column chemistry performed in December 2019 – January 2020, and measured in February 2020 immediately prior to the COVID-19 laboratory shutdown in March 2020, produced isotopic compositions for the BHVO-2 reference material significantly heavier than the recommended values (Table 2.3). Although the origin of this issue cannot be unambiguously determined, it was most likely associated with a change in the bottle of anion exchange resin used (AG1-X8, since the AG1-X4 had been used up), and a contamination of the acids used for the chemistry. After access to the laboratory was restored in August 2020, the issue was repeated in a trial and persisted through a series of resin and acid tests (Table 2.3), although the testing was delayed by problems with the mass spectrometer in November 2020 – June 2021. High Mg and Ca blanks were identified in the acid and MilliQ stock bottles, and higher levels of matrix elements (particularly Mg, Ca, Na) in the column-processed BHVO-2 than expected, particularly for standards processed through AG1-X8 resin. However, the isotopic offset was not resolved by using new acid stocks (Table 2.3), suggesting the source of the problem was not the high non-Fe blanks, although there was a slight improvement with the reduced Mg and Ca blanks. A trial of new AG1-X4 resin in August 2021 produced anomalously light isotopic compositions for BHVO-2, the origin of which remains unresolved but has not been repeated.

Subsequently, a new column calibration was performed in October 2021 using the new AG1-X4 resin. Although  $> 99\%$  Fe yield was achieved with the usual 7 ml of Fe collection, a small amount (0.5 %) of Fe was found to be present in the following millilitre of Fe elution for the BHVO-2 standard (Fig. 2.3). Therefore, to improve the Fe yield, the Fe collection window was expanded to 8 ml for all column chemistry performed in 2021–2022. No increase in other element concen-

**Table 2.3: Summary of isotopic compositions of BHVO-2 standard during column chemistry issues.** †Isotopic composition of 7 ml Fe collection; \*isotopic composition of 8 ml Fe collection.

| Measurement period<br>(columns in) | BHVO-2 $\delta^{57}\text{Fe}$ (‰)<br>ref. value = 0.17 ‰ | Note                                                        |
|------------------------------------|----------------------------------------------------------|-------------------------------------------------------------|
| Nov 2018–Aug 2019                  | average 0.17                                             |                                                             |
| Feb 2020 (Dec–Jan 2020)            | 0.22–0.29                                                | First identification of issue, after switch to AG1-X8       |
| Oct 2020 (Oct 2020)                | 0.28–0.34                                                | Test with different bottle of AG1-X8 resin vs AG1-X4        |
| July 2021 (Dec 2020)               | 0.24–0.27                                                | Replaced columns, new single distilled acids                |
| Aug 2021 (Aug 2021)                | –0.12                                                    | New AG1-X4 resin                                            |
| Oct 2021 (Oct 2021)                | 0.21*–0.22†                                              | Column calibration with new BHVO dissolution                |
| Nov 2021 (Nov 2021)                | 0.29                                                     | Double distilled (DD) acid (re-process of Oct 2021 samples) |
| Nov 2021 (Nov 2021)                | 0.19                                                     | DD acid, new BHVO dissolution, column-process IRMM          |



**Figure 2.3: Iron proportions in column calibration cuts for the BHVO-2 reference material.**

trations was found in the extra collection window. However, the isotopic composition of BHVO in this column calibration, even with the extended 8 ml collection, was still slightly heavy, although an improvement on previous measurements (Table 2.3). Repeated column processing of these calibration samples with double distilled HCl in the chemistry (to reduce any possible non-Fe blank issue further) showed that samples were made even heavier (by up to 0.07 ‰ in  $\delta^{57}\text{Fe}$ ) with reprocessing through a second column chemistry, consistent with newly processed samples also coming out slightly heavy. Given the problem was made worse by repeated processing despite using low blank double distilled acid and the extended Fe collection, in late November 2021 the elimination of any matrix effects was tried by processing the bracketing IRMM-014 standard through columns, following a suggestion from Helen Williams. Combined with a new dissolution of the BHVO-2 powder, bracketing the column-processed standards to column-processed IRMM-014 (from the same column chemistry session) during a mass spectrometer session worked very well, reproduc-

ing the expected isotopic compositions for the international reference materials, as well as for a test of the in-house  $\text{FeCl}_3$  through column chemistry.

Therefore, all column chemistry performed from November 2021 onwards used fresh dissolutions of samples and standards, double distilled HCl, and was bracketed to IRMM-014 processed in the same set of chemistry. This method generally reduced the analytical errors on the measurements of samples, with typical 2 S.D. on  $\delta^{57}\text{Fe}$  around 0.03 ‰, compared to 0.05 ‰ previously. This improvement is likely due to the better matrix matching of samples and standards when both have been through column chemistry.

## 2.2 Mantle melting and isotope fractionation model

Throughout the work in this thesis, I use a combined thermodynamic phase-equilibria and equilibrium isotope fractionation model, based on the model presented in Williams et al. (2021), to investigate the stable isotope signature of equilibrium melts from mantle peridotite and pyroxenite. The model for Fe isotope fractionation is described here, and is used in chapters 3, 4 and 5. The development of the model for other stable isotope systems is described in chapter 4.

### 2.2.1 Choice of lithology composition

The KLB1 composition was chosen to model peridotite melting. KLB1 is a commonly used experimental composition used as an analogue for the upper mantle, based on a Kilborne Hole spinel lherzolite xenolith (Davis et al., 2009). For pyroxenite, two compositions were studied, one a silica-enriched (SE) pyroxenite (G2; Pertermann and Hirschmann, 2003a) and the other a silica-deficient (SD) pyroxenite (MIX1G; Hirschmann et al., 2003; Lambart et al., 2016). G2 is an important MORB-like bulk composition used in melting experiments and models (Pertermann and Hirschmann, 2003a,b; Lambart et al., 2016), and is a low MgO quartz eclogite and a SE pyroxenite endmember (Lambart et al., 2016). MIX1G is a silica-deficient pyroxenite which plots close to the average global pyroxenite composition and can be considered as a mixture between KLB1 and MORB (Lambart et al., 2016), i.e., recycled crust mixed with ambient mantle. The ferric Fe content of MIX1G is taken as between that of KLB1 peridotite and MORB, following the approach used for KG1 by Jennings et al. (2016), with  $\text{Fe}^{3+}/\text{Fe}_T = 0.1$ . Further detail on the choice of pyroxenite lithologies is given throughout the thesis.

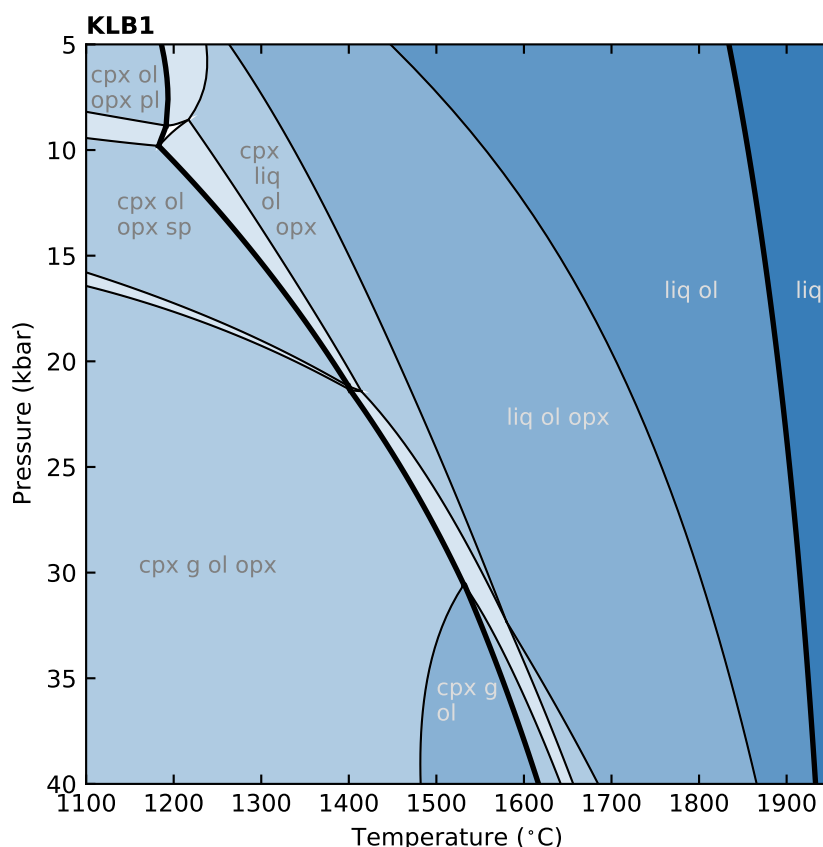
The compositions of the peridotite and pyroxenite lithologies used in the phase-equilibria calculations are given in Table 2.4. For the study in chapter 3, the model contained KLB1 and G2 lithologies, with MIX1G added for chapters 4 and 5.

**Table 2.4: Lithology compositions, in KNCFMASSTOCr system.** KLB1 composition from Davis et al. (2009), G2 from Pertermann and Hirschmann (2003a). Cr added to G2 pyroxenite composition in order to stabilise THERMOCALC model. MIX1G composition from Lambart et al. (2016), renormalised without MnO. All converted to mole % oxides.

|       | mole % oxide     |                                |       |       |                  |                  |                   |                  |                                |      |
|-------|------------------|--------------------------------|-------|-------|------------------|------------------|-------------------|------------------|--------------------------------|------|
|       | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | CaO   | MgO   | FeO <sub>t</sub> | K <sub>2</sub> O | Na <sub>2</sub> O | TiO <sub>2</sub> | Cr <sub>2</sub> O <sub>3</sub> | O    |
| KLB1  | 38.5             | 1.78                           | 2.82  | 50.58 | 5.52             | 0.01             | 0.25              | 0.07             | 0.11                           | 0.09 |
| G2    | 52.4             | 9.72                           | 13.17 | 12.33 | 5.64             | 0.02             | 3.09              | 1.55             | 0.02                           | 0.64 |
| MIX1G | 45.6             | 8.95                           | 12.31 | 24.86 | 6.50             | 0.03             | 1.40              | 0.67             | 0.04                           | 0.33 |

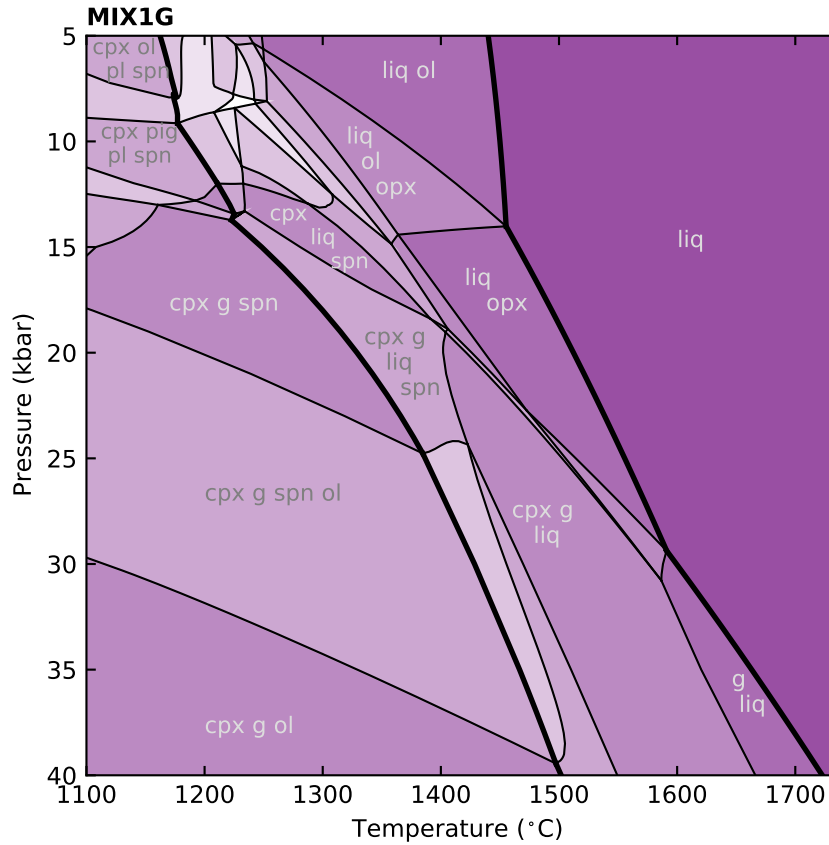
## 2.2.2 Pseudosection calculation

Pseudosections were constructed and mineral chemistries calculated for each lithology. The calculations were performed in the KNCFMASSTOCr system using THERMOCALC v3.47 (Powell et al., 1998), and the latest version of the thermodynamic dataset, ds633, of Holland and Powell (2011) with the activity-composition (a-X) models of Holland et al. (2018). The KLB1 pseudosection was initially calculated by Simon Matthews to test the subsequent model. Figs. 2.4–2.6 show the calculated pseudosections.



**Figure 2.4: Calculated pseudosection for peridotite lithology KLB1.** Bold lines show solidus and liquidus. Abbreviations: cpx = clinopyroxene, g = garnet, liq = liquid, ol = olivine, opx = orthopyroxene, pl = plagioclase, sp = spinel.

After the pseudosection calculations for this thesis were performed, an updated thermodynamic

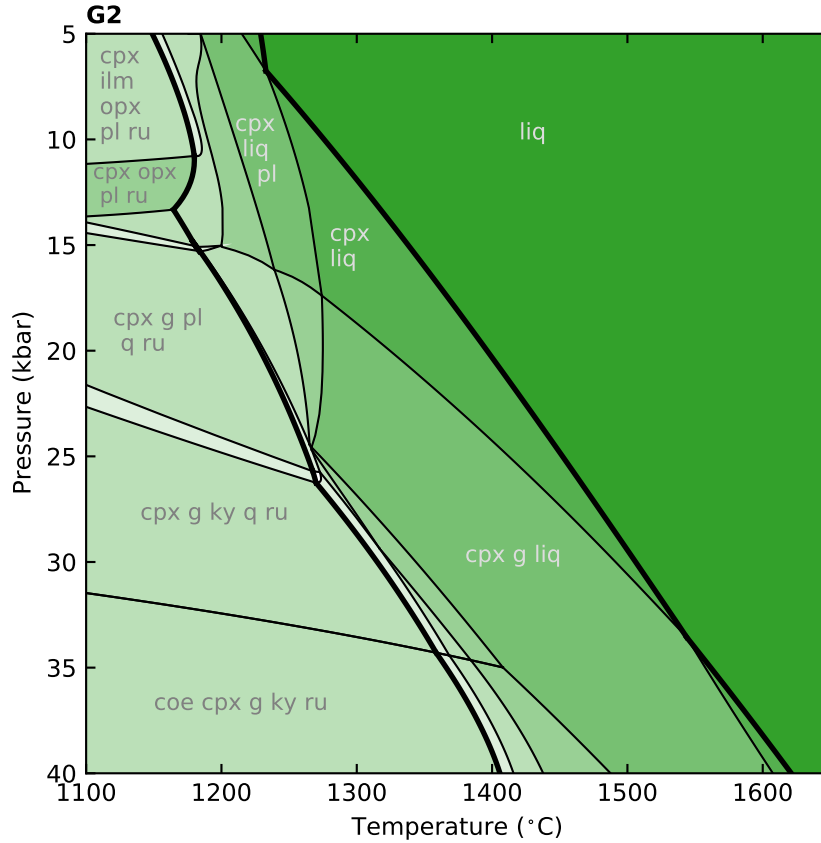


**Figure 2.5: Calculated pseudosection for pyroxenite lithology MIX1G.** Bold lines show solidus and liquidus. Abbreviations: cpx = clinopyroxene, g = garnet, liq = liquid, ol = olivine, opx = orthopyroxene, pig = pigeonite, pl = plagioclase, spn = spinel.

dataset for peridotite melting and phase relations, ds634, was published by Tomlinson and Holland (2021), which runs on THERMOCALC v3.50. The most relevant changes in the new model to work presented in this thesis are updates to the structure of the melt model, to allow better representation of melts undersaturated in silica, and an incorporation of more realistic levels of non-ideal Cr-Al mixing in spinel, which slightly raises the pressure of the spinel to garnet stability field transition at the solidus, generally widens the spinel stability field across P-T space and results in changes to Cr content of all mineral phases, notably garnet and orthopyroxene (Tomlinson and Holland, 2021). The most significant changes of this update to the results presented in this thesis are likely to relate to isotope systems where spinel has a distinct isotope signature or large budget of a given element compared to other mantle minerals, as presented in chapter 4, and are briefly discussed further there.

### 2.2.3 Calculation of equilibrium mineral and melt isotopic composition

The Python code used for the following calculations was initially written by Simon Matthews, with subsequent modifications and troubleshooting performed by me throughout the work for this thesis.



**Figure 2.6: Calculated pseudosection for pyroxenite lithology G2.** Bold lines show solidus and liquidus. Abbreviations: coe = coesite, cpx = clinopyroxene, g = garnet, ilm = ilmenite, ky = kyanite, opx = orthopyroxene, pl = plagioclase, q = quartz, ru = rutile.

After calculation of the phase boundaries, THERMOCALC was run over a grid of pressure-temperature (P-T) space, from 5–40 kbar and 1100–1950 °C (KLB1), 1100–1730 °C (MIX1G) and 1100–1650 °C (G2), with 0.5 kbar pressure steps and 1–10 °C temperature steps depending on the lithology and the resolution needed.

The THERMOCALC output includes the proportion of each phase present and information on the composition of each phase at any P-T point, including the distribution of elements on available cation sites, and the partitioning of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . The calculations assume chemical equilibrium and consider batch melting only. These results allow the equilibrium isotopic composition of the phases present (including melts) to be calculated, based on calculated equilibrium isotope fractionation factors,  $\alpha^{A-B}$  (‘ $\alpha$  factors’), between the phases A and B that are present, where

$$\alpha^{A-B} = \frac{\left(\frac{X_2}{X_1}\right)_A}{\left(\frac{X_2}{X_1}\right)_B}, \quad (2.1)$$

and X represents the amount of each isotope 1 or 2 of an element. To facilitate comparisons between different lithologies, results are all expressed relative to a bulk system of 0 ‰, for convenience (although I recognise that different mantle components may have non-zero initial bulk

stable isotope compositions).

$\alpha$  factors can be calculated using cation-oxygen bond force constants in each crystal site for the minerals,

$$\ln(\alpha^{A-B}) = C \frac{[K_A - K_B]}{T^2}, \quad (2.2)$$

where  $C$  is a constant dependent on the isotopes and element being considered (e.g., Sossi and O'Neill, 2017),  $T$  is the temperature in Kelvin, and  $K_A$  and  $K_B$  refer to the cation-oxygen force constants in minerals  $A$  and  $B$ .

Following the model used in Williams et al. (2021), the equations presented in Sossi and O'Neill (2017) (equations 2.3 and 2.4 below) were used to calculate the force constants for Fe–O bonds in each mineral site hosting Fe in each lithology. These equations use a simplified ionic bonding approach to the Fe isotope composition for each mineral. The input parameters used are shown in Table 2.5, and the other constants used are  $q$  (electronic charge,  $1.602 \times 10^{19}$  C),  $B$  (Born exponent, 12),  $1/4\pi\epsilon_o$  (Coulomb's constant,  $9 \times 10^9$  Nm<sup>2</sup>/C<sup>2</sup>),  $I$  (ionicity, 0.36) and  $r$ , bond length, is used in metres.  $\bar{s}_X$  is calculated as the average charge on ion  $X$  divided by the mean coordination number of ion  $X$  in the mineral (Young et al., 2009; Sossi and O'Neill, 2017).  $K_f$  represents an individual force constant for any particular Fe–O bond in a given mineral site,  $K_T$  represents the total force constant associated with any particular mineral site (i.e., considering the coordination number, CN, of the site and the proportion of the bond strength that is ionic). An average Fe–O force constant for each mineral was then calculated considering the number of each site in the structure, the  $K_T$  for each site, and the amount of Fe held in each site as calculated by THERMOCALC.

$$K_{f,Fe,O} = - \frac{\bar{s}_{Fe}\bar{s}_O q^2 (1 - B)}{4\pi\epsilon_o r^3} \quad (2.3)$$

$$K_T^{Fe-O} = \frac{1}{4} \frac{K_{f,Fe,O} \overline{CN}_{Fe}}{I} \quad (2.4)$$

For melt, the force constants estimated for basaltic melts of varying Fe<sup>3+</sup>/Fe<sub>T</sub> from Dauphas et al. (2014) were used, with the melt force constant at each P-T point calculated according to the Fe<sup>3+</sup>/Fe<sub>T</sub> calculated by THERMOCALC.

The force constants were used to calculate fractionation factors between each mineral and melt, with  $C = 4284$  in equation 2.2 for  $\Delta^{57/54}\text{Fe}$  following Sossi and O'Neill (2017), since for  $\alpha$  factors close to 1 (as is the case for equilibrium fractionation factors),

$$\Delta^{57}\text{Fe}_{A-B} = 1000 \ln \alpha_{A-B}. \quad (2.5)$$

With the temperature- and composition-dependent fractionation factors between each mineral and melt calculated at each P-T point, combined with the mineral assemblage information from

**Table 2.5: Input parameters for the Fe isotope fractionation model, based on ionic bonding environments.** Pigeonite, where present, was modelled as clinopyroxene. Input parameters collated by Simon Matthews.

| Mineral       | Fe species | Site | Fe coordination | Bond length (Å) | O coordination | No. sites |
|---------------|------------|------|-----------------|-----------------|----------------|-----------|
| spinel        | 2+         | M    | 6               | 2.15            | 4              | 2         |
| spinel        | 2+         | T    | 4               | 2.00            | 4              | 1         |
| spinel        | 3+         | M    | 6               | 2.03            | 4              | 2         |
| spinel        | 3+         | T    | 4               | 1.88            | 4              | 1         |
| garnet        | 2+         | M1   | 8               | 2.29            | 4              | 3         |
| garnet        | 3+         | M2   | 6               | 2.02            | 4              | 2         |
| olivine       | 2+         | M1   | 6               | 2.16            | 4              | 1         |
| olivine       | 2+         | M2   | 6               | 2.18            | 4              | 1         |
| orthopyroxene | 2+         | M1   | 6               | 2.14            | 3.66           | 1         |
| orthopyroxene | 3+         | M1   | 6               | 2.12            | 3.66           | 1         |
| orthopyroxene | 2+         | M2   | 6               | 2.23            | 3.33           | 1         |
| clinopyroxene | 2+         | M1   | 6               | 2.14            | 3.66           | 1         |
| clinopyroxene | 3+         | M1   | 6               | 2.03            | 3.66           | 1         |
| clinopyroxene | 2+         | M2   | 6               | 2.53            | 3.75           | 1         |
| ilmenite      | 2+         | A    | 6               | 2.14            | 4              | 1         |
| ilmenite      | 3+         | B    | 6               | 1.98            | 4              | 1         |
| ilmenite      | 3+         | A    | 6               | 2.14            | 4              | 1         |
| ilmenite      | 2+         | B    | 6               | 1.98            | 4              | 1         |

THERMOCALC, the deviation of  $\delta^{57}\text{Fe}$  in the melt with respect to the bulk composition of 0 ‰ (i.e.,  $\Delta^{57}\text{Fe}_{\text{melt-bulk}}$ , the partial melting isotope fractionation) was calculated.

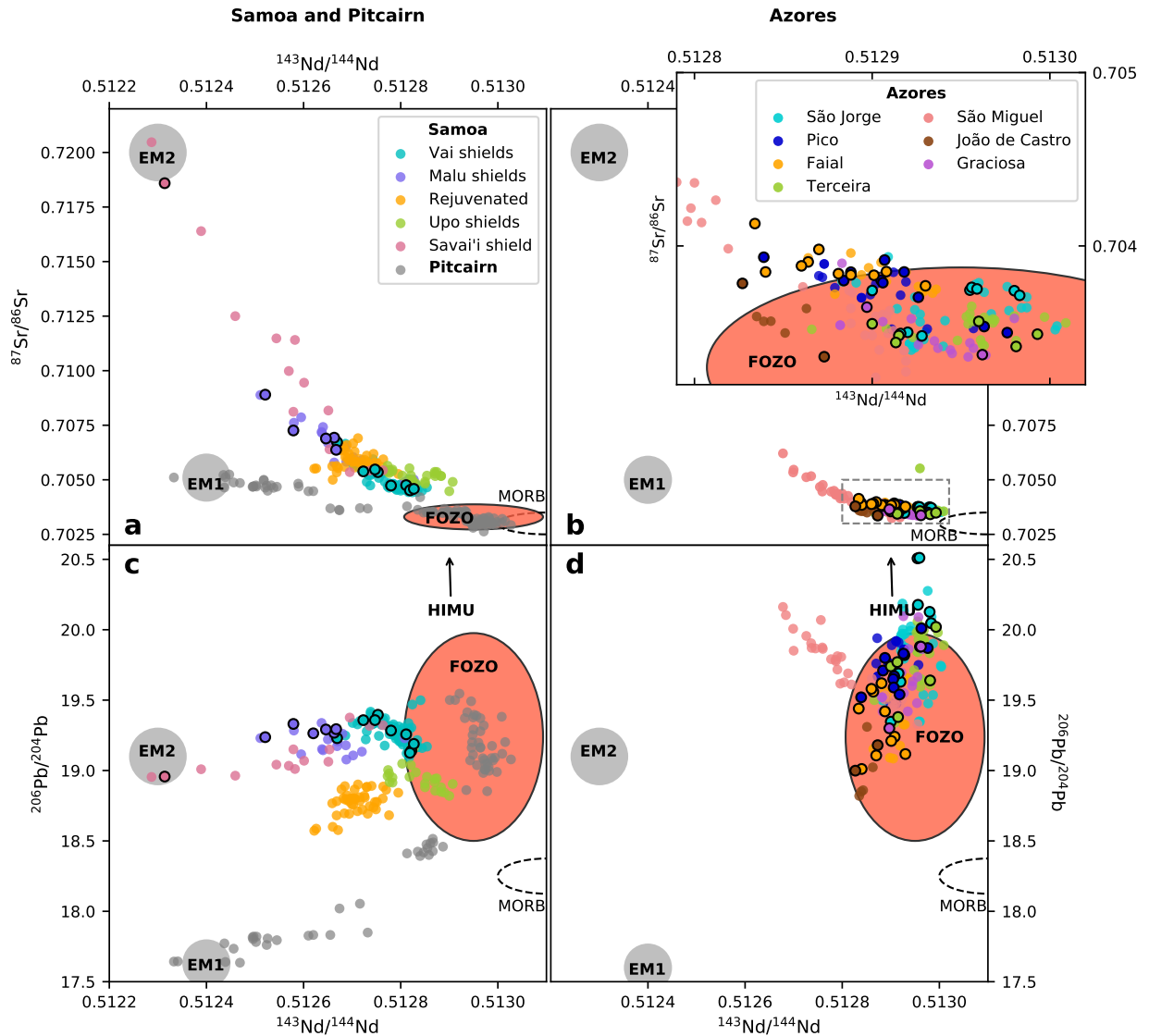


# **3 High $\delta^{57}\text{Fe}$ in ocean island basalts: A non-unique signature of processes and source lithologies in the mantle**

## **3.1 Introduction**

The ocean island basalts of Samoa, Pitcairn and the Azores offer complementary opportunities to study recycled crustal components in the source regions of plume-related basalts. The variance in long-lived radiogenic isotopic composition (Sr-Nd-Pb) in these OIB can be explained by mixing between at least four of the five primary mantle components identified in global OIB: depleted mantle, the prevalent mantle (PREMA)/focal zone (FOZO) component, two enriched mantle (EM1/EM2) components and a HIMU component (Stracke, 2012; Fig. 3.1).

Qualitatively consistent with predictions and observations that recycled pyroxenite components in the mantle, and melts derived from them, should be isotopically heavier than peridotite and peridotite-derived melts (Williams and Bizimis, 2014; Konter et al., 2016 [chapter 1]), OIB show variable  $\delta^{57}\text{Fe}$  relative to average N- and T-MORB (the latter two dominated by peridotite melting). Published  $\delta^{57}\text{Fe}$  data for global OIB generally extend to heavier isotopic compositions, such as over 0.25 ‰ in Samoa and Pitcairn (Konter et al., 2016; Nebel et al., 2019), than MORB. These heavy Fe isotopic compositions are suggested to relate to pyroxenitic mantle components in the OIB source, which may relate to the radiogenic isotope compositions of these OIB. There are some N-MORB with  $\delta^{57}\text{Fe}$  as high as 0.2 ‰, which could also be consistent with indications of small amounts of enriched pyroxenite or eclogite in the MORB source (c.f., Hirschmann and Stolper, 1996). The radiogenic isotope systematics of hotspots (plumes) that display high  $\delta^{57}\text{Fe}$  signatures show mixing between a common peridotitic mantle component and recycled crustal endmembers (Konter et al., 2016; Nebel et al., 2019; Fig. 3.1), and in several cases Fe isotopes correlate positively with indices of recycling (e.g., Sr-Nd-Pb isotopes; Nebel et al., 2019). However, it is unclear whether mixing between different mantle components is represented to the same extent in Fe isotopes as in long-lived radiogenic isotopes, and whether Fe and radiogenic isotopic systems can be linked to identify the mineralogy (e.g., pyroxene enrichment) of different mantle components identified in Fig. 3.1. In using heavy Fe isotopic compositions to better understand mantle heterogeneity, both the sources and processes generating high  $\delta^{57}\text{Fe}$  melts in OIB need to be considered.



The Fe isotope compositions recorded in OIB are heavier (and more variable) than the expected equilibrium isotopic compositions of melts from crustal endmembers contributing to mantle heterogeneity. Isotopic composition estimates for the mantle are  $\delta^{57}\text{Fe} = 0.03 \pm 0.03 \text{‰}$  (DM; Craddock et al., 2013; Johnson et al., 2020) to  $0.05 \pm 0.01 \text{‰}$  (BSE; Sossi et al., 2016); for average oceanic crust, represented by MORB, are  $\delta^{57}\text{Fe} = 0.15 \text{‰}$  (Teng et al., 2013; Sossi et al., 2016); and bulk continental crust is indistinguishable from, or lighter than, oceanic crust ( $\delta^{57}\text{Fe} = 0.08 - 0.16 \text{‰}$ ; Johnson et al., 2020). Highly differentiated ( $\text{SiO}_2 > 70 \text{ wt\%}$ ) crust, which could contribute to continentally-derived sediment, records  $\delta^{57}\text{Fe} < 0.9 \text{‰}$  (Du et al., 2017) although the average  $\delta^{57}\text{Fe}$  of rocks with  $\text{SiO}_2 > 60 \text{ wt\%}$  is around  $0.3 \text{‰}$  (Johnson et al., 2020). Experimental and theoretical estimates of fractionation during partial mantle melting are known to be small (e.g., Dauphas et al., 2009; Sossi and O'Neill, 2017; Gleeson et al., 2020), likely  $\Delta^{57}\text{Fe}_{\text{melt-mantle}} (= \delta^{57}\text{Fe}_{\text{melt}} - \delta^{57}\text{Fe}_{\text{mantle}}) < 0.1 \text{‰}$  depending on  $\text{Fe}^{3+}$  buffering in the mantle (Dauphas et al., 2014). However, data from Pitcairn and Galápagos Spreading Centre lavas require a mantle component with  $\delta^{57}\text{Fe} = 0.30 \text{‰}$  (Nebel et al., 2019; Gleeson et al., 2020). The heaviest isotopic values in OIB from Samoa have previously been explained by combining source heterogeneity, partial melting, and fractional crystallisation effects (Konter et al., 2016). However, even in this multi-process scenario, equilibrium fractionation factors for these processes are required to be high (crystallisation with  $\Delta^{57}\text{Fe}_{\text{olivine-melt}} = -0.45 \text{‰}$ , and mantle melting with  $\Delta^{57}\text{Fe}_{\text{melt-mantle}} > 0.15 \text{‰}$ ; Konter et al., 2016), and possibly unrealistically high (Gleeson et al., 2020). It therefore remains unclear if the heaviest Fe isotopic values in OIB ( $\delta^{57}\text{Fe} > 0.25 \text{‰}$ ) can be explained by simple melting processes of recycled crustal components embedded in ambient plume mantle.

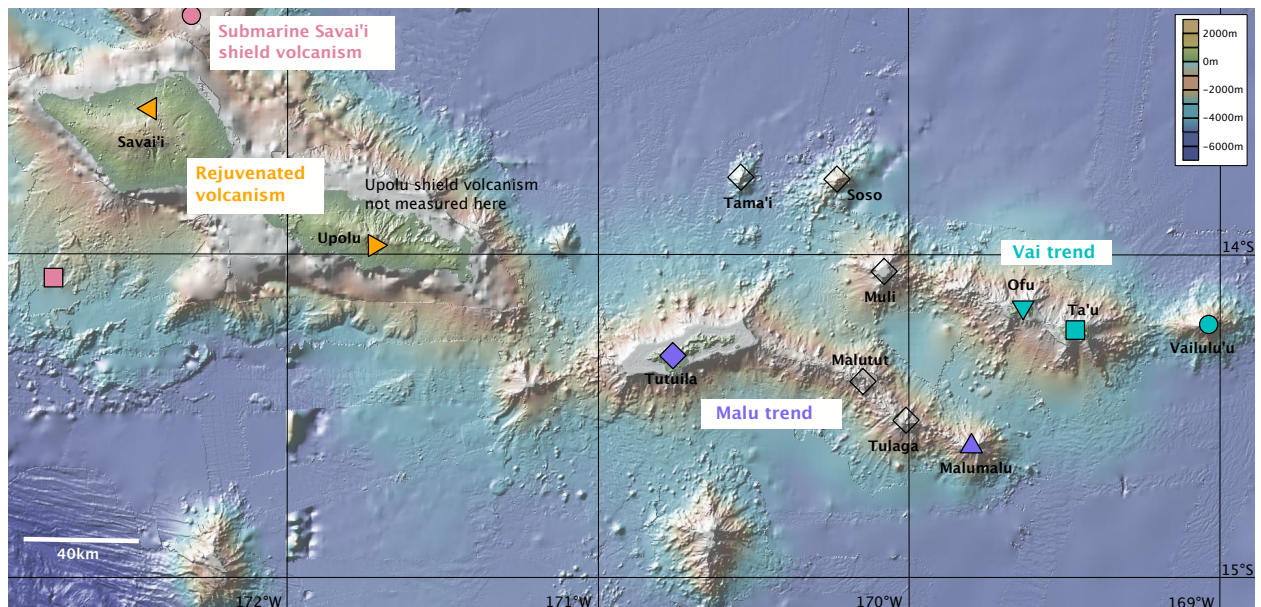
Samoaan rejuvenated lavas (a later, volumetrically less significant stage than the main shield lavas, erupted far from the plume; Natland, 1980) record the heaviest Fe isotopic compositions in the global OIB dataset (Konter et al., 2016). Samoaan shield samples also show correlated  $^3\text{He}/^4\text{He}$ - $\mu^{182}\text{W}$ , with  $^3\text{He}/^4\text{He} \leq 33.8 \text{ R/R}_a$  (Jackson et al., 2007b) and  $\mu^{182}\text{W} \geq -17.3$  (Mundl et al., 2017), proposed to relate to core-equilibrated material (Mundl-Petermeier et al., 2020). Thus, Samoaan lavas were selected for further Fe isotopic characterisation. I have expanded the shield lava dataset allowing me to study pyroxenite versus core contributions to high  $\delta^{57}\text{Fe}$  liquids, as the two contributions could be associated with other distinct geochemical signatures. The Azores was chosen as a second OIB locality to add to this study because it shows radiogenic isotopic mixing between a common Azores mantle component and recycled components, so could allow identification of recycled mantle pyroxenite. There may also be a minor lower mantle or core component associated with the Azores plume, identified by raised  $^3\text{He}/^4\text{He}$  relative to MORB ( $\leq 18.4 \text{ R/R}_a$ ; Moreira et al., 2012) and small negative  $\mu^{182}\text{W}$  anomalies ( $\geq -9.9$ ; Mundl-Petermeier et al., 2020). Unlike Samoa, the Azores is also (1) a cooler plume ( $> 1400 \text{ °C}$ ; Beier et al., 2012, compared to  $> 1600 \text{ °C}$  in Samoa; Putirka et al., 2018) meaning melts of enriched (and possibly high  $\delta^{57}\text{Fe}$ ) components will be minimally obscured by contemporaneous melting of ambient, relatively depleted mantle; and (2) shows a well spatially-resolved distribution of melts from different components sampled by volcanoes (Béguelin et al., 2017; Beier et al., 2018; Fig. 3.1). Therefore, Samoa and

the Azores offer different perspectives on the links between distinct mantle components and the source of high  $\delta^{57}\text{Fe}$  lavas.

## 3.2 Samples and methods

### 3.2.1 Samoa samples

The Samoan islands show an age-progressive volcanic track (Koppers et al., 2011), with a shield building stage influenced by multiple mantle components (Jackson et al., 2014; Fig. 3.1). These components include the global EM2 endmember, which is distinguished by high  $^{87}\text{Sr}/^{86}\text{Sr}$  relative to FOZO (but FOZO-like  $^{206}\text{Pb}/^{204}\text{Pb}$ ) and proposed to relate to recycled continental sediment (White and Hofmann, 1982; Jackson et al., 2007a); and a high  $^3\text{He}/^4\text{He}$ -negative  $\mu^{182}\text{W}$  common plume component (Jackson et al., 2007b; Mundl et al., 2017), proposed to relate to a contribution from the outer core (Mundl-Petermeier et al., 2020). Recent shield-stage volcanism is split into two sub-parallel and geochemically distinct volcanic chains (Fig. 3.1), similar to Hawai'i's Loa and Kea trends (Workman et al., 2004; Huang et al., 2011c; Koppers et al., 2011): the Vai and Kea trends. Subsequently, rejuvenated lavas have erupted on the older islands of Savai'i and Upolu (Konter and Jackson, 2012). Rejuvenated lavas record heavy Fe isotopic signatures of  $\delta^{57}\text{Fe} \geq 0.3\text{‰}$  (Konter et al., 2016), and an EM1-like component (Workman et al., 2004; Konter and Jackson, 2012; Reinhard et al., 2019; Fig. 3.1c). Metasomatism of the lithosphere by silicate melts and/or mineralogical heterogeneity (a pyroxenite component) are proposed as the most likely origin of the high  $\delta^{57}\text{Fe}$  in Samoa (Konter et al., 2016).



**Figure 3.2:** Map of the Samoan volcanic chain, showing the volcanoes/regions studied.

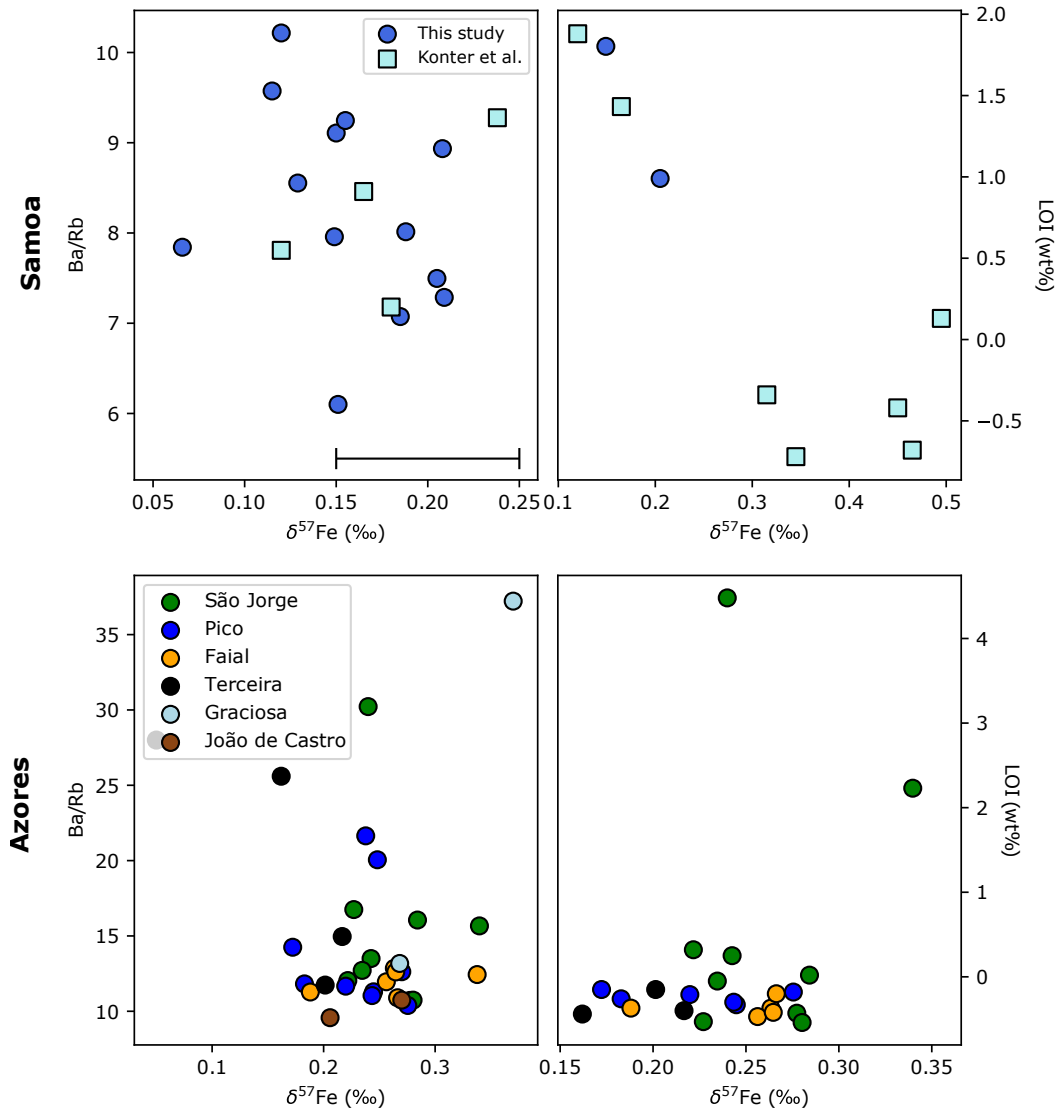
The 14 new Samoan samples I studied are subaerial and submarine shield lavas, covering six

volcanic centres (Savai'i, Tutuila, Malumalu, Ofu, Ta'u and Vailulu'u) (Fig. 3.2) and were provided as powders by Matt Jackson. These samples cover the range of the long-lived radiogenic isotope space spanned by Samoan shield lavas (Fig. 3.1), and include high  $^3\text{He}/^4\text{He}$ , negative  $\mu^{182}\text{W}$  samples (Ofu; Mundl et al., 2017).

Major and trace element, and radiogenic isotopic data has been published previously (Vailulu'u and Malumalu seamounts and subaerial Ta'u lavas from Workman et al., 2004; Ofu from Jackson et al., 2007b, 2010; Hart and Jackson, 2014). Petrographic descriptions or classifications of some samples have also been published. Vailulu'u basalts are mostly phenocryst-poor (e.g., trace olivine and clinopyroxene, AVON-3-70-9; trace clinopyroxene, AVON-3-73-1), but high MgO (22 wt%) sample AVON-3-71-22 contains 40 % olivine (Workman et al., 2004), consistent with olivine accumulation. The T'au sample T33, a basaltic lava flow (Hart and Jackson, 2014), is recorded with 10 % olivine, 2 % clinopyroxene phenocrysts (Workman et al., 2004), and the low MgO Malumalu samples both contain minor phenocryst phases, 3 % olivine  $\pm$  clinopyroxene. The high MgO Malumalu sample, AVON-3-78-1, contains 25 % olivine and 5 % clinopyroxene (Workman et al., 2004). Of the Ofu samples, Ofu-04-14 is described as an ankaramitic cumulate, and Ofu-05-18 is a resample of an ankaramitic dyke originally sampled as Ofu-04-06 (Jackson et al., 2007b, 2014; Hart and Jackson, 2014). Only samples with greater than 5 wt% MgO were selected, to limit the effects of fractional crystallisation, particularly magnetite fractionation (Williams et al., 2018). Three high MgO samples ( $> 18$  wt%) were chosen to explore the  $\delta^{57}\text{Fe}$  variability that could be introduced to lavas by olivine accumulation during melt storage and transport. The Savai'i sample (ALIA115-18) is a dredged lava (trachybasalt, from Jackson et al., 2014), with high  $\delta^{57}\text{Fe}$  (0.36 ‰) previously measured by Konter et al. (2016), which was suggested to have undergone seawater alteration based on trace element data (combined high LOI of 4.4 wt% and Ba/Rb  $< 6.7$ ; Konter et al., 2016). This sample was the only sample available where alteration is documented, and therefore was measured to get an idea of the Fe isotopic variability that could be induced by alteration. The other samples do not show a trace element signature of alteration, with no correlations between high LOI and low Ba/Rb, suggesting alteration has not strongly affected the Azores and Samoan samples that are used in this study (Fig. 3.3).

### 3.2.2 Azores samples

The Azores consist of nine volcanic islands, on the west and east of the Mid-Atlantic Ridge, and is associated with a triple junction. Many of the islands are still active, with most subaerial lavas less than 1 Myr old (Larrea et al., 2018). The Azores volcanoes sample a number of recycled components identified in radiogenic isotopic space, spanning much of the global variation of OIB (Beier et al., 2018), although the eastern São Miguel component is not a globally-defined endmember (Fig. 3.1). São Jorge lavas have the most radiogenic  $^{206}\text{Pb}/^{204}\text{Pb}$  from the Azores, a signature attributed to the presence of a HIMU-like recycled oceanic crustal component (Millet et al., 2009).



**Figure 3.3: Geochemical evidence for lack of significant alteration in the Samoa and Azores samples.** Ba/Rb and LOI for Samoa (top) and Azores (bottom) samples. Errorbar shows long term 2 S.D. of  $\pm 0.05$  ‰.

These recycled components are mixed with a common Azores component, but appear to undergo limited mixing with each other (Beier et al., 2018). Limited mixing is hypothesised to occur in part because the Terceira rift drains melts from fusible mantle components to the surface, allowing only short scale horizontal migration and mixing of melts between volcanoes towards the Mid-Atlantic Ridge (Béguélin et al., 2017). However, the presence of a recycled oceanic crustal component in Azores lavas is debated, with uranium series disequilibria (Prytulak and Elliott, 2009) and transition element ratios (Beier et al., 2013) consistent with a garnet peridotite source and not requiring pyroxenite/eclogite. It is also suggested that carbonated peridotitic mantle may be present in the Azores source region (Beier et al., 2013), explaining melting despite a relatively small thermal anomaly (Beier et al., 2012). Additionally, a negative  $\mu^{182}\text{W}$  signature has been recorded in the Azores, suggesting a lower mantle or core component entrained in the Azores plume (Rizo et al., 2019; Mundl-Petermeier et al., 2020).

In this chapter I use (previously unpublished, prior to Soderman et al., 2021) Fe isotope data for São Jorge, Terceira, Pico, Faial, João de Castro and Graciosa islands collected by Helen Williams at Durham University, and by Saskia Ruttor at Monash University. Major and trace element, and radiogenic isotopic data are from Turner et al. (1997); Beier et al. (2008); Millet et al. (2009); Watanabe (2010); Yu (2011); Beier et al. (2010, 2012); Béguelin et al. (2017); Waters et al. (2020). Less published petrographic information is available than for Samoan samples, but the Graciosa, São Jorge and João de Castro samples are classified as basalts (Beier et al., 2008; Millet et al., 2009). Some Pico and Faial samples are recorded with olivine pheno/xenocrysts (Beier et al., 2012). Only samples with MgO > 5 wt% were selected, to limit the effects of fractional crystallisation.

### 3.2.3 Methods

Iron isotope analyses were carried out following established procedures (Williams et al., 2005, 2009; Cheng et al., 2014) in the laboratories identified in Table 6.2. Measurements made in Cambridge (by me) and Durham (by Helen Williams) followed the procedures outlined in chapter 2. For the analyses performed in Cambridge and Durham, the international geological reference materials BHVO-2, BCR-2 and BIR-1 were used to evaluate column chemistry procedures, and give values in agreement with published values (Craddock and Dauphas, 2010; Table 6.1 in Appendix). The in-house FeCl<sub>3</sub> standard was used to assess mass dependence, reproducibility and accuracy in Cambridge and Durham, giving  $\delta^{56}\text{Fe} = -0.73 \pm 0.03 \text{‰}$  (2 S.D.),  $\delta^{57}\text{Fe} = -1.08 \pm 0.05 \text{‰}$  in Cambridge and  $\delta^{56}\text{Fe} = -0.69 \pm 0.03 \text{‰}$ ,  $\delta^{57}\text{Fe} = -1.03 \pm 0.05 \text{‰}$  in Durham. The long term 2 S.D. reproducibility of  $\delta^{57}\text{Fe}$  analyses in this chapter is therefore taken as  $\pm 0.05 \text{‰}$ .

#### 3.2.3.1 Isotopic measurements in Monash University

For measurements made in Monash University by Saskia Ruttor, Fe isotope analyses were carried out on dissolutions of  $\sim 25$  mg of whole-rock powders following established procedures (Cheng et al., 2014; Sossi et al., 2015). Powders were dissolved in 2 ml concentrated HF:HNO<sub>3</sub> (ratio 1:2), for a maximum of three days on a hotplate at 120 °C and evaporated to dryness once completely dissolved. After evaporation, samples were treated with several drops of concentrated nitric acid to ensure the absence of fluoride bonds. Afterwards, samples were taken up in 9 M HCl and pipetted onto AG-MP-1 anion resin, preconditioned with 9 M HCl. Column chromatographic extraction with 9 M HCl and 5 M HCl removed matrix elements as well as semi and transitional metals. The Fe fraction was eluted with 1 M HCl. The collected Fe fraction was placed on a hotplate at 90 °C. The dried samples were dissolved and taken up in 2 % HNO<sub>3</sub>. The Fe isotope analyses were performed on a ThermoFisher Scientific Neptune plus MC-ICP-MS in medium-resolution. The samples were introduced via a low flow quartz cyclonic spray chamber and a PFA nebuliser. Each

sample was analysed three times from a single dissolution batch in order to ensure precision and accuracy. Isotope ratios for each sample presented here are averaged from these three individual analyses. Each single dissolution batch was mixed with a Ni standard solution to correct for instrumental mass bias effects. To ensure reliability and comparability of the Fe isotope data, the basaltic reference material BCR-2 was analysed with the samples. The analyses are in agreement with previously published data. The reproducibility of the method is  $\pm 0.03\text{‰}$  (as a two-standard deviation) in  $^{57}\text{Fe}/^{54}\text{Fe}$  relative to the IRMM-524a external standard, based on repeated analyses of standard reference materials. The IRMM-524a standard is isotopically identical to the IRMM-014 standard (Craddock and Dauphas, 2010). The reproducibility of each sample was calculated as the standard deviation from 3 repeated analyses. Always the larger error (external vs. sample-averaged error) was used. At the end of the analysis a blank was analysed and showed values below detection level, and is thus negligible.

### 3.2.3.2 Measurement of Fe/Mn ratios at Florida State University

Fe/Mn data collection and analysis, as outlined below, was performed by Munir Humayan at Florida State University. Fe/Mn ratios were measured on dissolutions of the same powders used for iron isotope measurements and for which FeO contents have been reported (Turner et al., 1997). An aliquot of about 100 mg of sample powder was weighed into Savillex<sup>TM</sup> PFA beakers, and 1 ml  $\text{HNO}_3$  and 3 ml HF were added. The beakers were sealed and heated at  $150^\circ\text{C}$  for about three days, after which the solutions were dried down. The residue was taken up in 6 ml of 6 M HCl, resealed and heated at  $150^\circ\text{C}$  overnight to dissolve any residual fluorides. Each PFA vial was heated with 2 ml 12 M HCl to extract any traces of sample remaining, and this solution was combined with the sample stock solution. Ultrapure Seastar<sup>TM</sup> acids were used in preparing solutions. To avoid loss of volatile  $\text{FeCl}_3$ , none of the HCl-bearing solutions was dried down. The clear solutions were transferred to acid-washed LDPE bottles and diluted to 100 ml with MilliQ<sup>TM</sup> deionized water to form a matrix with 5 % HCl and 0.01 % HF. Aliquots for these stock solutions were diluted to form 1 % HCl, trace HF, solutions for ICP-MS analysis.

Precise Fe/Mn ratios were determined on a Thermo Element 1<sup>TM</sup> at the NHMFL, FSU following procedures described previously (Huang et al., 2007; Qin and Humayun, 2008). Gravimetrically prepared Fe/Mn standards with Fe/Mn ratios from 40–80 were used to prepare a calibration curve. Internal precision was  $\pm 0.2\%$  (1 sigma) and external reproducibility is better than  $\pm 0.5\%$  (1 sigma). Individual basalt rocks vary in their Fe/Mn during fractionation of olivine and clinopyroxene in Azorean magmas with an initial increase in Fe/Mn at high MgO followed by a decrease in Fe/Mn due to clinopyroxene fractionation producing a convex-upward curve in a plot of Fe/Mn vs. MgO. Each island produced distinct curves for Fe/Mn vs. MgO but, because of the small number of samples from each island, a single quadratic fit was used for Pico, Faial and Terceira and applied to samples from São Miguel and São Jorge that had significantly higher scatter around the

curve. The Fe/Mn of each sample was corrected to 8 wt% MgO using the quadratic interpolation, and an average reported for each island (see Soderman et al., 2021). Since prior work has shown that the errors in published Fe/Mn data is due to the errors in MnO, following Huang et al. (2007) precise MnO abundances were calculated from the measured Fe/Mn ratios and the reported FeO<sub>T</sub> abundances (Turner et al., 1997).

### 3.3 Results

The measured Fe isotope compositions for Samoa and the Azores are given in Table 6.2 in the Appendix. The Fe isotope systematics of the two localities are discussed separately below.

#### 3.3.1 Samoa Fe isotope compositions

The measured Fe isotope composition of Samoan shield lavas ranges from  $\delta^{57}\text{Fe} = 0.07\text{--}0.21\text{‰}$  ( $\pm 0.02\text{‰}$ , 2 S.E.), with an average of  $\delta^{57}\text{Fe} = 0.15\text{‰}$ , coinciding with average MORB (Teng et al., 2013). There is no systematic variation between Vai ( $\delta^{57}\text{Fe} = 0.07\text{--}0.20\text{‰} \pm 0.02\text{‰}$  2 S.E.) and Malu ( $\delta^{57}\text{Fe} = 0.15\text{--}0.21\text{‰} \pm 0.02\text{‰}$  2 S.E.) trend lavas. Duplicate dissolutions of samples ALIA115-18 and AVON-3-71-22 reproduce within 2 S.D. of each other (Table 6.2). The shield lava dataset measured in this study is comparable with previously published Samoan shield data (Konter et al., 2016). The rejuvenated lavas from Konter et al. (2016) are isotopically heavier ( $\delta^{57}\text{Fe} > 0.3\text{‰}$ ) than any of the combined dataset of shield lavas. The measurement of sample ALIA115-18, the common sample between the two studies, is  $\Delta^{57}\text{Fe} = 0.18\text{‰}$  lower than that reported by Konter et al. (2016).

#### 3.3.2 Azores Fe isotope compositions

The Fe isotope composition of Azores samples shows considerable variation, ranging from  $\delta^{57}\text{Fe} = 0.05\text{--}0.37\text{‰}$  ( $\pm 0.02\text{‰}$  2 S.E.), with all but three samples displaying  $\delta^{57}\text{Fe} > 0.15\text{‰}$  (average MORB, Teng et al., 2013) even at the same MgO content as MORB (Fig. 3.5). Two of these are Terceira samples (T2, AZT-03-016) with slightly low TiO<sub>2</sub> for their MgO (Fig. 3.4), which may indicate they have experienced early magnetite saturation (Williams et al., 2018) or formed as a result of mixing between primitive melts unsaturated in magnetite and magnetite-saturated evolved melts. At the onset of magnetite fractionation during crystallisation of a melt, studies have recorded a decrease in whole-rock  $\delta^{57}\text{Fe}$  (e.g., Williams et al., 2018; McCoy-West et al., 2018). This is because magnetite is generally expected to be an isotopically heavy phase ( $\delta^{57}\text{Fe} \leq 0.3\text{‰}$ , Shahar et al. 2008; Dauphas et al. 2017), although it may also have a low  $\delta^{57}\text{Fe}$  relative to melt depending on the melt Fe<sup>3+</sup> content, and amount of titanium in the crystallising phase (Schuessler, 2008;

Sossi et al., 2012). Consequently, samples that have undergone magnetite fractionation or possible mixing with magnetite-fractionated liquids should be carefully considered in Fe isotope work. The two Terceira samples are therefore not considered further. I note that these samples do not have high  $\delta^{57}\text{Fe}$  and therefore possible (titano-)magnetite saturation is ruled out as contributing to the high  $\delta^{57}\text{Fe}$  in the Azores, and notably all Samoa samples studied plot at higher MgO than magnetite saturation (Fig. 3.4). No Azores samples have  $\text{Ba/Rb} < 9$ , and there is no correlation between  $\delta^{57}\text{Fe}$  and  $\text{Ba/Rb}$  or LOI, which could be indicative of alteration (Fig. 3.3). There is no apparent difference in  $\delta^{57}\text{Fe}$  between different islands.

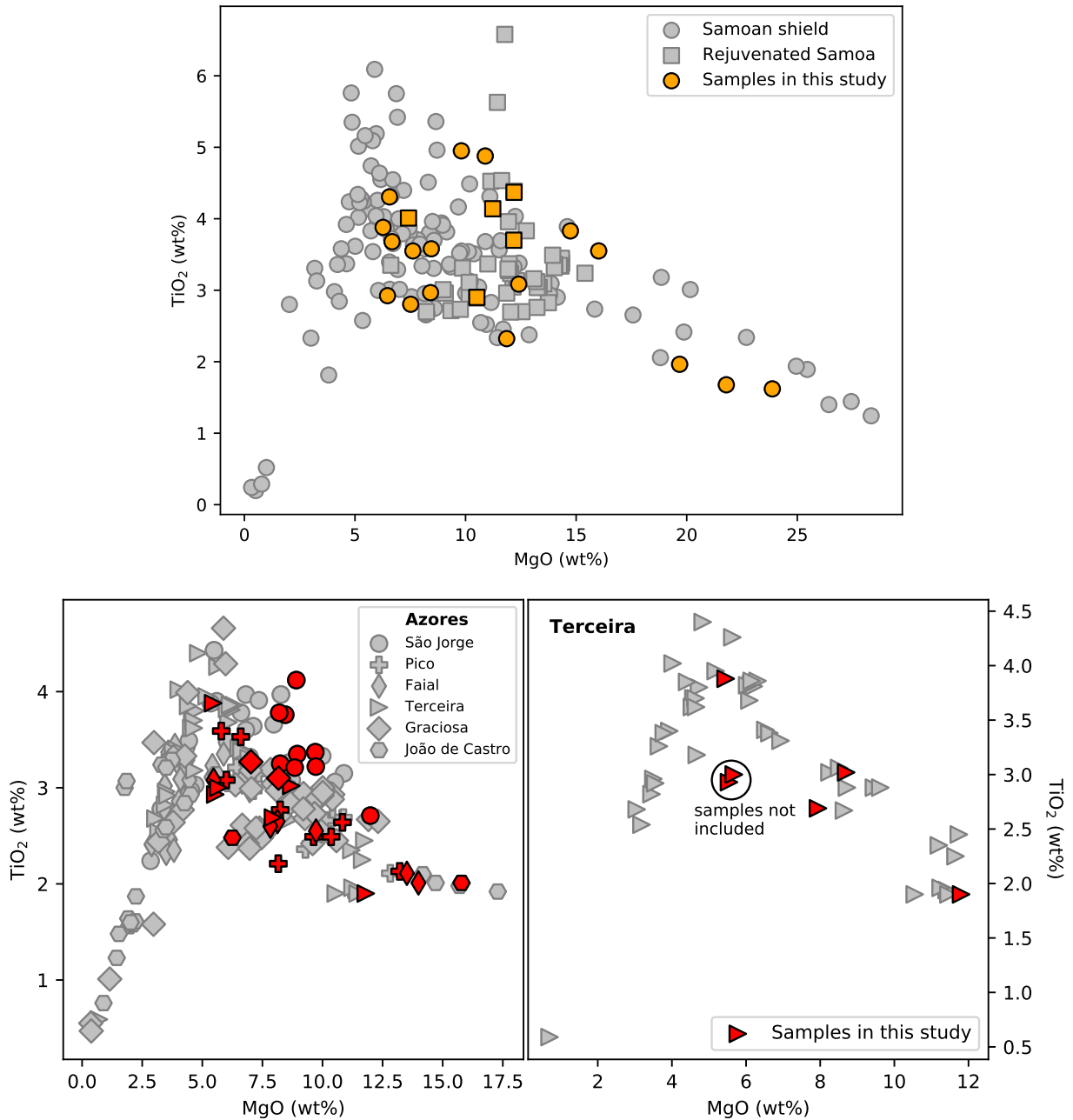
### 3.4 What processes could generate high $\delta^{57}\text{Fe}$ liquids?

Several processes can modify the whole rock  $\delta^{57}\text{Fe}$  from the primary liquid  $\delta^{57}\text{Fe}$ , and the primary liquid  $\delta^{57}\text{Fe}$  from the isotopic composition of ambient peridotite ( $0.03 - 0.05\text{‰}$ ). In this section, I consider how: (1) post-melt emplacement processing (fractional crystallisation, olivine accumulation); (2) partial melting; and (3) pre-melt emplacement considerations of mantle lithological heterogeneity, may contribute to the high  $\delta^{57}\text{Fe}$  ( $\geq 0.20\text{‰}$ ) seen in Samoa and the Azores.

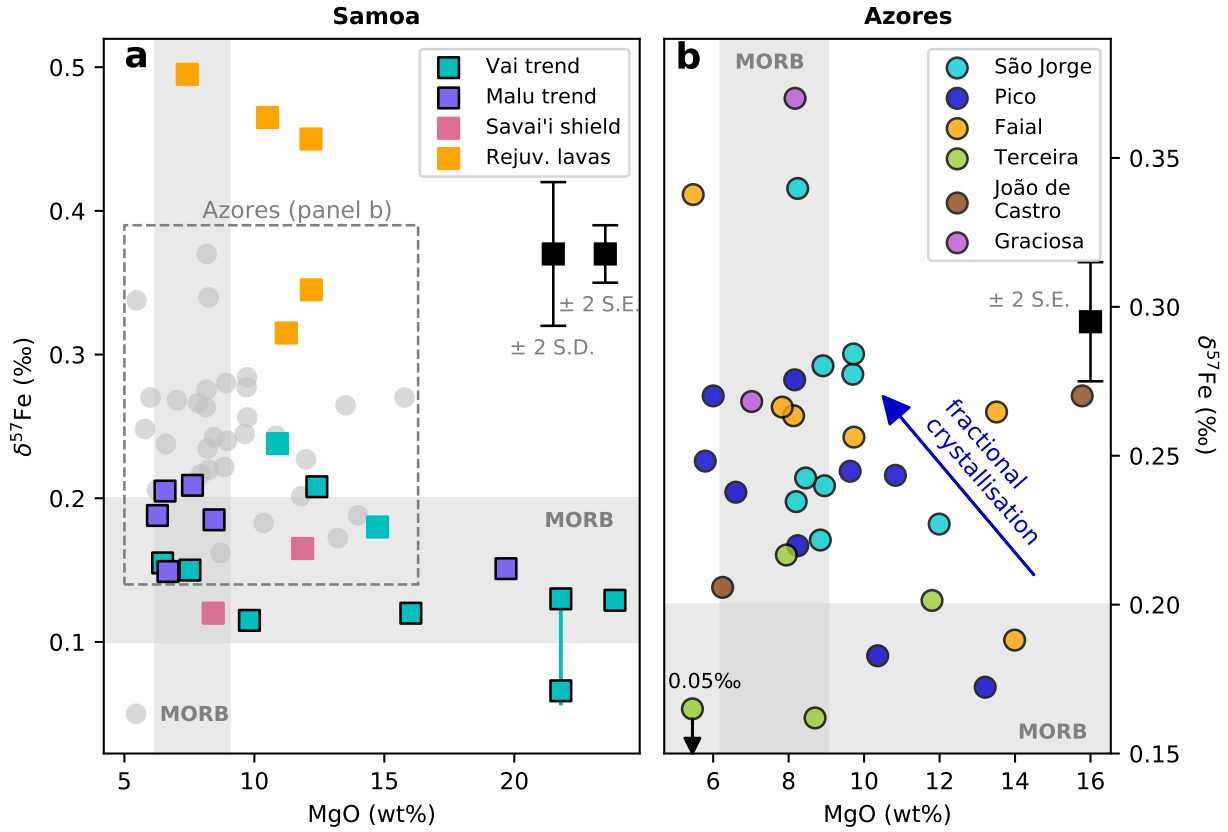
#### 3.4.1 Olivine accumulation and fractional crystallisation

Olivine accumulation is known to produce low whole-rock  $\delta^{57}\text{Fe}$  (Teng et al., 2008; McCoy-West et al., 2018). Olivine accumulation is likely for three Samoan samples measured here, as they have high ( $> 18\text{ wt\%}$ ) MgO content (Fig. 3.5), and petrographic descriptions available for two of the samples confirm a high proportion of olivine (Workman et al., 2004). It is possible to correct for olivine accumulation by modelling the removal of olivine (e.g., McCoy-West et al., 2018), however it is unlikely that the melt has accumulated olivine that is in equilibrium with the final bulk composition which makes the correction hard to use with reliability. Since there is no statistical  $\delta^{57}\text{Fe}$  difference between the high and low MgO shield lavas, the (uncorrected) high MgO samples are included in the following plots.

The removal of low  $\delta^{57}\text{Fe}$  mineral phases (e.g., olivine and pyroxene, both isotopically light relative to melt) by fractional crystallisation is an important control on driving the  $\delta^{57}\text{Fe}$  of residual melts to higher values (e.g., Teng et al., 2008). This isotopic fractionation is thought to be caused by the low  $\text{Fe}^{3+}$  content of olivine and pyroxene relative to silicate melt (Dauphas et al., 2014) and is consistent with the  $\text{MgO}-\delta^{57}\text{Fe}$  trend seen in Pico lavas (Fig. 3.5b). Previous studies have shown that fractional crystallisation corrections can be large ( $\Delta^{57}\text{Fe}$  up to  $-0.15\text{‰}$  for Pitcairn samples; Nebel et al., 2019, with the biggest corrections for the lowest wt% MgO samples), therefore the same correction was performed on samples with  $< 18\text{ wt\%}$  MgO in this dataset. For each sample, equilibrium olivine was incrementally added back into the measured melt composition until



**Figure 3.4:  $\text{TiO}_2$  vs  $\text{MgO}$  for Samoa (top) and Azores (bottom) samples. a)** Grey symbols are published data from Workman et al. (2004); Jackson et al. (2007b); Hart and Jackson (2014); orange symbols highlight samples with  $\delta^{57}\text{Fe}$  measured in this study. There is no difference in  $\text{TiO}_2$  between shield and rejuvenated lavas. **b, c)** Grey symbols are published data from Turner et al. (1997); Beier et al. (2008); Millet et al. (2009); Beier et al. (2012); Béguelin et al. (2017); Waters et al. (2020); red symbols highlight those samples with  $\delta^{57}\text{Fe}$  measured in this study. The Terceira samples are also shown, highlighting the two low  $\text{TiO}_2$  samples not considered in case of mixing with magnetite fractionated melts.



**Figure 3.5: Measured Samoa and Azores Fe isotope data vs whole-rock MgO:** black outlines, data from this study; no outline, data from Konter et al. (2016). At the same MgO content as MORB, the Azores lavas and Samoan rejuvenated lavas are relatively isotopically heavy. Samoan samples with MgO > 18 wt % that have accumulated olivine show no resolvable Fe isotopic difference from lower MgO samples. Some Azores volcanoes (Pico, Faial) show evidence for fractional crystallisation trends. Shaded region is average MORB ( $\delta^{57}\text{Fe}$  from Teng et al., 2013; MgO from range of ‘ALL MORB’ from Gale et al., 2013a). Errorbars show average long term 2 S.D. and average 2 S.E. on repeat measurements; duplicate dissolutions of the same sample linked by a vertical line.

the liquid was in equilibrium with  $\text{Fo}_{90}$  olivine. Given the MgO range of Samoa and Azores samples, and minor clinopyroxene noted in petrographic descriptions where available (Workman et al., 2004), pyroxene likely crystallised from these melts (e.g., Beier et al., 2012). However, pyroxene–melt fractionation is expected to be smaller than olivine–melt fractionation (Macris et al., 2015) due to the differing Fe bonding environment in olivine and pyroxene, although the fractionation is poorly constrained. Therefore, only olivine crystallisation is corrected for, which provides an upper limit on the fractional crystallisation correction.

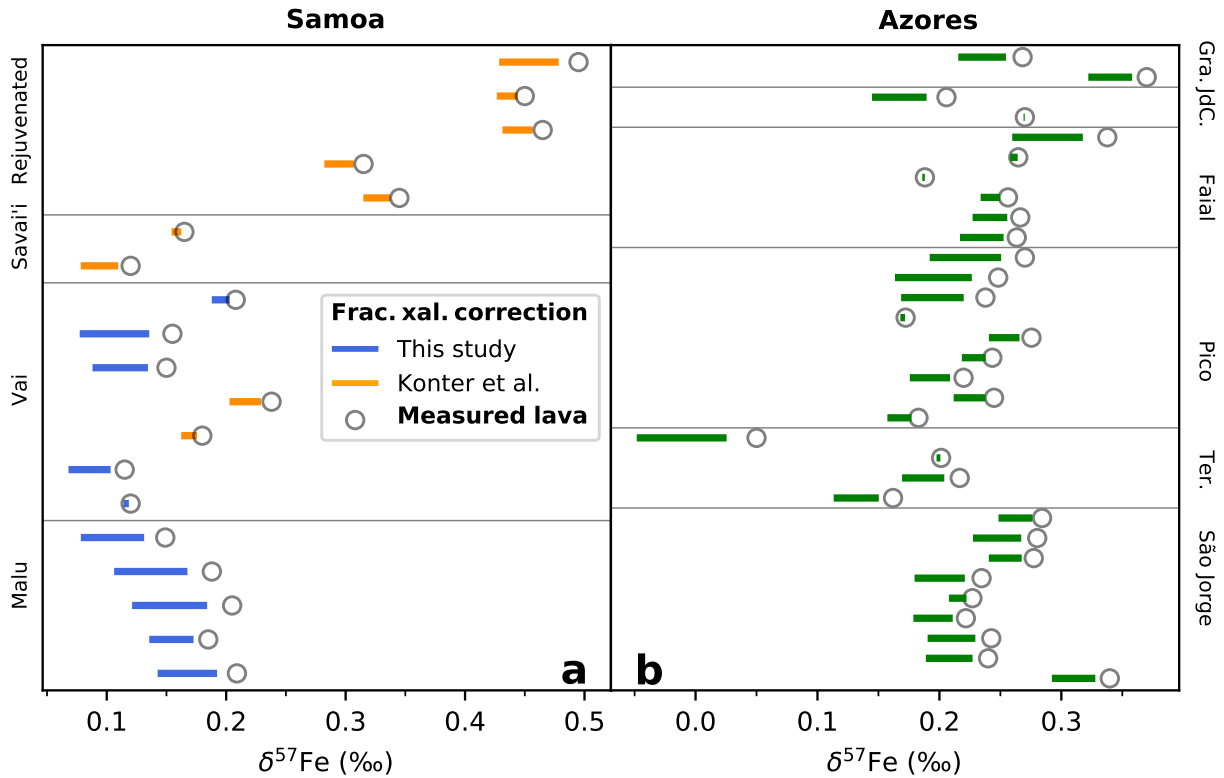
The olivine–melt fractionation factor ( $\Delta^{57}\text{Fe}_{\text{olivine–melt}}$ ) generates significant uncertainty in the fractional crystallisation correction used by Sossi et al. (2016) and Nebel et al. (2019). The fractionation factor can be calculated using either experimental or theoretical force constants for the relevant phases

$$\Delta^{57/54}\text{Fe}_{\text{ol–melt}} = 4284 \frac{K_{\text{ol}} - K_{\text{melt}}}{T^2}, \quad (3.1)$$

where  $K_i$  is the Fe–O force constant in phase  $i$  (Sossi and O’Neill, 2017). The force constants for olivine and basaltic melt are 197 and  $220 \pm 10$  N/m respectively (Dauphas et al., 2014; us-

ing basaltic glass as a proxy for melt and assuming melt  $\text{Fe}^{3+}/\text{Fe}_T = 0.15$ ). Using equation 3.1 gives  $\Delta^{57}\text{Fe}_{\text{ol-melt}} \approx -0.1 \times 10^6/T^2$ , producing  $\Delta^{57}\text{Fe}$  corrections of  $0.00 - 0.02\text{‰}$  for the Samoan dataset, which is less than the internal precision of sample analyses. Considering a more oxidised melt (up to  $\text{Fe}^{3+}/\text{Fe}_T = 0.3$ ), and allowing for uncertainties in the olivine force constant,  $\Delta^{57}\text{Fe}_{\text{ol-melt}}$  could increase to  $-0.3 \times 10^6/T^2$ . Nebel et al. (2019) use  $\Delta^{57}\text{Fe}_{\text{ol-melt}} = -0.4 \times 10^6/T^2$  for Pitcairn samples (corresponding to  $\Delta^{57}\text{Fe}_{\text{ol-melt}}$  of  $-0.15 - -0.2\text{‰}$  at magmatic temperatures): using this value gives maximum fractional crystallisation corrections of  $\Delta^{57}\text{Fe} = -0.08\text{‰}$  for the Samoan shield samples, and  $\Delta^{57}\text{Fe} = -0.05\text{‰}$  for the Azores samples.

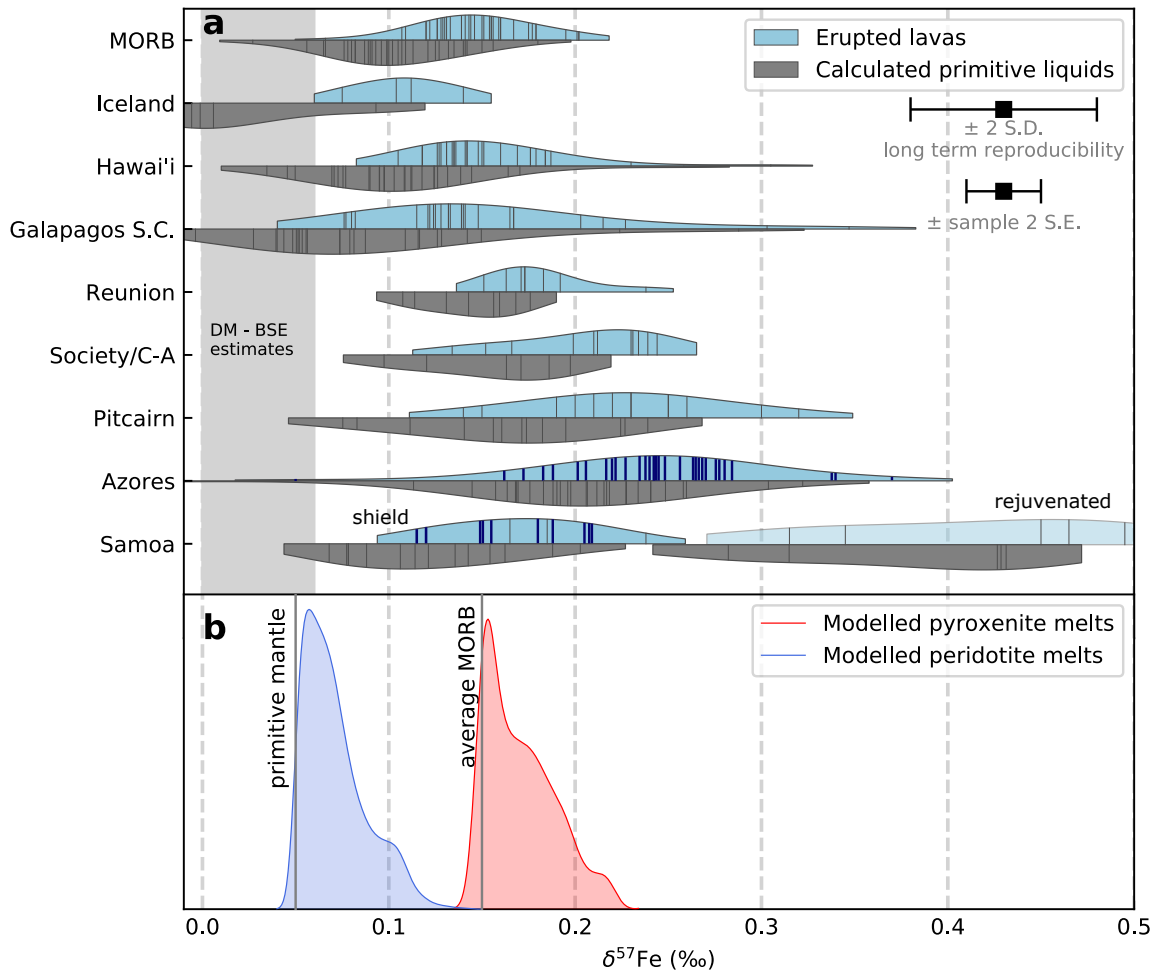
Fig. 3.6 shows how the magnitude of the fractional crystallisation correction varies with the value of  $\Delta^{57}\text{Fe}_{\text{ol-melt}}$ , from  $-0.1 \times 10^6/T^2$  to  $-0.4 \times 10^6/T^2$ . Since I am interested in the heavy Fe isotope signatures, I use the largest fractional crystallisation correction, even though this may be overcorrecting the data. The correction therefore represents an upper limit on  $\Delta^{57}\text{Fe}$  during fractional crystallisation, which will be conservative from the perspective of diminishing as much high  $\delta^{57}\text{Fe}$  enrichment that is observed as possible.



**Figure 3.6: Fractional crystallisation correction following Nebel et al. (2019) and Sossi et al. (2016).** The coloured bars show the magnitude of the correction for values of  $\Delta^{57}\text{Fe}_{\text{ol-melt}} = -0.1 \times 10^6/T^2 - -0.4 \times 10^6/T^2$ . Using the smaller correction gives corrected values that are unresolvable from the internal precision of the data collected in this study. Uncorrected data shown in outline for comparison. Samples with  $\text{MgO} > 18\text{ wt\%}$  were not corrected and are not shown. Abbreviations: ‘Gra.’: Graciosa; ‘JdC.’: João de Castro; ‘Ter.’: Terceira.

This calculation has been applied to all the MORB and OIB data shown in Fig. 3.7a. After accounting for the processes of olivine accumulation and fractional crystallisation, the Samoan

and Azores datasets still show heavy Fe isotopic compositions relative to MORB (Figs. 3.6, 3.7), which must then be a mantle source-derived signal.



**Figure 3.7: a) Compilation of kernel density plots of OIB and MORB Fe isotope data**, with each vertical line a sample (bold lines are samples measured in this study). OIB data filtered to only include samples with 5–16 wt% MgO; top errorbar shows long term reproducibility 2 S.D. on  $\delta^{57}\text{Fe}$  of standards run at the University of Cambridge. Samoan rejuvenated lavas record the highest  $\delta^{57}\text{Fe}$  in the global dataset, whereas the Samoan shield dataset is indistinguishable from MORB. The Azores show the isotopically heaviest lavas after Samoan rejuvenated lavas. Only normal (N-MORB) and transitional (T-MORB) class MORB data is shown, following the classification by Teng et al., 2013. Data sources: MORB, Teng et al. (2013); Pitcairn, Nebel et al. (2019); Iceland, Schuessler et al. (2009); La Réunion, Peters et al. (2019); Society and Cook-Austral, Teng et al. (2013); Galápagos Spreading Centre, Gleeson et al. (2020); Hawai'i, Teng et al. (2008, 2013); Samoa, Konter et al. (2016), this study; Azores, this study. Fractional crystallisation correction shows liquids calculated to be in equilibrium with Fo<sub>90</sub> olivine, described in section 3.4.1. Shaded region shows range of estimates, including quoted errors, for depleted mantle, DM (Craddock et al., 2013; Johnson et al., 2020) and Bulk Silicate Earth, BSE (Sossi et al., 2016). **b)** Model results of compositions of melts of a peridotite (KLB1) and pyroxenite (G2) lithology, discussed in section 3.4.2.1. Primitive mantle estimate of  $\delta^{57}\text{Fe} = 0.05\text{‰}$  (Sossi et al., 2016) is shown.

### 3.4.2 Heterogeneity derived from the mantle

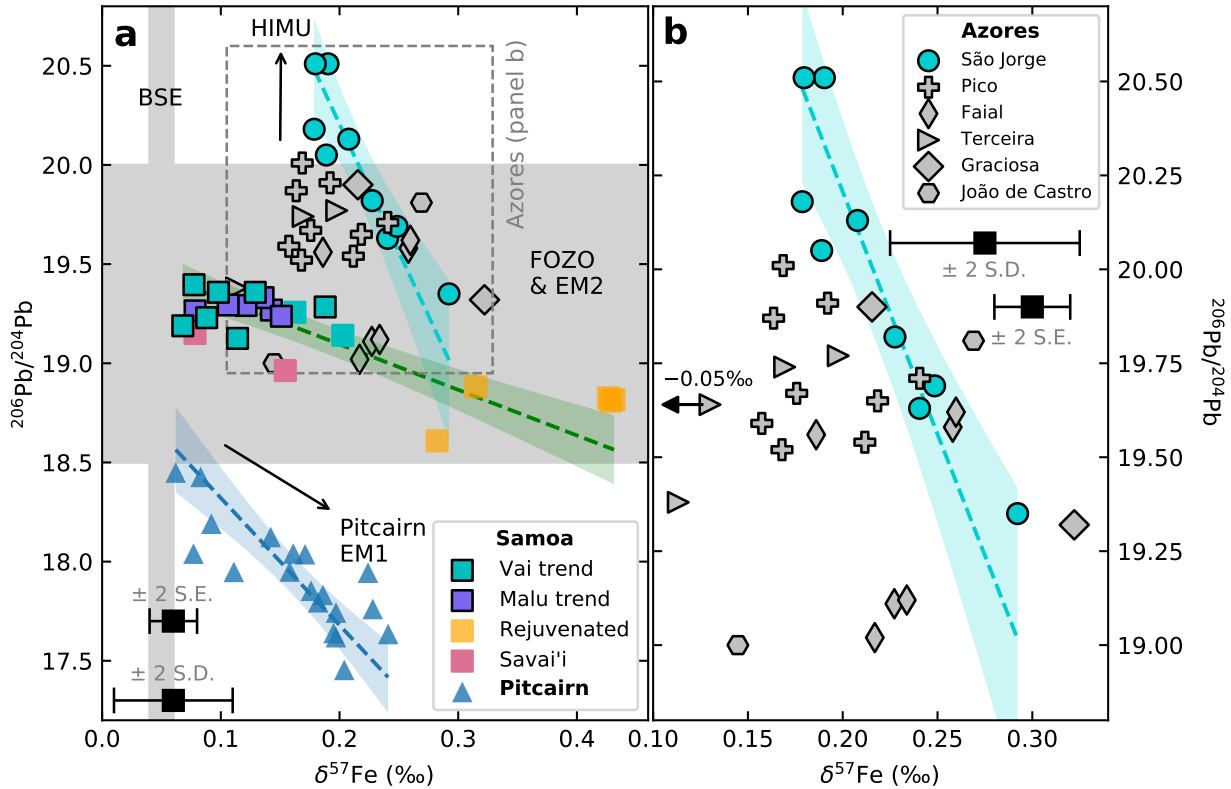
Variability in the Fe isotopic composition of primary mantle melts could be the result of partial melting and/or heterogeneous mantle domains. Mantle heterogeneity is well-studied in the Samoa, Pitcairn and Azores plumes, with different mantle components well-characterised in radiogenic isotope space (Eisele et al., 2002; Jackson et al., 2014; Beier et al., 2018; Waters et al., 2020; Fig. 3.1). Differences in mantle mineralogy associated with these components may account for variations in Fe isotope composition (Williams and Bizimis, 2014; Konter et al., 2016), as suggested for Pitcairn, where a negative Fe–Pb correlation is interpreted as mixing between a FOZO-like peridotite and an EM1, high  $\delta^{57}\text{Fe}$  pyroxenite (Nebel et al., 2019; Fig. 3.8). In Samoa, the distinct populations of shield and rejuvenated lavas also form a negative  $\delta^{57}\text{Fe}$ – $^{206}\text{Pb}/^{204}\text{Pb}$  array (Fig. 3.8); the high  $\delta^{57}\text{Fe}$  endmember is associated with the less radiogenic Pb component. Although the Azores data as a whole show no Fe–Pb correlation, despite Pb isotopic variability, the island of São Jorge does display a statistically significant correlation distinguishable with external 2 S.D. precision on each sample. However, while I note that the São Jorge samples with the more radiogenic Pb isotopic signature do not show the highest  $\delta^{57}\text{Fe}$  (Fig. 3.8), the spread of  $\delta^{57}\text{Fe}$  in São Jorge is small, so a link between the Pb isotopes and high  $\delta^{57}\text{Fe}$  may be largely masked by analytical precision in this case.

All three plumes produce melts that have higher  $\delta^{57}\text{Fe}$  than MORB, and show Pb isotopic variability reflecting different components in the mantle source. The likely dominant endmember lithologies responsible for mantle heterogeneity are peridotite (anhydrous or volatile-rich) and pyroxenite derived from recycled oceanic crust (section 3.1). Therefore, I first examine whether melting of these endmember lithologies can generate the high  $\delta^{57}\text{Fe}$  seen in Samoa, Pitcairn and the Azores.

#### 3.4.2.1 Iron isotope fractionation by peridotite melting

First, I consider the contribution of anhydrous peridotite melting to the generation of heavy Fe isotopic signatures in OIB. To estimate the heaviest Fe isotopic composition of melts generated from single-stage melting of mantle peridotite, I use the combined phase equilibria and isotope fractionation model as outlined in chapter 2, which contained the KLB1 and G2 lithologies at the time.

The KLB1 pseudosection, showing equilibrium phase assemblages, and melt  $\delta^{57}\text{Fe}$  fractionation results (reported as  $\Delta^{57}\text{Fe} = \delta^{57}\text{Fe}_{\text{melt}} - \delta^{57}\text{Fe}_{\text{bulk}}$ ) are shown in Fig. 3.11a & c. The maximum partial melting fractionation is small ( $\Delta^{57}\text{Fe} = 0.07\text{‰}$ ), consistent with estimates from previous studies of  $\Delta^{57}\text{Fe}$  (0.07–0.11 ‰; Dauphas et al., 2009; Williams and Bizimis, 2014; Sossi et al., 2016; Gleeson et al., 2020). Superimposing this melting fractionation onto the bulk BSE  $\delta^{57}\text{Fe}$  (0.05 ‰; Sossi et al., 2016) generates insufficiently isotopically heavy melts to explain many of

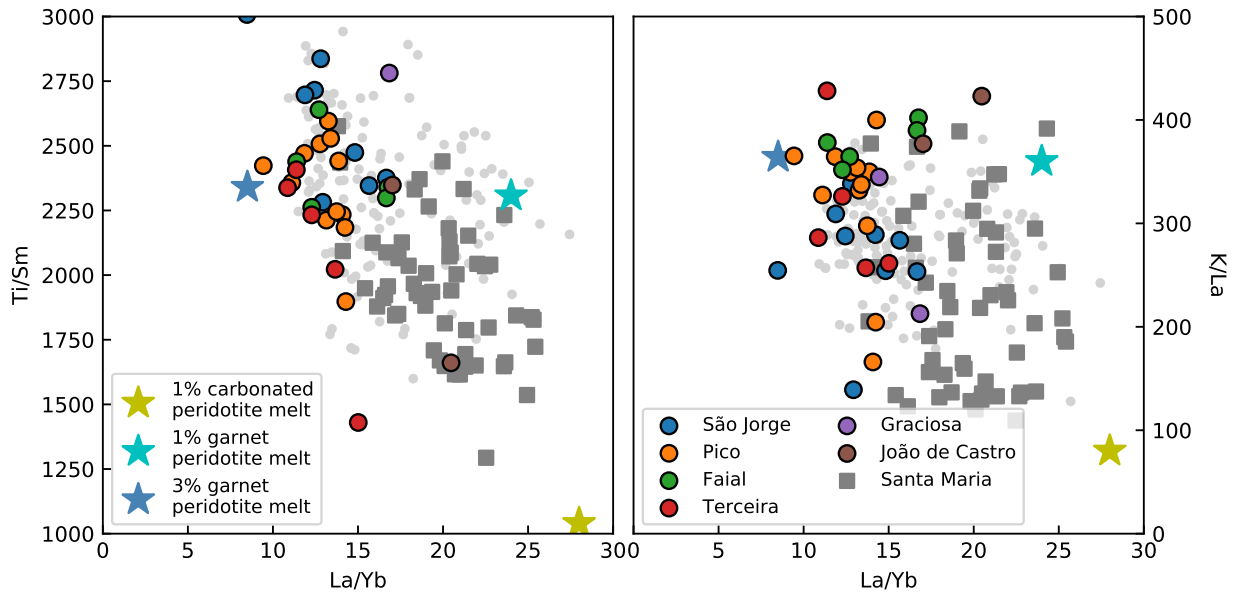


**Figure 3.8: Lead and Fe isotopic variability in the Samoan, Azores and Pitcairn plumes.** Data shown have been corrected for fractional crystallisation (section 3.4.1). Black outlines indicate iron isotope measurement in this study; no outline indicates published iron isotope data (Samoa, Konter et al., 2016; Pitcairn, Nebel et al., 2019). The plumes show negative arrays with high  $\delta^{57}\text{Fe}$  components also having less radiogenic Pb isotopic compositions within each array: orthogonal distance regression lines and  $2\sigma$  confidence bands for Pitcairn, Samoa, and São Jorge are shown, calculated by weighting each data point with the sample 2 S.D. if known, or the long term 2 S.D. whichever is greater, as errors on  $\delta^{57}\text{Fe}$ .

the fractional-crystallisation-corrected OIB data. Some MORB also show higher  $\delta^{57}\text{Fe}$  than would be expected for melting of homogeneous peridotite.

*Role of carbonated peridotite melting:* Small-degree (carbonatite) melts from a carbonated peridotite mantle have been proposed to explain geochemical variability in Azores lavas (Beier et al., 2013), and carbonatite metasomatism has been proposed to explain trace element data in peridotite xenoliths from Savai'i (Hauri et al., 1993). It is important to consider the role of carbonatite melts in generating high  $\delta^{57}\text{Fe}$  lavas because, although carbonatites in equilibrium with silicate mantle are predicted to have  $\delta^{57}\text{Fe} < -0.45\text{‰}$ , some measured intrusive carbonatites extend up to  $\delta^{57}\text{Fe} = 1.2\text{‰}$  (Johnson et al., 2010). Some of these heavy isotopic compositions are attributed to the addition of a high  $\delta^{57}\text{Fe}$  ( $\text{Fe}^{3+}$  rich) fluid at the edges of a carbonatite intrusion in the upper crust (generating isotopic compositions of  $\delta^{57}\text{Fe} \lesssim 0.6\text{‰}$ ), and other disequilibrium processes including phenocryst mixing, although the complete process of generation of the measured high  $\delta^{57}\text{Fe}$  in carbonatites relevant to OIB lavas is unclear.

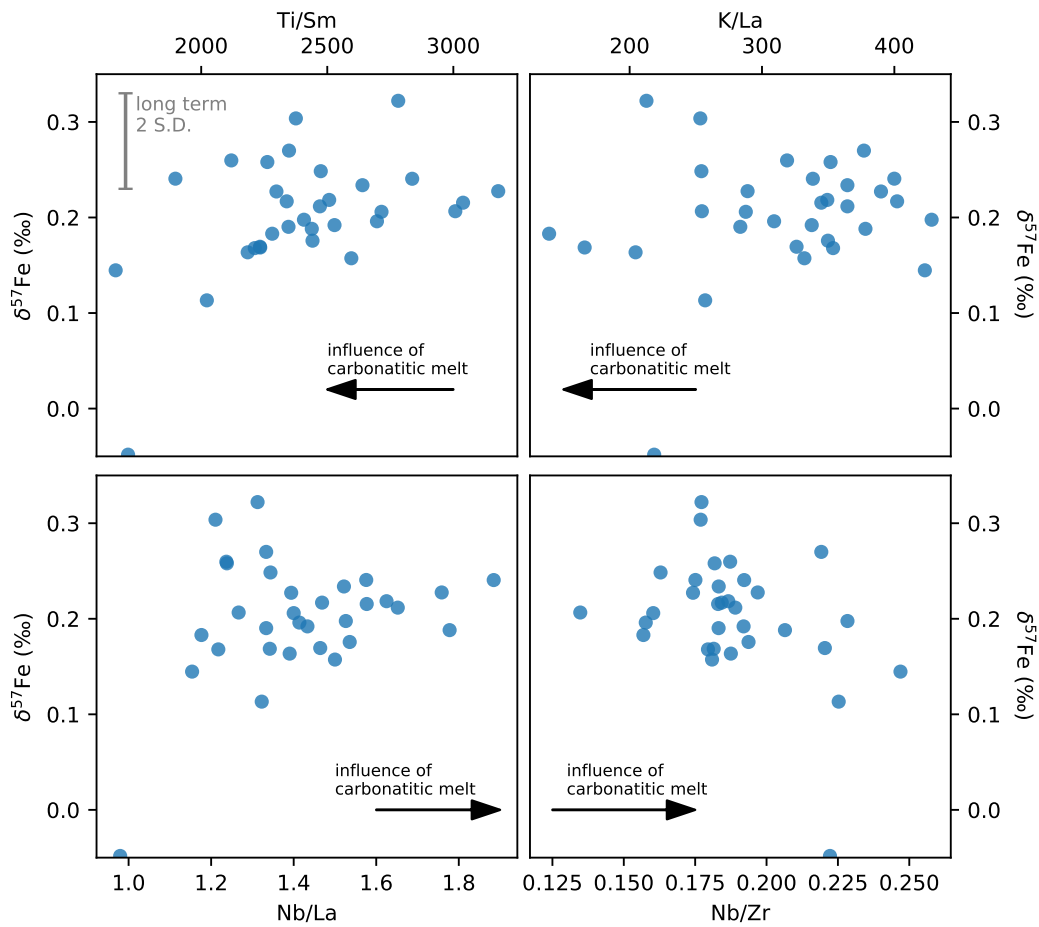
Carbonated peridotite melts can be identified by their fractionation of trace and major element ratios, including Nb/La, Ti/Sm and K/La (Cottrell and Kelley, 2013; Beier et al., 2013) relative



**Figure 3.9: Published Ti/Sm and K/La vs La/Yb for Azores samples measured in this study** (coloured circles, filtered for those  $> 5.5$  wt% MgO) compared to Santa Maria (Beier et al., 2013), an Azores volcano thought to sample a carbonated peridotite source. Compilation of Azores volcanoes, published by Béguelin et al. (2017), shown in small pale grey circles for reference. The coloured stars show modelled melts from carbonated and garnet peridotite sources calculated in Beier et al. (2013), highlighting the low Ti/Sm and K/La expected from carbonated peridotite melts.

to anhydrous peridotite melts. The Azores volcano of Santa Maria has been proposed to require at least 20 % of a 1 % carbonated peridotite melt in its source based on Ti/Sm and K/La (Beier et al., 2013), however the other volcanoes that are sampled in this study do not show evidence for a carbonated peridotite component in the source (Fig. 3.9). Consistent with a lack of significant carbonated peridotite component, the measured  $\delta^{57}\text{Fe}$  show no correlations with proposed tracers of carbonatite melt from Cottrell and Kelley (2013); Beier et al. (2013); Fig. 3.10.

Beier et al. (2013) suggest that the low Ti/Sm and K/La signature of carbonatite will be obscured by the contribution from peridotitic melts if the contribution of carbonatite in the final melt is  $< 20$  %, or the anhydrous ambient peridotite undergoes  $> 4$  % partial melting. By mass balance, with (1) 20% carbonatite; (2) equal proportions of Fe in carbonated peridotite melts and anhydrous peridotite melts (Dasgupta et al., 2009); and (3) volatile-free peridotite  $\delta^{57}\text{Fe} = 0.05$  ‰ (Sossi et al., 2016), producing an average fractional-crystallisation-corrected  $\delta^{57}\text{Fe}$  for Azores lavas of  $0.20$  ‰ requires  $\delta^{57}\text{Fe}_{\text{carbonatite}} = 0.8$  ‰. If the carbonatite contribution is 10 %, the required  $\delta^{57}\text{Fe}_{\text{carbonatite}} = 1.55$  ‰. While the lightest of these hypothetical carbonatite compositions are consistent with some measured intrusive carbonatites, in general carbonatite lavas show significantly lower  $\delta^{57}\text{Fe}$  compositions (Johnson et al., 2010). Therefore, it seems unlikely that carbonatite melts are contributing to the high  $\delta^{57}\text{Fe}$  in Azores lavas, despite the possible presence of a carbonated peridotite lithology in their source region (Beier et al., 2013).



**Figure 3.10: Primary  $\delta^{57}\text{Fe}$  in Azores lavas (corrected for fractional crystallisation) show no relationship to tracers of carbonatite melts in their source region.** Major and trace element data from Turner et al. (1997); Beier et al. (2008); Millet et al. (2009); Beier et al. (2012); Béguelin et al. (2017); Waters et al. (2020).

### 3.4.2.2 Iron isotope fractionation by pyroxenite melting

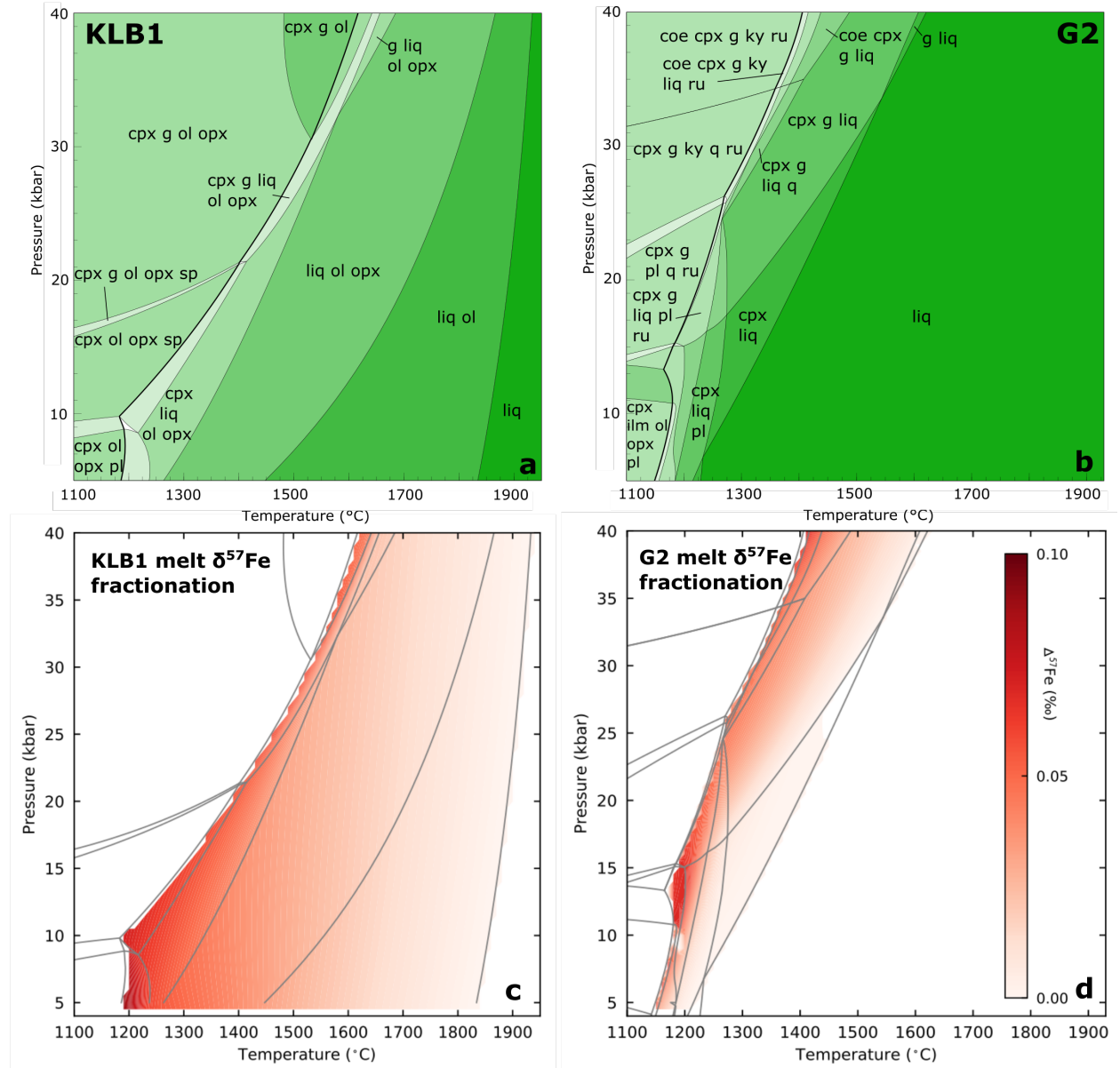
Given that pure peridotite melts cannot account for high  $\delta^{57}\text{Fe}$  in Samoa, Pitcairn and the Azores, I now consider the effect of using a pyroxenite lithology on  $\Delta^{57}\text{Fe}$  during partial melting. I follow Lambart et al. (2016) in using the term pyroxenite to refer to pyroxene-rich rocks with insufficient olivine ( $< 40\%$ ) to be considered peridotites (Le Maitre et al., 2005). There are a number of recorded natural pyroxenite compositions, but it is unclear which pyroxenite types may best explain global Fe isotopic variability. Natural pyroxenites can be broadly separated into two types: silica-deficient (SD) and silica-excess (SE); producing distinct partial melt compositions (Kogiso et al., 2004; Lambart et al., 2016). Most previously studied pyroxenites are SD type; those that are MgO-rich are thought to be cumulates produced by the fractional crystallisation of peridotite partial melts (Gonzaga et al., 2010; Lambart et al., 2016). Following Lambart et al. (2016), eclogites (from recycled oceanic crust or sediment) and pyroxenites produced from hybridisation between silica-rich eclogite melts and peridotite (Sobolev et al., 2005) are SE type. Previous studies have proposed that the pyroxenitic component in the OIB mantle source may be formed by this hybridisation process (e.g., Sobolev et al., 2005, 2007; Nebel et al., 2019), therefore I consider the melting of SE eclogitic pyroxenite first. Lithospheric pyroxenites with a cumulate origin, possibly through multi-stage processes, are discussed in section 3.5.4.

The G2 composition (Table 2.4), an important MORB-like bulk composition in melting experiments and models from Pertermann and Hirschmann (2003a,b) and Lambart et al. (2016), is a low MgO quartz eclogite and a SE pyroxenite endmember (Lambart et al., 2016). This eclogitic pyroxenite composition should have a higher bulk  $\delta^{57}\text{Fe}$  composition than peridotite, at least as heavy as mean MORB (section 3.4.2.3). The G2 equilibrium phase assemblage was modelled as outlined in chapter 2 (Figs. 2.6, 3.11b) to give the partial melting  $\delta^{57}\text{Fe}$  fractionation over P-T space (Fig. 3.11d).

The maximum calculated partial melting fractionation for G2 is small ( $\Delta^{57}\text{Fe} = 0.07\text{‰}$ ) and similar compared to that of KLB1, although the P-T distribution of melt compositions is different owing to the different melting behaviours of the two lithologies. Iron isotope fractionation during partial melting of individual endmember lithologies alone cannot explain the range in  $\delta^{57}\text{Fe}$  observed for OIB. Therefore, I consider the role of bulk  $\delta^{57}\text{Fe}$  enriched mantle compositions in producing the observed  $\delta^{57}\text{Fe}$  of melts from a two lithology mantle.

### 3.4.2.3 Effect of bulk $\delta^{57}\text{Fe}$ compositions of peridotite and pyroxenite

The pyroxenite bulk  $\delta^{57}\text{Fe}$  is not expected to be the same as that of peridotite (e.g., Williams and Bizimis, 2014; Konter et al., 2016). For eclogitic G2 pyroxenite, which was chosen to be similar in major element chemistry to average modern oceanic crust (Pertermann and Hirschmann, 2003a), my initial assumption of starting Fe isotopic composition is that of average MORB ( $\delta^{57}\text{Fe}$



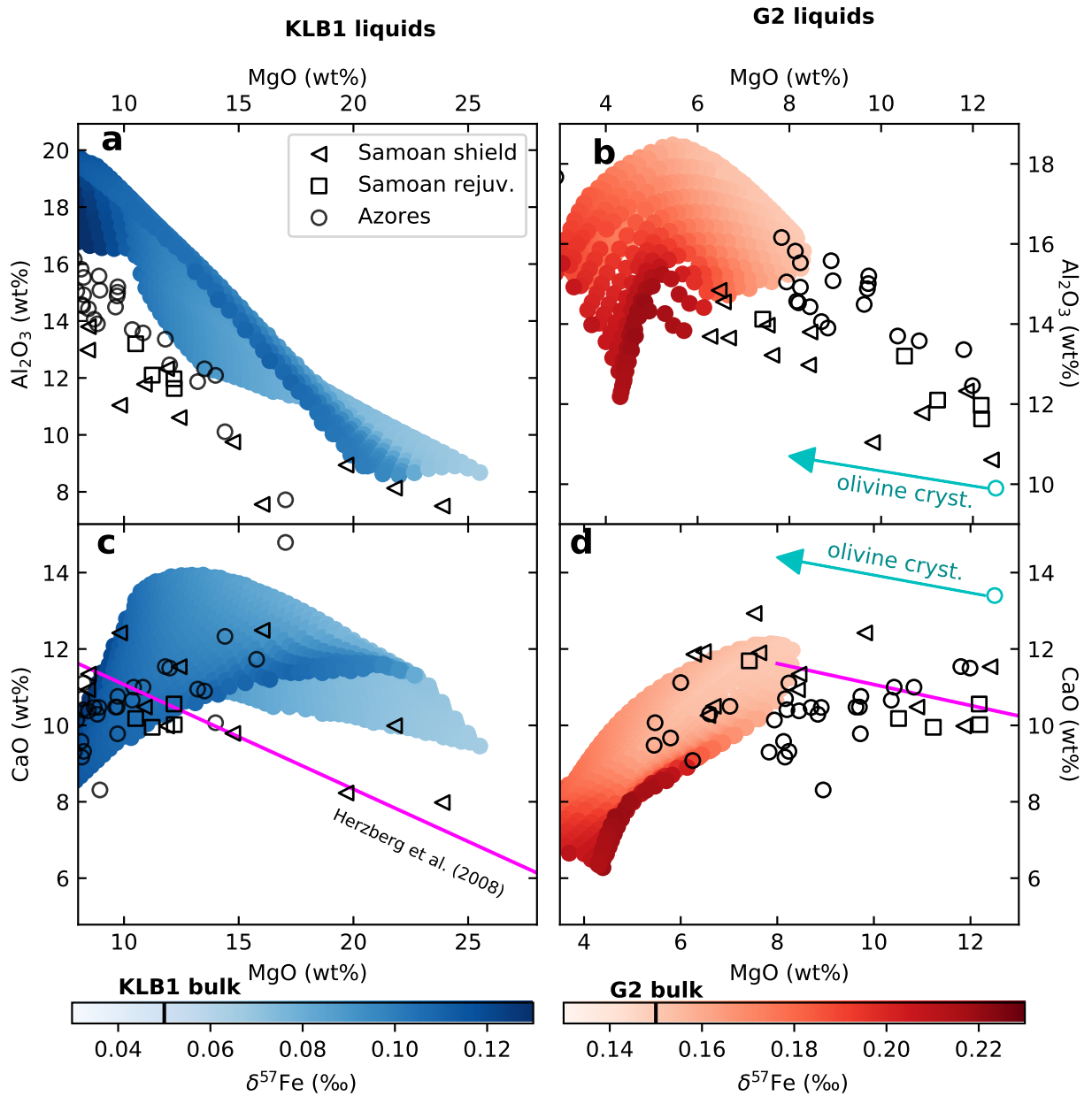
**Figure 3.11: Results of the combined phase equilibria and isotope fractionation model for KLB1 and G2 lithologies. a, b)** The stable mineral phases calculated using THERMOCALC, with the solidus highlighted in bold. **c, d)** The calculated partial melting fractionation from the pseudosections in **a** and **b**. The magnitude of the maximum partial melting Fe isotopic fractionation,  $\Delta^{57}\text{Fe}$ , is small and independent of the bulk composition used.

= 0.15 ‰; Teng et al., 2013; Williams and Bizimis, 2014), although the effect of subduction and eclogite formation during high P, low T metamorphism is poorly understood (section 3.5.2.1).

The model results (Fig. 3.7) show that, based on this assumed G2 starting composition and single-stage melting of each lithology, mixed peridotite and eclogitic pyroxenite melts span the Fe isotope range of Samoan shield and some Azores melts. However, the isotopically heaviest of the Samoan and Azores melts ( $\delta^{57}\text{Fe} > 0.2$  ‰) require that they are almost pure pyroxenite melts. Although melts derived from a dominantly or exclusively pyroxenitic source have been proposed for Hawai'i based on olivine compositions (Sobolev et al., 2005; Herzberg, 2011), a pure pyroxenite source is generally incompatible with other global OIB (e.g., Dasgupta et al., 2010; Herzberg, 2011) and is not supported by the major element compositions of the measured Samoan and Azores lavas relative to the model liquids (Fig. 3.12). The isotopically heaviest modelled pyroxenite melts are produced at low-degrees of melting, 13–14 kbar ( $\sim 50$  km depth) and  $\sim 1200$  °C (Fig. 3.11c & d). Plume geotherms are unlikely to intersect this part of the melting region, e.g., Azores melts are thought to form at  $> 1400$  °C and  $> 25$  kbar (Beier et al., 2012); Samoa melts at  $> 1600$  °C and  $> 30$  kbar (Putirka et al., 2018). Moreover, mixing between pyroxenite and peridotite melts would be expected upon ascent in the mantle, even if pyroxenite melts first (Lambart et al., 2016). Therefore, pure, high  $\delta^{57}\text{Fe}$  eclogitic pyroxenite melts are unlikely.

I also note that a contribution to a peridotite-dominated melt from an eclogitic pyroxenite melt could explain why average MORB, after correction for fractional crystallisation, sits at the higher end of predicted KLB1 melt  $\delta^{57}\text{Fe}$  compositions. An enriched, fertile lithology has been proposed previously to be a small, ubiquitously distributed component of the MORB source, to balance depleted components seen in abyssal peridotites (Salters and Dick, 2002; Byerly and Lassiter, 2014) and the garnet signature seen in trace elements in MORB (Hirschmann and Stolper, 1996). The Fe isotope data would be consistent with this enriched component being a refertilised peridotite (i.e., still an olivine-bearing lithology, but with more clinopyroxene than depleted mantle and a slightly elevated bulk  $\delta^{57}\text{Fe}$ ), or even a pyroxenite to match the highest MORB  $\delta^{57}\text{Fe}$  compositions. Sun et al. (2020) record MORB glass samples from EPR seamounts with  $\delta^{56}\text{Fe} \leq 0.36$  ‰ ( $\delta^{57}\text{Fe} \leq 0.54$  ‰), where the high Fe isotope variability relative to average MORB is suggested to relate to limited melt mixing with ambient mantle in the seamounts compared to the ridge axis. The high  $\delta^{57}\text{Fe}$  compositions are attributed to garnet pyroxenite veins in recycled, metasomatised oceanic lithosphere, processes which are discussed further in section 3.5.4.

The modelled major element chemistry could be made more consistent with the Samoa and Azores lavas by changing the type of pyroxenite: SD pyroxenites, such as MIX1G (a composition resembling average natural SD pyroxenites, produced by mixing MORB with peridotite), produce melts with  $\text{Al}_2\text{O}_3$  that overlap more OIB compositions than G2 (Hirschmann et al., 2003; Kogiso et al., 2003). In agreement with this hypothesis, mixing the modelled KLB1 and G2 melts in Fig. 3.12 could produce melts that cover more of the OIB major element compositions than each individual lithology. However, the results of the MIX1G lithology subsequently added to



**Figure 3.12: Comparison of modelled melt major element compositions with measured Samoa and Azores lavas.** Coloured circles show the compositions of KLB1 (left) and G2 (right) melts produced in the model, coloured for  $\delta^{57}\text{Fe}$  (KLB1 melts filtered for melt fraction < 30 % to give a realistic MgO range). Samoa and Azores lavas are superimposed. Although pure pyroxenite melts are implied by the Fe isotopic composition, observed lava compositions are not consistent with pure pyroxenite melts. Pink line shows the separation of accumulated fractional melts from pyroxenite and peridotite source melts in CaO-MgO space from Herzberg and Asimow (2008) — peridotite source melts mostly plot above the line, pyroxenite melts mostly below. An example vector of melts related by olivine fractional crystallisation is shown.

the model show that the maximum isotopic fractionation generated during melting of MIX1G is indistinguishable from that of G2 (see chapter 4).

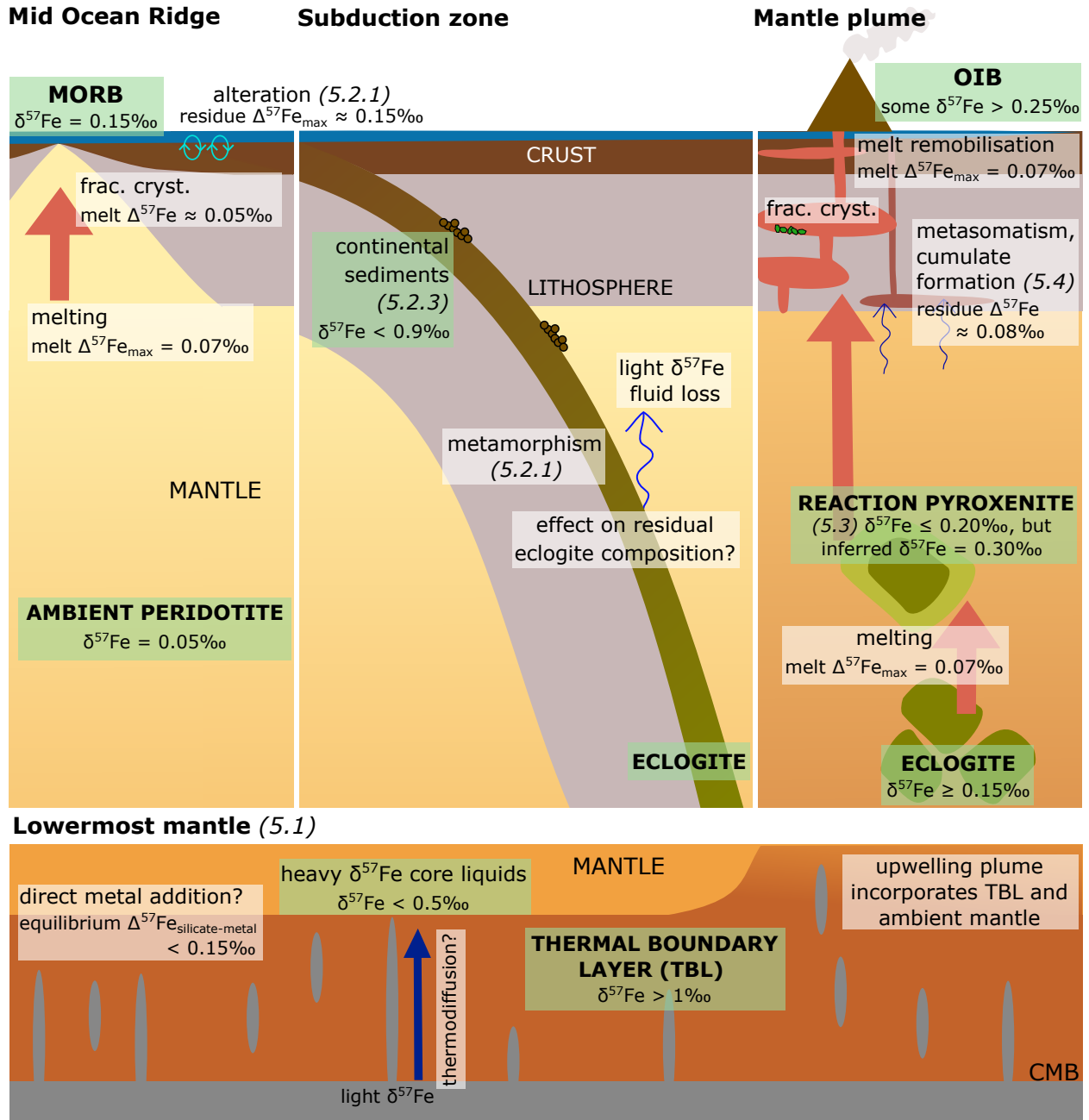
The isotopically heaviest Samoan shield and Azores melts, and all rejuvenated Samoan melts, are isotopically heavier than those produced from plausible conditions of a single-stage mixed peridotite–pyroxenite melting model.

## 3.5 How to generate high $\delta^{57}\text{Fe}$ mantle components?

The inability of a simple peridotite–eclogitic pyroxenite melting model (section 3.4.2.3) to generate the high  $\delta^{57}\text{Fe}$  of Samoa, Pitcairn and Azores melts means that pre-final melt emplacement processes (i.e., processes affecting the source  $\delta^{57}\text{Fe}$  composition) must be considered. After core contributions, I sequentially consider processes operating from a mid-ocean ridge setting, through subduction, to upwelling and melting in a mantle plume (summarised in Fig. 3.13).

### 3.5.1 Is high $\delta^{57}\text{Fe}$ a core component?

Many OIB are suggested to entrain lower mantle material. Short-lived radiogenic isotope systems and noble gases support that some OIB have incorporated small amounts of primordial, less-degassed mantle material from the first 0.5 Ga of Earth’s history, and/or core-equilibrated liquids, possibly stored near the CMB (e.g., Mukhopadhyay, 2012; Mundl et al., 2017; Peters et al., 2018; Rizo et al., 2019; Mundl-Petermeier et al., 2019, 2020). Calculated equilibrium silicate-metal fractionation factors at high pressures and temperatures are small ( $\Delta^{57}\text{Fe}_{\text{silicate-metal}} \lesssim 0.15\text{‰}$ ; Polyakov, 2009; Shahar et al., 2016; Liu et al., 2017c). Given that W and He isotope data support  $< 0.3\text{‰}$  core-equilibrated material in OIB (Mundl-Petermeier et al., 2020), this small equilibrium fractionation is unlikely to contribute to high  $\delta^{57}\text{Fe}$  in OIB. However, it has been proposed (Leshner et al., 2020) that high  $\delta^{57}\text{Fe}$  in OIB could be generated by the incorporation of a kinetically-fractionated high  $\delta^{57}\text{Fe}$  liquid iron and silicate layer from the lowermost mantle into an upwelling plume (Fig. 3.15). In this model, isotopic fractionation occurs by thermodiffusion (Soret diffusion), due to the relative motion of heavy and light isotopes in a liquid in response to a temperature gradient. In the case of liquid iron infiltrating the lowermost mantle near the CMB, high  $\delta^{57}\text{Fe}$  migrates towards lower temperatures further from the CMB, forming a thin, high  $\delta^{57}\text{Fe}$  ( $< 0.5\text{‰}$ , average  $\approx 0.1\text{‰}$ ) boundary layer just above the CMB, which can be entrained by a rising mantle plume. As the plume rises, the core liquids freeze to preserve the isotopic anomaly, and the resultant plume is a mixture of this core component and ambient silicate mantle. This process produces a plume with average  $\delta^{57}\text{Fe} > 0.05\text{‰}$  higher than chondritic mantle depending on the core contribution (Leshner et al., 2020). The proposed average  $\delta^{57}\text{Fe}$  offset of the plume relative to ambient mantle could explain part of the range of high  $\delta^{57}\text{Fe}$  in OIB relative to MORB, so the process is



**Figure 3.13: Schematic showing processes that may contribute to OIB liquids with higher  $\delta^{57}\text{Fe}$  than those predicted by single-stage melting of eclogite** (section 3.4.2.3). Processes including hydrothermal alteration (El Korh et al., 2017) and metamorphism (Debret et al., 2016) may increase subducted eclogite  $\delta^{57}\text{Fe}$  ( $> 0.15\text{‰}$ ), and the addition of continental sediments could contribute to recycled crustal domains with  $\delta^{57}\text{Fe} > 0.15\text{‰}$ . Reaction pyroxenites have inferred  $\delta^{57}\text{Fe} \approx 0.30\text{‰}$  from erupted lavas (Nebel et al., 2019; Gleeson et al., 2020), however generation of this component requires eclogite to have  $\delta^{57}\text{Fe}$  significantly greater than  $0.15\text{‰}$  (section 3.5.3). Metasomatism (Konter et al., 2016), fractional crystallisation and secondary melting may further contribute to high  $\delta^{57}\text{Fe}$  ( $> 0.25\text{‰}$ ) liquids measured in OIB. Contributions from core liquids have also been proposed to generate high  $\delta^{57}\text{Fe}$  in OIB (Leshner et al., 2020). Numbers in italics refer to the sections each process is discussed in.

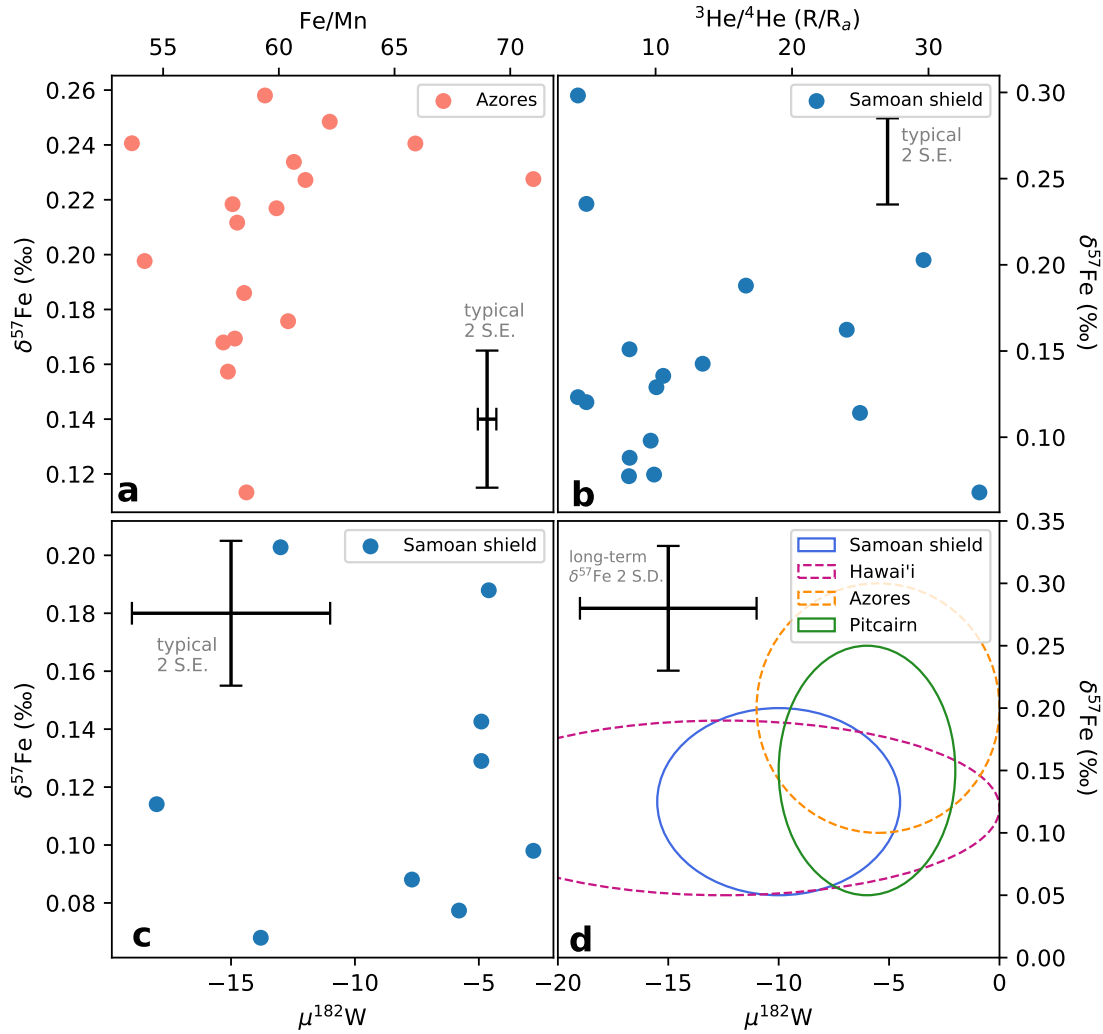
discussed below, but the addition of the core liquids modelled by Leshner et al. (2020) still cannot explain the isotopically heaviest ( $\delta^{57}\text{Fe} \gtrsim 0.25\text{‰}$ ) OIB.

High  $\delta^{57}\text{Fe}$  in OIB generated from the core-contribution model should be linked to other geochemical signatures of core material: specifically, low  $^{182}\text{W}/^{184}\text{W}$  (negative  $\mu^{182}\text{W}$ ) and high  $^3\text{He}/^4\text{He}$  (Leshner et al., 2020), as well as high  $^{186,187}\text{Os}/^{188}\text{Os}$ , strong HSE enrichment (Brandon and Walker, 2005), and possibly high Fe/Mn (Humayun et al., 2004; Rizo et al., 2019). However, HSE enrichment in OIB that show negative  $\mu^{182}\text{W}$  signatures is generally not observed (Mundl et al., 2017; Mundl-Petermeier et al., 2019), which could be attributed to the presence of a core-equilibrated reservoir rather than direct incorporation of core material providing the  $\mu^{182}\text{W}$  signatures (Mundl-Petermeier et al., 2020).

The global OIB  $\delta^{57}\text{Fe}$  dataset does not show a relationship between high  $\delta^{57}\text{Fe}$  and volcanoes or plumes that show negative  $\mu^{182}\text{W}$  and high  $^3\text{He}/^4\text{He}$ , or high Fe/Mn (Fig. 3.14; although as discussed by Leshner et al. (2020) it is not known how well coupled we might expect Fe and W isotopes to be).

Fe/Mn ratios in samples studied here were measured as outlined in section 3.2.3.2. The Fe/Mn ratios of the Azores define two groups: volcanics from the islands of Pico, Faial and Terceira are similar to those from Iceland (Humayun et al., 2004; Qin and Humayun, 2008), while volcanics from São Jorge and São Miguel exhibit variations in Fe/Mn that range (60–68) between Icelandic and Hawaiian lavas (Humayun et al., 2004; Huang et al., 2007). Since Fe isotope data from São Miguel samples are not presented in this manuscript, there is little reason to expect a strong core-mantle exchange effect on the Fe isotope dataset presented here from the Fe/Mn, with the exception of some São Jorge samples.

The Samoan volcano of Ofu records  $^3\text{He}/^4\text{He} \leq 33.8 \text{ R/R}_a$  (Jackson et al., 2007b) and negative  $\mu^{182}\text{W}$  ( $\geq -17.3$ ; Mundl et al., 2017; Mundl-Petermeier et al., 2020). However, the same Ofu samples measured here have  $\delta^{57}\text{Fe}$  indistinguishable from MORB. This result is inconsistent with the presence of frozen core liquid contributing to high  $\delta^{57}\text{Fe}$  melts in the upwelling plume. There is a small negative  $\mu^{182}\text{W}$  anomaly (and slightly raised Fe/Mn) recorded in the Azores plume as a whole (Rizo et al., 2019; Mundl-Petermeier et al., 2020), but Fe/Mn ratios for Pico (with a negative  $\mu^{182}\text{W}$ ; Rizo et al., 2019) show the least evidence of high-Fe in the Azores mantle, being similar to Icelandic lavas (Humayun et al., 2004; Qin and Humayun, 2008). The highest Fe/Mn ratio were measured in lavas from São Jorge (and São Miguel) that have not all been analysed for Fe or W isotopes (see Appendix, Table 6.2), but where samples have both Fe/Mn and  $\delta^{57}\text{Fe}$  data there is no relationship between the two (Fig. 3.14). Other high  $^3\text{He}/^4\text{He}$  lavas (e.g., Baffin) also show no high  $\delta^{57}\text{Fe}$  anomaly relative to average MORB (McCoy-West et al., 2018), although this could be related to the high mantle potential temperatures associated with the Icelandic plume and plume head (Matthews et al., 2016; Spice et al., 2016) and therefore high degrees of melting of ambient peridotite. Overall, current data do not support a link between high  $\delta^{57}\text{Fe}$  and the presence of



**Figure 3.14: Comparison of proposed geochemical tracers of core material compared to  $\delta^{57}\text{Fe}$ .** **a–c)** Available Fe/Mn,  $\mu^{182}\text{W}$  or  $^3\text{He}/^4\text{He}$  data for the same samples with  $\delta^{57}\text{Fe}$  measured in this study (corrected for fractional crystallisation). Typical 2 S.E. on  $\mu^{182}\text{W}$  from Mundl-Petermeier et al. (2020), typical 2 S.E. on  $\delta^{57}\text{Fe}$  from average 2 S.E. for repeat analyses of a sample within a sample run. In **a)**, the Fe/Mn data is corrected for fractional crystallisation following procedures described in section 3.2.3.2. Error shown on Fe/Mn is a typical error from repeats of the same sample. **d)** The distribution of  $\delta^{57}\text{Fe}$  and  $\mu^{182}\text{W}$  for 4 plume systems, although these are not necessarily measurements from the same samples.  $\mu^{182}\text{W}$  taken from Mundl-Petermeier et al. (2020),  $\delta^{57}\text{Fe}$  from this study; Konter et al. (2016); Nebel et al. (2019). Long term 2.S.D reproducibility used as  $\delta^{57}\text{Fe}$  errorbar.

core liquids entrained in an upwelling plume, and I instead consider modifications to the model of subducted, recycled material.

### 3.5.2 The Fe isotope composition of subducted material

Pyroxenite melts that are isotopically heavier than the model melts shown in Fig. 3.7b, and therefore more consistent with measured OIB melts, could be generated if subducted material had  $\delta^{57}\text{Fe} > 0.15$  ‰. This high  $\delta^{57}\text{Fe}$  could be caused by: (i) alteration of oceanic crust either hydrothermally at the seafloor, or during devolatilisation and metamorphism associated with subduction; (ii)

ancient MORB being inherently isotopically heavier than modern MORB; or (iii) contributions from isotopically heavy subducted sediments.

### 3.5.2.1 Hydrothermal alteration and subduction processes

Studies of subduction zone metabasites suggest that hydrothermal alteration of basalt at shallow crustal levels could make subducted basalt isotopically heavier than MORB. For example, in Île de Groix, France (a HP-LT metamorphic belt), hydrothermal alteration makes subducted basalt isotopically heavier by  $\Delta^{56}\text{Fe} = 0.06\text{--}0.10\text{‰}$  (equivalent to  $\Delta^{57}\text{Fe} = 0.09\text{--}0.15\text{‰}$ ), contributing to the heavy Fe compositions of eclogites ( $\delta^{57}\text{Fe} = 0.25\text{--}0.28\text{‰}$ ; El Korh et al., 2017). Taking the maximum amount of Fe isotope variability attributed to hydrothermal alteration by El Korh et al. (2017), partial melts of hydrothermally altered crust could be as isotopically heavy as  $\delta^{57}\text{Fe} = 0.37\text{‰}$ . Melting of this material, if present in mantle plumes, could explain the entire range of Samoan shield and Azores melts, and some of the rejuvenated Samoan liquids. Further geochemical studies, such as oxygen isotopes (Day et al., 2010), could help test the role of crustal alteration on high  $\delta^{57}\text{Fe}$ . Alteration may also introduce sample heterogeneity, which could explain the different  $\delta^{57}\text{Fe}$  found between this study and Konter et al. (2016) for sample ALIA115-18, and highlights that samples chosen for Fe isotope analyses should be carefully picked (due to this heterogeneity, the sample is not included in Figs. 3.5, 3.6, 3.7 & 3.8). However, Rouxel et al. (2003) showed that on a scale larger than a few metres, bulk hydrothermally altered oceanic crust is indistinguishable in  $\delta^{57}\text{Fe}$  from MORB.

Therefore, the ability of hydrothermal alteration to generate large scale high  $\delta^{57}\text{Fe}$  recycled crustal domains in the mantle remains uncertain, but is likely small. Any contribution from hydrothermally altered MORB protolith to OIB melts may not be distinguishable in major element compositions, as large major element variability in altered basalts is only recorded where a large proportion of alteration (e.g.,  $> 30\%$   $\text{Fe}^{2+}$  loss) has taken place (Rouxel et al., 2003).

Isotopically heavy mantle components could also be generated by metamorphic and/or devolatilisation reactions, driving metabasites to higher  $\delta^{57}\text{Fe}$  values than their protolith. For example, Île de Groix blueschists have high  $\delta^{57}\text{Fe}$  ( $0.26\text{--}0.51\text{‰}$ ; El Korh et al., 2017), which could be partly explained by the loss of isotopically light fluids during prograde metamorphism: progressive serpentinite devolatilisation in the Western Alps records an increase of  $\Delta^{56}\text{Fe}_{\text{blueschist-serpentinite}} = 0.12\text{‰}$  ( $\Delta^{57}\text{Fe} = 0.18\text{‰}$ ) from abyssal serpentinites to blueschists (Debret et al., 2016). Increasing  $\delta^{57}\text{Fe}$  with devolatilisation is ascribed to loss of  $\text{Fe(II)-Cl}$  or  $\text{Fe(II)-S}$  complexes in serpentinite-derived fluids (Debret et al., 2016), which is consistent with low  $\delta^{57}\text{Fe}$  in secondary olivines precipitated from serpentinite fluids (Debret et al., 2018). Infiltration by isotopically light slab-derived fluids has also been proposed to explain isotopically light ( $\delta^{57}\text{Fe} < 0\text{‰}$ ) peridotite fragments observed above the Philippine arc (Turner et al., 2018).

However, the origin of high  $\delta^{57}\text{Fe}$  in Île de Groix blueschists is unclear, with El Korh et al. (2017) suggesting that much of the variability is likely to have been inherited from the original protolith, rather than generated during subduction. Studies have also shown that Fe is not fractionated in the downgoing oceanic crust during prograde metamorphism: orogenic eclogites preserve a MORB-like Fe isotope composition ( $\delta^{57}\text{Fe} = 0.15\text{‰}$ ; Williams et al., 2009; Li et al., 2016); Western Alpine eclogites also record no Fe isotope fractionation from MORB  $\delta^{57}\text{Fe}$ , despite evidence from associated metagabbros of infiltration by a low  $\delta^{57}\text{Fe}$  fluid (Inglis et al., 2017). Preserved eclogite MORB-like  $\delta^{57}\text{Fe}$  could be the result of mass balance between the slab and fluid, leaving no resolvable Fe isotope heterogeneity after fluid loss in the subducted, dehydrated eclogitic material. The role of the loss of slab-derived fluids on the Fe isotopic composition of subducted material is further complicated by sources of fluids other than serpentinites, such as fluids derived from the altered oceanic crust, which could have high  $\delta^{57}\text{Fe}$  as isotopically heavy hydrous minerals (e.g., amphibole, epidote) break down (Huang et al., 2020a).

### 3.5.2.2 The composition of ancient MORB

While the Fe isotopic composition of modern oceanic crust is well-studied, the material that now contributes to mantle heterogeneity may have been subducted more than a billion years ago (Montanini and Tribuzio, 2015). If ancient oceanic crust was isotopically heavier than the modern equivalent, it may have contributed to the formation of high  $\delta^{57}\text{Fe}$  mantle domains sampled by OIB. Factors introducing temporal variability in the bulk isotopic composition of oceanic crust could be: (i) isotopic fractionation during partial melting and fractional crystallisation; and (ii) the amount and/or isotopic effect of hydrothermal alteration.

*Magnitude of isotopic fractionations:* Isotopic fractionation during ancient mantle partial melting, and/or fractional crystallisation of the subsequent melts, would need to be greater than modern values to generate oceanic crust with  $\delta^{57}\text{Fe} > 0.15\text{‰}$  from a silicate mantle with  $\delta^{57}\text{Fe}$  similar to the present-day value. However, hotter average upper mantle temperatures in the past (Herzberg et al., 2010) argue against larger  $\Delta^{57}\text{Fe}$ , both because equilibrium isotopic fractionation factors decrease with temperature (Urey, 1947) and partial melting fractionation is smaller at higher degrees of melting (Fig. 3.11). This relationship is consistent with komatiites, generally ascribed to high melting temperatures, recording an average  $\delta^{57}\text{Fe}$  more similar to BSE than average terrestrial basalts (Hibbert et al., 2012; Johnson et al., 2020). Mantle  $f\text{O}_2$  may also affect the composition of mantle melts due to varying  $\text{Fe}^{3+}/\text{Fe}_\text{T}$  over time (Williams et al., 2004), hence the crustal  $\delta^{57}\text{Fe}$  composition. However, Hibbert et al. (2012) records no difference in  $\delta^{57}\text{Fe}$  from komatiites from the late Archean to the Tertiary associated with a mantle  $f\text{O}_2$  effect, which is in agreement with other work suggesting that the mantle oxidation state has remained approximately fixed since the Archean (e.g., Berry et al., 2008).

*Ancient hydrothermal alteration:* Different processes operating in ancient hydrothermal sys-

tems compared to modern MORB could have contributed to  $\delta^{57}\text{Fe}$  variability in subducted crust. Whereas modern hydrothermal systems generally precipitate more low  $\delta^{57}\text{Fe}$  sulphides (e.g., Rouxel et al., 2004) than high  $\delta^{57}\text{Fe}$  oxides, Precambrian hydrothermal systems precipitated fewer sulphides due to higher Fe/S and  $\text{Fe}^{2+}$  content in the fluids (Kump and Seyfried Jr, 2005). Therefore, Precambrian vent fluids may have precipitated dominantly high  $\delta^{57}\text{Fe}$  minerals in the crust, and had lower  $\delta^{57}\text{Fe}$  than the present-day fluids (Johnson et al., 2020). However, even for modern hydrothermal systems, their influence on bulk altered crust  $\delta^{57}\text{Fe}$  remains uncertain (section 3.5.2.1), and so it is not possible to discern whether or not ancient hydrothermal systems could have generated higher  $\delta^{57}\text{Fe}$  in altered MORB than today.

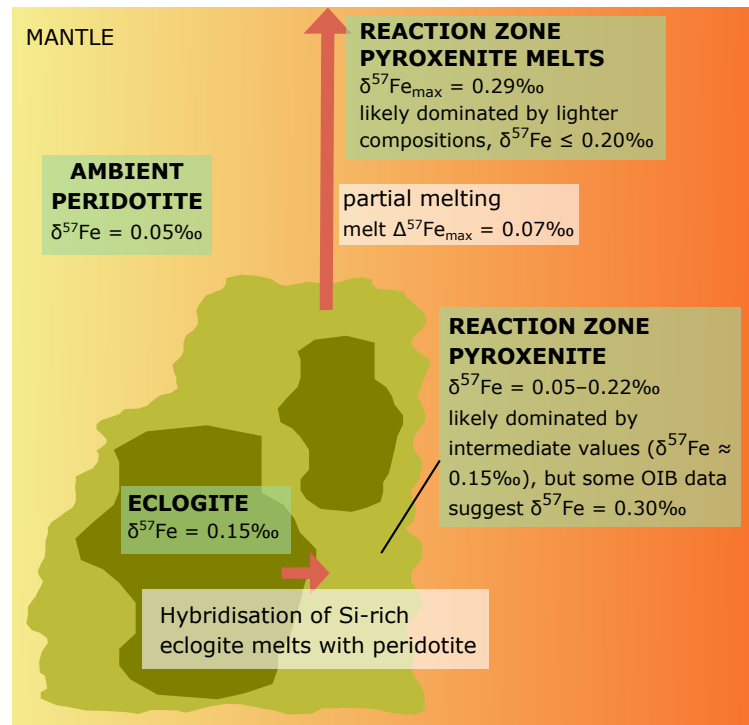
### 3.5.2.3 Contributions from sediments

Subducted slab material includes oceanic lithosphere, crust, and sediments. Downgoing sediments are suggested to contribute to mantle heterogeneity (White and Hofmann, 1982; Plank and Langmuir, 1998), with small amounts of continental sediments traced in enriched mantle reservoirs ( $\leq 10\%$ ; e.g., Jackson et al., 2007a; Rapp et al., 2008). Continental sediments could contribute to high  $\delta^{57}\text{Fe}$  mantle domains, since differentiated igneous rocks record variable  $\delta^{57}\text{Fe}$  ( $\leq 0.9\text{‰}$ ; Du et al., 2017). However, bulk upper continental crust (the main component of recycled sediment in the mantle; Stracke, 2012), is thought to be isotopically indistinguishable from MORB (Johnson et al., 2020), and direct measurements of arc system sediments show  $\delta^{57}\text{Fe} = 0.17\text{‰}$  (Nebel et al., 2015). Moreover, large-scale sediment input into the mantle is not expected because most sediment is scraped off in the forearc and never subducted; much of the sediment that does subduct may melt early and be returned to the surface in arc volcanism (Jackson et al., 2007a).

The Vai (weak HIMU) and Malu (EM2; Jackson et al., 2014) trends in Samoa, as distinguished in radiogenic isotope space (Fig. 3.1), are proposed to reflect the sampling of different mantle heterogeneities, including sediments. These heterogeneities may originate from different recycled material, explaining their radiogenic isotopic differences, hence might be expected to show  $\delta^{57}\text{Fe}$  variability related to the recycled material. However, the melts of any recycled mantle component (e.g., sediments, oceanic crust) are likely to be mixed with ambient peridotite melts during shield stage volcanism. Since the contribution of Fe from non-peridotitic components will not dominate the Fe content of melts (unlike incompatible radiogenic isotopes), mass balance would argue against small fractions of non-peridotitic components in the mantle source being resolved using  $\delta^{57}\text{Fe}$  where melt fraction is sufficiently high for peridotite melts to dominate. The Fe isotopic composition of melts is dependent on both mantle processes and source lithology and, in this case, processing rather than source composition may dominate melt  $\delta^{57}\text{Fe}$  – small variations in the  $\delta^{57}\text{Fe}$  of isotopically heavy melts from dilute HIMU and EM2 components may be eliminated by mixing with isotopically light peridotite melts.

### 3.5.3 Generating pyroxenites by peridotite hybridisation

In existing studies, the proposed formation of a solid pyroxenite component in the mantle that contributes to melts in OIB (e.g., the Pitcairn EM1 mantle component; Nebel et al., 2019) is a two-stage process, rather than only eclogite subduction and recycling. Reaction-zone pyroxenite is proposed to form by the reaction of high pressure ( $> 30$  kbar) Si-rich melts from recycled oceanic crust with ambient peridotite, producing an olivine-free hybrid pyroxenite lithology (Sobolev et al., 2005, 2007; Rosenthal et al., 2014; Nebel et al., 2019; Fig. 3.15), which is suggested to have  $\delta^{57}\text{Fe} = 0.30\text{‰}$  based on measured OIB data (Nebel et al., 2019; Gleeson et al., 2020). Here I examine whether my modelled eclogite melts can generate this isotopically heavy pyroxenite mantle component.



**Figure 3.15:** Schematic showing formation of a reaction zone pyroxenite, following Sobolev et al. (2005); Nebel et al. (2019), and the subsequent generation of high  $\delta^{57}\text{Fe}$  melts. Eclogite melts hybridise with ambient peridotite, generating a pyroxenite mantle component with  $\delta^{57}\text{Fe} \leq 0.22\text{‰}$ , assuming a subducted eclogite composition of  $\delta^{57}\text{Fe} = 0.15\text{‰}$ .

Based on a single-stage melting process (section 3.4.2.1), the isotopically heaviest melts that can be formed from subducted oceanic crust (with bulk  $\delta^{57}\text{Fe} = 0.15\text{‰}$ ) have  $\delta^{57}\text{Fe} = 0.22\text{‰}$ . Mixing of these melts with peridotite ( $\delta^{57}\text{Fe} = 0.05\text{‰}$ ) would produce a lithology of  $\delta^{57}\text{Fe} = 0.05\text{--}0.22\text{‰}$ , assuming equilibrium fractionation and depending on the proportion of eclogite melt involved. Remelting of this component could then produce liquids isotopically heavy enough to explain the isotopic compositions of Samoan shield and some of the Azores melts, but would require: (i) the solid reaction-zone pyroxenite to have an isotopic composition close to that of the Si-rich eclogite melt (maximum  $\delta^{57}\text{Fe} = 0.22\text{‰}$ ), and (ii) that pyroxenite melt (with  $\delta^{57}\text{Fe}$  up to  $0.29\text{‰}$ , taking the upper limit of melting fractionation from section 3.4.2.1) was extracted

without mixing with ambient peridotite melts (Fig. 3.15). It is also likely that the subsequent melts would have major element compositions similar to G2 melts and therefore not match the OIB major element geochemistry. Overall, this process cannot generate a sufficiently isotopically heavy solid mantle component to match previous estimates of pyroxenite composition ( $\delta^{57}\text{Fe} \geq 0.30\text{‰}$ ; Nebel et al., 2019), nor subsequently produce the isotopically heaviest observed OIB melt compositions. Instead, forming pyroxenite by hybridisation produces a range of subsequent melt compositions likely dominated by  $\delta^{57}\text{Fe}$  similar to MORB, but could produce some higher  $\delta^{57}\text{Fe}$  melts that contribute to the high  $\delta^{57}\text{Fe}$  seen in OIB.

### 3.5.4 Lithospheric processing and remobilisation

Remobilisation of small-degree pyroxenite melts, frozen in the lithosphere during the passage of the main plume head, could generate liquids isotopically heavier than those from a single-stage mantle melting process. Melt remobilisation superimposes a further partial melting fractionation of  $\Delta^{57}\text{Fe} \leq 0.07\text{‰}$  onto the resultant melts, which are likely to be small-degree melts. Therefore, partial melting fractionations may be at the upper limit of the melting fractionation range; and minimal melting of, and thus minimal dilution by, isotopically light peridotite is expected. If the isotopically heaviest possible reaction-zone pyroxenite melts ( $\delta^{57}\text{Fe} = 0.29\text{‰}$ ; Fig. 3.15) could become trapped in the lithosphere and subsequently remobilised, it would be possible to generate small-degree melts with  $\delta^{57}\text{Fe} \lesssim 0.35\text{‰}$ . These melts could explain some of the rejuvenated Samoan lavas, since the Samoan lithosphere has previously passed over at least two hotspots (Jackson et al., 2010) so is likely to contain trapped veins of melt. The rejuvenated lavas have been proposed to be small-degree melts remobilised by decompression melting due to plate flexure near the Tonga trench, consistent with their low  $\text{SiO}_2$ , alkalic nature relative to shield samples, and may be an expression of ‘petit spot’ volcanism (Hawkins Jr and Natland, 1975; Natland, 1980; Konter and Jackson, 2012; Reinhard et al., 2019). However, erupted melts with compositions close to  $\delta^{57}\text{Fe} = 0.35\text{‰}$  would require that: (i) reaction-zone pyroxenite melts were extracted through two partial melting events without mixing with ambient peridotite melts, and (ii) at each melting stage, Fe isotopic fractionation was at a maximum ( $\Delta^{57}\text{Fe} = 0.07\text{‰}$ ), despite the limited P-T conditions where this  $\Delta^{57}\text{Fe}$  is possible (Fig. 3.11). In addition, to generate any large volume of small-degree, maximum  $\Delta^{57}\text{Fe}$  melts requires a residual source that is much larger in mass than the melts for both melting events. This volume problem would make it difficult to generate appreciable quantities of eruptable high  $\delta^{57}\text{Fe}$  melt, but it is possible that remobilisation of melts with less extreme melting  $\Delta^{57}\text{Fe}$  (hence a smaller volume problem) could provide a small contribution to high  $\delta^{57}\text{Fe}$ .

Metasomatic reactions of source peridotite with a melt or fluid, generating isotopic and chemical disequilibrium and forming pyroxene-rich domains, may also be able to contribute to heavy isotopic signatures in OIB. Where metasomatism involves enrichment by a Fe-rich, Si-undersaturated melt (e.g., a silicate liquid that has evolved in mantle magma chambers and veins; Weyer and

Ionov, 2007), formation of secondary clinopyroxene (as seen in some Samoan xenoliths; Finlayson et al., 2015) and generation of wehrlites (Ionov et al., 2005) could generate a high  $\delta^{57}\text{Fe}$  metasomatised source (Weyer and Ionov, 2007; Konter et al., 2016). The precipitation of garnet and clinopyroxene at the interface between subsolidus lherzolite and eclogite-derived melts has also been shown experimentally and has occurred within the lithosphere of the North China Craton (Wang et al., 2020a). Sun et al. (2020) propose that metasomatic garnet pyroxenite veins in recycled oceanic lithosphere could melt and react with ambient peridotite to produce secondary pyroxenites with  $\delta^{57}\text{Fe} > 0.3\text{‰}$  although, as discussed in section 3.5.3, it is unclear how these heavy isotopic compositions will be generated. Metasomatic phlogopite has also been recorded with high  $\delta^{57}\text{Fe}$  in cratonic mantle xenoliths ( $> 0.30\text{‰}$ ; Zhao et al., 2012), although Beier et al. (2012) argue against phlogopite in the Azores source on the basis of trace elements.

The suggested magnitude of the metasomatic effect, based on xenolith data from Samoa (Finlayson et al., 2015), is  $\Delta^{56}\text{Fe} = 0.05\text{‰}$  ( $\Delta^{57}\text{Fe} = 0.08\text{‰}$ ; Konter et al., 2016), which cannot generate the full  $\delta^{57}\text{Fe}$  range of liquids observed in Samoa, but could contribute to producing high  $\delta^{57}\text{Fe}$ . Some mantle samples affected by metasomatism record a strong negative correlation between  $\delta^{56}\text{Fe}$  and  $\delta^{26}\text{Mg}$ , which is consistent with an inter-diffusion disequilibrium origin to the isotopic signatures (Zhao et al., 2012; Su et al., 2015), and likely due to coupled diffusion into/out of mantle minerals. Therefore, Mg isotopic measurements might be able to identify heavy Fe isotopic signatures of a metasomatic origin, which could be particularly applicable for rejuvenated Samoan lavas (Konter et al., 2016).

Some SD pyroxenites are suggested to be lithospheric cumulates from low-degree mantle melts, e.g., some Hawaiian pyroxenite xenoliths, which have  $\delta^{57}\text{Fe} \leq 0.27\text{‰}$  (Bizimis et al., 2013; Williams and Bizimis, 2014). These compositions have been explained by the progressive fractional crystallisation in the lithosphere of an initial melt with  $\delta^{57}\text{Fe} = 0.15\text{‰}$ . However, the highest  $\delta^{57}\text{Fe}$  xenolith is required to be a cumulate fraction in equilibrium with a highly evolved ( $> 90\%$  fractionally crystallised) melt (Williams and Bizimis, 2014). For major elements, cumulate pyroxenite compositions can produce primary magmas that have higher CaO than eclogite-derived melts, plotting above the dividing line in Fig. 3.12 (Herzberg and Asimow, 2008), although this CaO enriched composition would be inconsistent with the major element chemistry of most of the Azores and Samoan lavas shown here. Therefore, while xenoliths record the presence of high  $\delta^{57}\text{Fe}$  ( $> 0.25\text{‰}$ ) lithospheric components, their mode of formation and relevance to high  $\delta^{57}\text{Fe}$  in OIB, particularly large-volume melts, remains uncertain.

The pre-final melting processes that have been discussed are summarised in Table 3.1, highlighting key points about the possibility of each consideration in explaining  $\delta^{57}\text{Fe}$  of melts.

**Table 3.1: Summary of processes that are discussed to contribute to high  $\delta^{57}\text{Fe}$  melts in OIB.** I consider the potential effects on melt  $\delta^{57}\text{Fe}$ , in addition to major elements; and potential melt volume generated from this contribution to mantle heterogeneity, to identify plausible processes that are traced by  $\delta^{57}\text{Fe}$  in OIB melts.

| Process                                                                      | Contribution to:                                                                    |                                                         |                                                | Section |
|------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|---------------------------------------------------------|------------------------------------------------|---------|
|                                                                              | $\delta^{57}\text{Fe}$                                                              | Major elements                                          | Melt volume                                    |         |
| <b>Core contribution</b>                                                     | $> 0.05\text{‰}$ higher than silicate mantle but not consistent with other isotopes | No difference                                           | Could be mixed into whole plume to some extent | 3.14    |
| <b>Make eclogite <math>\delta^{57}\text{Fe} &gt; 0.15\text{‰}</math> by:</b> |                                                                                     |                                                         |                                                |         |
| (i) Hydrothermal alteration of oceanic crust                                 | Bulk effect suggested to be small                                                   | Large variability only from highly altered protolith    | Could be large component                       | 3.5.2.1 |
| (ii) Metamorphism and/or dehydration of subducted basalt                     | Bulk effect uncertain, could be small due to mass balance in slab                   | Likely small due to mass balance in slab                | Could be large component                       | 3.5.2.1 |
| (iii) Composition of ancient MORB                                            | Poorly constrained, but likely negligible                                           | Poorly constrained                                      | Could be large component                       | 3.5.2.2 |
| (iv) Sediment input to the mantle                                            | Sediments $\leq 0.9\text{‰}$ , but bulk effect could be small                       | Bulk effect likely small                                | Likely small                                   | 3.5.2.3 |
| <b>Generate reaction-zone pyroxenites</b>                                    | Melts $\leq 0.29\text{‰}$ , likely closer to $0.15\text{‰}$                         | Mix between peridotite and pyroxenite melt compositions | Could be large component                       | 3.5.3   |
| <b>Lithospheric processing</b>                                               |                                                                                     |                                                         |                                                |         |
| (i) Melt remobilisation                                                      | Superimposes a further $\Delta^{57}\text{Fe}_{\text{max}} = 0.07\text{‰}$           | Small-degree OIB melts likely alkalic                   | Likely small                                   | 3.5.4   |
| (ii) Metasomatism                                                            | Could increase melt $\delta^{57}\text{Fe}$ due to pyroxene enrichment               | Measurable e.g., CaO enrichment                         | Likely small                                   | 3.5.4   |

### 3.6 Preservation of high $\delta^{57}\text{Fe}$ : Importance of plume variables

Not all OIB record high  $\delta^{57}\text{Fe}$  (e.g., Hawai'i, Samoan shield, Réunion), which suggests that the processes controlling the generation and preservation of high  $\delta^{57}\text{Fe}$  in erupted lavas may rely on factors that differ between plumes, e.g., melt fraction and potential temperature, in addition to the  $\delta^{57}\text{Fe}$  of source material.

The Azores records high  $\delta^{57}\text{Fe}$  and is a relatively cool plume (Putirka, 2008a; Beier et al., 2012), and the high  $\delta^{57}\text{Fe}$  rejuvenated Samoan lavas are small-degree melts (Konter and Jackson, 2012). Therefore, high  $\delta^{57}\text{Fe}$  melts may be more likely to be preserved in plumes where they are not diluted by extensive degrees of melting and/or mixing with ambient peridotite mantle melts, regardless of how a high  $\delta^{57}\text{Fe}$  source component is generated. Hawai'i and Samoa have notably high excess temperatures, with a potential temperature anomaly of  $> 200^\circ\text{C}$  (Putirka, 2005) compared to only  $35^\circ\text{C}$  in the Azores (Beier et al., 2012), and record no high  $\delta^{57}\text{Fe}$  in erupted shield stage melts (Teng et al., 2008, 2013; Konter et al., 2016). However, a link between plume excess temperature and  $\delta^{57}\text{Fe}$  is likely to be complicated by other factors affecting melt fraction, such as lithospheric thickness and mantle source components, and I note that some plumes (for example Réunion) with a similar excess temperature to Pitcairn (Putirka, 2008a) have no measured high  $\delta^{57}\text{Fe}$  lavas.

### 3.7 Summary

Stable Fe isotopes have increasingly been used as a tracer of mineralogical heterogeneity in the mantle, but there are multiple processes that could generate high  $\delta^{57}\text{Fe}$  mantle melts. I show that the existing dataset of  $\delta^{57}\text{Fe}$ ,  $\mu^{182}\text{W}$  and  $^3\text{He}/^4\text{He}$  of OIB are inconsistent with a contribution from high  $\delta^{57}\text{Fe}$  core liquids. In agreement with previous work, I also calculate that the magnitude of partial melting fractionation of peridotite is small. I show that the partial melting fractionation of an eclogitic pyroxenite is similar to that of peridotite, and less than that required to explain the highest  $\delta^{57}\text{Fe}$  seen in basalts — therefore, heterogeneity in melt  $\delta^{57}\text{Fe}$  derives from the bulk  $\delta^{57}\text{Fe}$  of source lithologies. Mixed melts of KLB1 peridotite and G2 eclogitic pyroxenite (with bulk compositions of  $\delta^{57}\text{Fe} = 0.05$  and MORB-like  $0.15\text{‰}$  respectively) produce liquids that match some of the Samoan shield and Azores melts, but would need to comprise nearly pure pyroxenite melts to explain the highest  $\delta^{57}\text{Fe}$ , and cannot explain any of the rejuvenated Samoan samples.

I show that to produce a mantle source capable of generating melts that match the OIB  $\delta^{57}\text{Fe}$  range requires consideration of processes operating from MORB generation, through mantle heterogeneity development and lithospheric processing, to eruption at ocean islands. The dominant contributor to geochemical heterogeneity recorded in OIB is recycled oceanic crust, which could generate high  $\delta^{57}\text{Fe}$  ( $\geq 0.2\text{‰}$ ) melts if recycled crust was higher in  $\delta^{57}\text{Fe}$  than modern MORB

(> 0.15 ‰). High  $\delta^{57}\text{Fe}$  in recycled material could be created by hydrothermal alteration, metamorphic reactions during subduction, or Fe isotope contributions from sediments, but I suggest no single, unique factor can explain the isotopically heaviest OIB ( $\delta^{57}\text{Fe} > 0.25$  ‰) lavas. Reaction-zone pyroxenites in the mantle, formed by the hybridisation of modelled equilibrium eclogitic melts and peridotite, will not be sufficiently isotopically heavy to match the proposed high  $\delta^{57}\text{Fe}$  mantle component beneath Pitcairn and the Galapagos (Nebel et al., 2019; Gleeson et al., 2020), unless eclogite in the mantle has  $\delta^{57}\text{Fe} > 0.15$  ‰, i.e., has been modified from MORB values. Further processes contributing to high  $\delta^{57}\text{Fe}$  melts could include the formation of isotopically heavy metasomatic pyroxene-rich domains and cumulates in the lithosphere, which may be remelted during late stages of plume activity (such as small-scale rejuvenated volcanism).

Any high  $\delta^{57}\text{Fe}$  mantle or lithospheric component may most likely be observed in erupted lavas where overall melt volume and/or degree of melting is small, e.g., plumes with relatively low potential temperature. The measurement of MORB-like  $\delta^{57}\text{Fe}$  signatures in an ocean island system therefore does not rule out the presence of a high  $\delta^{57}\text{Fe}$  component in the mantle, as melts derived from this component may be too dilute in the erupted liquid to be distinguished by Fe isotopes.

High  $\delta^{57}\text{Fe}$  in OIB may have an important role to play in identifying mantle source lithologies, but the presence or absence of a high  $\delta^{57}\text{Fe}$  signature in melts is unlikely to simply relate to a uniform recycled component in the mantle. Instead, Fe isotopes in OIB reflect a variety of often poorly-understood, difficult-to-distinguish and plume-specific processes that have contributed to variable  $\delta^{57}\text{Fe}$  in the mantle and erupted melts.



# 4 Global trends in novel stable isotopes: theory and observations

## 4.1 Introduction

A key window into Earth's mantle is through the petrology and geochemistry of its melts, which include both MORB and OIB. MORB may be able to tell us about the composition and temperature of the upper mantle across multiple length scales (e.g., Allègre et al., 1984; Zindler and Hart, 1986; Mahoney et al., 1994; Agranier et al., 2005; Janney et al., 2005; Herzberg et al., 2007; Gale et al., 2013b; Shorttle, 2015). Key questions about MORB-source mantle concern the various roles of temperature, crustal thickness, lithological heterogeneity, melt mixing and melt-rock reaction and the degree to which they can explain the trace, major element, and radiogenic isotope arrays of global MORB. Decades of investigation have produced a broad consensus that in the MORB-source mantle thermally-driven variations in melting degree create global signals in major and/or trace elements (Klein and Langmuir, 1987; Dalton et al., 2014; Gale et al., 2014). On a local scale MORB also show considerable isotopic and trace element variability, linked to small-scale lithological heterogeneity in the upper mantle (e.g., Zindler et al., 1984; Langmuir et al., 1986; Fornari et al., 1988; Hekinian et al., 1989; Schiano et al., 1997; Castillo et al., 2000; Waters et al., 2011; Gill et al., 2016; Liu and Liang, 2017a; Jiang et al., 2021; Zhong et al., 2021b). OIB also sample a heterogeneous mantle over short and long lengthscales including significant lithological heterogeneity (e.g., Cohen and O'Nions, 1982; Weaver, 1991; Chauvel et al., 1992; Kogiso et al., 2003; Sobolev et al., 2007; Jackson and Dasgupta, 2008; Dasgupta et al., 2010; Day and Hilton, 2011; Shorttle and MacLennan, 2011), elemental and isotopic heterogeneity (e.g., Zindler and Hart, 1986; Dupuy et al., 1988; Hauri and Hart, 1993; Hofmann, 1997, 2003; Stracke et al., 2005; Willbold and Stracke, 2006; Prytulak and Elliott, 2007; Jackson and Dasgupta, 2008; MacLennan, 2008; Dasgupta et al., 2010; Jackson et al., 2012; Mundl et al., 2017), and record large temperature variations relative to MORB (e.g., Putirka, 2005; Herzberg et al., 2007; Putirka, 2008a,b; Herzberg and Gazel, 2009; Herzberg and Asimow, 2015; Matthews et al., 2021).

In this study, I investigate the use of novel stable isotopes of major and minor elements in basalts (magnesium [ $\delta^{26/24}\text{Mg}$ ], calcium [ $\delta^{44/40}\text{Ca}$ ], iron [ $\delta^{57/54}\text{Fe}$ ], vanadium [ $\delta^{51/50}\text{V}$ ], chromium [ $\delta^{53/52}\text{Cr}$ ]) as new tools for studying temperature and lithological heterogeneity in the mantle, complementary to existing work on MORB and OIB mantle sources using major and trace elements (e.g., Klein and Langmuir, 1987; Langmuir et al., 1992; McKenzie et al., 2004; Putirka, 2005; Herzberg

et al., 2007; Jackson and Dasgupta, 2008; Niu and O'Hara, 2008; Dasgupta et al., 2010; Le Roux et al., 2011; Jackson et al., 2012; Lambart et al., 2013; Gale et al., 2014; Yang et al., 2019; Mallik et al., 2021). The chosen isotope systems may trace thermal and mineralogical heterogeneity in the source region of melts through their temperature and mineral-dependent equilibrium fractionation factors (e.g., Schauble, 2004; Young et al., 2015; see chapters 1 and 3), and I include detail on the choice of these isotope systems in section 4.1.3.

### 4.1.1 Temperature and lithological heterogeneity in the mantle

Mantle-derived melts, particularly MORB, show global geochemical arrays that can be explained by the conditions of melt generation in the mantle (e.g., temperature, lithology; Klein and Langmuir, 1987; Langmuir et al., 1992; Niu and O'Hara, 2008; Arevalo Jr and McDonough, 2010; Gale et al., 2014) and/or subsequent melt transport and storage processes (e.g., melt mixing, melt-rock reaction, fractional crystallisation; Devey et al., 1994; Arevalo Jr and McDonough, 2010; Liang et al., 2011; Kimura and Sano, 2012; Till et al., 2012; Shorttle, 2015; Bo et al., 2018; Mallik et al., 2021; Stracke, 2021). Once corrected for crystal fractionation, moderately incompatible element concentrations (e.g., Na, Al) in global MORB correlate positively with ridge depth, commonly interpreted to equate to a control by mantle potential temperature variations of around 220 °C (Klein and Langmuir, 1987; Langmuir et al., 1992; Brandl et al., 2013; Gale et al., 2014). Correlations between fractionation-corrected major element compositions in MORB (e.g., FeO-Na<sub>2</sub>O, CaO-Al<sub>2</sub>O<sub>3</sub>) are consistent with the same mantle temperature variations (Langmuir et al., 1992; Gale et al., 2014). Although mantle composition has also been invoked instead of temperature variation to explain these trends (by applying a different fractionation correction; Niu and O'Hara, 2008), major element compositions measured in OIB and their constituent olivine, as well as olivine crystallisation thermometry and geophysical observations, argue in favour of there being regions of mantle up to 250 °C hotter than typical mid-ocean ridge mantle (e.g., Putirka, 2005; Herzberg et al., 2007; Putirka, 2008a; Dalton et al., 2014; Herzberg and Asimow, 2015; Spice et al., 2016; Ball et al., 2021; Matthews et al., 2021).

Although temperature may be a dominant control on MORB geochemical variability, mantle compositional heterogeneity is also clear in the elemental and isotopic compositions of both MORB and OIB. For example, in MORB highly incompatible element enrichment (e.g., fractionation corrected K concentrations) correlates roughly with radiogenic isotopes, which must relate to source heterogeneity, such as through the addition or removal of low-degree melts (e.g., McKenzie and O'Nions, 1995; Donnelly et al., 2004; Gale et al., 2011, 2013b, 2014). Radiogenic and stable isotopes and trace elements have also been used to argue for the presence of incompatible trace element-enriched, recycled components in the MORB source (e.g., Hirschmann and Stolper, 1996; Schiano et al., 1997; Salters and Dick, 2002; Bezard et al., 2016). In OIB, there is extensive evidence for mantle heterogeneity in the form of radiogenic and stable isotope compositions

and the concentrations of major elements in basalt and trace elements in olivine (e.g., Zindler and Hart, 1986; Weaver, 1991; Hauri, 1996; Hofmann, 1997; Sobolev et al., 2005; Stracke et al., 2005; Sobolev et al., 2007; Jackson and Dasgupta, 2008; Day et al., 2009; Herzberg, 2011; Shorttle and MacLennan, 2011; Konter et al., 2016; Mundl et al., 2017; Neave et al., 2018; Nebel et al., 2019; Gleeson et al., 2020). This mantle heterogeneity is thought to relate largely to the recycling of crust, and the reaction between recycled lithologies (and their melts) and ambient mantle peridotite (e.g., Cohen and O’Nions, 1982; Hofmann and White, 1982; Allègre and Turcotte, 1986; Schiano et al., 1997; Sobolev et al., 2005, 2007; Herzberg, 2011; Mallik and Dasgupta, 2012; Stracke, 2012; Rosenthal et al., 2014; Lambart, 2017).

Many tools are available to study the contributions of temperature and lithological heterogeneity in these two types of basalts, for example: rare earth element inversion modelling (INVMEL: McKenzie and O’Nions, 1991, 1995), major element calculations (PRIMELT: Herzberg and Asimow, 2008, 2015; the thermodynamic model of Jennings and Holland, 2015; Jennings et al., 2016), trace element and radiogenic isotope composition forward modelling (REEBOX PRO: Brown and Leshner, 2016), and models combining trace elements, crystallisation temperatures and magma productivity (Shorttle et al., 2014; Matthews et al., 2016, 2021). However, achieving success in linking the elemental and radiogenic isotope variability in MORB and OIB to temperature and/or lithological heterogeneity is complicated by uncertainty in the nature of enriched lithologies, metasomatism by small volumes of melt (which are usually highly enriched in incompatible elements, so can overwhelm evidence of the original source lithology), magma recharge and mixing, diffusional re-equilibration and fractional crystallisation (e.g., Niu and O’Hara, 2003; Workman et al., 2004; Niu and O’Hara, 2008; Lambart et al., 2013; Matzen et al., 2017; Gleeson and Gibson, 2019). Stable isotopes of major and minor elements complement radiogenic isotopes and major element calculations and could provide new constraints on understanding global basalt chemistry: stable isotope systems are time-independent, and since their equilibrium partitioning is a function of mineral chemistry, they are the natural extension of major element calculations based on thermodynamic data. In addition, some of these stable isotopes are major elements whose budgets in the mantle source and subsequent erupted melts reflect contributions from both enriched and depleted lithologies, and are not dominated by small-degree melt metasomatism.

#### **4.1.2 Stable isotopes as a probe of mantle temperature and compositional heterogeneity**

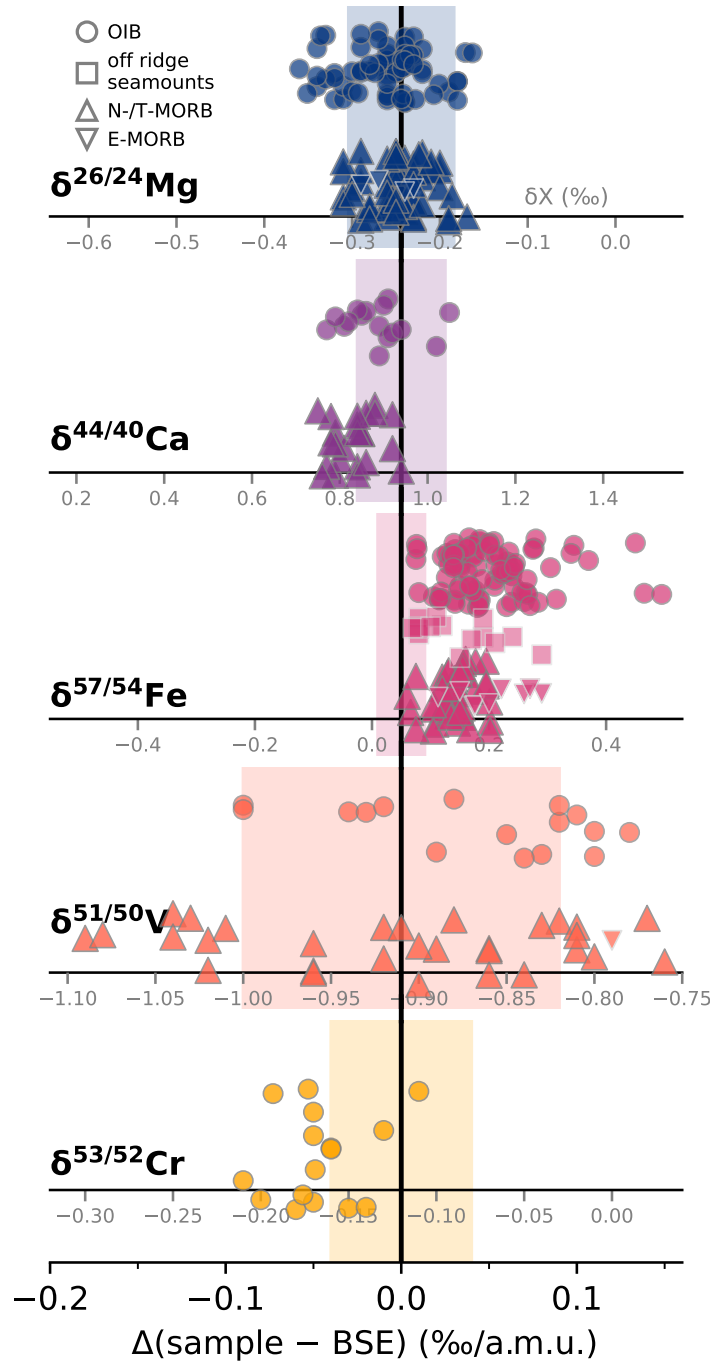
Stable isotopes may trace thermal and mineralogical heterogeneity in the mantle through their temperature and mineral-dependent equilibrium fractionation factors (e.g., Schauble, 2004; Young et al., 2015). Our understanding of the equilibrium high temperature fractionation effects experienced by novel stable isotope systems is improving, and many studies (both theoretical and from natural samples) suggest controls from mantle temperature and lithology on the isotopic compo-

sition of the melts produced. Previous studies (Table 4.1) have shown considerable variability in stable isotope ratios in MORB and OIB even where the geochemical signals of fractional crystallisation are considered to be negligible, or have been removed (Fig. 4.1), but understanding the origin of the variability remains challenging. For example, Fig. 4.1 shows that natural basalt stable isotope data for the isotope systems considered here have different systematics relative to the bulk silicate Earth (BSE). Magnesium and V stable isotope compositions in MORB and OIB scatter both sides of the BSE value, whereas Fe stable isotope compositions of basalts are heavier than the BSE, and for Cr and Ca basalts are (mostly) isotopically lighter than the BSE. The Mg and Fe stable isotope compositions of OIB show greater variability than MORB for the same isotope system, whereas the opposite is true for V stable isotopes (although this may be a sampling bias, given the greater amount of V isotope data for MORB than OIB).

**Table 4.1: Literature data sources for stable isotope data compilation used in this chapter.**

| Isotope                | Type        | Literature sources                                                                                                                                                                                                                                                        |
|------------------------|-------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\delta^{26}\text{Mg}$ | MORB<br>OIB | Wiechert and Halliday (2007); Bourdon et al. (2010); Teng et al. (2010); Zhong et al. (2021a)<br>Bourdon et al. (2010); Teng et al. (2010); Zhong et al. (2017); Wang et al. (2021)                                                                                       |
| $\delta^{44}\text{Ca}$ | MORB<br>OIB | Zhu et al. (2018b); Chen et al. (2020a); Zhu et al. (2020)<br>Huang et al. (2011b); Valdes et al. (2014, 2019); Feng et al. (2017); Chen et al. (2020a)                                                                                                                   |
| $\delta^{57}\text{Fe}$ | MORB<br>OIB | Teng et al. (2013); Nebel et al. (2013); Zhong et al. (2021b) (seamounts: Sun et al., 2020)<br>Teng et al. (2008); Schuessler et al. (2009); Konter et al. (2016); Nebel et al. (2019)<br>Peters et al. (2019); Gleeson et al. (2020); Soderman et al. (2021) [chapter 3] |
| $\delta^{51}\text{V}$  | MORB<br>OIB | Prytulak et al. (2013); Wu et al. (2018); Novella et al. (2020)<br>Prytulak et al. (2013); Ding et al. (2020)                                                                                                                                                             |
| $\delta^{53}\text{Cr}$ | OIB         | Bonnand et al. (2020); Shen et al. (2020)                                                                                                                                                                                                                                 |

Modelling of expected stable isotopic behaviour has led to questions about the origin of isotopic signatures observed in natural samples. For example, some studies have modelled Ca stable isotope fractionation using composition-dependent inter-mineral fractionation factors and concluded that partial melting of eclogite cannot produce the variability measured in OIB (Chen et al., 2020b), whereas others have predicted and measured that garnet has a higher  $\delta^{44}\text{Ca}$  than coexisting clinopyroxene (Antonelli et al., 2019b; Huang et al., 2019; Kang et al., 2019; Wang et al., 2019; Chen et al., 2020b; Dai et al., 2020; Smart et al., 2021; Tappe et al., 2021), and have used this observation to predict that melts from recycled oceanic crust (garnet-bearing eclogite) will have low  $\delta^{44}\text{Ca}$ , thus explaining the low  $\delta^{44}\text{Ca}$  measured in some OIB (Kang et al., 2019; Dai et al., 2020). Lithological heterogeneity (specifically, recycled pyroxenite) has also been linked to Mg and Fe isotope variability in MORB and OIB (e.g., Williams and Bizimis, 2014; Konter et al., 2016; Zhong et al., 2017; Stracke et al., 2018; Nebel et al., 2019; Gleeson et al., 2020; Sun et al., 2020; Zhong et al., 2021b). However, some recent models of Fe and Mg isotope fractionation have led to uncertainty in whether equilibrium fractionation associated with the presence of garnet can unambiguously identify a garnet-bearing pyroxenite source lithology in natural OIB samples (Stracke et al., 2018; Soderman et al., 2021 [chapter 3]), and whether the heaviest Fe isotope data in the global dataset



**Figure 4.1: Literature MORB and OIB data for the isotope systems** (for sources, see Table 4.1). Samples are filtered for  $7.2 < \text{MgO wt \%} < 16$ , but included if MgO is not known, to limit the effects of fractional crystallisation and olivine accumulation. Where MORB type is known, samples are classified as N-/T- or E-type (as classified by Teng et al., 2013); if classification is not known, samples are plotted as N-/T-type. Ca and Mg isotope data is filtered to exclude samples with  $^{87}\text{Sr}/^{86}\text{Sr} > 0.7037$ , which excludes samples with  $> 1\%$  carbonate component in the source (Huang et al., 2011b). The main axis shows the variability in natural data from the BSE value for each isotope system, scaled by the difference in the atomic mass units (a.m.u.) of the isotopes being measured (e.g., for  $\delta^{26/24}\text{Mg}$ , this a.m.u. factor is 2). The coloured bars show 2 S.D. on the BSE estimates. BSE values used are  $\delta^{26}\text{Mg} = -0.24 \pm 0.06\text{‰}$  (Stracke et al., 2018),  $\delta^{44}\text{Ca} = 0.94 \pm 0.10\text{‰}$  (Kang et al., 2017; Chen et al., 2019a),  $\delta^{57}\text{Fe} = 0.05 \pm 0.04\text{‰}$  (Sossi et al., 2016),  $\delta^{51}\text{V} = -0.91 \pm 0.09\text{‰}$  (Qi et al., 2019),  $\delta^{53}\text{Cr} = -0.12 \pm 0.04\text{‰}$  (Jerram et al., 2020). The pale secondary axis for each isotope shows the raw isotope ratios. The isotope ratios and reference materials used in the delta notation throughout are:  $\delta^{26/24}\text{Mg}$  [DSM3];  $\delta^{44/40}\text{Ca}$  [SRM915a];  $\delta^{57/54}\text{Fe}$  [IRMM-014];  $\delta^{51/50}\text{V}$  [AA];  $\delta^{53/52}\text{Cr}$  [NIST979].

can be matched by models of mantle melting (Sun et al., 2020; Soderman et al., 2021 [chapter 3]).

Given the framework of MORB and OIB data that the geochemical community now has (Fig. 4.1), growing theoretical information on bond strength and predicted inter-mineral fractionations for multiple stable isotope systems, and a variety of published isotope fractionation models that both can and cannot explain all the natural data, it is timely to develop a self-consistent model for the behaviour of multiple stable isotopes during mantle melting. Here, I use the thermodynamically self-consistent model for mantle melting of peridotite and two pyroxenite lithologies presented in chapter 2, combined with a model for equilibrium Mg-Ca-V-Cr stable isotope fractionation based on the Fe isotope fractionation model outlined in chapter 2. This model responds to changes in mantle mineralogy, intrinsic variations in oxygen fugacity (i.e., at constant O content), temperature and pressure. These models allow me to investigate the potential for the stable isotope composition of basalts to be a tracer of mantle temperature and lithological heterogeneity.

### 4.1.3 Approach

This contribution explores the behaviour of Mg-Ca-Fe-V-Cr stable isotopes during mantle melting, using the modelling approach outlined in chapter 2. These isotope systems were chosen as they have been documented to show resolvable mineral-specific fractionation effects that may make them sensitive to partial melting or source lithology effects (e.g., Konter et al., 2016; Xia et al., 2017; Stracke et al., 2018; Wu et al., 2018; Kang et al., 2019; Nebel et al., 2019; Dai et al., 2020; Gleeson et al., 2020; Shen et al., 2020; Novella et al., 2020), and their bonding environments and/or expected isotopic fractionation in mantle minerals and melt are sufficiently well-studied to provide reasonable inputs for an isotopic fractionation model. The isotope systems represent both major and trace elements in basalts, and monovalent and heterovalent elements. The major elements (Mg, Ca, Fe) are abundant in the mantle with comparable or lower concentrations in pelitic sediments and crustal material (Plank and Langmuir, 1998; Rudnick and Gao, 2003; Workman and Hart, 2005), meaning the isotopic signatures of mantle components are not easily affected by metasomatism, and their isotopic compositions in basalts should track the bulk mass contributions of both fertile and depleted mantle lithologies to the melt. This is an important property of major element stable isotope systems that contrasts with radiogenic isotope systems of incompatible trace elements, which cannot probe the proportions of different lithologies directly, as incompatible element concentrations vary widely between enriched and depleted mantle lithologies. I note that carbonates, whose presence has been invoked in the source regions of mantle melts (e.g., Huang et al., 2011b; Liu et al., 2017b; Wang et al., 2018), have Ca concentrations  $\sim 10$  times higher than the mantle (e.g., Huang et al., 2011b), but I do not discuss carbonates here; instead I filter natural data used in this study by  $^{87}\text{Sr}/^{86}\text{Sr}$  to exclude significant contributions from carbonate components.

Section 4.2 contains specific details of the inputs and associated uncertainties of the combined

thermodynamic melting and equilibrium isotope fractionation model, beyond the approach outlined in chapter 2. A summary of the results is presented in this section.

Section 4.3 contains full graphical results of the Mg, Ca, V and Cr isotope fractionation model.

Sections 4.4 and 4.5 address the degree to which different stable isotope measurements (individual isotope systems, or in combination) can identify the relative importance of mantle temperature variability and mantle lithological heterogeneity in generating the observed variability in basalts. I also discuss where stable isotope systems have the potential to be useful in identifying these processes, if measurement uncertainties can be reduced.

Finally, section 4.6 combines MORB and OIB data for the isotope systems studied with the modelled equilibrium melts, to assess to what extent our present understanding of the isotope behaviour can explain global basalt variability. I do not include arc basalts in my discussion for a number of reasons, including but not limited to the complicating effects of H<sub>2</sub>O, slab fluids and redox variability in an arc setting, which have been linked to stable Fe and Mg isotope variability recorded in arc basalts (e.g., Dauphas et al., 2009; Nebel et al., 2013, 2015; Sossi et al., 2016; Teng et al., 2016; Li et al., 2017; Brewer et al., 2018; Hu et al., 2020) and which are beyond the applicable scope of the modelling presented here.

## 4.2 Modelling equilibrium isotopic composition of mantle melts

The equilibrium melting isotopic fractionation over P-T space for  $\delta^{26/24}\text{Mg}$ ,  $\delta^{44/40}\text{Ca}$ ,  $\delta^{57/54}\text{Fe}$ ,  $\delta^{51/50}\text{V}$  and  $\delta^{53/52}\text{Cr}$  was calculated for three representative mantle lithologies, following the model outlined in chapter 2. The calculated modal mineralogies over P-T space of KLB1 peridotite (an experimental composition used as an analogue for the upper mantle; Davis et al., 2009) and G2 silica-excess pyroxenite (a MORB-like bulk composition; Pertermann and Hirschmann, 2003a) presented in Soderman et al. (2021), and chapters 2 and 3, were used. Following the methods used for KLB1 and G2, for this study the P-T-dependent modal mineralogy of MIX1G, a silica-deficient pyroxenite which plots close to the average global pyroxenite composition, was also calculated. This lithology can be considered as a mixture between KLB1 and MORB (Lambart et al., 2016), i.e., recycled crust mixed with ambient mantle [chapter 2]. This set of lithologies spans a range of fertile compositions, both ambient mantle and those derived from recycled crust, thought to be present in the mantle (Hirschmann and Stolper, 1996; Shorttle and MacLennan, 2011; Lambart et al., 2016; Mallik et al., 2021).

Iron isotope compositions of minerals and melts were calculated for MIX1G, following Soderman et al. (2021) [chapters 2 and 3]; and Ca, Mg, Cr and V isotope compositions were newly calculated for all three lithologies. The approach of the model for each isotope, and the full results, are described below.

I do not consider  $\text{H}_2\text{O}$  in my phase-equilibrium calculations, as the THERMOCALC peridotite dataset used does not account for  $\text{H}_2\text{O}$  accommodation in the mantle phases (Holland et al., 2018). However, for the comparison of my models to MORB and OIB, I consider this dry system to be suitable: non-arc mantle is generally considered to have small amounts of water stored in nominally anhydrous minerals (Bell and Rossman, 1992; Hirschmann et al., 2005). While  $\text{H}_2\text{O}$ , if present in the mantle source, would result in a deeper onset of melting than in dry melting, it does not result in significant changes to the maximum extent of melting and most water would be extracted in the first degrees of melting (e.g., Hirth and Kohlstedt, 1996; Hirschmann et al., 1999; Katz et al., 2003), so I consider that the  $\text{H}_2\text{O}$  concentrations will be very low throughout most of the melting region. Therefore, the conclusions reached here will not be significantly changed by the inclusion of water in the thermodynamic system.

#### 4.2.1 Modelling approach: Ca, Mg and Fe

The partitioning of Ca, Mg and Fe ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) between the phases present at any P-T point is taken from the THERMOCALC results. To calculate the isotope fractionation factors ( $\alpha$ ) for Ca and Mg isotopes between each phase, published temperature-dependent  $\beta$ -values (a reduced partition function ratio; Young et al., 2015) are used, where

$$\alpha^{A-B} = \frac{\beta(T)_A}{\beta(T)_B}. \quad (4.1)$$

Bulk  $\beta$ -values for each mineral (i.e., not using crystal site occupancy information) are calculated based on vibrational frequencies from first-principle calculations.

For Mg,  $\beta^{\text{Mg}}$  factors for Mg-bearing mantle minerals (spinel, clinopyroxene, orthopyroxene, olivine, garnet; Table 4.2) are taken from Huang et al. (2013), with the exception of spinel, which is taken from Schauble (2011) and scaled relative to a reference  $\beta^{\text{Mg}}$  of olivine which is calculated in both studies. Pigeonite (a stable phase in MIX1G) is modelled with the same  $\beta^{\text{Mg}}$  as clinopyroxene; liquid (melt) is taken as having no fractionation from olivine in the main model (Stracke et al., 2018, see section 4.9 for discussion), so  $\beta_{\text{melt}}^{\text{Mg}} = \beta_{\text{olivine}}^{\text{Mg}}$ .

**Table 4.2: Parameters for  $\beta^{\text{Mg}}$  factors from Huang et al. (2013).**  $1000\ln\beta = a/T^6 + b/T^4 + c/T^2$ , where T = temperature (Kelvin).

| Mineral       | a                      | b                     | c                  |
|---------------|------------------------|-----------------------|--------------------|
| spinel        | $-2.74 \times 10^{16}$ | $2.08 \times 10^{11}$ | $2.93 \times 10^6$ |
| orthopyroxene | $-8.10 \times 10^{15}$ | $6.65 \times 10^{10}$ | $2.25 \times 10^6$ |
| clinopyroxene | $-1.17 \times 10^{16}$ | $1.03 \times 10^{11}$ | $2.24 \times 10^6$ |
| olivine       | $-1.19 \times 10^{16}$ | $1.05 \times 10^{11}$ | $2.07 \times 10^6$ |
| garnet        | $-5.50 \times 10^{15}$ | $4.92 \times 10^{10}$ | $1.30 \times 10^6$ |
| melt          | $-1.19 \times 10^{16}$ | $1.05 \times 10^{11}$ | $2.07 \times 10^6$ |

**Table 4.3:**  $\beta^{\text{Ca}}$  factors for isotope fractionation model, given as  $1000 \ln \beta$ , at a temperature of 1000K, from Antonelli et al. (2019b).

| Mineral       | Structure used          | $1000 \ln \beta$ |
|---------------|-------------------------|------------------|
| plagioclase   | anorthite               | 1.06             |
| orthopyroxene | Ca/Mg = 1/32            | 1.84             |
| clinopyroxene | diopside                | 1.32             |
| olivine       | forsterite Ca/Mg = 1/64 | 2.11             |
| garnet        | pyrope Ca/Mg = 1/24     | 2.00             |
| liquid        |                         | 1.19             |

The  $\beta^{\text{Ca}}$  factors used for Ca-bearing mantle minerals (plagioclase, clinopyroxene, orthopyroxene, olivine, garnet) are given in Table 4.3, and are taken from Antonelli et al. (2019b). Where options exist for minerals with different structures and/or compositions, those with the most similar Ca/Mg to the typical phase compositions calculated by THERMOCALC for KLB1 were used. Pigeonite is modelled with the same  $\beta^{\text{Ca}}$  as clinopyroxene; liquid is taken as having  $\beta^{\text{Ca}}$  intermediate between clinopyroxene and plagioclase (anorthite), following observations from natural samples (Zhang et al., 2018b; Antonelli et al., 2019a) and consistent with the approach used by Antonelli et al. (2021).  $\beta^{\text{Ca}}$  factors are made temperature-dependent by

$$\ln \beta_{(T)} = \ln \beta_{(1000K)} \times \frac{10^6}{T^2} \quad (4.2)$$

following Antonelli et al. (2021).

Where suitable  $\beta$ -values are not published, as for Fe and outlined in chapter 2,  $\alpha$  factors can be calculated using cation-oxygen bond force constants in each crystal site for the minerals,

$$\ln(\alpha^{\text{A-B}}) = C \frac{[K_A - K_B]}{T^2}, \quad (4.3)$$

where C is a constant dependent on the isotopes and element being considered (e.g., Sossi and O'Neill, 2017), T is the temperature in Kelvin, and  $K_A$  and  $K_B$  refer to the cation-oxygen force constants in minerals A and B. These force constants are based on an ionic bonding model for Fe (Sossi and O'Neill, 2017), as employed in Macris et al. (2015); Young et al. (2015); Soderman et al. (2021); Williams et al. (2021), and described in chapter 2.

## 4.2.2 Modelling approach: V and Cr

### 4.2.2.1 Parameterising the proportion of each valence state in the melt

The THERMOCALC a-X models of Holland et al. (2018) do not model V partitioning, nor heterovalent Cr (Cr is assumed to have a valence of 3+ in the Holland et al., 2018 models). Therefore, the

**Table 4.4: Optical basicity values for each major element oxide**, from Mills (1993), used in equation 4.8.

| optical basicity, $\Lambda$ |                  |                                |                                |                                |     |     |      |                   |                  |
|-----------------------------|------------------|--------------------------------|--------------------------------|--------------------------------|-----|-----|------|-------------------|------------------|
| SiO <sub>2</sub>            | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | FeO | CaO | MgO  | Na <sub>2</sub> O | K <sub>2</sub> O |
| 0.48                        | 0.61             | 0.60                           | 0.75                           | 0.58                           | 1   | 1   | 0.78 | 1.15              | 1.4              |

proportion of  $V^{3+/4+/5+}$  was calculated following Toplis and Corgne (2002), using the FeO/Fe<sub>2</sub>O<sub>3</sub> ratio of the melt (calculated in THERMOCALC) at each point in P-T space, with

$$\log(XV^{3+}/XV^{4+}) = \log(XFe^{2+}/XFe^{3+}) - 2.4 \quad (4.4)$$

and

$$\log(XV^{4+}/XV^{5+}) = \log(XFe^{2+}/XFe^{3+}) - 0.3 \quad (4.5)$$

where X is the mole fraction of cation.

The proportion of  $Cr^{2+/3+}$  was calculated using the parameterisation of Berry et al. (2021)

$$\frac{Cr^{2+}}{Cr_T} = \frac{1}{1 + 10^{(0.25 \log fO_2 + \log K')}} \quad (4.6)$$

with  $fO_2$  at each point calculated using the ‘fO<sub>2</sub>melt’ software (Holland et al., 2018), hence Cr speciation also depends on the Fe redox equilibria. The modified equilibrium constant was calculated by

$$\log K' = \frac{9770}{T} - 7.69 + 6.22\Lambda + \frac{(900P - 172P^2)}{T} \quad (4.7)$$

where T is in Kelvin, P is in GPa.  $\Lambda$  is the optical basicity, a composition-dependent term (Duffy, 1993) which reflects equilibrium between bridging oxygens, non-bridging oxygens and free oxide anions in a melt (Humphreys et al., 2015). Since optical basicity values can be assigned to individual oxides (Duffy, 1993), an ideal optical basicity for a melt can be calculated, following Mills (1993), as

$$\Lambda = \frac{\sum X_i n_i \Lambda_i}{\sum X_i n_i} \quad (4.8)$$

where  $X_i$  is the mole fraction of oxide i, n is the number of O associated with oxide i, and  $\Lambda$  is the theoretical  $\Lambda$  of oxide i (see Table 4.4). At each P-T point, the calculated  $\Lambda$  was used with equations 4.6 and 4.7 to calculate Cr redox state.

#### 4.2.2.2 Oxygen distribution amongst the redox-sensitive elements

Here, I note that the requirement to handle heterovalent Cr and V outside of the THERMOCALC calculations means that the calculations of the redox state (hence, ultimately isotopic fractionation) are not fully self-consistent for the redox-sensitive elements. The  $Cr^{3+}/Cr_T$ ,  $V^{4+}/V_T$  and  $V^{5+}/V_T$  ratios change across P-T space without taking oxygen from anywhere else (i.e., the  $Fe^{3+}/Fe_T$  ratio

calculated at each P-T point does not vary when Cr and V redox equilibria are considered). Instead, the calculations of the valence states of Cr and V at each P-T point are dictated by the calculated Fe redox equilibria at that point. Nonetheless, tying the redox equilibria of Cr and V to that of Fe is a reasonable approximation of the natural system, given that the abundance of Fe in the mantle is significantly greater than that of the other redox-variable elements (Anenburg and O'Neill, 2019).

To quantify the dominance of Fe amongst the redox-sensitive elements in the mantle, I have calculated the fraction of oxygen associated with oxidised valence states of the each redox-sensitive element out of the total oxygen associated with the oxidised valence states, e.g.,

$$\frac{O_{\text{Fe}^{3+}}}{O_{\text{Fe}^{3+}} + O_{\text{Cr}^{3+}} + O_{\text{V}^{4+}} + O_{\text{V}^{5+}}} \quad (4.9)$$

where  $O_X$  represents the number of moles of oxygen associated with cation X at any given P-T point. At  $T = 1300^\circ\text{C}$  and  $P = 12$  kbar, I calculate that 73 % of the oxygen associated with oxidised cations is associated with  $\text{Fe}^{3+}$ , 27 % with  $\text{Cr}^{3+}$ , and  $< 0.01$  % with  $\text{V}^{4+,5+}$ , for total Fe, Cr and V contents in peridotite (Davis et al., 2009; Salters and Stracke, 2004). This result confirms that tying the redox equilibria of Cr and V to that of Fe is a reasonable approximation of the natural system.

It is important to note that, as a consequence of my model's implementation of Cr/V redox, the changes in Cr/V speciation in the model will represent upper limits: i.e., in a more complex system coupled Fe-Cr-V redox equilibria will dampen the variability of  $\text{Fe}^{3+}/\text{Fe}_T$ ,  $\text{Cr}^{3+}/\text{Cr}_T$  and  $\text{V}^{4+,5+}/\text{V}_T$  compared to my models. This is because the combined effect of considering three redox equilibria able to accommodate oxygen via their oxidised cations together is that each system will have to shift its redox equilibria less compared to a scenario where only one redox-sensitive element is considered. To approximately quantify the effect of this redox feedback, I took an extreme case of reducing all the  $\text{Cr}_2\text{O}_3$  in the melt at a given P-T point, accommodating the released oxygen by increasing the amount of  $\text{Fe}_2\text{O}_3$  and reducing the amount of FeO accordingly. I then calculated the  $f\text{O}_2$  of this new composition through the  $f\text{O}_2\text{melt}$  software (Holland et al., 2018), and recalculated the expected  $\text{Cr}^{3+}/\text{Cr}_T$  given the new  $f\text{O}_2$ . I find that, for this calculation performed using at  $T = 1350^\circ\text{C}$  and  $P = 12$  kbar, the  $f\text{O}_2$  change produces a 1 % change in  $\text{Cr}^{3+}/\text{Cr}_T$  and negligible impact on the calculated  $\delta^{53}\text{Cr}$ .

#### 4.2.2.3 Partitioning and isotopic fractionation of V and Cr amongst the mantle phases

The total V and Cr in the system were partitioned, dependent on the relative proportions of each valence state, between the phases present based on valence-specific partition coefficients mostly from Mallmann and O'Neill (2009) (Tables 4.5, 4.6). Garnet was assumed to have similar V partitioning to clinopyroxene (Mallmann and O'Neill, 2007, 2009), and pigeonite was modelled as clinopyroxene. The  $\alpha$  factors for V were calculated following the approach used for Mg and

Ca above, using  $\beta^V$  values for V in different coordination environments in solution systems from Wu et al. (2015) (Table 4.5), extrapolated to magmatic systems at high temperature following Wu et al. (2018).

**Table 4.5: Parameters for V partitioning and isotopic fractionation.** Partition coefficients (D) from Mallmann and O'Neill (2009).  $\beta^V$  factors are from Wu et al. (2015).  $1000\ln\beta = a/T^6 + b/T^4 + c/T^2$ , where T = temperature (Kelvin).

| Mineral       | Valence         | $D_{\text{min-liq}}$ | a                    | b                      | c                  |
|---------------|-----------------|----------------------|----------------------|------------------------|--------------------|
| olivine       | V <sup>3+</sup> | 0.18                 | $1.0 \times 10^{14}$ | $-7.70 \times 10^9$    | $6.28 \times 10^5$ |
|               | V <sup>4+</sup> | 0.0227               | $4.0 \times 10^{14}$ | $-1.80 \times 10^{10}$ | $9.43 \times 10^5$ |
|               | V <sup>5+</sup> | 0.00255              | $7.0 \times 10^{14}$ | $-3.06 \times 10^{10}$ | $1.26 \times 10^6$ |
| orthopyroxene | V <sup>3+</sup> | 1                    | $1.0 \times 10^{14}$ | $-7.70 \times 10^9$    | $6.28 \times 10^5$ |
|               | V <sup>4+</sup> | 0.674                | $4.0 \times 10^{14}$ | $-1.80 \times 10^{10}$ | $9.43 \times 10^5$ |
|               | V <sup>5+</sup> | 0.00338              | $7.0 \times 10^{14}$ | $-3.06 \times 10^{10}$ | $1.26 \times 10^6$ |
| clinopyroxene | V <sup>3+</sup> | 3.88                 | $1.0 \times 10^{14}$ | $-7.70 \times 10^9$    | $6.28 \times 10^5$ |
|               | V <sup>4+</sup> | 1.13                 | $4.0 \times 10^{14}$ | $-1.80 \times 10^{10}$ | $9.43 \times 10^5$ |
|               | V <sup>5+</sup> | 0.0142               | $7.0 \times 10^{14}$ | $-3.06 \times 10^{10}$ | $1.26 \times 10^6$ |
| spinel        | V <sup>3+</sup> | 15.3                 | $1.0 \times 10^{14}$ | $-7.70 \times 10^9$    | $6.28 \times 10^5$ |
|               | V <sup>4+</sup> | 1.44                 | $4.0 \times 10^{14}$ | $-1.80 \times 10^{10}$ | $9.43 \times 10^5$ |
|               | V <sup>5+</sup> | 0.00303              | $7.0 \times 10^{14}$ | $-3.06 \times 10^{10}$ | $1.26 \times 10^6$ |
| garnet        | V <sup>3+</sup> | 3.88                 | $1.0 \times 10^{14}$ | $-7.70 \times 10^9$    | $6.28 \times 10^5$ |
|               | V <sup>4+</sup> | 1.13                 | $4.0 \times 10^{14}$ | $-1.80 \times 10^{10}$ | $9.43 \times 10^5$ |
|               | V <sup>5+</sup> | 0.0142               | $7.0 \times 10^{14}$ | $-3.06 \times 10^{10}$ | $1.26 \times 10^6$ |
| melt          | V <sup>3+</sup> | 1                    | $1.0 \times 10^{14}$ | $-7.70 \times 10^9$    | $6.28 \times 10^5$ |
|               | V <sup>4+</sup> | 1                    | $4.0 \times 10^{14}$ | $-1.80 \times 10^{10}$ | $9.43 \times 10^5$ |
|               | V <sup>5+</sup> | 1                    | $7.0 \times 10^{14}$ | $-3.06 \times 10^{10}$ | $1.26 \times 10^6$ |

For Cr, for partition coefficients not published by Mallmann and O'Neill (2009), those for spinel were taken from the supplement of Shen et al. (2018), and for garnet from Sutton et al. (2008).  $\alpha$  factors were calculated from Cr-O force constants following an ionic model (Shen et al., 2018, 2020), as for Fe isotopes (Soderman et al., 2021 [chapter 2]). The ionic model inputs (Table 4.6) are based on the supplement of Shen et al. (2018); for garnet, where no ionic inputs are presented in Shen et al. (2018), coordination information was taken from Deer et al. (2013), with the relevant ionic radii as used by Shen et al. (2018). The force constants for Cr-O bonds were then calculated based on the equations presented in Sossi and O'Neill (2017) for Fe isotopes.

### 4.3 Modelling results

A summary of the modelled equilibrium isotopic fractionation of peridotite melts (relative to the source), is shown in Fig. 4.2. In Fig. 4.2, melt isotope ratios are shown along isentropic decompression melting paths calculated from THERMOCALC output – the isentropic approach (McKenzie, 1984; McKenzie and Bickle, 1988) assumes the adiabatic upwelling of the mantle is reversible, which is generally considered to be a good approximation of decompression melting in the mantle (e.g., McKenzie, 1984; McKenzie and Bickle, 1988; Asimow, 2002).

**Table 4.6: Parameters for Cr partitioning and isotopic fractionation model.** Partition coefficients (D) from Mallmann and O'Neill (2009); Shen et al. (2018); Sutton et al. (2008). Mineral site and bonding information is based on Shen et al. (2018). cpx = clinopyroxene, opx = orthopyroxene.

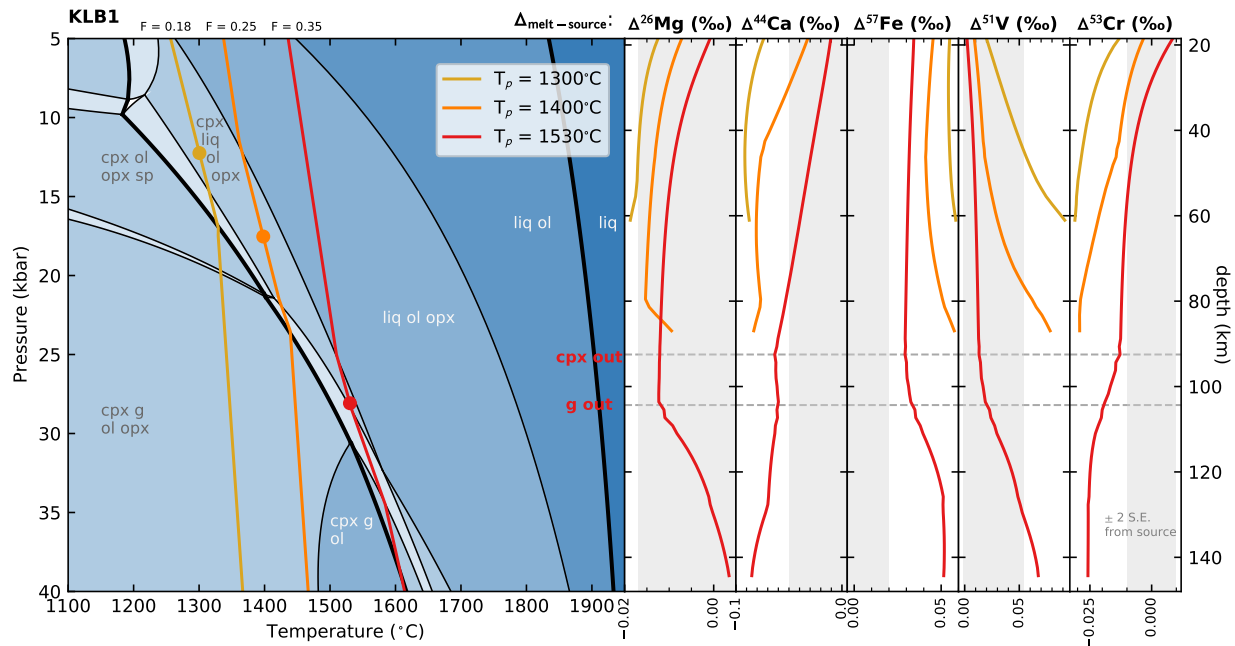
| Mineral | Cr species | $D_{\text{min-melt}}$ | Site | Cr coordination | Bond length (Å) | O coordination | No. sites |
|---------|------------|-----------------------|------|-----------------|-----------------|----------------|-----------|
| spinel  | 2+         | 0                     | n/a  | n/a             | n/a             | n/a            | n/a       |
| spinel  | 3+         | 220                   | M    | 6               | 1.995           | 4              | 2         |
| garnet  | 2+         | 0                     | n/a  | n/a             | n/a             | n/a            | n/a       |
| garnet  | 3+         | 12                    | M2   | 6               | 1.995           | 4              | 2         |
| olivine | 2+         | 0.85                  | M2   | 6               | 2.18            | 4              | 1         |
| olivine | 3+         | 0.85                  | M1   | 6               | 1.995           | 4              | 1         |
| opx     | 2+         | 0.843                 | M2   | 7               | 2.305           | 3.57           | 1         |
| opx     | 3+         | 3.52                  | M1   | 6               | 1.988           | 3.67           | 1         |
| cpx     | 2+         | 0.587                 | M2   | 7               | 2.305           | 3.57           | 1         |
| cpx     | 3+         | 12.6                  | M1   | 6               | 1.988           | 3.67           | 1         |
| liquid  | 2+         | 1                     |      | 4               | 1.913           | 4              |           |
| liquid  | 3+         | 1                     |      | 6               | 1.995           | 4              |           |

Table 4.7 summarises how the modelled stable isotope compositions of pyroxenite melts compare to the peridotite melts from Fig. 4.2. Due to the wider range of melting degrees reached by pyroxenites compared to peridotite for a given  $T_p$ , generally the pyroxenite melts show a wider range of isotope ratios than peridotite melts for the same  $T_p$ .

**Table 4.7: Maximum magnitude  $\Delta_{\text{melt-source}}$  for modelled isentropic decompression melting of KLB1 (peridotite), MIX1G (silica-deficient pyroxenite) and G2 (silica-excess pyroxenite), all following KLB1 isentropes, when  $T_p = 1300^\circ\text{C}$  ('cold'),  $T_p = 1400^\circ\text{C}$  ('mid') and  $T_p = 1530^\circ\text{C}$  ('hot').** Typical analytical uncertainties used throughout this study are also given, taken from recent studies: for Mg, Wang et al. (2021); for Ca, Zhu et al. (2018b, 2020); Chen et al. (2019a); for Fe, Soderman et al. (2021); for V, Wu et al. (2018); Qi et al. (2019); Novella et al. (2020); for Cr, Xia et al. (2017); Sossi et al. (2018a).

| Lithology                             | Temperature | Maximum modelled melt-source fractionation |                        |                        |                       |                        |
|---------------------------------------|-------------|--------------------------------------------|------------------------|------------------------|-----------------------|------------------------|
|                                       |             | $\Delta^{26}\text{Mg}$                     | $\Delta^{44}\text{Ca}$ | $\Delta^{57}\text{Fe}$ | $\Delta^{51}\text{V}$ | $\Delta^{53}\text{Cr}$ |
| KLB1                                  | cold        | -0.019                                     | -0.092                 | 0.058                  | 0.092                 | -0.031                 |
|                                       | mid         | -0.015                                     | -0.083                 | 0.058                  | 0.078                 | -0.029                 |
|                                       | hot         | -0.012                                     | -0.085                 | 0.052                  | 0.067                 | -0.026                 |
| MIX1G                                 | cold        | -0.081                                     | -0.081                 | 0.050                  | 0.093                 | -0.058                 |
|                                       | mid         | -0.024                                     | -0.137                 | 0.045                  | 0.090                 | -0.049                 |
|                                       | hot         | 0.099                                      | -0.087                 | 0.026                  | 0.022                 | -0.036                 |
| G2                                    | cold        | 0.088                                      | -0.125                 | 0.048                  | 0.074                 | -0.095                 |
|                                       | mid         | 0.088                                      | -0.113                 | 0.036                  | 0.041                 | -0.054                 |
|                                       | hot         | 0.00                                       | 0.00                   | 0.00                   | 0.00                  | 0.00                   |
| 1 S.D. long-term analytical precision |             | 0.03                                       | 0.07                   | 0.025                  | 0.04                  | 0.02                   |
| 2 S.E. typical sample error           |             | 0.02                                       | 0.05                   | 0.02                   | 0.05                  | 0.01                   |

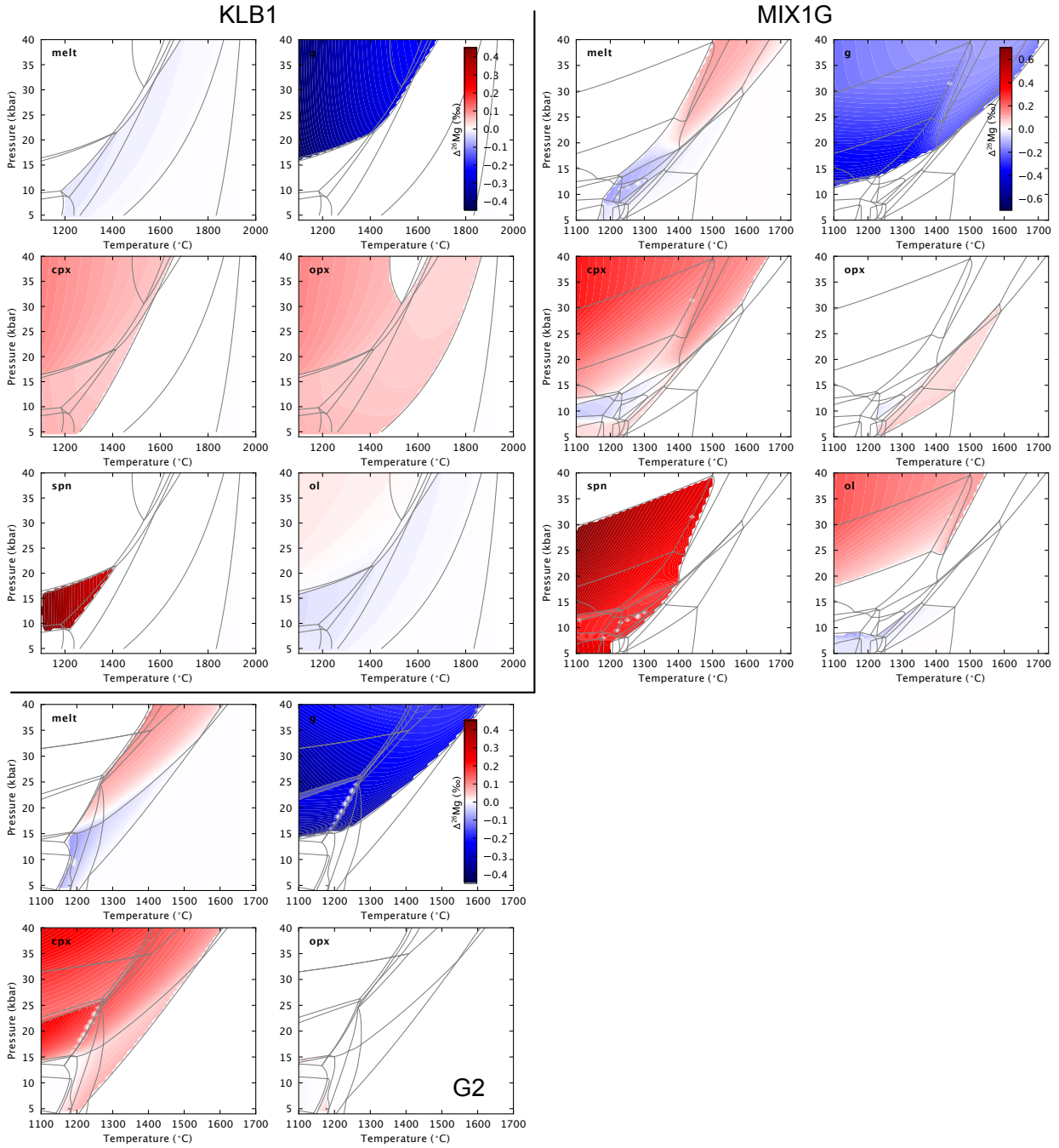
The full results for each isotope system are shown in the following figures, Figs. 4.3–4.6. Note that stable isotope fractionation of V and Cr can only be calculated where there is liquid present, i.e., where the proportion of each valence state can be calculated.



**Figure 4.2: Pseudosection and modelled instantaneous equilibrium melt isotopic fractionation along isentropic decompression melting paths for KLB1.** The left hand panel shows the pseudosection for KLB1 peridotite calculated in THERMOCALC, with the solidus and liquidus marked in bold, and three isentropic melting paths also calculated using THERMOCALC. The average pressure of melting for each isentrope (see section 4.10) is shown by the small circles, and maximum melt fraction ( $F$ ) labelled at the top of each isentrope. The right hand panels show the modelled instantaneous equilibrium melt isotopic fractionation relative to the bulk isotopic composition along both isentropes. Key mineralogical controls on the isotopic composition of the melt are highlighted (colour-coded by the isentropic path they refer to; here both for  $T_p = 1530^\circ\text{C}$ ). Vertical grey bars show the source composition (0‰) with typical sample 2 S.E. analytical precision for each isotope system. The analytical precisions used are based on representative errors from recent studies: for Mg from Wang et al. (2021), for Ca from Zhu et al. (2018b, 2020); Chen et al. (2020b), for Fe from Soderman et al. (2021) [chapter 3], for V from Wu et al. (2018); Novella et al. (2020), for Cr from Sossi et al. (2018a). Note that long-term analytical 2 S.D. uncertainty is usually greater than sample 2 S.E. for each isotope system; see Table 4.7.

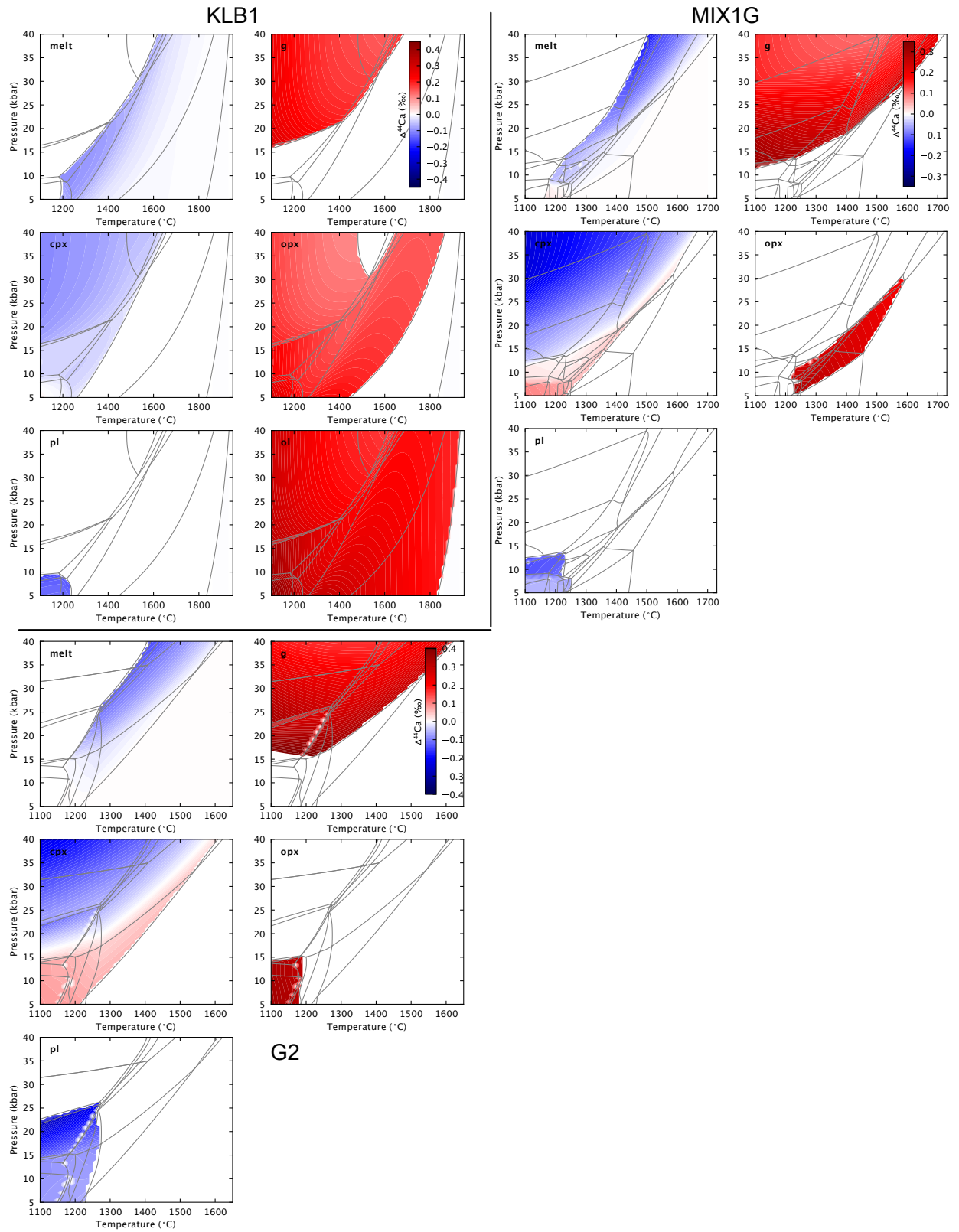
## 4.4 Stable isotope sensitivity to mantle temperature variations

To explore the sensitivity of stable isotopes in basalts to variations in mantle potential temperature, I use the results of the equilibrium melt fractionation model for KLB1, since for MORB, the dominant source lithology is peridotite (Hirschmann and Stolper, 1996; Sobolev et al., 2007). Generally, all equilibrium source-melt isotopic fractionations are expected to decrease in magnitude with increased temperature (e.g., Bigeleisen and Mayer, 1947), although this effect will be small at high temperatures (typically scaling with  $1/T^2$ ). However, the complexity of mineral reactions during melting and the mineral-specific fractionation effects shown by the stable isotope systems means some isotopes may show larger temperature (and extent of melting) sensitivity than others as modal mineralogy and mineral chemistry changes across P-T space. When using stable isotopes as a tool to understand mantle melting processes and source compositions, I am interested in two aspects of equilibrium stable isotope fractionation: 1) the mineralogy-dependent fractionation on melting, and 2) the degree-of-melting-dependent fractionation.



**Figure 4.3:** Full results of the Mg isotopic fractionation model,  $\Delta^{26}\text{Mg}_{\text{phase-source}}$ , for the three lithologies.

MORB generated from different mantle potential temperatures will vary in 1) the modal mineralogy of their mantle source, 2) source oxygen fugacity ( $f\text{O}_2$ ), as this changes with pressure and temperature (e.g., Stolper et al., 2020), and 3) the degree of partial melting of the mantle source (Fig. 4.2; also Fig. 4.20). For MORB, the mean pressure and composition of melts produced in the mantle, hence the aggregate MORB composition, can be calculated using equations for 2D melting regimes (e.g., Klein and Langmuir, 1987; McKenzie and Bickle, 1988; Langmuir et al., 1992; Asimow et al., 2001). These calculations show that the mean melting pressure varies from  $\approx 12$  kbar for mantle potential temperatures around  $1300^\circ\text{C}$ , to  $> 25$  kbar for potential temperatures over  $1500^\circ\text{C}$  (see section 4.10 at end of chapter for details). The THERMOCALC results show that



**Figure 4.4:** Full results of the Ca isotopic fractionation model,  $\Delta^{44}\text{Ca}_{\text{phase-source}}$ , for the three lithologies.

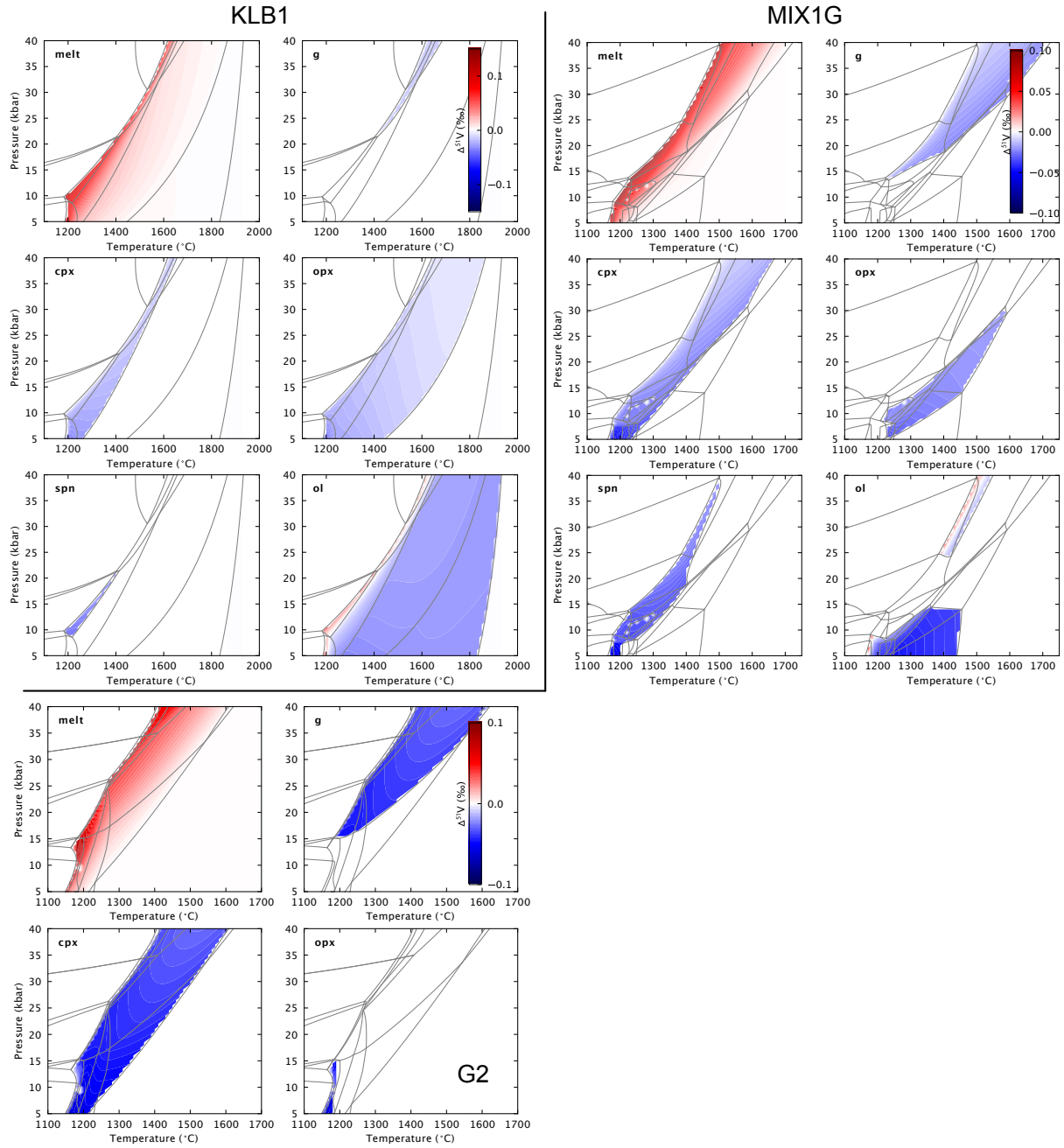


Figure 4.5: Full results of the V isotopic fractionation model,  $\Delta^{51}\text{V}_{\text{phase-source}}$ , for the three lithologies.

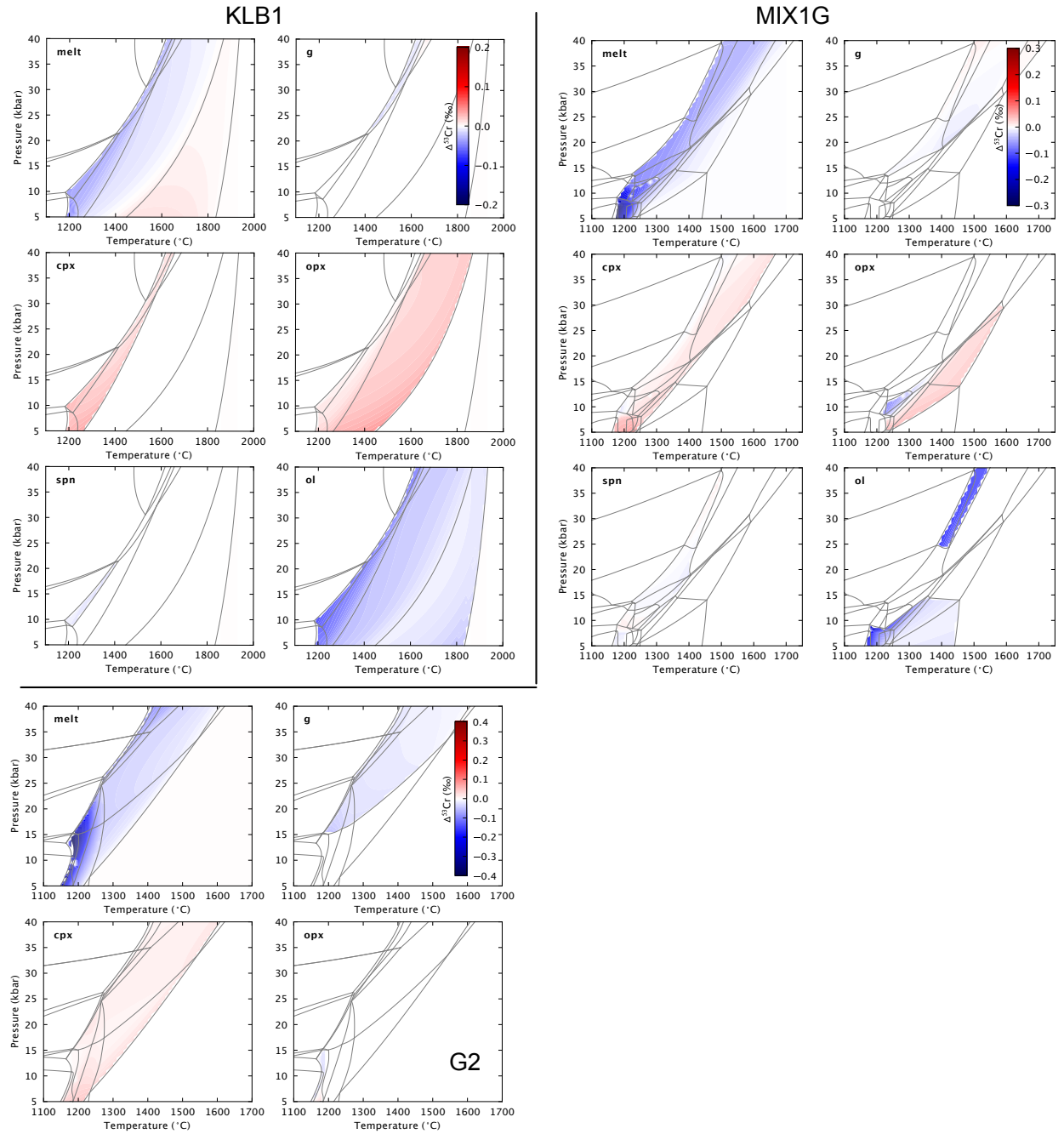
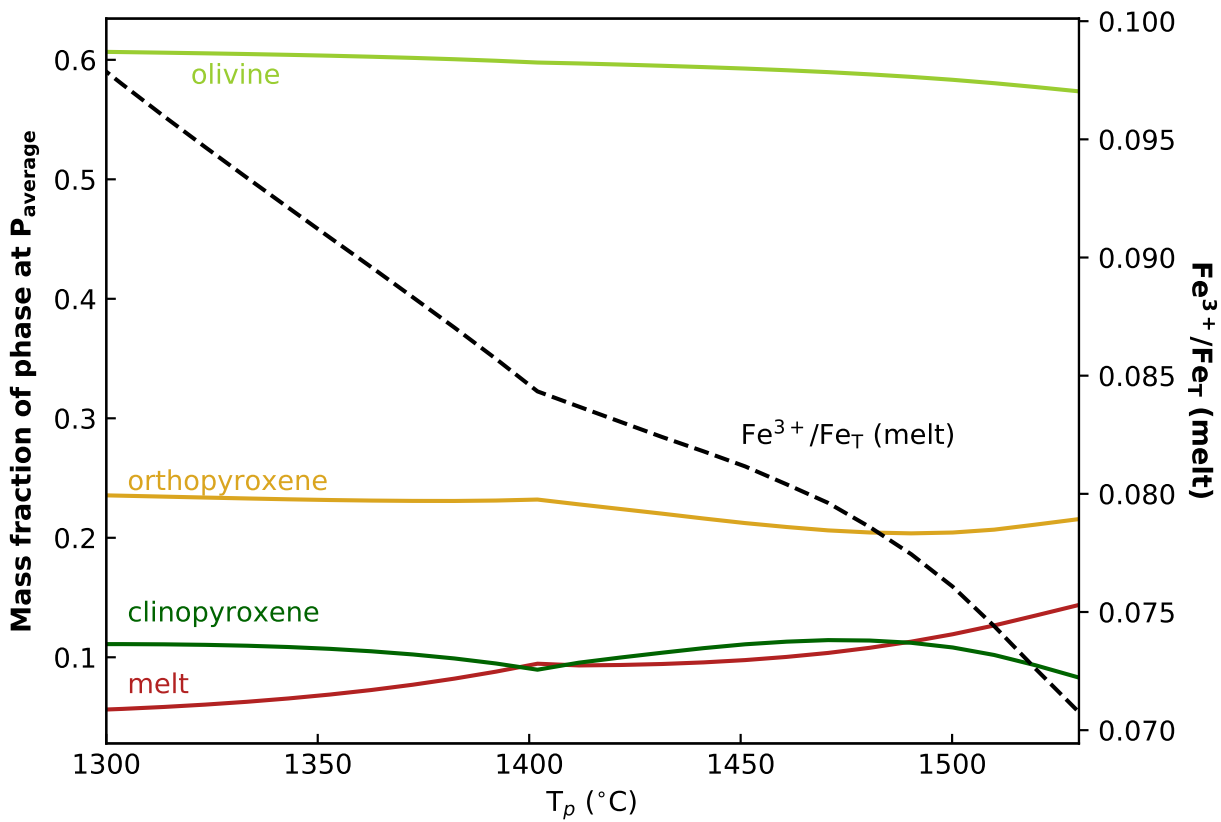


Figure 4.6: Full results of the Cr isotopic fractionation model,  $\Delta^{53}\text{Cr}_{\text{phase-source}}$ , for the three lithologies.

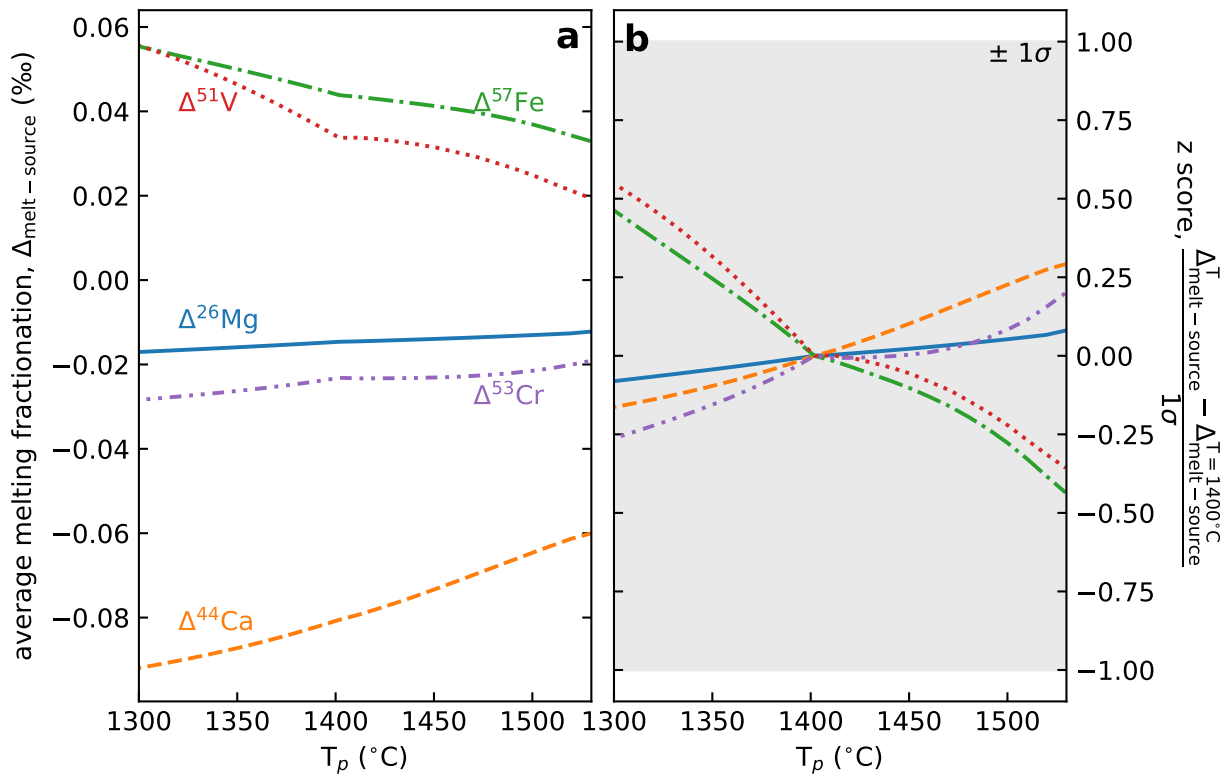
increasing mantle temperature, with a corresponding deepening of the average pressure of melting reflecting the ‘aggregate’ melt, leads to progressively increasing melt fraction and progressively decreasing  $\text{Fe}^{3+}/\text{Fe}_T$  in the melt (due to changing mineral chemistry; Stolper et al., 2020), with minimal changes in the proportions of solid phases in the stable assemblage at the mean melting pressure for each  $T_p$  (Figs. 4.2, 4.7). Therefore, the stable isotope compositions of melts could be dependent on mantle temperature through an  $f\text{O}_2$  dependence, which will arise due to the existence of multiple valence states, and the different melt partitioning behaviour of each valence state of the cation (e.g., Fe, Cr and V). Isotopes that are most sensitive to melting degree, such as those with large magnitude melt-source isotope fractionations at low melting degrees, may also show temperature-related melt isotope composition variations.



**Figure 4.7: Mass fraction of phases present in the equilibrium KLB1 mineral assemblage and melt  $\text{Fe}^{3+}/\text{Fe}_T$ , at the mean pressure of melt generation calculated for increasing mantle potential temperature.** Mantle potential temperature,  $T_p$ , is calculated by assuming a linear interpolation between the isentropes calculated in THERMOCALC for  $T_p = 1300, 1400$  and  $1530$  °C. The solid phase proportions are fractions of the whole assemblage (including melt). The average pressure of melting was calculated for  $T_p = 1300, 1400$  and  $1530$  °C (see details in section 4.10), and interpolated between.

Fig. 4.8 shows how the estimated isotopic composition of aggregate melts relative to the source, taken as the isotope ratio of the melt at the mean pressure of melting for each temperature, varies with mantle potential temperature. Using the mean melting pressure approach, which is a simplification of polybaric melting occurring in the Earth (Langmuir et al., 1992), gives similar results to polybaric decompression melting (see section 4.10 for a comparison of the approaches). The approach used here does not reflect accumulated fractional melting – the mean pressure of melt-

ing is in the spinel stability field, and therefore the isotope ratios of the final aggregate melts do not show a clear garnet signature. The isotope fractionation models show that relatively large magnitude temperature-related effects are seen in the heterovalent Fe and V isotope systems, in agreement with the predictions above that  $fO_2$  sensitivity will be the driver of  $T_p$ -related isotopic fractionation variation. The Cr isotope ratio of the melt does not show large variability with potential temperature despite being a heterovalent system – this is because the  $Cr^{2+}/Cr_T$  ratio in the system is dependent on pressure and temperature (equation 4.6), as well as  $fO_2$  (Berry et al., 2021). Therefore, the  $fO_2$  effect is not dominant when changing  $T_p$ , in contrast to V stable isotopes where the V valence state parameterisation is only linked to the  $Fe^{3+}/Fe_T$  at any point. Calcium isotope compositions of accumulated mantle melts also show dependence on temperature. This variation is linked to the increase in average melt fraction with increasing temperature; this effect is large for Ca compared to Mg isotopes, the other monovalent system, because of the much larger magnitude of melt-source Ca isotope fractionation (nearly 0.1 ‰ at low melt fraction), which results in an increased sensitivity to melting degree.



**Figure 4.8: a) The estimated average isotopic fractionation of accumulated model peridotite melts relative to the source, across reasonable mid-ocean ridge and mantle plume temperatures.** Mantle potential temperature,  $T_p$ , is calculated as in Fig. 4.7, and the average melt fractionation is taken as the fractionation at the mean melting pressure at each temperature (see details in the text, Fig. 4.7, section 4.10). **b) The z score is calculated as  $(\Delta_{\text{melt-source}}(T) - \Delta_{\text{melt-source}}(T = 1400^\circ\text{C})) / 1\sigma$  typical analytical precision, for each isotope system.** This calculation reflects how the magnitude of expected isotopic variability compares to reasonable measurable isotopic differences: a z score of 1 represents predicted isotopic variability resolvable at typical  $1\sigma$  uncertainty. The errors used are the representative long-term analytical uncertainty for each isotope system; see Table 4.7.

The relative enrichment of the heavy stable isotopes of Fe and V in the melt relative to the source

(because oxidised, isotopically heavy cations behave more incompatibly during mantle melting than the reduced, isotopically lighter cations of the same element; Canil, 1999; Toplis and Corgne, 2002; Williams et al., 2004; Dauphas et al., 2009; Mallmann and O'Neill, 2009, 2013; Davis et al., 2013) decreases with increasing  $T_p$  (Fig. 4.8), and is qualitatively consistent with the positive  $\delta^{51}\text{V}$ – $\text{Na}_{8.0}$  correlation in global MORB (Wu et al., 2018; Qi et al., 2019; Novella et al., 2020;  $\text{Na}_{8.0}$  is the  $\text{Na}_2\text{O}$  content corrected for crystallisation to  $\text{MgO} = 8 \text{ wt } \%$ , and therefore removes the variable chemical effects of low-pressure processes allowing for more direct comparison between samples). However, the predicted magnitude of V isotope variability with  $T_p$  is smaller than the range of MORB V isotope data presented by Wu et al. (2018). Due to the enrichment of melts with heavy isotopes, MORB should have a higher  $\delta^{51}\text{V}$  than fertile mantle. This prediction is in agreement with observed data: Wu et al. (2018) measure an average global MORB value of  $-0.84 \pm 0.10 \text{ ‰}$  (2 S.D.), Qi et al. (2019) propose BSE is  $-0.91 \pm 0.09 \text{ ‰}$  (2 S.D.) based on the isotopic composition of peridotite xenoliths and komatiites. Similar behaviour is observed for Fe isotopes: global MORB, after correction for fractional crystallisation, has  $\delta^{57}\text{Fe} = 0.10 \pm 0.01 \text{ ‰}$  (2 S.E.); BSE is estimated at  $0.05 \pm 0.01 \text{ ‰}$  (2 S.E.) from primitive lherzolites (Sossi et al., 2016). The magnitude of the modelled  $\Delta^{51}\text{V}_{\text{melt-source}}$  and  $\Delta^{57}\text{Fe}_{\text{melt-source}}$  of aggregate KLB1 melts at  $T_p \approx 1300^\circ\text{C}$  ( $\sim 0.055 \text{ ‰}$  for both isotope systems) is similar to the  $0.07 \text{ ‰}$  and  $0.05 \text{ ‰}$  difference observed between BSE and average MORB for V and Fe, respectively. However, I note that the large uncertainties on the  $\delta^{51}\text{V}$  values estimated for the BSE and MORB mean that the  $\Delta^{51}\text{V}_{\text{melt-source}}$  predicted by the model would match the BSE and MORB data for all  $T_p$ .

Fig. 4.8b shows how the magnitude of isotopic variability across the  $T_p$  range compares to typical long-term analytical precision for each isotope system (see Table 4.7 for the errors used), highlighting that the magnitude of variability in the isotope ratio of melts produced between  $T_p = 1300^\circ\text{C}$  and  $1530^\circ\text{C}$  (a reasonable  $T_p$  range for melt generation at mid-ocean ridges and mantle plumes) is currently analytically unresolvable. Even considering analytical uncertainty in individual measurement sessions (i.e., the typical sample 2 S.E. rather than the long-term uncertainty; Table 4.7), the temperature-related variations associated with varying melt  $\text{Fe}^{3+}/\text{Fe}_T$  and modal mineralogy are not resolvable in the modelled average melt isotope ratios. The analytical precision therefore currently precludes mantle temperature variations in the global MORB dataset being resolved; this is consistent with Sossi et al. (2016) finding a homogenous global MORB  $\delta^{57}\text{Fe}$ , despite global MORB major element chemistry indicating  $200^\circ\text{C}$  variability (Gale et al., 2014). I note that the Mg and Cr stable isotope compositions of basalts are unlikely to be sensitive to temperature effects even with improved analytical precision; significant improvements in V and Ca analytical precision (both currently systems with relatively large errors), down to 2 S.D. of  $< 0.04 \text{ ‰}$ , offer the most potential to resolve the predicted temperature-related variations.

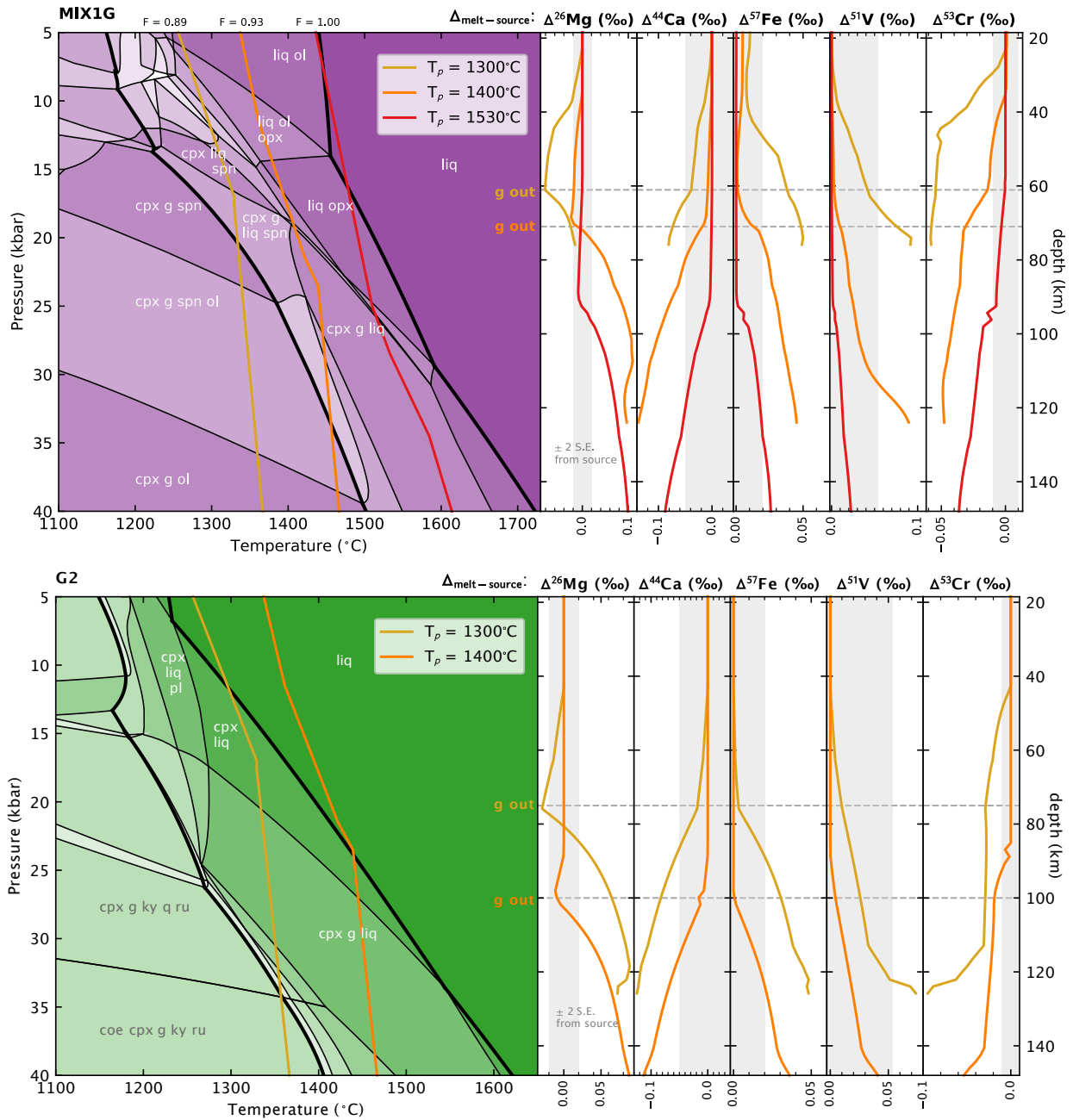
## 4.5 Stable isotope sensitivity to mantle lithology

I next investigate the use of stable isotopes as tracers of lithological heterogeneity in the mantle, using two pyroxenite lithologies, MIX1G (silica deficient, SD pyroxenite) and G2 (silica excess, SE pyroxenite). Silica-deficient pyroxenites may be the most representative type of pyroxenites found in the convecting mantle (the majority of pyroxenite xenoliths sampled in OIB are SD; Lambart et al., 2016 – natural SD pyroxenites are considered to be formed by metasomatism of peridotite by eclogite melts, as shown in experiments; Yaxley and Green, 1998; Yaxley, 2000; Mallik and Dasgupta, 2012). Natural SE pyroxenites include eclogites (Lambart et al., 2016).

### 4.5.1 Mineralogic control on melt isotope composition

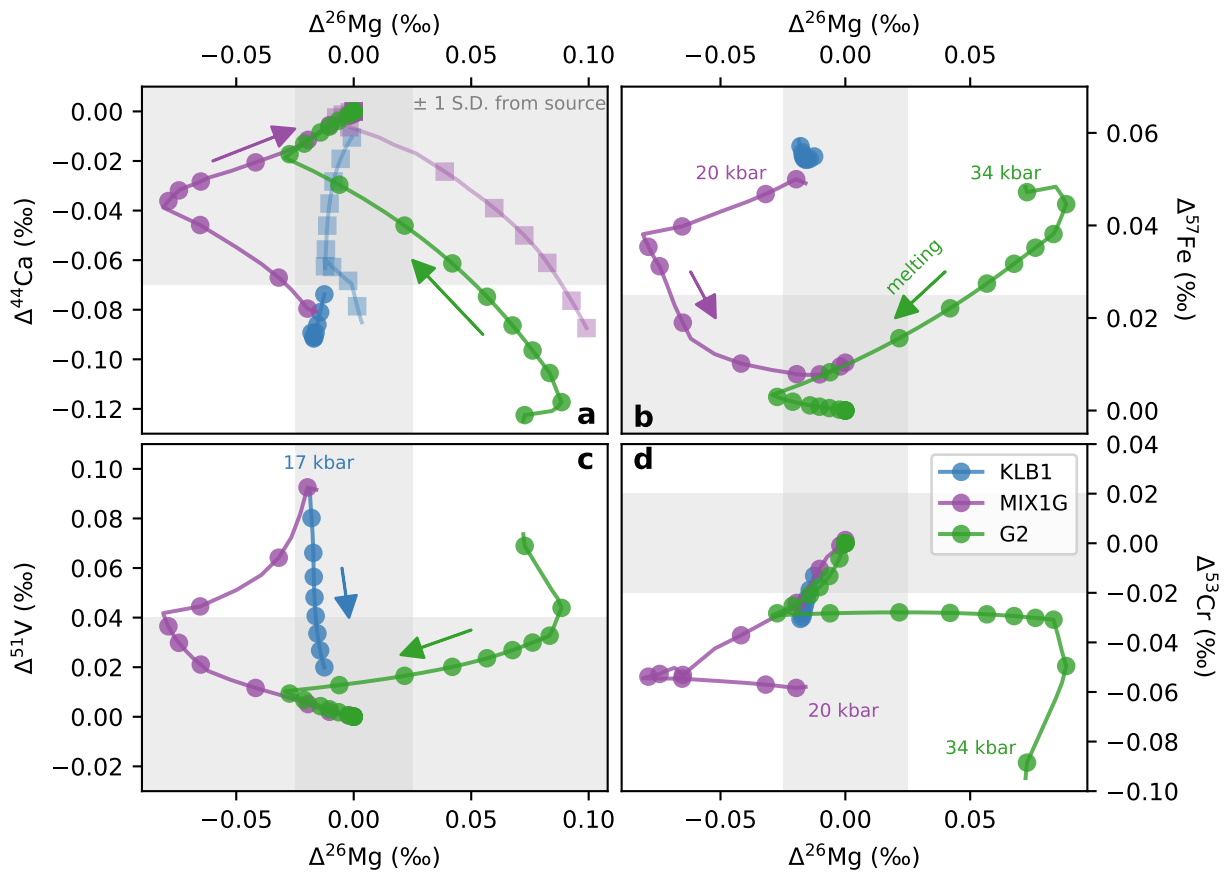
Fig. 4.9 shows the pseudosections and melt isotope ratios along peridotite isentropic decompression melting paths (see Fig. 4.2) for the two pyroxenite lithologies considered in this study. I have used peridotite isentropes since the thermal budget of multi-lithologic mantle will be buffered by melting of the dominant lherzolitic peridotite lithology, not pyroxenite melting (Phipps Morgan, 2001; Katz and Rudge, 2011). For example, peridotite (lherzolite + harzburgite) is estimated to make up  $\geq 95\%$  of the multi-lithologic mantle in the MORB mantle source (e.g., Hirschmann and Stolper, 1996; Matthews et al., 2016), and  $> 90\%$  of the Icelandic mantle source (e.g., Shorttle et al., 2014). While a multi-lithologic mantle will not follow pure peridotite isentropic decompression paths, I consider this approach the most realistic reflection of mantle melting processes. Isentropic decompression melting paths for pure MIX1G and G2 are shown in Figs. 4.21 and 4.22 at the end of the chapter for reference. The melt isotope ratios shown in Fig. 4.9 are all calculated relative to a bulk system isotopic composition of 0‰, for convenience. In this respect Fig. 4.9 is strictly looking at the direct lithological (i.e., mineralogic) control on the stable isotope composition of melts independent of any additional source compositional effects that may have been imprinted by the processes forming the source in the first place. For example, MORBs (and hence MORB-derived mantle components) are isotopically distinct from the BSE, due to their formation by partial melting (Fig. 4.2), crystal fractionation, and low temperature alteration by the time of their subduction (e.g., as for  $\delta^{57}\text{Fe}$ ; Teng et al., 2013; Sossi et al., 2016,  $\delta^{44}\text{Ca}$ ; Zhu et al., 2018b; Chen et al., 2020a; Antonelli and Simon, 2020 and  $\delta^{51}\text{V}$ ; Wu et al., 2018). If MORB, or MORB-derived components, then form part of the mantle source during a subsequent melting episode, the new melts will be isotopically fractionated compared to lherzolite melts both because of their distinct mineralogy and their inherited initial isotope compositions. This subject is considered further in sections 4.5.2 and 4.6.

I first consider how the isotopic composition of pyroxenite melts compares to peridotite melts (Table 4.7) in the context of the two questions posed in section 4.4: the magnitude of melt-source isotopic fractionation, and how melt-source isotopic fractionation varies with progressive melting.



**Figure 4.9: Pseudosection and modelled instantaneous equilibrium melt isotopic fractionation along isentropic decompression melting paths for MIX1G and G2 pyroxenites.** As in Fig. 4.2, the left hand panels show the pseudosections calculated in THERMOCALC for MIX1G (top) and G2 (bottom) pyroxenites, with the solidus and liquidus marked in bold. Isentropic melting paths for peridotite calculated using THERMOCALC for  $T_p = 1300^\circ\text{C}$ ,  $1400^\circ\text{C}$  and  $1530^\circ\text{C}$  are superimposed. For MIX1G, maximum melt fractions (F) are marked at the top of each isentrope (for G2  $F = 1$ ). The right hand panels show the modelled instantaneous equilibrium melt isotopic fractionation relative to the bulk isotopic composition ( $\Delta_{\text{melt-source}}$ ) along the isentropes. The  $T_p = 1530^\circ\text{C}$  isentrope has not been shown on G2 as the isentrope sits hotter than the liquidus. Key mineralogical controls on the isotopic composition of the melt are highlighted (colour-coded by the isentropic path they refer to). Vertical grey bars show the source composition (0‰ for convenience) with typical 2 S.E. sample error for each isotope system – see Table 4.7 for details.

Generally, the pyroxenite melts show a wider range of melt isotope ratios than peridotite melts for the same  $T_p$  (compare Figs. 4.2 and 4.9; see also Fig. 4.20), because the pyroxenite melts represent a wider range of melting degrees than the peridotite and a greater proportion of these melts are generated in the garnet stability field (garnet generally imparts a large isotopic fractionation compared to olivine and pyroxene; see Figs. 4.3–4.6). I find that stable V isotopes are predicted to have no direct sensitivity to different source lithologies (because the modelled  $\Delta^{51}\text{V}_{\text{melt-source}}$  for peridotite and pyroxenite lithologies are both similar to each other and well within current analytical precision; Fig. 4.10).

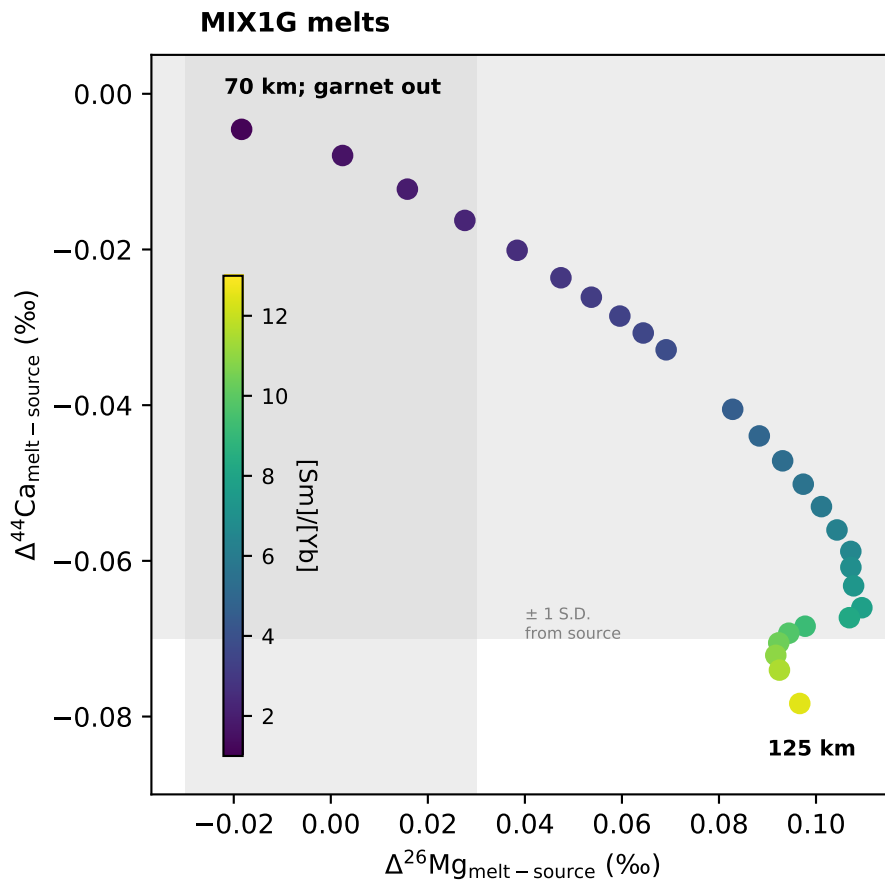


**Figure 4.10: Melting fractionation ( $\Delta_{\text{melt-source}}$ ) plotted along the  $T_p = 1300^\circ\text{C}$  isentrope;** squares in Mg–Ca space show  $T_p = 1530^\circ\text{C}$  isentrope for reference. High or low pressure end of isentrope is marked, and arrows show the direction of progressive melting (decompression). Markers are plotted every 3 pressure steps (each pressure step is 0.5 kbar). Grey shaded regions show the source ( $0\text{‰}$ )  $\pm$  typical long-term analytical 1 S.D. (see Table 4.7 for details).

However my results show that Fe, Cr, Ca and Mg could show some (weak) direct sensitivity to mantle lithology (Fig. 4.10), assuming equilibrium fractionation behaviour and in the absence of any pre-imposed source heterogeneity (i.e., where all lithologies have the same bulk isotope ratio). By direct lithological sensitivity, I refer to sensitivity related to mineralogy – these isotope systems may also trace lithology via each lithology’s different bulk isotope composition. On balance, given that melts from any pyroxenite lithology are likely to be diluted with ambient peridotite melts when extracted from the mantle (e.g., Hirschmann and Stolper, 1996; Sobolev et al., 2005; Shorttle and MacLennan, 2011; Soderman et al., 2021 [chapter 3]), my results in Fig. 4.10 are prob-

ably representative of maximum isotope fractionation signatures we might see in natural systems, and the subsequent discussion in section 4.5.2 (which takes into account both this dilution effect and non-identical bulk isotope compositions of the lithologies) may better represent the predicted resolvability of each isotope system to lithology.

Progressive melting of a garnet-bearing source (such as G2, or MIX1G at depth) produces the opposite sense of melt-source isotope fractionation in Mg and Ca isotopes (both in direction, i.e., positive or negative  $\Delta_{\text{melt-source}}$ , and trend, i.e.,  $\Delta_{\text{melt-source}}$  becoming more negative or more positive; Figs. 4.2, 4.9) due to the presence of isotopically light and heavy garnet respectively ( $\Delta^{26}\text{Mg}_{\text{garnet-source}} \sim -0.3\text{‰}$ ;  $\Delta^{44}\text{Ca}_{\text{garnet-source}} \sim 0.25\text{‰}$ ). Therefore, if lithological heterogeneity (specifically, the proportion of garnet in a melt source) is the principal control on the chemical heterogeneity of a suite of basalts, the two isotope systems should show a negative correlation. This relationship is shown in Fig. 4.11 for MIX1G melts. Fig. 4.11 also shows how the isotopic compositions of the melts might be predicted to relate to a more traditional geochemical tracer of garnet in the source region, Sm/Yb ratio (e.g., Pertermann et al., 2004; details of the calculation below), and similar patterns would be predicted for other garnet tracers such as Dy/Yb (Fig. 4.20).



**Figure 4.11: Instantaneous equilibrium melt-source Mg and Ca stable isotope fractionation for MIX1G melts produced at depths greater than 70 km (i.e., where garnet is present in the source) along a peridotitic isentropic decompression melting path ( $T_p = 1400\text{ °C}$ ).** Grey shading shows the source ( $0\text{‰}$ )  $\pm$  typical 1 S.D. long-term analytical error (Table 4.7). Details of trace element modelling in section 4.5.1.1.

The correlation between Ca isotopes and garnet-sensitive trace element ratios is in agreement with measurements and predictions by Wang et al. (2019); Antonelli et al. (2021). Magnesium-Ca isotope systematics of basalts could therefore have future potential as a tracer of garnet (hence, depth of melting and/or lithological heterogeneity) in the mantle source, as predicted for both stable isotope systems individually (e.g., Stracke et al., 2018; Kang et al., 2019; Wang et al., 2019; Dai et al., 2020; Antonelli et al., 2021).

However, further work on the effect of garnet on  $\Delta^{44}\text{Ca}_{\text{melt-source}}$  by taking garnet composition into account, following measurements by Chen et al. (2020b) and predicted composition-dependent  $\beta^{\text{Ca}}$  from Antonelli et al. (2019b), is required. I note that Antonelli et al. (2019b) predict that composition-dependent isotope fractionation effects (‘concentration effects’) for other mineral solid solutions (olivine, pyroxene) are smaller using their PBE (Perdew, Burke, Ernzerhof) functionals to calculate  $\beta$  relative to previous studies that have employed different approaches (LDA functionals; e.g., Feng et al., 2014; Wang et al., 2017), which supports only small concentration effects in garnet. Currently, typical analytical precision on Ca isotope measurements (long-term external 2 S.D. of  $\delta^{44}\text{Ca} = 0.14\text{‰}$  on the SRM915b standard, although typical 2 S.E. on measurements of individual samples is smaller, average 0.05 ‰, Chen et al., 2019a; Dai et al., 2020) precludes some of the predicted equilibrium variability in  $\Delta^{44}\text{Ca}_{\text{melt-source}}$  due to the presence of garnet from being resolved (Fig. 4.11). However, as analytical precision improves, the garnet signature in Mg-Ca isotopes could be further tested.

Overall, whether melts from pyroxenite lithologies will ultimately be resolvable in an erupted melt will depend on two factors in addition to the direct mineralogic control: the bulk isotope composition of a pyroxenite lithology relative to peridotite, and the amount of each element that each of the melting lithologies contributes to the final melt.

#### 4.5.1.1 Trace element calculations

Table 4.8 gives the mineral-melt partition coefficients and mantle concentrations for Sm, Dy and Yb used in the calculations for Figs. 4.11 and 4.20.

**Table 4.8: Input parameters (partition coefficients relative to melt, mantle concentrations) for calculating the Sm, Dy and Yb concentrations in the model melts.**  $D_{\text{gt,cpx,ol,opx}}$  and element concentrations from Gibson and Geist (2010);  $D_{\text{spinel}}$  from Liu et al. (2019) (average values from high P experiments);  $D_{\text{plag}}$  from Aigner-Torres et al. (2007) (from ‘run 31’);  $D_{\text{rutile}}$  from Klemme et al. (2005) (Sm), Foley et al. (2000) (Dy, Yb);  $D_{\text{ilmenite}}$  from Zack and Brumm (1998).  $\text{Conc.}_{\text{DM}}$  = concentration in depleted mantle (used for KLB1);  $\text{Conc.}_{\text{plume}}$  = concentration in plume mantle (used for pyroxenites); mineral abbreviations as previous with rut. = rutile, ilm. = ilmenite.

| Element | $D_{\text{gt}}$ | $D_{\text{cpx}}$ | $D_{\text{ol}}$ | $D_{\text{opx}}$ | $D_{\text{spn}}$ | $D_{\text{plag}}$ | $D_{\text{rut}}$ | $D_{\text{ilm}}$ | $\text{Conc.}_{\text{DM}}$ | $\text{Conc.}_{\text{plume}}$ |
|---------|-----------------|------------------|-----------------|------------------|------------------|-------------------|------------------|------------------|----------------------------|-------------------------------|
| Sm      | 0.25            | 0.293            | 0.0011          | 0.02             | 0.198            | 0.081             | 0.00135          | 0.00059          | 0.299                      | 0.35                          |
| Dy      | 2.2             | 0.4              | 0.0027          | 0.011            | 0.069            | 0.049             | 0.00076          | 0.01             | 0.525                      | 0.57                          |
| Yb      | 6.6             | 0.4              | 0.02            | 0.08             | 0.812            | 0.025             | 0.0093           | 0.17             | 0.347                      | 0.372                         |

The concentration of each element in the melt was calculated at each P-T point by:

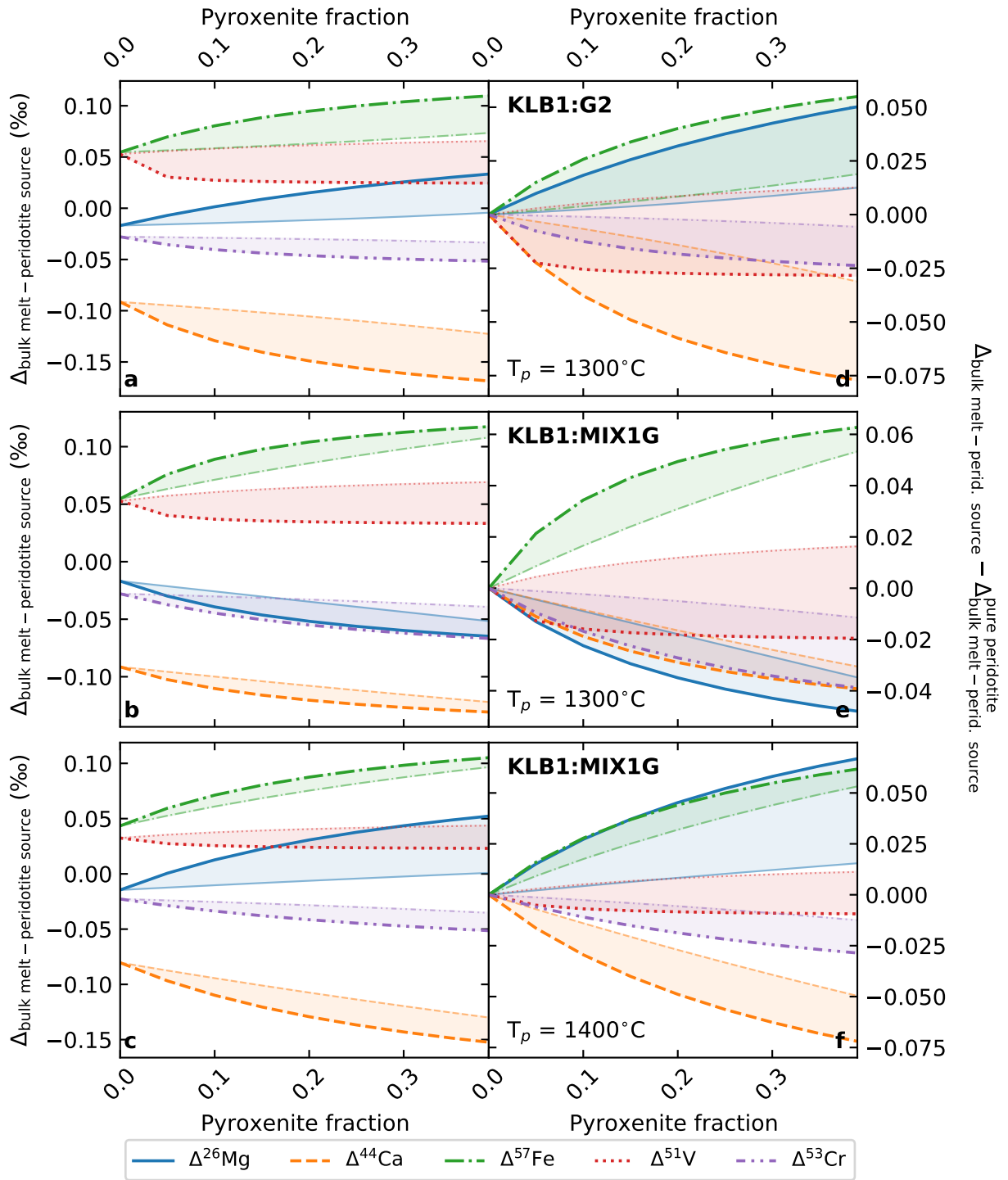
$$C_{\text{liquid}} = \frac{C_{\text{bulk}}}{\sum D_{\text{mineral}} F_{\text{mineral}} + F_{\text{liquid}}} \quad (4.10)$$

where C = concentration, D = partition coefficient, F = fraction of phase.

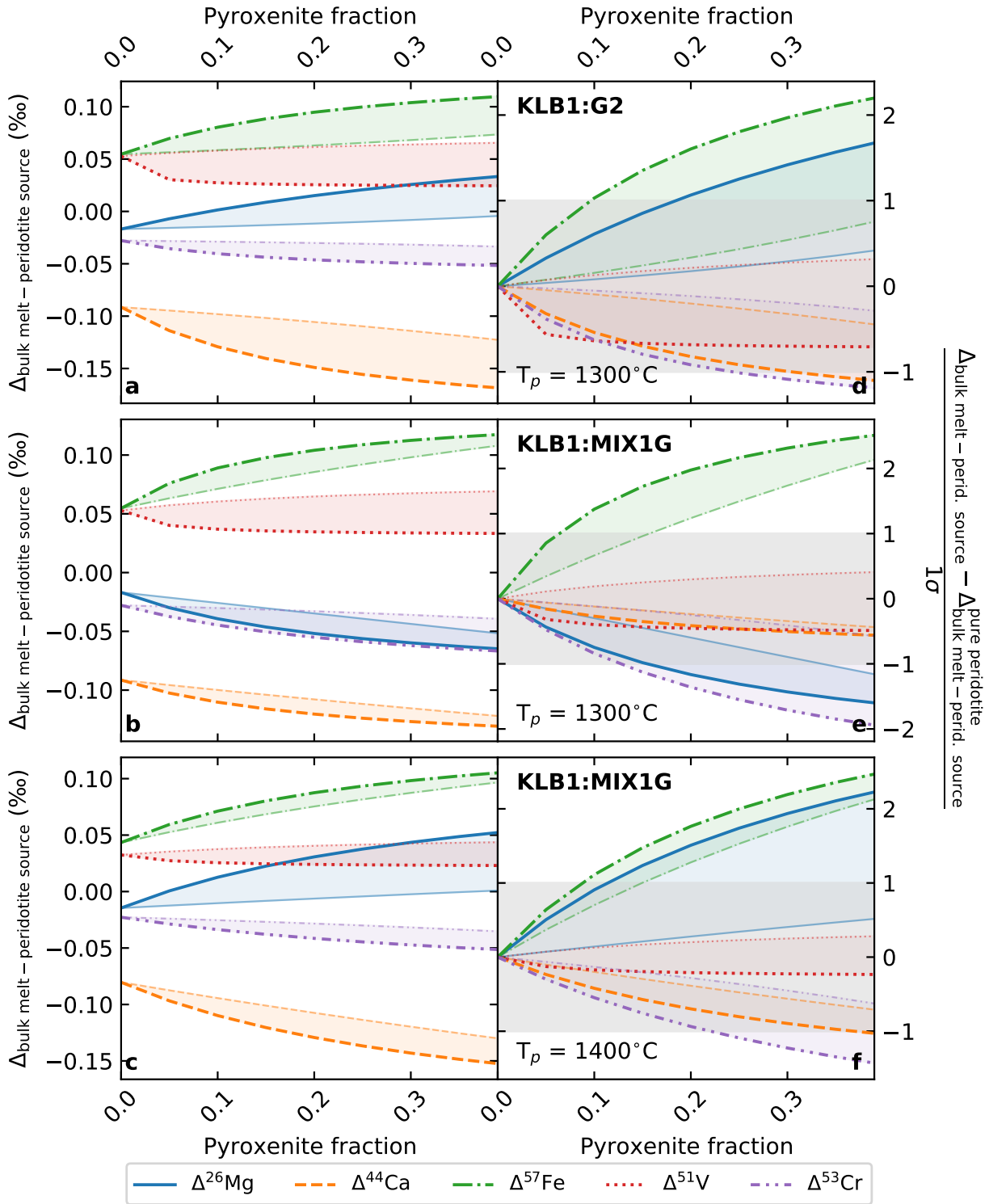
I note that McKenzie and O’Nions (1991) suggest  $D_{\text{spinel}}$  of 0.01 for the elements considered here, following a review of experimental studies by Irving (1978), which is much lower than the values of 0.07–0.81 used here from high pressure experiments of Liu et al. (2019). Given the purpose of the trace element modelling in this thesis, to provide a more traditional geochemistry reference point for the presence of garnet in a melt’s source, this possible uncertainty in spinel partition coefficients is not considered further, although should be addressed if further trace element work using the framework of this model is undertaken.

#### 4.5.2 Resolving pyroxenite source components in erupted melts

Fig. 4.12 shows the results of mass balance calculations for the aggregate bulk melt-source isotope fractionation of a multi-lithologic mantle relative to a pure pyroxenite source, with varying proportions of pyroxenite. The peridotite lithology is taken to have a bulk isotope composition equal to BSE (see Fig. 4.1 caption for data sources; isotopic reference materials used are DSM3, SRM915a, IRMM-014, AA, NIST979 for Mg-Ca-Fe-V-Cr respectively); pyroxenite lithologies are taken to have a bulk isotope composition of average MORB for each isotope, except for Cr where no known MORB data are published and the modelled aggregate KLB1 melt isotope composition for  $T_p = 1300^\circ\text{C}$  is used. Full details of the mass balance calculation are found in section 4.5.2.1 below. The right hand panels show the same data referenced to the pure peridotite melt, allowing a simple assessment of the required analytical precision if pyroxenite is to be detected by each system. Fig. 4.13 shows the same data as Fig. 4.12, instead scaled to typical current 1 S.D. analytical precision. Each isotope system is shown with a range of isotope compositions, reflecting two end-member conditions of thermal behaviour of the pyroxenite in multi-lithologic mantle. The bold line reflects a pyroxenite decompressing along a peridotite decompression path, as used in Fig. 4.9. This approximation will be most valid for small ( $< 10\%$ ) pyroxenite fractions. The other end-member is pyroxenite following its own decompression melting path (the paths shown in Figs. 4.21 and 4.22). I acknowledge that these results are still an approximation, as peridotite is assumed to be melting along its own geotherm regardless of pyroxenite fraction. From Figs. 4.12 and 4.13, I find that none of the considered isotope systems will be able to resolve the presence of minor (less than  $\sim 5\%$ ) pyroxenite components in mantle source regions, given levels of current analytical precision as given in Table 4.7.



**Figure 4.12: Aggregate bulk melt isotope fractionation (relative to a pure peridotite source, left hand panels; relative to pure peridotite melt; right hand panels) for multi-lithologic mantle.** At each  $T_p$ , the aggregate melt composition (including isotope composition, and element proportion) at the average pressure and temperature of melting for each lithology is used to calculate the resulting bulk melt isotope composition by mass balance. A range of bulk melt-source isotope fractionations are given for each isotope system, reflecting two endmembers for the thermal behaviour of pyroxenite upwelling in a peridotite host. The bolder line for each isotope system represents the case for pyroxenite following peridotite geotherms (as used throughout this study); the paler line reflects pyroxenite following its own geotherm, as in Figs. 4.21 and 4.22.



**Figure 4.13: Aggregate bulk melt isotope fractionation (relative to a pure peridotite source, left hand panels; relative to a pure peridotite melt and scaled to current typical long-term analytical 1 S.D., right hand panels) for multi-lithologic mantle.** At each  $T_p$ , the aggregate melt composition (including isotope composition, and element proportion) at the average pressure and temperature of melting for each lithology is used to calculate the resulting bulk melt isotope composition by mass balance. A range of bulk melt-source isotope fractionations are given for each isotope system, reflecting two endmembers for the thermal behaviour of pyroxenite upwelling in a peridotite host. The bolder line for each isotope system represents the case for pyroxenite following peridotite geotherms (as used throughout this study); the paler line reflects pyroxenite following its own geotherm, as in Figs. 4.21 and 4.22. Grey horizontal bars in the right hand panels highlight 1 S.D.

#### 4.5.2.1 Element budgeting between lithologies

To produce Fig. 4.12, I use a mass balance calculation for each isotopic system, X, where

$$\delta X_{\text{bulk}} = (F_{\text{pyroxenite}}^X \times \delta X_{\text{pyroxenite}}) + (F_{\text{peridotite}}^X \times \delta X_{\text{peridotite}}) \quad (4.11)$$

and  $F^X$  is the fraction of the total element in the final melt coming from each lithology,  $\delta X_{\text{lithology}}$  is the isotopic composition of each lithology (bulk isotope composition of lithology + melt-source isotope fractionation). The F term considers both the amount of the element in the melt from each lithology, and the melt fraction of each lithology. Table 4.9 gives the inputs used: these inputs are taken from the full model results at the average P-T melting condition (as in section 4.10) for each  $T_p$ . This calculation cannot be done for a  $T_p$  of 1530 °C (MIX1G & G2) or 1400 °C (G2) because the isentropic melting paths intersect the solidus at pressures below the base of my model, so an accurate average pressure of melting cannot be calculated. The bulk isotope compositions of each lithology are the BSE values for peridotite (see Fig. 4.1 caption for sources), and average MORB composition for pyroxenite (except for Cr where no known MORB data are published and the modelled aggregate KLB1 melt isotope composition for  $T_p = 1300$  °C is used).

#### 4.5.2.2 Isotope systems with minimal sensitivity to pyroxenite: V and Ca

My results show that the presence of even moderate amounts of pyroxenite in the mantle source cannot be resolved using V stable isotopes, assuming a MORB-like bulk pyroxenite isotope composition. This result is consistent with Novella et al. (2020) who show that  $\delta^{51}\text{V}$  cannot detect pyroxenite in the source of Reykjanes Ridge basalts. Given the similar predicted V isotope compositions of pyroxenite and peridotite melts, with pyroxenite fractions up to 40 % producing bulk melt isotope compositions that only differ from a peridotite source by  $< 0.03$  ‰ (Fig. 4.12), improvements in V stable isotope analytical precision are unlikely to make V isotopes sensitive to the pyroxenite lithologies modelled here.

I also predict that partial melting of peridotite and pyroxenite produces unresolvable Ca isotopic fractionation relative to the source (for peridotite,  $\Delta^{44}\text{Ca}_{\text{melt-source}}$  smaller than  $-0.09$  ‰; Fig. 4.2, in agreement with Kang et al., 2017; Chen et al., 2019a but smaller than  $\Delta^{44}\text{Ca}_{\text{melt-residue}} = -0.09 - -0.2$  ‰ suggested by Zhu et al., 2018b; Ionov et al., 2019; Chen et al., 2020a). Although bulk MORB-like pyroxenite may have an isotopically lighter composition than peridotite (see Fig. 4.14), which is further amplified by negative melt-source isotopic fractionation to produce pyroxenite melts that are isotopically lighter than peridotite melts, Fig. 4.12 suggests that Ca isotope ratios measured with current typical long-term uncertainty will only be able to detect MORB-like pyroxenite in a mantle source if the proportion of pyroxenite is greater than 30 % (which may be unrealistic of multi-lithologic mantle, e.g., Sobolev et al., 2005; Pietruszka et al., 2013; Shorttle et al., 2014; Matthews et al., 2016; Brown et al., 2020). When considering a current best 2 S.E.,

**Table 4.9: Inputs used to calculate bulk melt-source isotope fractionation in Figs. 4.12 and 4.13.** \* indicates inputs using the pure pyroxenite isentropes at that  $T_p$ , rather than peridotite isentropes. The MIX1G 1400\* inputs are actually for an isentrope of  $T_p = 1436^\circ\text{C}$ . The P-T given are the closest P-T pair in the model output files to the average P-T of melting along each isentrope, as calculated in section 4.10. For V and Cr, where element partitioning is not calculated by THERMOCALC, the melt element concentrations are calculated as described in section 4.2.2, using the following bulk compositions for each lithology: KLB1  $\text{Cr}_2\text{O}_3 = 0.32\text{ wt \%}$ , G2  $\text{Cr}_2\text{O}_3 = 0.08\text{ wt \%}$ , MIX1G  $\text{Cr}_2\text{O}_3 = 0.11\text{ wt \%}$  (Jennings et al., 2016); KLB1 V = 85 ppm (typical primitive mantle value from Lee et al., 2003; Prytulak et al., 2013), MIX1G and G2 V = 350 ppm (typical MORB value; Prytulak et al., 2013).

|                                            | KLB1  |       | MIX1G |       |       |       | G2    |       |
|--------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| $T_p$ ( $^\circ\text{C}$ ):                | 1300  | 1400  | 1300  | 1300* | 1400  | 1400* | 1300  | 1300* |
| Pressure (kbar)                            | 12    | 17.5  | 15    | 13.5  | 24.5  | 22    | 27    | 25.5  |
| Temperature ( $^\circ\text{C}$ )           | 1300  | 1400  | 1317  | 1248  | 1440  | 1380  | 1345  | 1269  |
| Melt fraction                              | 0.061 | 0.099 | 0.323 | 0.093 | 0.369 | 0.155 | 0.458 | 0.048 |
| Melt element conc.                         |       |       |       |       |       |       |       |       |
| Mg (mol % oxide)                           | 16.50 | 20.43 | 15.44 | 11.01 | 19.42 | 16.59 | 5.92  | 4.48  |
| Ca (mol % oxide)                           | 12.72 | 13.62 | 12.66 | 10.63 | 13.09 | 11.83 | 9.47  | 7.53  |
| Fe (mol % oxide)                           | 6.36  | 7.64  | 8.93  | 7.46  | 9.27  | 10.21 | 4.22  | 3.07  |
| V (wt % element)                           | 0.002 | 0.003 | 0.014 | 0.008 | 0.015 | 0.009 | 0.021 | 0.011 |
| Cr (wt % element)                          | 0.005 | 0.009 | 0.004 | 0.001 | 0.007 | 0.002 | 0.004 | 0.001 |
| Melt-source isotopic fractionation (‰)     |       |       |       |       |       |       |       |       |
| $\Delta^{26}\text{Mg}$                     | -0.02 | -0.02 | -0.08 | -0.10 | 0.08  | 0.02  | 0.06  | 0.09  |
| $\Delta^{44}\text{Ca}$                     | -0.09 | -0.08 | -0.04 | -0.05 | -0.08 | -0.08 | -0.08 | -0.12 |
| $\Delta^{57}\text{Fe}$                     | 0.06  | 0.04  | 0.03  | 0.06  | 0.03  | 0.04  | 0.03  | 0.06  |
| $\Delta^{51}\text{V}$                      | 0.05  | 0.03  | 0.03  | 0.08  | 0.02  | 0.05  | 0.03  | 0.07  |
| $\Delta^{53}\text{Cr}$                     | -0.03 | -0.02 | -0.05 | -0.06 | -0.04 | -0.05 | -0.03 | -0.12 |
| Bulk isotopic composition of lithology (‰) |       |       |       |       |       |       |       |       |
| $\delta^{26}\text{Mg}$                     | -0.24 |       | -0.25 |       |       |       | -0.25 |       |
| $\delta^{44}\text{Ca}$                     | 0.94  |       | 0.83  |       |       |       | 0.83  |       |
| $\delta^{57}\text{Fe}$                     | 0.05  |       | 0.14  |       |       |       | 0.14  |       |
| $\delta^{51}\text{V}$                      | -0.91 |       | -0.92 |       |       |       | -0.92 |       |
| $\delta^{53}\text{Cr}$                     | -0.12 |       | -0.15 |       |       |       | -0.15 |       |

this detection limit only improves to  $\sim 20\%$  of pyroxenite in the source. The small variability in melt isotope ratios with increasing pyroxenite fraction compared to resolvable variability is consistent with DMM, EM1 and HIMU basalts recording no resolvable  $\delta^{44}\text{Ca}$  variability (Valdes et al., 2014), and measured mantle pyroxenites and associated peridotites recording indistinguishable  $\delta^{44}\text{Ca}$  (Dai et al., 2020). However, even a small improvement in analytical precision could enable greater sensitivity to pyroxenite fraction: for example Figs. 4.12a and 4.13 show that  $\sim 15\%$  of G2 pyroxenite in a mantle source produces an isotopic offset in the bulk melt of  $-0.05\text{‰}$  relative to a pure peridotite source. Given that the typical 2 S.E. for  $\delta^{44}\text{Ca}$  is around  $0.05\text{‰}$  (Table 4.7), there is potential for these small pyroxenite fraction signatures to be theoretically resolved with only minor improvements in analytical precision. I note that currently resolvable variability in the measured  $\delta^{44}\text{Ca}$  of igneous rocks is found (specifically in ultramafic rocks including dunites and komatiites), but that pyroxenite source contributions are not proposed to be the origin of this  $\delta^{44}\text{Ca}$  heterogeneity (Antonelli and Simon, 2020).

#### 4.5.2.3 Distinguishing lithologies: Fe, Mg, Cr

The Fe isotope variability of MORB and OIB has been previously linked to source heterogeneity (e.g., Williams and Bizimis, 2014; Konter et al., 2016; Nebel et al., 2019; Sun et al., 2020; Zhong et al., 2021b), through the inherent (initial; presumably derived from its formation or protolith) Fe isotope compositions of the different source components, rather than directly through any large mineralogy-dependent partial melting Fe isotope fractionation. Consistent with these conclusions, I find that the calculated partial melting  $\Delta^{57}\text{Fe}$  fractionations are small ( $\leq 0.06\text{‰}$ ) for peridotite and pyroxenite lithologies (in agreement with previous studies, e.g., Dauphas et al., 2009; Williams and Bizimis, 2014; Sossi et al., 2016; Gleeson et al., 2020; Soderman et al., 2021 [chapter 3]). I also find that the main driver of melt Fe isotope ratio sensitivity to pyroxenite fraction (Fig. 4.12) is the expectation that MORB-like pyroxenite will have a heavier bulk Fe isotope ratio than peridotite, which in combination with a positive melt-source isotopic fractionation drives pyroxenite melts to heavier isotope compositions than peridotite melts. The contribution of high  $\delta^{57}\text{Fe}$  pyroxenite melts (from both SD and SE pyroxenites) compared to melting of a pure peridotite source is resolvable at greater than 8–9% pyroxenite with current typical 1 S.D. (Figs. 4.12, 4.13), making Fe isotopes one of the most sensitive systems to source considered here. However, it should be noted that equilibrium isotopic fractionation associated with pyroxenite sources cannot generate the full range of natural stable isotope OIB data from a single stage melting model (Soderman et al., 2021 [chapter 3], see section 4.6). For G2 pyroxenite however, the choice of thermal behaviour of the pyroxenite (i.e., whether the upwelling pyroxenite component follows a peridotite or pyroxenite decompression path) strongly affects the sensitivity to pyroxenite fraction. At high proportions of G2 pyroxenite, when a pyroxenite decompression path becomes more appropriate, the multi-lithologic mantle melt may no longer be resolvable from a pure peridotite source (Fig. 4.12d).

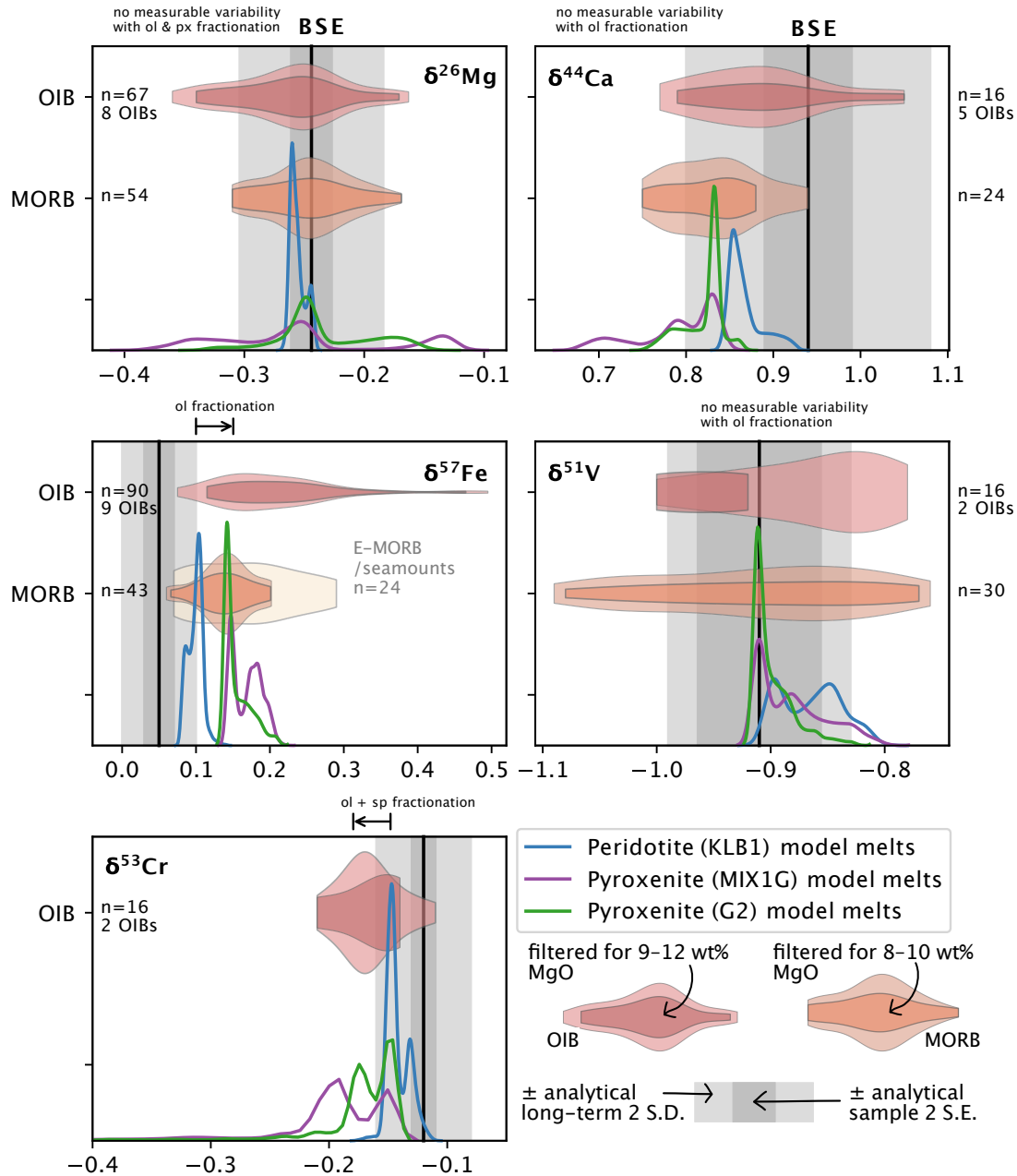
In agreement with most existing studies (e.g., Teng et al., 2007, 2010; Huang et al., 2011a; Stracke et al., 2018), but in contrast to Zhong et al. (2017), I find that partial melting of peridotite produces unresolvable Mg isotopic fractionation ( $\Delta^{26}\text{Mg} < 0.02\text{‰}$ ; Fig. 4.2). Melting of MIX1G and G2 pyroxenite lithologies produces larger magnitude melt-source fractionations than peridotite (Fig. 4.9) due to the presence of isotopically light garnet and isotopically heavy clinopyroxene in the source, in varying proportions over P-T space (Fig. 4.3). By comparison, olivine and orthopyroxene, which dominate peridotite melting, have less extreme  $\delta^{26}\text{Mg}$  compositions. The presence of garnet producing more extreme isotopic fractionations than a non-garnet-bearing source is consistent with melting models from Stracke et al. (2018). However, a key difference is that the modelled melting of garnet pyroxenite by Stracke et al. (2018) produces isotopically light melts (i.e., a negative  $\Delta_{\text{melt-source}}$ ), compared to the mostly isotopically heavy (a positive  $\Delta_{\text{melt-source}}$ ) melts at depths where garnet is present in the source in this model (Fig. 4.9). This difference in behaviour is due to the choice of initial  $\alpha_{\text{melt-source}} = 1$  in Stracke et al. (2018). I do not use this initial condition, and in the melting assemblage considered here, garnet is largely a residual phase (i.e., not contributing to melting), and therefore initial melts are isotopically heavy relative to the source. Both models agree that with progressive melting of isotopically light garnet in the source, melts will become isotopically lighter. Some isotopically light (i.e.,  $\Delta^{26}\text{Mg}_{\text{melt-source}} < 0\text{‰}$ ) melts are produced by melting G2 and MIX1G in this model, but these are at depths where garnet is nearly or completely absent from the stable assemblage (Fig. 4.9). It is this garnet effect that is responsible for the opposite behaviours of  $\Delta^{26}\text{Mg}_{\text{melt-source}}$  in Fig. 4.12d, f compared to Fig. 4.12e: the aggregate pyroxenite melt sits in the spinel stability field for MIX1G at  $T_p = 1300^\circ\text{C}$  (Fig. 4.12b), but in the garnet stability field for MIX1G at  $T_p = 1400^\circ\text{C}$  (Fig. 4.12c) and G2 at  $T_p = 1300^\circ\text{C}$  (Fig. 4.12d). Melting of multi-lithologic mantle (with MIX1G pyroxenite) is resolvable from pure peridotite at current 1 S.D. at  $\sim 10\text{--}15\%$  pyroxenite fraction (Fig. 4.13); my results show that Mg isotopes are more sensitive to MIX1G than G2 pyroxenite. With continued improvements in analytical precision, such as the  $0.02\text{‰}$  2 S.E. reported by Wang et al. (2021), pyroxenite fractions  $< 10\%$  could be resolved in the Mg isotope composition of the bulk melt, as a  $10\%$  pyroxenite fraction produces a bulk melt  $> 0.02\text{‰}$  different from a pure peridotite melt (Figs. 4.12e, f).

Chromium stable isotope fractionation during partial melting of different lithologies is relatively understudied compared to Mg and Fe, however Fig. 4.12 shows that melt Cr isotopic composition could show resolvable sensitivity to the fraction of pyroxenite in the source. This is due both to variable modelled melting fractionations dependent on lithology, and comparatively small analytical uncertainty. Equilibrium Cr stable isotope fractionation is controlled by both bonding environment and redox conditions (e.g., Shen et al., 2018, 2020; Bonnand et al., 2020). Chromium stable isotope fractionation during partial melting of peridotite is probably small (magnitude of  $\Delta^{53}\text{Cr} < 0.07\text{‰}$ ; Schoenberg et al., 2016; Xia et al., 2017; Shen et al., 2018; Bonnand et al., 2020), in agreement with my results. Isotopically heavy spinel, where present, has a large influence on the isotopic fractionation between melt and residue due to the compatibility of Cr in

spinel, and this has been used to explain observations from peridotite xenoliths that partial melting appears to generate isotopically light melts ( $\Delta^{53}\text{Cr}_{\text{melt-source}} < 0$ ) and heavy residues (Xia et al., 2017; Shen et al., 2020). However, due to the small area of the KLB1 melting regime in which spinel is stable in my model (Figs. 4.2, 4.6), spinel does not control the magnitude of stable isotope fractionation associated with melting in this case. I find a slightly larger magnitude of melting-induced Cr stable isotope fractionation for MIX1G pyroxenite than for peridotite (as large as  $-0.06\text{‰}$ ). Like MIX1G, G2 pyroxenite melts all have a negative  $\Delta^{53}\text{Cr}$  with respect to the source, with melting fractionations as large as  $\Delta^{53}\text{Cr} = -0.1\text{‰}$  (Fig. 4.9). This result is because the main Cr bearing phase in much of the melting region is isotopically heavy (relative to olivine) clinopyroxene, and this produces consistently isotopically light melts, consistent with observations by Xia et al. (2017); Shen et al. (2020). Therefore, combined with a predicted bulk pyroxenite isotope composition that is also isotopically lighter than peridotite, bulk melts are predicted to become progressively Cr-isotopically lighter with increasing pyroxenite fraction in the mantle source. This effect is generally small ( $< 0.04\text{‰}$  offset from pure peridotite melts even at 30 % pyroxenite; Fig. 4.12) and at current typical 2 S.D. is only resolvable at more than 20 % MIX1G in the source at comparatively low temperatures ( $T_p = 1300^\circ\text{C}$ ). However, as with Mg, recent improvements in analytical precision for Cr isotopes (Sossi et al., 2018a; Wagner et al., 2021) may permit greater sensitivity to pyroxenite components: for a 2 S.E. of  $0.01\text{‰}$ , multi-lithologic mantle melts become resolvable from pure peridotite melts at around 8 % pyroxenite upwards, assuming upwelling pyroxenite follows the peridotite geotherm (Figs. 4.12, 4.13).

## 4.6 Comparisons to natural data

Fig. 4.14 shows how literature MORB and OIB data compare to modelled melts. The modelled melts are filtered for those produced at cooler temperatures than the  $T_p = 1530^\circ\text{C}$  peridotite isentrope for a given pressure, to limit the contribution of unrealistic high melt fraction and high pressure melts. The same potential temperature isentrope has been chosen for all lithologies for consistency, although because of its fusibility this filter includes some 100 % melts of G2 at all pressures. Natural samples are filtered for those with  $7.2 < \text{MgO (wt\%)} < 16$  to minimise the effects of fractional crystallisation and olivine accumulation, which can result in measurable isotopic fractionations in several isotope systems (e.g., Sossi et al., 2016; McCoy-West et al., 2018; Nebel et al., 2019; Shen et al., 2020). The KLB1 melts are shown as the calculated melting fractionation applied to an accessible mantle isotopic composition (presumptive bulk silicate earth, BSE); G2 and MIX1G melts are shown as the melting fractionation applied to the average fresh MORB isotopic composition, since G2 is a MORB-like eclogite in composition. For Cr, where I can find no published MORB data, I use the isotope ratio of BSE + the aggregate KLB1 melt isotope ratio for  $T_p = 1300^\circ\text{C}$  (Fig. 4.8) to predict the isotopic composition of fresh MORB, and reference G2 and MIX1G melts to this value.



**Figure 4.14: Literature MORB (N- and T- MORB, if classification is known) and OIB data for the isotope systems (data sources in Table 4.1), compared to the model instantaneous melts** (all data shown as ‰ variation from the reference materials outlined in Fig. 4.1). Samples are filtered for  $7.2 < \text{MgO wt \%} < 16$ , but included if MgO is not known. ‘n’ refers to the total number of samples included, and the number of OIBs given shows how many unique ocean island settings are sampled. The central darker violin shows a more limited subset of samples: 9–12 wt % MgO in OIB, 8–10 wt % MgO in MORB, to highlight isotope compositions of the most primitive lavas. Ca and Mg isotope data is filtered to exclude samples with  $^{87}\text{Sr}/^{86}\text{Sr} > 0.7037$ , which excludes samples with  $> 1\%$  carbonate component in the source (Huang et al., 2011b). Modelled melts are filtered for those cooler than the  $T_p = 1530^\circ\text{C}$  peridotite isentrope at any given pressure. KLB1 melts are shown assuming a bulk source isotope composition of BSE; G2 and MIX1G melts are shown assuming a bulk source isotope composition of average MORB (for Cr, the isotope ratio of BSE + the aggregate KLB1 melt isotope ratio for  $T_p = 1300^\circ\text{C}$  is used due to the lack of published MORB data). BSE values are  $\delta^{26}\text{Mg} = -0.24\text{‰}$  (Stracke et al., 2018),  $\delta^{44}\text{Ca} = 0.94\text{‰}$  (Kang et al., 2017; Chen et al., 2019a),  $\delta^{57}\text{Fe} = 0.05\text{‰}$  (Sossi et al., 2016),  $\delta^{51}\text{V} = -0.91\text{‰}$  (Qi et al., 2019),  $\delta^{53}\text{Cr} = -0.12\text{‰}$  (Jerram et al., 2020). The outer pale grey shaded region shows typical long term 2 S.D. analytical uncertainty in recent studies, the inner dark grey shaded region shows typical sample 2 S.E. (S.E. = S.D./ $\sqrt{n}$ ) in recent studies (see Table 4.7). The fractionation arrows for Fe and Cr isotopes represent the direction and approximate magnitude of isotopic fractionation associated with differentiation to form samples with minimum 7 wt % MgO. Fractionation information from Sossi et al. (2016) for Fe, Teng et al. (2007, 2010); Wang et al. (2021) for Mg, Zhang et al. (2018b) for Ca, Shen et al. (2020) for Cr, Ding et al. (2020) for V.

#### 4.6.1 Can peridotite melting explain MORB Mg-Ca-Fe-V isotope ratios?

The mean MORB Mg isotope ratio agrees well with the average peridotite melt produced (BSE plus the melt-source isotope fractionation) when  $T_p = 1300^\circ\text{C}$ . The mean MORB Ca and V isotope ratios are also well within analytical uncertainty of the average peridotite melt produced (BSE plus the melt-source isotope fractionation) when  $T_p = 1300^\circ\text{C}$  (see Figs. 4.8, 4.14), since both Ca and V have relatively large analytical uncertainties. For Fe, the isotope ratios of mean MORB and average peridotite melt at  $T_p = 1300^\circ\text{C}$  agree just within analytical uncertainty, requiring almost the maximum long-term error on natural sample measurements to match. Considering typical 2 S.E. analytical precision, mean MORB  $\delta^{57}\text{Fe}$  are slightly higher than predicted by the model even when considering only extremely small melt fractions (hence maximum partial melting isotopic fractionation). This discrepancy could be due to the effect of fractional crystallisation on the Fe isotope ratio of melts, since even high MgO MORB are almost never primary liquids (e.g., Langmuir et al., 1992), and fractional crystallisation produces isotopically heavy residual melts compared to the primary liquid (Teng et al., 2008; Chen et al., 2019b). Sossi et al. (2016) use a fractional crystallisation correction on the MORB dataset and calculate an average primitive MORB liquid with  $\delta^{57}\text{Fe} = 0.10\text{‰}$ , compared to  $0.15\text{‰}$  in the uncorrected (and non-MgO filtered) dataset (maximum correction on individual samples is  $\sim 0.07\text{‰}$ ). This result matches well with my calculated average peridotite melt at  $T_p = 1300^\circ\text{C}$ . However, the fractional crystallisation correction applied by Sossi et al. (2016) (e.g.,  $\Delta^{57}\text{Fe}_{\text{ol-melt}} \approx -0.18\text{‰}$  at  $T = 1200^\circ\text{C}$ ) is likely to represent the maximum limit of isotopic fractionation during olivine differentiation (Soderman et al., 2021 [chapter 3]).

In addition to comparing my results with mean MORB isotope compositions, I also examine how the ranges of measured MORB stable isotope compositions (for the systems Mg-Ca-Fe-V) compares to the spread of modelled melts. MORB samples have a wider range of isotopic compositions than the equilibrium KLB1 model melts (Fig. 4.14). In the Ca isotope system, some of this variability may be attributed to analytical uncertainty on measurements: here the width of the measured distributions of MORB data are within long-term analytical precision of the modelled KLB1 melt compositions (although, the errors on individual sample Ca isotope measurements are smaller and hence cannot account for all the difference between MORB and peridotite melts). In the Fe, Mg and V systems, the variability of measured MORB isotope compositions relative to the single-stage equilibrium peridotite melts is greater than can be explained by analytical uncertainty alone (Sossi et al., 2016) – this is particularly evident in  $\delta^{51}\text{V}$  (Fig. 4.14). Stable isotope fractionation during differentiation may play a role, as discussed for Fe isotopes above, but V isotopes are not thought to be significantly fractionated by olivine differentiation (Prytulak et al., 2013; Ding et al., 2020). Fractional crystallisation of clinopyroxene and Fe-Ti oxides, although unlikely for the MgO-filtered data here, is shown to drive melts to higher  $\delta^{51}\text{V}$  (Wu et al., 2018; Ding et al., 2020), which may explain some of the samples with high  $\delta^{51}\text{V}$ . However, the isotopically light (relative to BSE) MORB  $\delta^{51}\text{V}$  values remain unexplained by my calculations of peridotite melt-

ing. For Fe, even with a large Fe isotope fractionation correction applied (up to 0.07 ‰ for some MORB samples; Sossi et al., 2016) some MORB samples with extreme high  $\delta^{57}\text{Fe}$  values still remain isotopically heavy relative to modelled KLB1 melts that I consider most realistic of mantle melting (Soderman et al., 2021; see also Chen et al., 2019b). I find that neither long-term analytical uncertainty nor equilibrium peridotite partial melting from realistic regions of P-T space (see Fig. 3.11 in chapter 3) can reproduce the heaviest MORB Fe isotope ratios.

The Mg-Ca-Fe-V-Cr stable isotope compositions of mantle-derived melts are not expected to show large heterogeneity as a consequence of the mantle potential temperature variability (with associated changes in mineralogy and melt redox state; Fig. 4.8) of around 220 °C known from major and trace element studies in MORB (Klein and Langmuir, 1987; Langmuir et al., 1992; Gale et al., 2014). Therefore, I do not predict that the differences in either mean MORB stable isotope composition or the variance in MORB isotope ratios from predicted peridotite melts generated at  $T_p = 1300^\circ\text{C}$  can be explained by potential temperature variability. Instead, additional processes beyond single-stage equilibrium peridotite partial melting are required to explain the full range of Mg-Ca-Fe-V stable isotope ratios of MORB. In some cases, the addition of single-stage pyroxenite melts (derived from a source with a MORB-like bulk isotope composition) may explain some of the MORB range, and small amounts of pyroxenite in the MORB source is consistent with conclusions using other tracers of lithological heterogeneity (e.g., Zindler et al., 1984; Langmuir et al., 1986; Castillo et al., 2000; Waters et al., 2011). For example, 10 % pyroxenite in the MORB source (at  $T_p = 1300^\circ\text{C}$ ) could produce melts with  $\delta^{26}\text{Mg} = 0.02\text{‰}$  and  $\delta^{44}\text{Ca} = 0.04\text{‰}$  (using G2 pyroxenite) lower than, and  $\delta^{57}\text{Fe} = 0.03\text{‰}$  higher than (using MIX1G pyroxenite), pure peridotite melts (Fig. 4.12), explaining some but not all of the MORB data range for these three isotope systems. However, some of the MORB Fe isotope data (including the seamounts and E-MORB data), would require the source of pyroxenite melts to be isotopically fractionated relative to a protolith of pristine MORB ( $\sim 0.05\text{--}0.15\text{‰}$  heavier than mean MORB to explain the full range of data, depending on proportion of pyroxenite contributing to the final melt and P-T conditions of melting). A pyroxenite component in the MORB source that is isotopically fractionated from pristine recycled MORB has previously been proposed to explain MORB Fe and Mg isotope data (Sun et al., 2020; Zhong et al., 2021b). Multi-stage melting processes and reaction of pyroxenite-derived melts with ambient peridotite have also been proposed to fractionate the bulk Fe isotope composition of mantle pyroxenite away from that of the subducted material (e.g., Konter et al., 2016; Nebel et al., 2019; Sun et al., 2020), although achieving the suggested large isotopic fractionations (e.g.,  $\Delta^{57}\text{Fe}_{\text{melt-source}} \geq 0.1\text{‰}$ ; Konter et al., 2016) during repeated partial melting events may be unrealistic [chapter 3].

I note that the large range in MORB V isotope ratios cannot be explained by pyroxenite in the source, and that the lowest  $\delta^{44}\text{Ca}$  pyroxenite melts (which appear able to explain the full range of Ca isotope MORB data not matched by peridotite melting, Fig. 4.14) are only generated at pressures  $> 35\text{ kbar}$ . For  $T_p = 1300^\circ\text{C}$ , pyroxenite fractions in the MORB source would need

to be  $\geq 40\%$  to match all the Ca isotope MORB data (Fig. 4.12); alternatively, a pyroxenite component with a bulk isotope composition  $\sim 0.05\%$  lighter than average pristine MORB could reduce the pyroxenite fraction required in the source to explain the Ca isotope data to lower levels. While the  $^{87}\text{Sr}/^{86}\text{Sr}$  filter I use where Sr isotope data is available attempts to remove effects from recycled carbonates, I also note that since marine carbonates can have very low  $\delta^{44}\text{Ca}$  (up to  $2\%$  lighter than BSE; e.g., DePaolo, 2004; Fantle and DePaolo, 2005; Antonelli and Simon, 2020), a contribution from recycled carbonates could also be involved in the generation of light Ca isotopic compositions of basalts, as reported by e.g., Huang et al. (2011b); Liu et al. (2017b).

The range of Mg-Ca-Fe-V isotopic compositions of MORB with respect to modelled equilibrium melts leaves open the possibility of disequilibrium processes playing a role in the erupted stable isotope composition of MORB. Disequilibrium associated with melt transport can arise as low melt fractions are extracted from the mantle and rapidly migrate (Faul, 2001; Connolly et al., 2009), as has been recorded using U-series disequilibria in MORB (e.g., McKenzie, 1985; Lundstrom, 2003; Van Orman et al., 2006), and could be responsible for some major element trends in the global MORB dataset (Oliveira et al., 2020). As disequilibrium during melt extraction and transport is related to the timescales of chemical diffusion of major and trace elements in the melt, disequilibrium could generate kinetic (rather than equilibrium) stable isotope fractionation as seen in chemical diffusion studies (e.g., Richter et al., 2003, 2009b; Watkins et al., 2017). Disequilibrium processes could therefore influence both the isotopic composition of melt source regions via metasomatism, and the isotopic composition of melts as they migrate and erupt. In samples recording kinetic isotope fractionation signatures, the direction of isotopic fractionation from the source isotope ratio will be the same for all isotope systems which behave similarly during mantle melting, as the light isotopes of a given element will diffuse faster than the heavier isotopes of the same element (e.g., Dauphas, 2007; Richter et al., 2008, 2009b; Teng et al., 2011), and the recorded isotopic fractionation should scale with the mass of the isotopes considered. Kinetic processes in melts can produce much larger isotopic fractionations than equilibrium processes (see Watkins et al., 2017) even for small concentration gradients in the diffusing element (and therefore can be seen even in the diffusion of major elements in silicate melts; Richter et al., 2003; Xiao et al., 2013; Watkins et al., 2014; Kang et al., 2020). Positive correlations would be expected between all isotope ratios measured for the same samples if their isotope ratio was controlled by kinetic fractionation and chemical diffusion during disequilibrium (for pairs of elements diffusing in the same direction, such as solid to melt), as reported in e.g., Zhao et al. (2017a,b); Kang et al. (2020). Key pairs of isotopes to identify a kinetic vs equilibrium process recorded in suites of natural samples would be those that behave similarly (from an elemental perspective) during partial melting but would show opposite directions of isotopic fractionation from the source under equilibrium conditions (e.g., Fe and Ca, with positive and negative melt-source isotopic fractionation respectively). Supporting this prediction, kinetic effects during metasomatism have been proposed to generate positively correlated  $\delta^{44}\text{Ca}$ – $\delta^{57}\text{Fe}$  values measured in ultramafic rocks (with a low  $\delta^{44}\text{Ca}$ ,  $\delta^{57}\text{Fe}$  metasomatic endmember; Zhao et al., 2017b).

Low temperature alteration (relative to mantle temperatures) could also be responsible for causing significant stable isotope variability in measured MORB. Due to the  $1/T^2$  dependence of equilibrium stable isotope fractionations (Bigeleisen and Mayer, 1947), low temperature processes generate larger magnitude isotope fractionation effects than magmatic processes. For example, Fe leaching during hydrothermal fluid circulation is generally shown to preferentially remove light Fe isotopes from the host rock, recorded in low  $\delta^{57}\text{Fe}$  hydrothermal fluids (e.g., Rouxel et al., 2003; Severmann et al., 2004). Correspondingly high  $\delta^{57}\text{Fe}$  is measured in heavily leached basalts (up to 2.05 ‰ with 80 % Fe loss; Rouxel et al., 2003), although Rouxel et al. (2003) also show that on a scale larger than a few metres, bulk hydrothermally altered oceanic crust is indistinguishable in  $\delta^{57}\text{Fe}$  from MORB. Without significant Fe loss, altered crust may not show such extreme Fe isotope variations (Williams et al., 2009), although alteration can generate measurable Fe isotope fractionation in komatiites (Dauphas et al., 2010). By contrast, Ca isotope data from mid-ocean ridge hydrothermal fluids suggest that the fluids and MORB have similar  $\delta^{44}\text{Ca}$  (Schmitt et al., 2003; Amini et al., 2008; Scheuermann et al., 2018). A Mg isotope study of altered oceanic crust from the East Pacific Rise also shows that limited bulk rock Mg isotope fractionation occurs during alteration, irrespective of alteration temperature (Huang et al., 2015), but I note that the measured  $\delta^{26}\text{Mg}$  range of altered crustal samples does exceed the range of MORB data. Altered oceanic crust also records MORB-like  $\delta^{51}\text{V}$  (Wu et al., 2018), and Prytulak et al. (2013) show that  $\delta^{51}\text{V}$  is generally insensitive to the range of common alteration processes (serpentinisation, seafloor weathering – although an effect of increased  $\delta^{51}\text{V}$  by 0.2–0.3 ‰ may be seen in extreme cases – and hydrothermal alteration) in the oceanic crust. By contrast, alteration and serpentinisation in near-surface settings generate large variations in  $\delta^{53}\text{Cr}$  in ultramafic rocks (Farkaš et al., 2013; Wang et al., 2016), but altered oceanic crust does not show the same isotopic variability (Wang et al., 2016). Given these studies, for the isotope systems considered here mildly altered MORB is not expected to show significant isotopic fractionation from erupted values, but given the potential for large low temperature isotopic fractionations, alteration (both of the basaltic rocks analysed and oceanic crustal material that serves as a protolith for mantle pyroxenite components) remains a consideration.

#### 4.6.2 Understanding the diversity of OIB Mg-Ca-Fe-V-Cr stable isotope compositions

For Mg, Ca and Fe, measured OIB stable isotope ratios are more variable relative to those measured in MORB (Fig. 4.14). This variability in OIB compared to MORB has been interpreted as a potential signature of lithological heterogeneity in the OIB source (Mg: Zhong et al., 2017; Stracke et al., 2018; Wang et al., 2018, Ca: Kang et al., 2019; Wang et al., 2019, Fe: Williams and Bizimis, 2014; Konter et al., 2016; Nebel et al., 2019; Gleeson et al., 2020). Carbonates and/or their derived melts have also been invoked for Mg and Ca isotopic heterogeneity in OIB (e.g., Huang et al.,

2011b; Liu et al., 2017b; Wang et al., 2018) but this topic is not discussed here. An important caveat of interpreting data shown in Fig. 4.14 is that the ocean islands sampled for each isotope system are different, and therefore the same localities are not present in each OIB dataset – Mg, Ca and Fe have data for a wider range of OIBs than V and Cr, and so it is possible that more variability would be seen in both V and Cr if more OIB are explored. However, despite the wide variability, the mean OIB is analytically indistinguishable (using long-term 2 S.D.) from mean MORB for Mg, Ca and V isotopes.

The mean measured OIB values can be explained both by modelled peridotite and pyroxenite melts for the Mg, Ca, V and Cr stable isotope systems. For Fe, modelled pyroxenite melts match mean OIB isotopic compositions better than peridotite melts, due to the use of mean MORB as the bulk isotopic composition for the pyroxenites, offsetting the resulting pyroxenite melts to heavier isotope ratios than peridotite melts. This potential Fe isotope signature of lithological heterogeneity in some OIB data due to a bulk isotopic offset of the source relative to ambient mantle has been suggested for several mantle plume systems (e.g., Hawai'i, Williams and Bizimis, 2014; Samoa, Konter et al., 2016; Pitcairn, Nebel et al., 2019; Galápagos, Gleeson et al., 2020).

The greater diversity of OIB Mg-Ca-Fe-V-Cr stable isotope compositions displayed in OIB compared to MORB and the modelled melts raises further questions, and I discuss only a few here. Firstly, for Cr, the contribution of isotopically light pyroxenite melts to multi-lithologic mantle melting means that a peridotite + pyroxenite mantle source is better able to explain the measured OIB data range than pure peridotite melts, especially considering the good analytical precision (2 S.D. < 0.04 ‰) compared to sample variability achieved in the Cr isotope studies shown in Fig. 4.14. However, it is possible that the apparently better fit of a pyroxenite model seen here is instead a result of fractionation from a peridotite-derived melt, as cotectic crystallisation of olivine and spinel in basalts has been proposed to drive residual melts to lighter Cr isotope ratios (Shen et al., 2020). Given the MgO filter used for OIB data in Fig. 4.14 however, spinel crystallisation is unlikely to have affected all the OIB samples. The Cr stable isotope data therefore provide tantalising evidence for the presence of lithological heterogeneity in OIB mantle source regions, particularly in the case of the lightest measured Cr isotope compositions. Nonetheless, without equivalent MORB Cr isotope data for comparison, and with a very limited published sample set, it is difficult to confirm how well natural Cr isotope data matches equilibrium isotope fractionation models. Fig. 4.12f suggests that even 20 % SD pyroxenite in a mantle source melting at  $T_p = 1400^\circ\text{C}$  will produce a bulk melt only 0.02 ‰ lighter than a pure peridotite melt, which would not be able to explain the full range of Cr isotope OIB data. An expanded study of MORB and OIB Cr isotope ratios would be an important step in both learning more about Cr isotope behaviour and exploring stable isotopes as a new tool for studying mantle melting conditions, given the potential for Cr isotope sensitivity to lithology discussed in this study.

For Mg stable isotopes, the extra range in isotope composition displayed by OIB relative to MORB is small (<  $\pm 0.05$  ‰) relative to analytical precision, and the extreme MORB and OIB

isotope ratios are only resolvable from each other using a typical sample 2 S.E., rather than values quoted for long-term reproducibility (Table 4.7). The pyroxenite melts show a much wider range of melt stable Mg isotope ratios than peridotite melts, and therefore could be contributing to the small extra variability in OIB compared to MORB: for example, Fig. 4.12 shows that 10–20 % pyroxenite could generate melt isotopic variability of  $\pm 0.04$ – $0.05$  ‰ compared to a pure peridotite source. Noticeably in the Mg isotope data, and particularly in comparison to Fe, the natural data is less variable than the full range predicted for pyroxenite melts by my models (Fig. 4.14). This is despite the sampled OIB including St Helena, Society and the Cook-Austral Islands, thought to sample various recycled crustal components (which will form pyroxenites in the mantle) based on multiple studies including radiogenic isotopes, trace elements and other stable isotopes (e.g., Chauvel et al., 1992; Stracke et al., 2005; Kawabata et al., 2011; Teng et al., 2013; Hanyu et al., 2014). The limited Mg isotope variability in OIB compared to possible pyroxenite melts could relate to the location of the melting region, and the dilution of pyroxenite melts with peridotite, as highlighted in Fig. 4.12. For example, the most negative  $\Delta^{26}\text{Mg}_{\text{melt-source}}$  for MIX1G is generated at low melt fraction close to the solidus, at temperatures of around 1200–1250 °C and pressures of 8–15 kbar, and the most positive  $\Delta^{26}\text{Mg}_{\text{melt-source}}$  at depths of over 100 km (Fig. 4.3). The isotopically lightest melts are not sampled by pyroxenite decompressing along a peridotite isentrope even at  $T_p = 1300$  °C (Fig. 4.9), and it is unlikely that deep, isotopically heavy melts will be extracted without mixing with shallower, isotopically lighter melts. This is in agreement with Fig. 4.12, which shows that typical aggregate melts from melting of multi-lithologic mantle at 1300–1400 °C will have a much narrower range in isotopic composition than the full range of pyroxenite melts shown in Fig. 4.14. Therefore, the process of melt extraction and mixing from a multi-lithologic mantle will act to minimise the isotopic signature from any deep pyroxenite melts, and result in relatively homogeneous OIB Mg isotope ratios seen in the OIB erupted at the surface.

In contrast to the Mg isotope system, OIB isotope ratios for Fe, Ca and V extend outside the range of any of the modelled peridotite or pyroxenite melts. For Ca and V isotopes, some OIB data fall to the opposite side of BSE than expected for mantle melting. In both cases, measurement uncertainties (particularly long-term 2 S.D.) are large and could account for all the difference between modelled melts and natural data, and it will be important to continue to improve analytical precision to better understand the natural data and be able to make comparisons between OIB sample sets, especially given the minimal sensitivity to lithology predicted for these isotope systems (section 4.5.2.2). In the case of V, fractional crystallisation of Fe-Ti oxides has been shown to drive melts up to 0.3 ‰ higher than their initial isotope composition, therefore able to match the spread of V isotope data to values higher than BSE, although this effect has only been recorded in basalts with < 5 wt % MgO (Wu et al., 2018; Ding et al., 2020). Therefore it is unlikely that the basalts with V isotope ratios heavier than BSE shown in Fig. 4.14 reflect Fe-Ti oxide crystallisation. For Ca, non-pyroxenitic origins of isotopic variability have been proposed for komatiite data, such as the generation of  $\delta^{44}\text{Ca}$  as low as 0.64 ‰ from serpentinised oceanic crust in the mantle source (John et al., 2012; Amsellem et al., 2019). If improved analytical precision confirms the Ca isotope

data variability shown in Fig. 4.14 is real, similar non-pyroxenitic origins may be able to explain some or all of the spread of OIB data.

For Fe, measurement uncertainties are small compared to the variability in the OIB Fe isotope data, which extends to much higher  $\delta^{57}\text{Fe}$  values than matched by the melts presented here (Fig. 4.12; see also Soderman et al., 2021 [chapter 3]). Heavier Fe stable isotope compositions than can be explained by single-stage melting of garnet-bearing lithologies are also seen in seamounts from close to the EPR (Sun et al., 2020) – the heaviest isotope ratios are found in samples with  $< 7$  wt % MgO, and therefore not shown in Fig. 4.14, but Sun et al. (2020) find that these are still isotopically heavier than can be explained by single-stage melting once they correct their samples for differentiation. One solution to explaining the heavy Fe isotope data could be to invoke a mantle source with unusually high  $\delta^{57}\text{Fe}$  (i.e., Fe-isotopically heavier than average MORB as assumed in Figs. 4.12 and 4.14), generated for example as a frozen melt that has been through multiple melting and remobilisation stages, and now stalled in the lithosphere. While the limitations of multiple melting events with regards to mass balance and plausible melting degrees are discussed in Soderman et al. (2021) [chapter 3], multiple melting stages of garnet-bearing lithologies and reaction with ambient mantle have been proposed to generate the required isotopically heavy mantle sources ( $\delta^{57}\text{Fe} > 0.3$  ‰) to explain some of the highest  $\delta^{57}\text{Fe}$  in the global dataset (Nebel et al., 2019; Sun et al., 2020). However, based on my modelled small melt-source isotope fractionations, the isotopically heaviest Fe isotope OIB data would require a mantle source with an even heavier overall bulk composition of  $\delta^{57}\text{Fe} > 0.4$  ‰. Alternatively, large stable isotope effects may be attributed to disequilibrium and/or low temperature alteration processes, as discussed for MORB above. A further possibility to explain heavy Fe isotope ratios in OIB could be the mixing of isotopically heavy components derived from the lower mantle (such as bridgmanite cumulates with  $\delta^{57}\text{Fe} \approx 0.3$  ‰, Williams et al., 2021) into upwelling plumes. High  $\delta^{44}\text{Ca}$  lower mantle components from Ca-perovskite crystallisation related to early Earth magma ocean processes have also been proposed as the origin of isotopically heavy Ca isotope komatiite data (up to 1.54 ‰; Amsellem et al., 2019).

## 4.7 Other potential isotopes

Other stable isotope systems not considered here might also have potential for investigating mantle heterogeneity (in either lithology or temperature). However, a better understanding of the bonding environment in melts or relevant minerals is required before these isotope systems can be implemented into the stable isotope fractionation models used here.

Like other stable isotope systems, the equilibrium  $\delta^{30}\text{Si}$  value of a phase will depend on the strength of the Si-O bonds. A more polymerised (or, more Si-rich) phase will have more Si-O bonds, therefore a stronger average Si-O bond force constant, hence high  $\delta^{30}\text{Si}$  (Grant, 1954).

However, density functional theory (DFT) calculations show this simple prediction is complicated by the role of other network-modifying cations in silicates (Méheut et al., 2009; Méheut and Schauble, 2014). Silicon isotope fractionation factors have been calculated using DFT for appropriate mantle minerals (Huang et al., 2014), however there is a lack of work on the crucial mineral-melt fractionation information required for the equilibrium fractionation model here. Furthermore, it has been suggested that Si isotopic fractionation in liquids may be correlated with chemical composition (Qin et al., 2016), an effect that is too complicated (and under-constrained) to model here. This knowledge gap could provide scope for future work, however the mantle is currently thought to be homogeneous in Si isotopes (within current limits of analytical precision), and there seems to be only a small partial melting effect (Savage et al., 2014).

Titanium stable isotopes have been suggested as tracer of magmatic processes (Millet et al., 2016), since Ti can exist in multiple coordination states in silicate melts and Ti-oxides (Farges and Brown Jr, 1997). However, Ti stable isotope fractionation in magmatic systems is dominated by the behaviour of Fe-Ti oxides, with no partial melting fractionation from mantle lithologies expected unless under conditions of Ti-oxide saturation. DFT calculations predict no significant Ti isotope fractionation between pyroxenes, olivine or garnet (Wang et al., 2020b), and both eclogites and MORB have the same measured  $\delta^{49}\text{Ti}$  value (Millet et al., 2016). Therefore, Ti isotopes are not investigated in this work, as there is no existing data to support for their use in tracing temperature or lithological heterogeneity in the mantle associated with MORB or OIB.

## 4.8 Summary

I have combined a thermodynamically self-consistent model for mantle melting of peridotite and pyroxenite with a model for equilibrium Mg-Ca-Fe-V-Cr stable isotope fractionation to quantitatively predict melt-source stable isotope fractionation over P-T conditions relevant to mantle melting at mid-ocean ridges and within mantle plumes. The results allow me to assess the potential of these stable isotope systems for investigating mantle temperature variations, source heterogeneity, and their record in the erupted basalts (MORB, OIB).

I used my results for the melting of KLB1 peridotite to explore the sensitivity of melt stable Mg-Ca-Fe-V-Cr isotope compositions in each isotope system to variations in mantle potential temperature. Redox-sensitive isotopes (Fe, V) show most variability in accumulated melt isotopic composition with potential temperature, due to the variation in  $\text{Fe}^{3+}/\text{Fe}_T$  (and  $\text{V}^{4+,5+}/\text{V}_T$ ) as the average depth of melting increases with  $T_p$ . The predicted variability in the V isotopic composition of melts is qualitatively consistent with  $\delta^{51}\text{V}$ - $\text{Na}_{8,0}$  trends in natural data. However, analytical precision improvements upon current levels would be necessary for variability to be clearly resolved in the compositions of erupted basalts. At present, the equilibrium fractionation of the stable isotopes considered here during peridotitic mantle melting is not predicted to be a

useful tool in identifying temperature variations in MORB or OIB melting regimes.

I also obtained model results for Mg-Ca-Fe-V-Cr fractionation during melting of MIX1G silica-deficient pyroxenite and G2 silica-excess pyroxenite. My results show that Mg and Ca isotopes have the most sensitivity to the presence of garnet in a melt source, with melts predicted to record a negative Mg-Ca isotope correlation if garnet is present in the mantle source, although improvements in analytical precision would be needed to clearly resolve this trend. My results also demonstrate that Fe, Mg and Cr stable isotopes are sensitive to the proportion of pyroxenite (with a MORB-like bulk isotope composition) in a mantle source, although with current analytical precision only pyroxenite fractions greater than around 10 % are resolvable. Moderate improvements in analytical precision could result in Ca stable isotopes being added to this list, and potentially allow pyroxenite fractions < 10 % to be identified in these isotope systems. However, Cr stable isotope partitioning in the mantle is generally understudied (both in measurements of natural samples, and studies of its bonding and fractionation in relevant mantle phases): while this system has the potential to be sensitive to lithological heterogeneity, we require improvements in the certainty of model inputs and/or more natural data to confidently use this isotopic tool in the mantle.

Comparison of the global datasets of stable isotope data for MORB and OIB with modelled melt isotope ratios generated by equilibrium fractionation highlight both agreements and disagreements between equilibrium melting models and measured data. Generally, mean MORB Mg-Ca-Fe-V-Cr stable isotope compositions, within typical long-term analytical precision, can be matched to the mean peridotite melt isotope ratio produced for a mantle potential temperature of 1300 °C. However, the range of MORB data is wide compared to modelled peridotite melts – even after analytical uncertainty on data and fractional crystallisation are considered, some MORB record stable isotope ratios that appear unable to be matched by equilibrium peridotite melting (notably in Mg, Fe and V, and Ca may show a similar result as measurement precision improves). Lithological heterogeneity (pyroxenite) in the MORB source can contribute to some of this variability but not all, and disequilibrium and/or low temperature processes may also be required to match the observed data. For OIB, the variability in natural data, even for isotope systems such as Fe and Cr where analytical precision is good compared to the data variability, could suggest that the involvement of pyroxenite may be recorded in the existing Mg, Fe and Cr stable isotope datasets. However, differences between the range of natural data and modelled pyroxenite melts suggest that additional processes such as the offset of the isotope ratio of recycled components from pristine MORB values and kinetic fractionations may also be important in understanding the current Mg-Ca-Fe-V-Cr stable isotope datasets available for primitive global oceanic basalts.

I conclude that stable isotopes in basalts have variable potential as a tracer of heterogeneity in the mantle, complementing existing tools well – however there are knowledge and data gaps that need to be filled before these systems can be used to their full potential.

## 4.9 Supplement: Alternative input parameters and results

The inputs into the isotope fractionation models are better constrained for some of the stable isotope systems considered relative to others. These uncertainties limit our ability to predict the behaviour of some isotope systems in high temperature settings, and therefore limit the utility of stable isotopes as a tool for exploring global basalt systematics. Here I discuss the results of using alternative inputs.

### 4.9.1 Mg: if $\alpha_{\text{orthopyroxene-melt}} = 1$

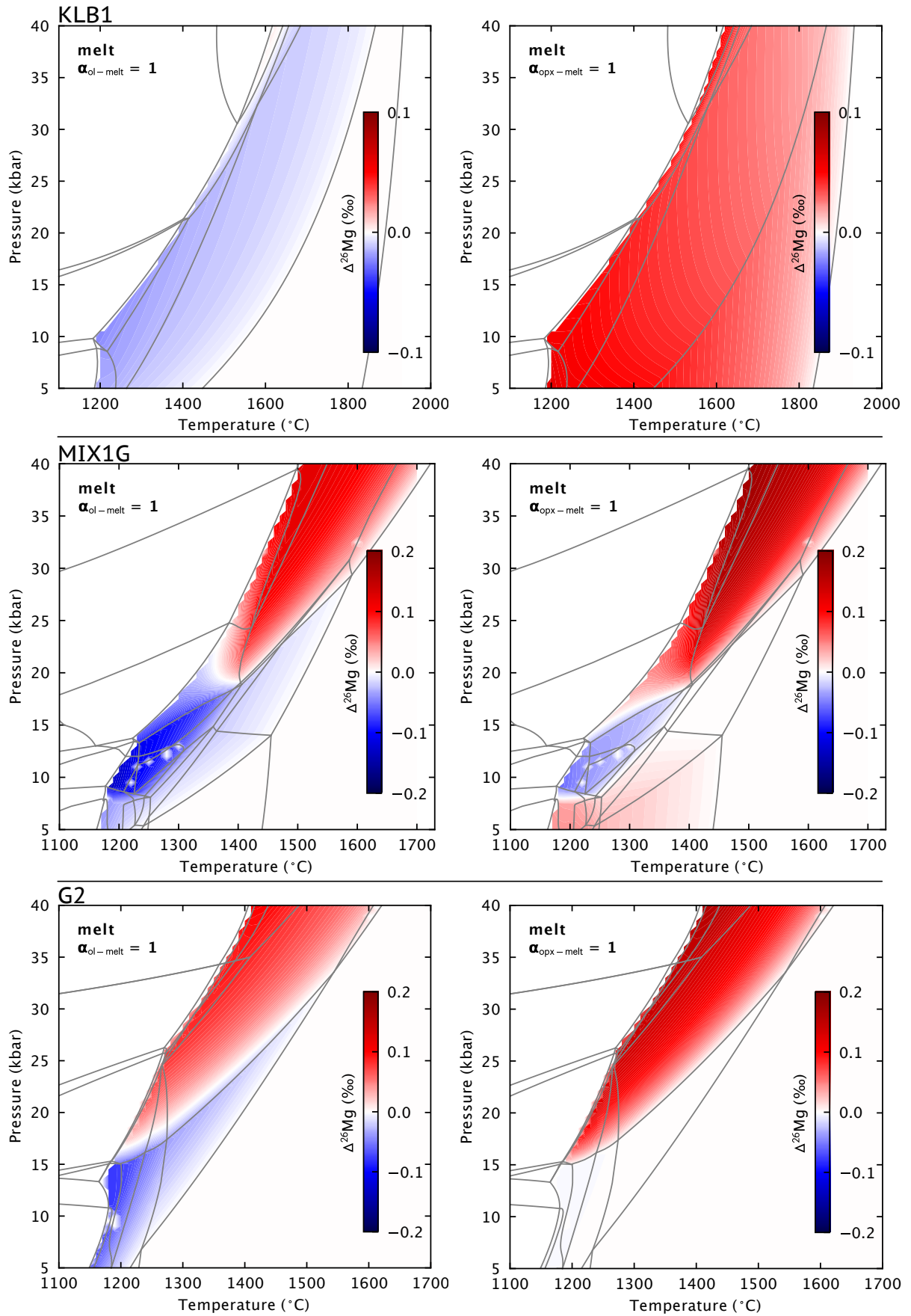
While the bonding of Mg in crystal lattices can be used to calculate a self-consistent set of  $\beta^{\text{Mg}}$  factors (Schauble, 2011; Huang et al., 2013) to input into the melting model,  $\beta^{\text{Mg}}$  factors do not exist for silicate liquid. However, Stracke et al. (2018) show that  $\alpha_{\text{olivine, orthopyroxene-melt}} \approx 1$  based on equilibrated peridotite xenoliths. Mg is also similarly coordinated ([5–6] fold) in melt and olivine/orthopyroxene (George and Stebbins, 1998; Shimoda et al., 2007; Stracke et al., 2018), providing further evidence for minimal olivine/orthopyroxene–melt Mg stable isotope fractionation at magmatic temperatures.

I have chosen to use  $\alpha_{\text{olivine-melt}} = 1$ ; i.e., using the same  $\beta^{\text{Mg}}$  values for liquid as for olivine. The alternative is to use  $\alpha_{\text{orthopyroxene-melt}} = 1$ . Fig. 4.15 compares the  $\Delta^{26}\text{Mg}_{\text{melt-source}}$  for an input of  $\alpha_{\text{olivine-melt}} = 1$  (left hand panels; these are the results used throughout the chapter) with an input of  $\alpha_{\text{orthopyroxene-melt}} = 1$  (right hand panels). The new input parameters replace the melt in Table 4.2 with Table 4.10.

**Table 4.10: Alternative parameters for Mg isotope  $\beta^{\text{Mg}}$  factors** from Huang et al. (2013).  $1000\ln\beta = a/T^6 + b/T^4 + c/T^2$ , where T = temperature (Kelvin).

| Mineral | a                      | b                     | c                  |
|---------|------------------------|-----------------------|--------------------|
| melt    | $-8.10 \times 10^{15}$ | $6.65 \times 10^{10}$ | $2.25 \times 10^6$ |

For KLB1 peridotite, the magnitude of the difference in melt isotope composition between the two models is  $\approx 0.05\text{‰}$  (small compared to the average analytical uncertainty of  $0.1\text{‰}$  suggested in Stracke et al., 2018, and similar to the long-term 2 S.D. of  $0.06\text{‰}$  given in Wang et al., 2021), however the direction of partial melting fractionation is different. In the case of  $\alpha_{\text{olivine-melt}} = 1$ , KLB1 melts are isotopically lighter than the bulk, and get heavier with increasing degree of melting (the latter part of this behaviour is consistent with fractional melting modelled by Stracke et al., 2018). For  $\alpha_{\text{orthopyroxene-melt}} = 1$ , partial melts are isotopically heavier than the bulk, and get progressively lighter with increasing degree of melting (the former part of this behaviour is consistent with Stracke et al., 2018).



**Figure 4.15:**  $\Delta^{26}\text{Mg}_{\text{melt-source}}$  compared for a model where  $\alpha_{\text{olivine-melt}} = 1$  (left hand plots) and  $\alpha_{\text{orthopyroxene-melt}} = 1$  (right hand plots) for all three lithologies considered.

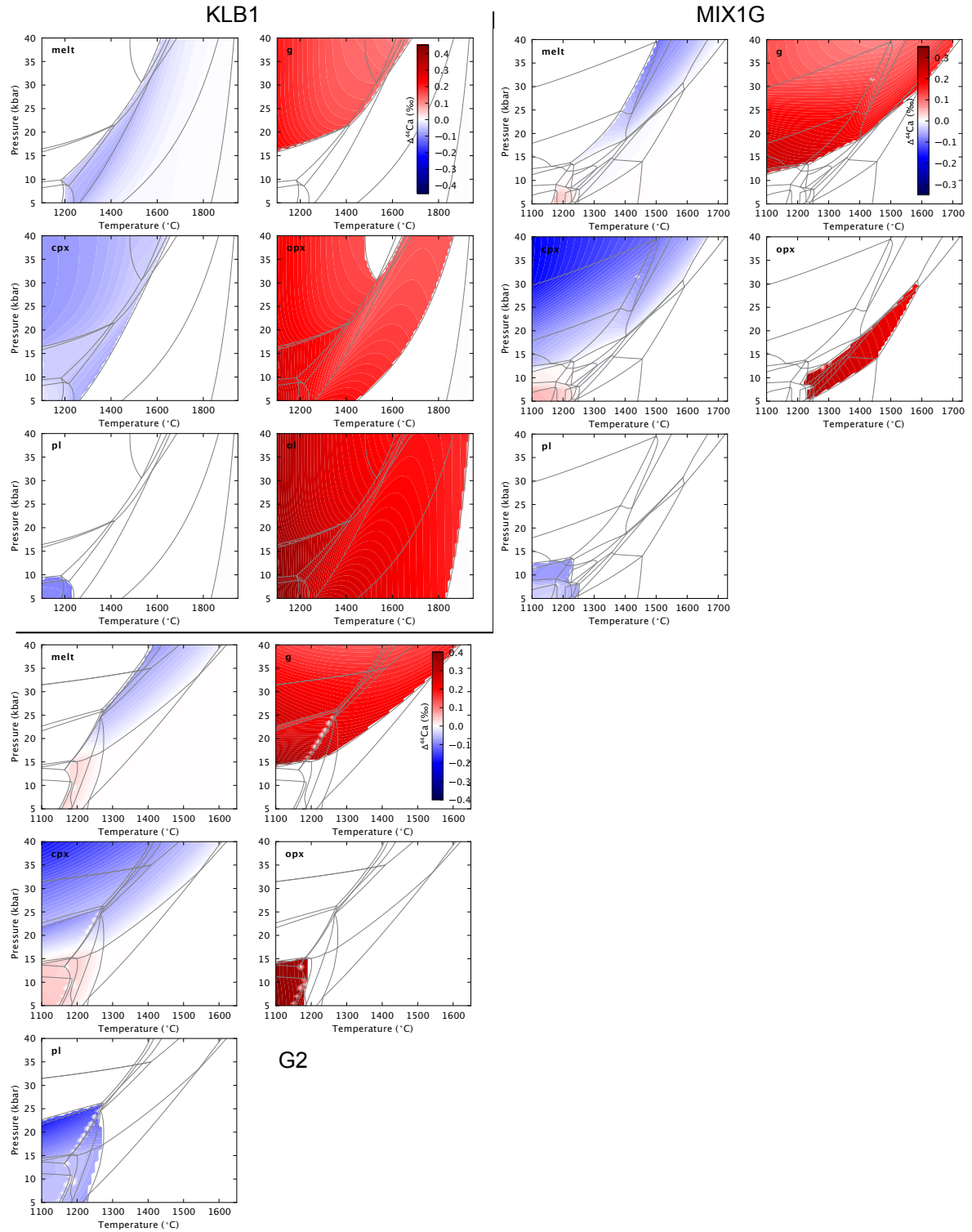
For KLB1, the similar differences in modelled melting isotopic fractionation relative to the analytical uncertainty means that the choice of  $\alpha_{\text{olivine-melt}} = 1$  or  $\alpha_{\text{orthopyroxene-melt}} = 1$  for liquid does not greatly alter any conclusions drawn from the peridotite melting. Minimal difference between the models is also seen for MIX1G. However, low pressure melts from G2 ( $< 15$  kbar) show effectively no stable isotope fractionation when  $\alpha_{\text{orthopyroxene-melt}} = 1$  is used, compared to fractionations as large as  $\Delta^{26}\text{Mg} = -0.1\text{‰}$  with  $\alpha_{\text{olivine-melt}} = 1$ . This is because, for these shallow depths, the only stable Mg-bearing phases in G2 are clinopyroxene and liquid (garnet is not stable). Orthopyroxene and clinopyroxene have similar  $\beta^{\text{Mg}}$  factors and therefore, when liquid is given the same  $\beta^{\text{Mg}}$  factor as orthopyroxene, the coexisting liquid and clinopyroxene are only minimally isotopically fractionated from each other. These results highlight how important accurate experimental  $\alpha_{\text{mineral-melt}}$  are for understanding the behaviour of stable isotope systems, and the important role analytical precision plays in being able to identify these effects in nature. Magnesium stable isotopes would benefit from further work in both of these areas.

#### 4.9.2 Alternative literature $\beta^{\text{Ca}}$ values

The  $\beta^{\text{Ca}}$  value approach reduces uncertainties associated with an ionic model, as the bond lengths and Ca, O coordination numbers in the relevant mineral structures required for the ionic model are variable in the literature (e.g., Feng et al., 2014; Huang et al., 2019). Huang et al. (2019) present an alternative set of  $\beta^{\text{Ca}}$  values for the Ca-bearing minerals we are concerned with, although Antonelli et al. (2019b) argue that the PBE functionals used in their own study better represent Ca isotope fractionation between species than the less accurate LDA functionals used by Huang et al. (2019). Additionally, Antonelli et al. (2019b) calculate  $\beta^{\text{Ca}}$  for pyrope garnet, which is more representative of mantle garnet than the grossular endmember used in Huang et al. (2019). My model uses  $\beta_{\text{plagioclase}}^{\text{Ca}} < \beta_{\text{melt}}^{\text{Ca}} < \beta_{\text{clinopyroxene}}^{\text{Ca}}$  (see explanation in section 4.2), but some studies do suggest that  $\beta_{\text{melt}}^{\text{Ca}} = \beta_{\text{clinopyroxene}}^{\text{Ca}}$  (e.g., Chen et al., 2019a) based on observations from natural equilibrated peridotite and pyroxenite samples that there is minimal Ca isotope fractionation between clinopyroxene and basaltic melt. Independent estimates of the force constants in silicate liquids and further experimental constraints on the behaviour of Ca isotopes in silicate melts are therefore needed to improve the Ca isotope fractionation model.

Fig. 4.16 shows the results of using the  $\beta^{\text{Ca}}$  values from Huang et al. (2019) with  $\beta_{\text{melt}}^{\text{Ca}} = \beta_{\text{clinopyroxene}}^{\text{Ca}}$  (equivalent to  $\alpha_{\text{clinopyroxene-melt}} = 1$ ). The use of isotopically lighter grossular garnet and isotopically heavier melt (relative to the Antonelli et al. (2019b) inputs) result in overall less negative melt-source isotope fractionation than in the main model, making all Ca isotope fractionations harder to resolve with current analytical precision. However, none of the conclusions presented in the main body of this chapter are altered by these alternative parameter choices.

The composition of the phases involved further complicates models of Ca isotope fractionation. Feng et al. (2014) and Wang et al. (2017) show that Ca-O bond strength, hence isotopic



**Figure 4.16: Model results of  $\Delta^{44}\text{Ca}_{\text{phase-source}}$  for  $\beta_{\text{Ca}}^{\text{Ca}}$  inputs from Huang et al. (2019), and using  $\beta_{\text{Ca}}^{\text{Ca}}_{\text{melt}} = \beta_{\text{Ca}}^{\text{Ca}}_{\text{clinopyroxene}}$ .** Generally, the calculated  $\Delta^{44}\text{Ca}_{\text{phase-source}}$  is less negative than using the  $\beta_{\text{Ca}}^{\text{Ca}}$  inputs from Antonelli et al. (2019b) as shown in Fig. 4.4.

fractionation, in orthopyroxene is dependent on the Ca and Fe content of the pyroxene, although the concentrations of these elements in natural orthopyroxenes may produce negligible concentration effects on isotopic fractionation (Wang et al., 2017). The isotopic fractionation associated with garnet, in particular, is sensitive to Ca content for typical mantle compositions, with a garnet-composition-sensitive fractionation factor producing smaller melting isotopic fractionations in eclogite than using a fixed composition model (Chen et al., 2020b). My model has not implemented composition-specific fractionation factors, although does use the pyrope garnet end-member which is most representative of mantle garnet. I also note that Antonelli et al. (2019b) calculate compositional effects for olivine and pyroxene solid solutions that are smaller than those predicted using LDA functionals (e.g., Feng et al., 2014; Wang et al., 2017).

### 4.9.3 Constraints on Fe model inputs

The model inputs for Fe isotope fractionation are relatively well constrained. The bonding environment of Fe in mineral phases is well studied, making an ionic model approach possible (e.g., Sossi and O'Neill, 2017). The model based on ionic inputs produces isotopic fractionation and force constant predictions consistent with predictions by other methods and observations (e.g., Dauphas et al., 2014; Macris et al., 2015). In addition, the Fe-O force constants in basaltic glass as a function of  $\text{Fe}^{3+}$  content have been experimentally determined (Dauphas et al., 2014), allowing the melt isotopic fractionation to be independently parameterised into the model (although I note the potential complication induced by quenching effects, and by melt generation in the mantle at non-atmospheric pressure). As discussed by Sossi and O'Neill (2017), some terms in the ionic model approach (such as the ionicity of the bonds) are less well constrained than the bonding environment of Fe in mineral structures, however the resultant fractionation factors are minimally affected by these uncertainties.

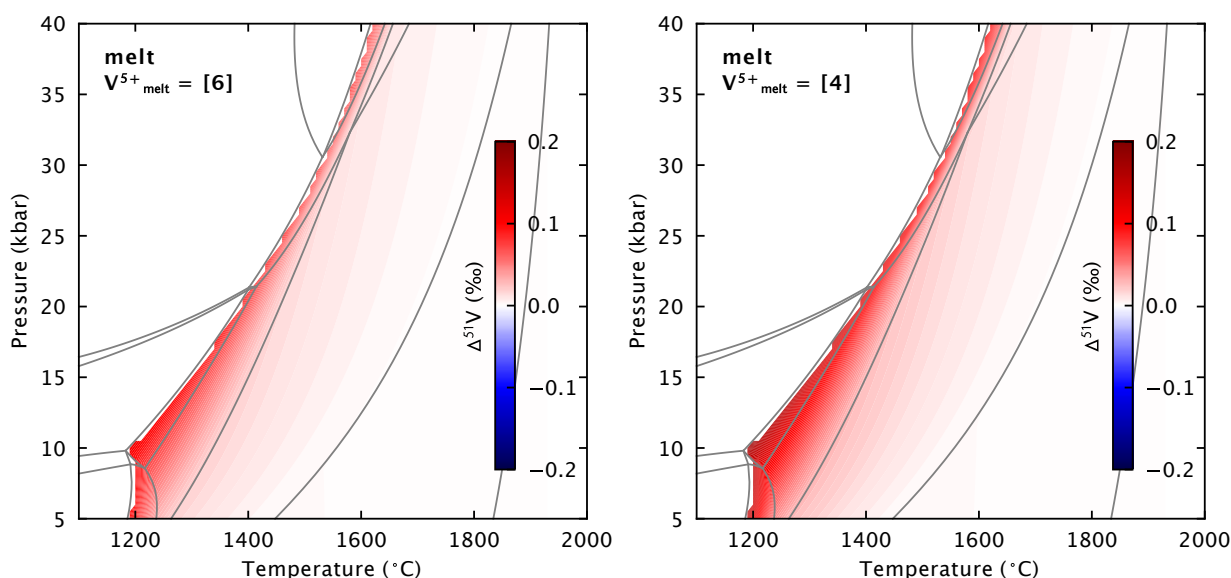
### 4.9.4 V: if $\text{V}_{\text{melt}}^{5+} = 4\text{-fold coordinated}$

It has been suggested that vanadium isotopes may track magmatic redox (Prytulak et al., 2013, 2017; Sossi et al., 2018b; Wu et al., 2018) due to the existence of three valence states (3+, 4+, 5+) in terrestrial magmatic systems (Canil, 1999), though a better understanding of V isotope behaviour during magmatic processes is required to exploit the system's full potential as a redox tracer (Prytulak et al., 2017). The successful modelling of V isotope fractionation therefore relies on an understanding of the behaviour of each V valence state.

Although slightly variable V partition coefficients for each valence state into mineral phases can be found from experimental studies (Mallmann and O'Neill, 2009), these variations make no significant difference to the calculated melt isotopic compositions. The main uncertainty in the V fractionation model inputs is the coordination of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  in silicate melts (and associated

$\beta^V$  factors).  $V^{4+}$  in silicate liquid is [5–6] coordinated (Sutton et al., 2005), and  $V^{4+}$  coordination of both [5.33] and [6] have been used in existing studies discussing V isotope behaviour during melting (Qi et al., 2019; Wu et al., 2018 respectively).  $V^{5+}$  coordination in silicate melts is [4–6] (Sutton et al., 2005; Richter et al., 2006), with Qi et al. (2019) quoting an average of [5] coordination. As one of the main causes of V isotope fractionation during melting is predicted to be the relative compatibility of  $V^{5+}$  (and to a lesser extent  $V^{4+}$ ) in melts relative to minerals (e.g., Canil, 2002; Mallmann and O'Neill, 2009; Wu et al., 2018), the bonding environment and force constants of V species in the melt is a particularly important input. The choice of coordination number for the V species controls the  $\ln \beta$  value chosen for that species:  $\beta^V$  values are taken from those calculated for different bonding environments in aqueous solutions (Wu et al., 2015), assumed to be a good approximation to the case of silicate melts following Wu et al. (2018). [5] coordination of  $V^{5+}$  is not modelled in Wu et al. (2015), and therefore only the cases of  $V^{5+}$  in [4] and [6] coordination can be used, for which  $\beta^V$  values have been calculated. No calculations are available for  $V^{4+}$  in [5] coordination, and therefore the model only considers  $V^{4+}$  in [6] coordination.

Fig. 4.17 compares the  $\Delta^{51}V_{\text{melt-source}}$  for an input of  $V_{\text{melt}}^{5+} = [6]$ -fold coordination (left hand panels; these are the results used in the main chapter) with an input of  $V_{\text{melt}}^{5+} = [4]$ -fold coordination (right hand panels). There are two aqueous complexes with [4]-fold  $V^{5+}$  in Wu et al. (2015). Here I have chosen the  $\beta^V$  factors for the  $[V^{5+}O_2(OH)_2]^-$  (Table 4.11) complex since this complex has the greatest  $\ln \beta^V$  difference from the [6]-fold coordinated case, therefore covering the greatest range of input uncertainty.



**Figure 4.17:**  $\Delta^{51}V_{\text{melt-source}}$  compared for a model where  $V_{\text{melt}}^{5+} = [6]$  coordinated (left hand plots) and  $V_{\text{melt}}^{5+} = [4]$  coordinated (right hand plots) for KLB1.

The model discussed in the main text of this chapter is the result of using the upper limit of [6] coordinated  $V^{5+}$ : this value will provide the minimum melting fractionation, since a higher coordination number results in weaker V-O bonds, and less extreme isotopic fractionation. Using an

**Table 4.11: Alternative parameters for V isotope  $\beta^V$  factors from Wu et al. (2015), where  $V_{\text{melt}}^{5+} = [4]$  coordinated.**  $1000\ln\beta = a/T^6 + b/T^4 + c/T^2$ , where T = temperature (Kelvin).

| Mineral | Valence  | a                     | b                      | c                  |
|---------|----------|-----------------------|------------------------|--------------------|
| melt    | $V^{5+}$ | $7.00 \times 10^{14}$ | $-3.25 \times 10^{10}$ | $1.42 \times 10^6$ |

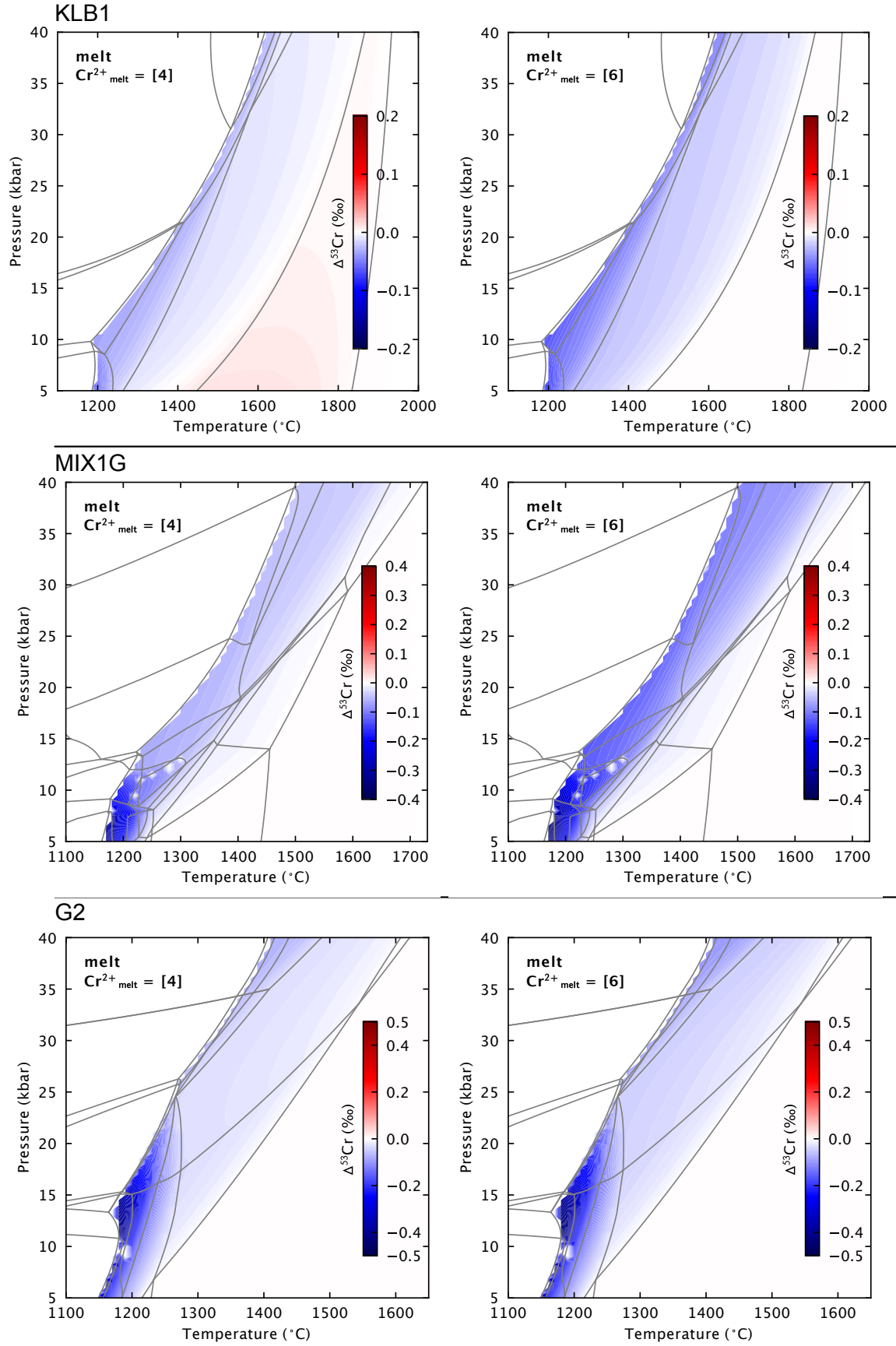
input of [4] coordinated  $V^{5+}$  results in isotopically heavier melts, with the maximum KLB1 melting stable isotope fractionation increasing from  $\approx 0.1$  ‰ in the [6] coordinated case to  $\approx 0.15$  ‰ close to the solidus around 10 kbar (Fig. 4.17 for full results) in the [4] coordinated case. However, the difference between the two models decreases at higher temperature, and for the temperature range of interest here (potential temperatures from 1300–1530 °C), at 5 kbar the difference in melt isotopic composition between the two models is  $\approx 0.01$  ‰, and therefore negligible. However, to improve understanding of high temperature V behaviour and link natural data to specific processes, experimental and/or theoretical work on equilibrium isotopic fractionation factors for silicate melt and minerals for different V species is needed.

#### 4.9.5 Cr: if $Cr_{\text{melt}}^{2+} = 6$ -fold coordinated

As chromium is a first-group transition element, the properties controlling isotopic fractionation behaviour (e.g., valence, ionic radius hence bonding environment) of  $Cr^{2+}$  and  $Cr^{3+}$  ions may be expected to be similar to  $Fe^{2+}$  and  $Fe^{3+}$  ions (Xia et al., 2017). The main Cr-bearing phases in the mantle are spinel, garnet and pyroxenes, although some Cr will partition into olivine (Mallmann and O'Neill, 2009), and as with V, partition coefficients depend on the valence state of Cr (Mallmann and O'Neill, 2009).

As a set of  $\beta^{Cr}$  factors for mantle minerals does not exist, my models of Cr stable isotope fractionation use force constants in each mineral calculated from an ionic bonding model (Shen et al., 2018), following the approach used for Fe isotopes. An ionic model has been shown to produce inter-mineral fractionation in agreement with the magnitude of isotope fractionation inferred from studies of lherzolite mineral pairs (Shen et al., 2018). As with V isotopes, the main uncertainty relating to species coordination is in liquid.  $Cr^{2+}$  in silicate melt is reported to be in [4] coordination (Miletich et al., 1999; O'Neill and Berry, 2006; Shen et al., 2020), but may also be in [6] coordination in a square planar arrangement (O'Neill and Berry, 2006). The isotope fractionation model presented here calculates force constants using effective anionic and cationic radii based on Shannon (1976), following the approach outlined in Shen et al. (2018), and these radii depend negatively on the coordination number chosen (Gibbs et al., 2014).

Fig. 4.18 compares the  $\Delta^{53}Cr_{\text{melt-source}}$  for an input of  $Cr_{\text{melt}}^{2+} = [4]$  coordinated (left hand panels; these are the results used in the main chapter text) with an input of  $Cr_{\text{melt}}^{2+} = [6]$  coordinated (right hand panels). The input parameters for the [6] coordinated case are in Table 4.12.



**Figure 4.18:**  $\Delta^{53}\text{Cr}_{\text{melt-source}}$  compared for a model where  $\text{Cr}^{2+}_{\text{melt}} = [4]$  coordinated (left hand plots) and  $\text{Cr}^{2+}_{\text{melt}} = [6]$  coordinated (right hand plots) for all three lithologies.

**Table 4.12: Alternative parameters for Cr isotopic fractionation model, where  $\text{Cr}_{\text{melt}}^{2+} = [6]$  coordinated.** Mineral site and bonding information is based on Shen et al. (2018).

| Mineral | Cr species | Site | Cr coordination | Bond length (Å) | O coordination |
|---------|------------|------|-----------------|-----------------|----------------|
| melt    | 2+         | n/a  | 6               | 2.18            | 4              |

The model presented in the main text of this chapter uses an input of  $\text{Cr}^{2+}$  in [4] coordination in the melt. Inputting [6] coordinated  $\text{Cr}^{2+}$  in the melt results in isotopically lighter peridotite melts across all of P-T space (Fig. 4.18) than the [4] coordinated case as a consequence of weaker Cr–O bonds in a [6] coordinated environment than [4] coordinated. A similar effect is seen in MIX1G and G2 melts. The melt-source isotopic fractionation is always negative, consistent with modelling by Shen et al. (2018), and melts get progressively isotopically heavier (towards 0‰ fractionation from the source) with increasing degree of melting, consistent with observations from OIB (Bonnand et al., 2020). The cationic radii are likely to be overestimates, as the radii for [6] coordinated Cr used in Shen et al. (2018) assume octahedral, not square planar, coordination. Square planar bonds would be expected to be longer than octahedral, and this would result in even isotopically lighter melts. Therefore, although the model uses the most appropriate available inputs for the more commonly quoted [4] coordination of  $\text{Cr}^{2+}$  in melts, our understanding of the behaviour of Cr isotopes in silicate melts would benefit from further work on the force constants of  $\text{Cr}^{2+}$  in glasses, or the inputs required to calculate these such as bonding environment or effective Cr–O bond lengths.

#### 4.9.6 Updates to THERMOCALC thermodynamic datasets

As mentioned in chapter 2, after the pseudosection calculations for this thesis were performed, an updated thermodynamic dataset for peridotite melting and phase relations, ds634, was published by Tomlinson and Holland (2021). Although a different peridotite composition was studied than the KLB-1 used in this thesis, some key changes produced using the updated dataset compared to ds633 used here are changes in the pressure of the garnet-spinel transition, an widened spinel stability field above the solidus, and changes to phase chemistry, particularly with respect to Cr (Tomlinson and Holland, 2021). A widened spinel stability field would most affect the results for isotope systems where spinel has a significant mineral-melt fractionation, such as Mg (Fig. 4.3) or contains a lot of the element budget, such as Cr. Although Cr contents of phases are also changed using the new dataset, I note that my model partitions Cr outside of THERMOCALC, because of the need to include both  $\text{Cr}^{2+}$  and  $\text{Cr}^{3+}$  in my isotope fractionation model, and therefore there would be minimal change in the budgeting of Cr between the phases from the new dataset. From Fig. 4.6, spinel does not have an extreme isotope composition relative to other mantle minerals in my Cr isotope fractionation model, but the high partition coefficient for Cr in spinel (Table 4.6) means that spinel stability will be important to the final melt fractionation. I also note that

my partitioning and isotope calculations for Cr do not account for changes in spinel or garnet composition across P-T space (bond lengths and partition coefficients for the Cr<sup>3+</sup>-bearing site in both minerals are taken as fixed; Table 4.6). We would expect changes in composition of phases across P-T space, including in Cr content as demonstrated by Tomlinson and Holland (2021), and therefore an improved version of this modelling, particularly for Cr, should combine the new ds634 dataset with a consideration of composition-dependent Cr partitioning.

## 4.10 Supplement: Calculating average pressure of melting

The mean melt pressure,  $\bar{P}$ , for isentropic melting at any  $T_p$  is calculated by the following integral, based on Asimow et al. (2001) with an additional geometric weighting factor to account for the triangular shape of the melting region

$$\bar{P} = \frac{\int_{P_0}^{P_f} P \Delta F g dP}{\int_{P_0}^{P_f} \Delta F g dP} \quad (4.12)$$

where  $P_0$  and  $P_f$  are the initial and final pressures of melting respectively,  $\Delta F$  is the amount of melt produced at each pressure step ( $dP$ ) along the isentropic melting path, and  $g$  is the geometric weighting factor.  $P_0$  is taken as the intersection of the isentrope with the solidus,  $P_f$  is used as 5 kbar in this model as melt compositions have not been calculated for shallower pressures – this is an overestimate (i.e., final melting will be shallower) for  $T_p = 1300^\circ\text{C}$  and an underestimate for  $T_p = 1530^\circ\text{C}$  (Asimow et al., 2001), but will provide the correct behaviour. Pressure steps used are the 0.5 kbar intervals used in the P-T grid.  $\Delta F$  is calculated for each step from the difference in melt fractions calculated by THERMOCALC for consecutive  $dP$  steps. The geometric weighting factor is a linear scaling running from 1 at the base of the melting region to 0 at the top, to account for the wider base of the triangular melting region beneath ridges. I calculate the average melting pressure for the three  $T_p$ s for which I have calculated isentropes in KLB1, and linearly interpolate between them (this will not be a linear relationship in reality, e.g., Asimow et al., 2001, but the approach will provide a good approximation) to get average melt pressures for temperatures between  $T_p = 1300^\circ\text{C}$  and  $1530^\circ\text{C}$ . For KLB1, I calculate an average melting pressure of approximately 12 kbar at  $T_p = 1300^\circ\text{C}$ , and 28 kbar at  $T_p = 1530^\circ\text{C}$ . The average  $\Delta_{\text{melt-source}}$  for each  $T_p$  is then taken as the  $\Delta_{\text{melt-source}}$  at the calculated average melting pressure.

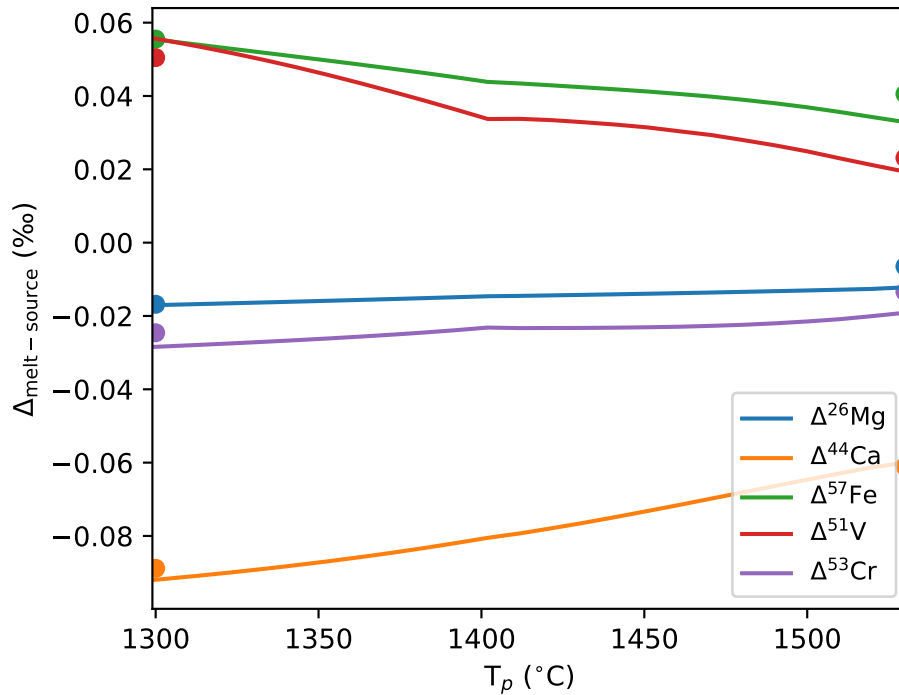
The approach above, however, uses an equilibrium melt isotope composition at a single pressure to approximate the fractional, multibaric melting thought to occur in the mantle (McKenzie, 1984; von Bagen and Waff, 1986; Langmuir et al., 1992; Asimow et al., 2001). To assess the suitability of the equilibrium melting at single pressure approach, I have also calculated the average melt isotopic composition by considering the stable isotope composition and elemental concentration for each new step of melt generated during isentropic decompression at  $T_p = 1300^\circ\text{C}$  and  $1530^\circ\text{C}$

by

$$\bar{\Delta}_{\text{melt-source}} = \frac{\int_{P_0}^{P_f} \Delta_x c \Delta F_g dP}{\int_{P_0}^{P_f} c \Delta F_g dP} \quad (4.13)$$

where  $\Delta_x$  is the  $\Delta_{\text{melt-source}}$  of the melt produced in the pressure step, and  $c$  is the wt % of the element being considered in the melt, and other terms as above. The approach of equation 4.13, while considering polybaric melting, is still not a fractional melting model, but fractional melting is beyond the scope of this work. Nonetheless, the chemical composition of pooled fractional melts from a ridge melting regime has been shown to closely resemble that of a simple equilibrium batch melt (Langmuir et al., 1992). Equation 4.13 therefore allows me to broadly assess whether the approach taken in equation 4.12 produces estimates of mean melt isotope ratios very different from a more realistic polybaric approach, although it should be noted that the polybaric method of equation 4.13 only allows me to calculate the average melt isotopic composition for the  $T_p$ s for which I have calculated isentropes.

Fig. 4.19 shows the comparison of the two calculations of average  $\Delta_{\text{melt-source}}$ . The dots show the average melt isotope composition when calculated as a sum along the isentrope; the solid lines show the approximation using the melt composition at the average pressure of melting.



**Figure 4.19: Comparison of estimates of average melt isotope composition along a decompression path.**  $\Delta_{\text{melt-source}}$  for KLB1 calculated by taking the isotopic fractionation at the average melt pressure (solid lines) is compared to a calculation of the average melt composition by considering polybaric melts (equation 4.13), shown as coloured dots.

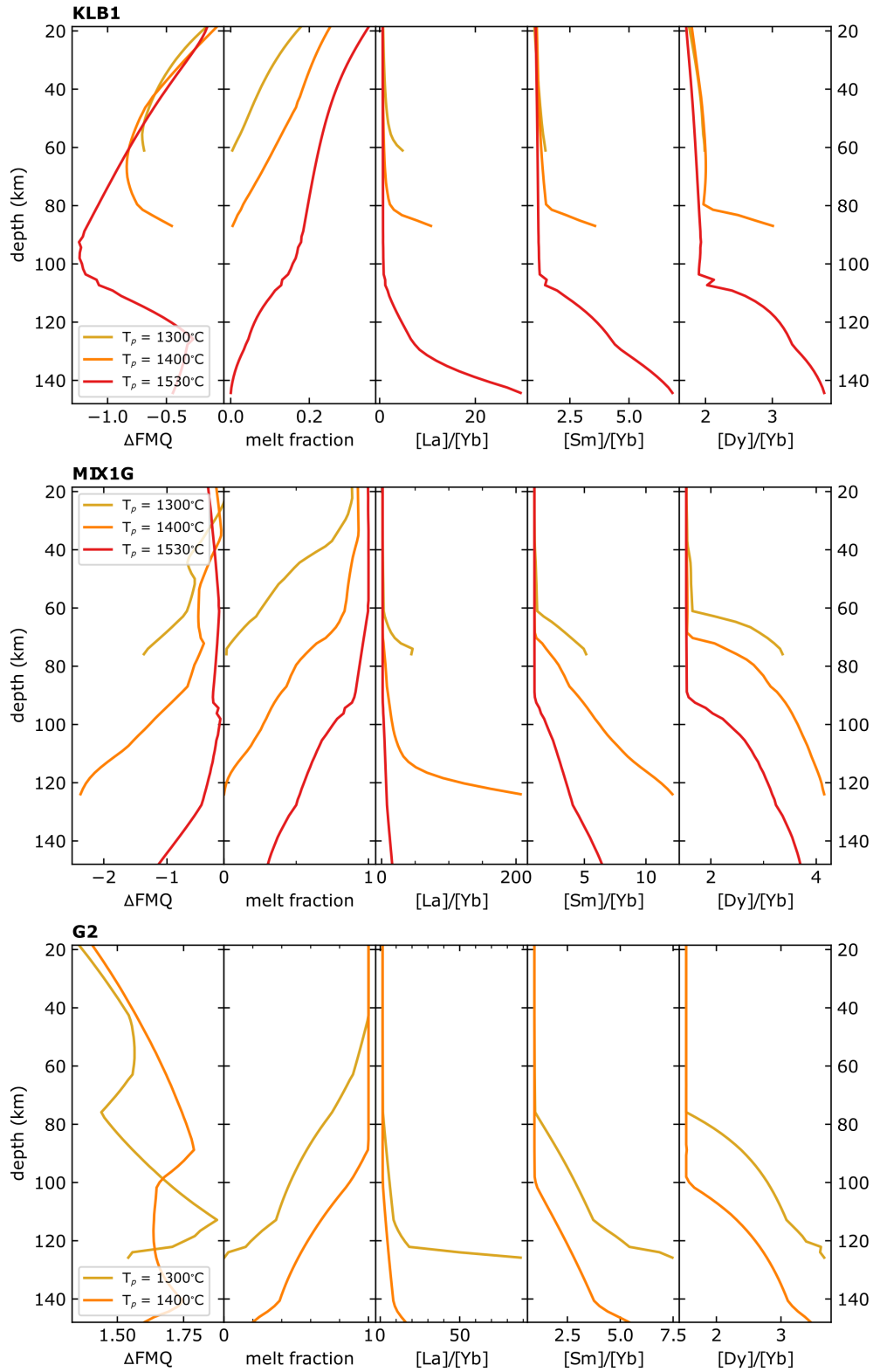
The calculation using the average melt pressure is a good approximation of the calculated average melt isotope compositions. Therefore I use this pressure approach in this chapter: the limitation of the calculated average melt isotope composition is that I only have information for the

$T_p$ s for which I have calculated isentropes, hence use a linear interpolation between them, whereas the average pressure approach allows me to use more information from the calculated P-T map of melt compositions, reflecting the changing of stable mineral assemblage, for example.

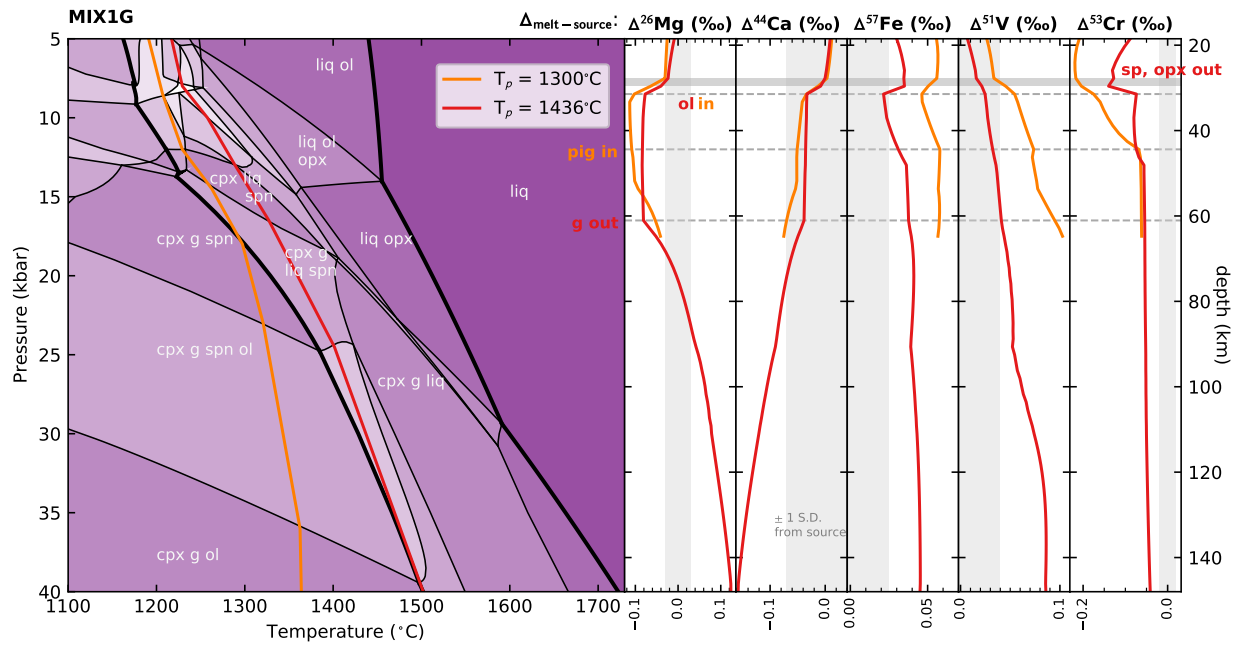
## **4.11 Supplement: Additional reference figures**

Fig. 4.20 provides a reference for how oxygen fugacity, melt fraction, and selected trace element ratios vary along the isentropes shown in Figs. 4.2 and 4.9. The trace element concentrations are calculated using depleted mantle (DM) inputs for KLB1, and plume inputs for the enriched MIX1G and G2 lithologies (see Table 4.8).

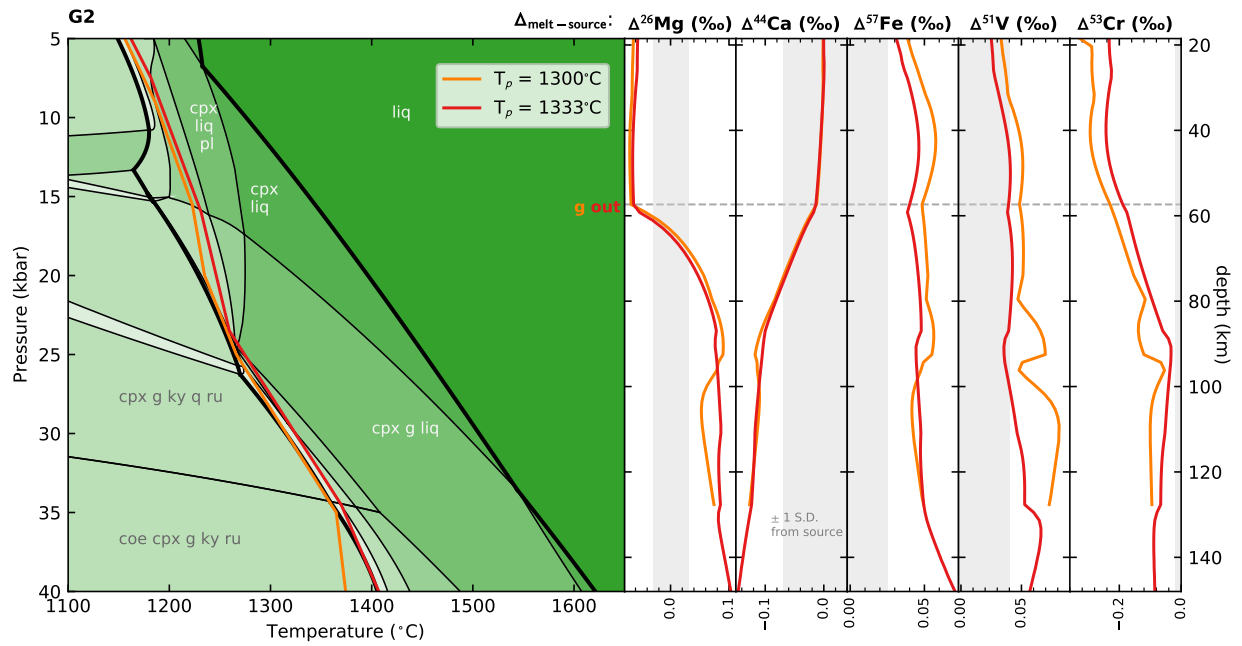
I choose to use peridotite isentropic decompression paths for the two pyroxenite lithologies, as discussed in the main text of the chapter. Figs. 4.21, 4.22 show results for the other endmember case for the two pyroxenite lithologies, i.e., where the lithologies decompress along isentropic paths calculated for each pure pyroxenite lithology.



**Figure 4.20: Reference parameters along the peridotite isentropic decompression paths for all three lithologies:** oxygen fugacity (from the  $f\text{O}_2\text{melt}$  software; Holland et al., 2018), melt fraction (from THERMOCALC output), and selected trace element ratios in the melts (calculated using the model described in section 4.5.1.1). The isentropes match those in Figs. 4.2 and 4.9.



**Figure 4.21:** Isentropic melting paths for pure MIX1G, and  $\Delta_{\text{melt-source}}$  along these isentropes. Errors are shown as 1 S.D. long-term uncertainty.



**Figure 4.22:** Isentropic melting paths for pure G2, and  $\Delta_{\text{melt-source}}$  along these isentropes. Errors are shown as 1 S.D. long-term uncertainty.

# **5 The evolution of lithology in the Galápagos mantle plume: an Fe isotope perspective**

## **5.1 Introduction**

The identity of the large low shear velocity provinces (LLSVPs) present at the core-mantle boundary is enigmatic. One interpretation is that they represent the remains of dense subducted oceanic crust recycled back into the mantle by tectonic processes (Christensen and Hofmann, 1994; Nakagawa and Tackley, 2004; Hirose et al., 2005; Ohta et al., 2008; Tackley, 2012; Mulyukova et al., 2015; Niu, 2018; Thomson et al., 2019; Huang et al., 2020b; Jones et al., 2020). Such recycled material is widely considered to form eclogite and pyroxenite lithologies, sampled in the upper mantle source regions of some OIB erupted from mantle plumes – pure pyroxenite melt has been proposed for the Hawaiian plume using trace elements in olivine (Herzberg, 2006, 2011), with other global estimates of up to 10 % pyroxenite in the Iceland plume (Sobolev et al., 2007; Shorttle and MacLennan, 2011; Shorttle et al., 2014) and up to 20 % in parts of the modern Galápagos plume (Vidito et al., 2013; Gleeson et al., 2020). These mantle plumes, which appear to originate from regions of the mantle associated with LLSVPs (Castillo, 1988; Ritsema et al., 1998; Dziewonski et al., 2010; Cottaar and Lekic, 2016; Garnero et al., 2016), may therefore be carrying LLSVP material and so provide a window into Earth's lower mantle (Weis et al., 2011; Hoernle et al., 2015; Jackson et al., 2018; Harpp and Weis, 2020).

However, the interpretation of plume pyroxenite components and their potential link to LLSVPs is not straightforward. Most geodynamic models do not support large fractions of pyroxenite being entrained from LLSVPs into the upper mantle, either because 1) the LLSVPs are not mostly made of recycled crust, instead formed of iron-rich primordial mantle (Kellogg et al., 1999; Wen et al., 2001; Wen, 2001; Deschamps et al., 2011; Li and McNamara, 2013; Williams et al., 2019), and/or 2) recycled crust is dense, thus it should only constitute < 10 % of buoyant plumes, irrespective of whether it is stored within an LLSVP or at its boundary (Lin and van Keken, 2006; Deschamps et al., 2011; Li et al., 2014; Deschamps et al., 2015).

A further complication is that most geochemical studies of plume lithology take snapshots in time (usually, the modern day expression of a plume), missing the geodynamically critical information on how plume lithology, and therefore buoyancy, evolves. Plumes progress from a hot plume head stage to a subsequent narrower, cooler, conduit ('tail'), which produces steady-state

OIB volcanism (Farnetani and Richards, 1994; Campbell, 2005). This well-documented plume cooling (Thompson and Gibson, 2000; Herzberg and Gazel, 2009; Spice et al., 2016; Trela et al., 2017) should result in a decrease in a plume's ability to carry dense material, such as recycled crust (Jones et al., 2019), but this evolution of plume lithology is rarely documented (Trela et al., 2015; Gazel et al., 2018).

Stable Fe isotopes in basalts trace mineralogical heterogeneity in their mantle source through their sensitivity to recycled crust (Schauble, 2004; Young et al., 2015; Soderman et al., 2021, 2022 [chapters 3 and 4]). Modelling and studies of natural samples have shown that both mantle temperature and lithological heterogeneity in a melt's source could be reflected in the Fe isotope composition of the erupted basalt (Nebel et al., 2019; Gleeson et al., 2020; Soderman et al., 2021; Williams et al., 2021; Soderman et al., 2022 [chapters 3 and 4]). Because the Fe abundances of melts derived from pyroxenite and peridotite are similar, the  $\delta^{57}\text{Fe}$  of mantle-derived melt reflects the relative contributions of the pyroxenite and peridotite to the bulk melt (Williams and Bizimis, 2014). Mantle pyroxenites are proposed to have a heavier Fe isotope composition (higher  $\delta^{57}\text{Fe}$ ) than mantle peridotite, either due to heavier (MORB-like) bulk Fe isotope composition than peridotite (Soderman et al., 2021 [chapter 3]), or from the role of residual garnet during pyroxenite melting (Nebel et al., 2019; Ruttor et al., 2021) and increased isotopically heavy pyroxene in the source compared to peridotite (Williams and Bizimis, 2014). Therefore, high  $\delta^{57}\text{Fe}$  has been used as an indication of mantle pyroxenite in several OIBs (Konter et al., 2016; Nebel et al., 2019; Shi et al., 2022), including for the plume-influenced Galápagos Spreading Centre (Gleeson et al., 2020).

Here, I use the stable Fe isotope composition of basalts erupted throughout the 90 million year (Myr) evolution of the Galápagos mantle plume, which overlies the eastern margin of the Pacific LLSVP (Jackson et al., 2018; Harpp and Weis, 2020), to show that the Galápagos mantle plume has contained < 10 % pyroxenite throughout its lifetime, in contrast to larger and geodynamically implausible pyroxenite fractions proposed for some plumes (Herzberg, 2011).

## 5.2 Samples

The Galápagos mantle plume presents an outstanding opportunity to study lower mantle composition and plume evolution because all stages of its 90 Myr history are recorded in erupted basalts either in the Pacific, in terranes accreted onto Central America (Alvarado et al., 1997; Hoernle et al., 2002; Denyer and Gazel, 2009; Gazel et al., 2018), or in the modern Galápagos (the present-day products of the plume tail). The Galápagos plume is thought to have cooled by over 300 °C since the plume-head stage, with a maximum mantle potential temperature ( $T_p$ ) of 1700–1800 °C proposed in the Tortugal suite (Costa Rica), and present-day plume-tail estimates of  $T_p = 1360\text{--}1490$  °C (Alvarado et al., 1997; Herzberg and Gazel, 2009; Trela et al., 2015, 2017; Matthews

**Table 5.1: Range of mantle potential temperature estimates for Galápagos plume-related localities used in this study.** Where possible, I have used average estimates for the whole locality from each source rather than taking the maximum and minimum on a sample by sample basis.

| Locality  | $T_p$ max., °C ( <i>source</i> ) | $T_p$ min., °C ( <i>source</i> ) |
|-----------|----------------------------------|----------------------------------|
| Tortugal  | 1800 (Trela et al., 2017)        | 1750 (Trela et al., 2017)        |
| Gorgona   | 1660 (Trela et al., 2017)        | 1620 (Herzberg and Gazel, 2009)  |
| Curaçao   | 1615 (Hastie and Kerr, 2010)     | 1540 (Herzberg and Gazel, 2009)  |
| Quepos    | 1530 (Herzberg and Gazel, 2009)  | 1490 (Trela et al., 2015)        |
| Azuero    | 1530 (Trela et al., 2015)        | 1450 (Trela et al., 2015)        |
| Galápagos | 1490 (Herzberg and Gazel, 2009)  | 1360 (Gazel et al., 2019)        |

et al., 2021); Table 5.1. Geochemically distinct mantle components similar to those measured in the modern Galápagos have been identified in the plume-head stage using radiogenic isotopes (Hoernle et al., 2000; Geldmacher et al., 2003; Gazel et al., 2018), although trace elements in olivine only show a crustal component after the plume-head (Trela et al., 2017; Gazel et al., 2018), and multiple studies suggest pyroxenite is present in the modern plume (Hoernle et al., 2000; Harpp and White, 2001; Vidito et al., 2013; Harpp et al., 2014a; Gleeson et al., 2020, 2021). The geochemical and lithological heterogeneity in the modern Galápagos has been linked to recycled crust stored within or near the Pacific LLSVP (Harpp et al., 2014b; Harpp and Weis, 2020; Gleeson et al., 2021). Additionally, a compositionally distinct ultra-low velocity zone (ULVZ) on the LLSVP margin has been associated with the plume and may also contain recycled crust (Ma et al., 2019). A primordial mantle component – recorded by high  $^3\text{He}/^4\text{He}$  and near-solar Ne isotopic compositions in basalts erupted in Fernandina (Kurz et al., 2009, 2014) – is also proposed to be present in the LLSVP (Harpp and Weis, 2020). However, because pyroxenite is enriched in most geochemical tracers relative to peridotite, and pyroxenite preferentially melts as a mixed-lithology melts, most traditional geochemical tracers are dominated by contributions from pyroxenite melts, which makes calculating the proportion of pyroxenite in the mantle source difficult. Therefore, it is unclear whether pyroxenite has been present throughout the Galápagos plume’s history, having been diluted by higher degrees of melting in the plume-head stage, or only appeared after 20 Myr of plume cooling (Gazel et al., 2018).

To address this question I measured  $\delta^{57}\text{Fe}$  of a suite of well-characterised basalts and picrites covering the whole age range of the Galápagos plume from the plume head (Tortugal, Curaçao [Lesser Antilles], Gorgona Island [Colombia]), head-tail transitional accreted terranes (Quepos [Costa Rica], Azuero peninsula [Panama]) and modern steady-state plume (Galápagos; Fig. 5.1). I analyzed samples from five Galápagos volcanoes, which span multiple isotopic domains of the recent archipelago (Harpp and White, 2001). Samples from Fernandina volcano are proposed to overlie the current plume location, and are where the most significant signatures of primordial mantle (the highest  $^3\text{He}/^4\text{He}$ , near-solar  $^{20}\text{Ne}/^{22}\text{Ne}$  and most negative  $\mu^{182}\text{W}$ ) have been recorded in the plume’s history (Kurz et al., 2009, 2014; Mundl-Petermeier et al., 2020). Radiogenic isotope

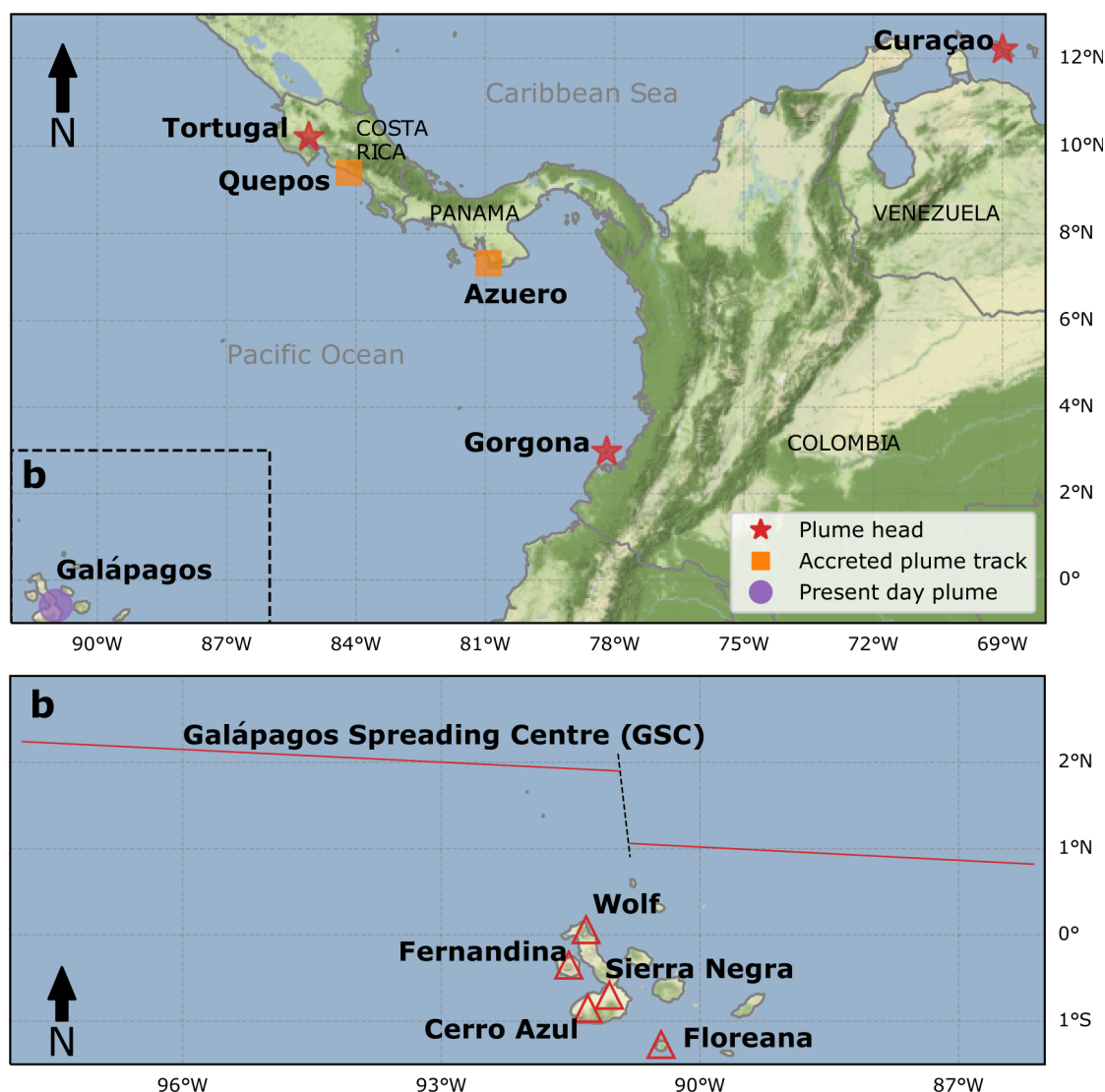


Figure 5.1: Map of Galápagos plume-related localities used in this study.

and olivine trace element data exists for some of the samples. Iron separation and isotope measurements were performed at the Department of Earth Sciences, University of Cambridge following established procedures [chapter 2]. Measurements were made on a NeptunePlus MC-ICP-MS in wet plasma, with typical 2 S.E. on multiple  $\delta^{57/54}\text{Fe}$  measurements of the same sample better than 0.02 ‰, and measurements of in-house standards and international reference materials ( $\text{FeCl}_3$ , BHVO-2, BCR-2, BIR-1) in agreement with accepted values (Table 6.1).

### 5.2.1 Petrography

Samples from Tortugal, Curaçao, Azuero and Quepos were provided by Esteban Gazel as rock powders. Prior to powdering, the samples had been classified by lithology, with most being basalts (lower MgO samples) or picrites (higher MgO samples, which have accumulated olivine). The lithological identification is given in Table 6.3. Unpublished thin section images of a subset of the

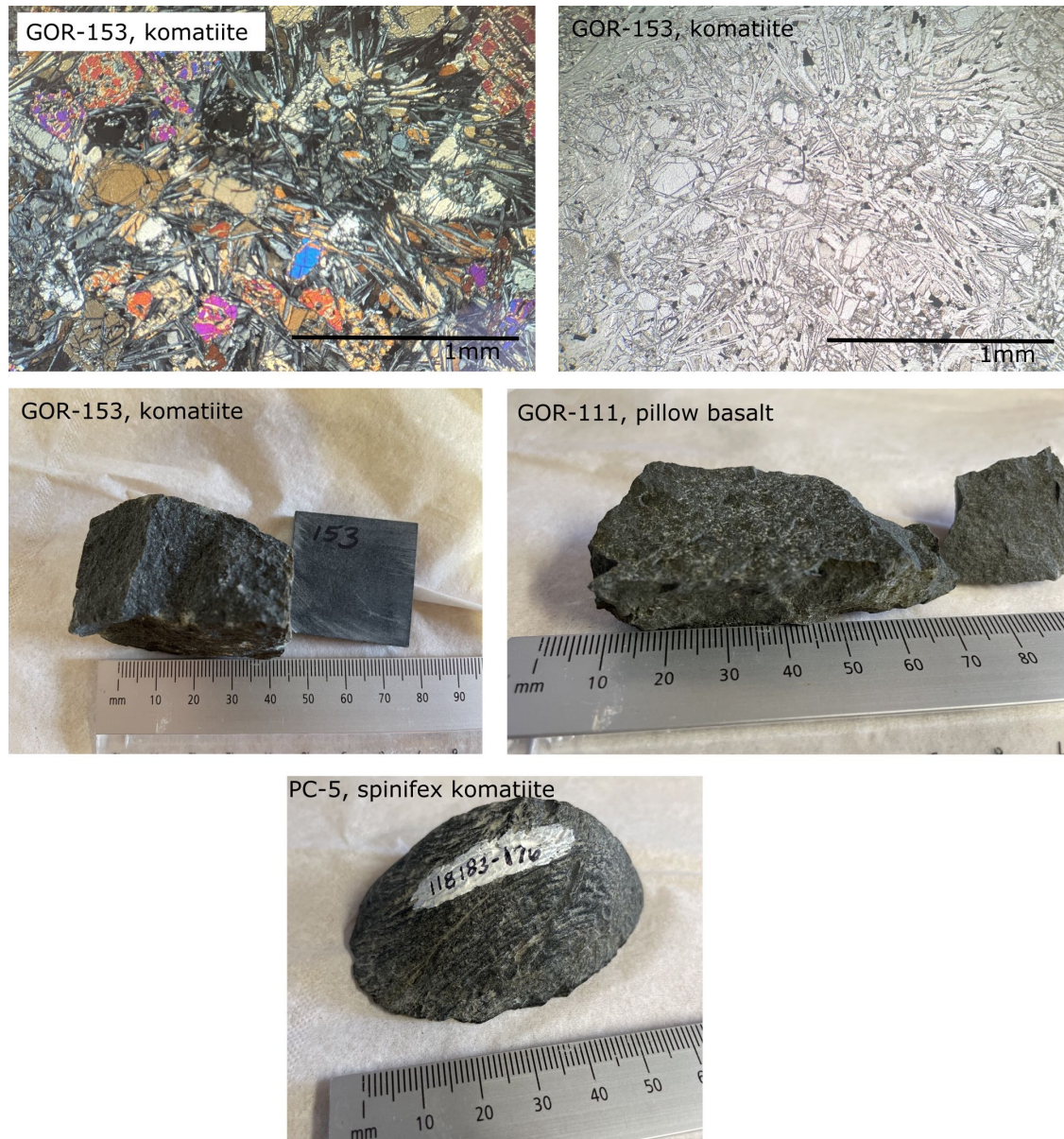
samples were also provided by Esteban Gazel. The samples classified as picrites contain large (0.5–2.5 mm) rounded olivine crystals and glomerocrysts in a finer-grained groundmass (most glassy in CUR-02 and CUR-13, whereas QP-121211-7 and QP-121211-10 contain identifiable groundmass feldspar  $\pm$  pyroxene), with varying levels of visible alteration (e.g., To-010513-7 showing most serpentinisation of olivine). The basaltic sample QP121211-8 shows a fine-grained groundmass, with small ( $< 1$  mm, and most  $< 0.5$  mm) olivine crystals. One sample, QP121311-11, is classified as a medium-grained diabase – although this sample has relatively high MgO (10.22 wt%), it is clearly not representative of a primary liquid, having crystallised pyroxene.

Gorgona samples were provided as powders by the Department of Mineral Sciences, Smithsonian Institution, from the collection of Lina Echeverría. Lithological classification of samples, as referenced in the museum's catalogue, is given in Table 6.3. Of the samples classified as komatiites, two are identified as having spinifex texture (PC-5, GOR-2P), and of the basalts, samples GOR-111, GOR-38 and GOR-6A are additionally classified as pillow basalts. Thin sections and hand specimens of some of these samples were also provided (Fig. 5.2). In thin section, GOR-153 is a fine-grained komatiite, with abundant fresh olivine (euhedral, typically  $< 0.5$  mm) and acicular feldspar. In hand specimen, sample PC-5 clearly shows its spinifex texture.

Modern Galápagos samples were provided as whole rocks by Dennis Geist, and were powdered by hand in an agate pestle and mortar. In hand specimen, most samples are variably vesicular basalts, but three are highly vesicular, largely glassy samples that contain occasional  $> 1$  mm olivine phenocrysts (W95-3, Fe-06-02, FLO3-128). Two samples have thin sections: SN91-31 (basalt from Sierra Negra) has  $\sim 5\%$  plagioclase and pyroxene phenocrysts, set in a fine-grained groundmass of olivine, pyroxene and feldspar; Fe-06-02 (vesicular glass from Fernandina) has a glassy groundmass, with occasional small olivine and feldspar phenocrysts.

## 5.3 Results

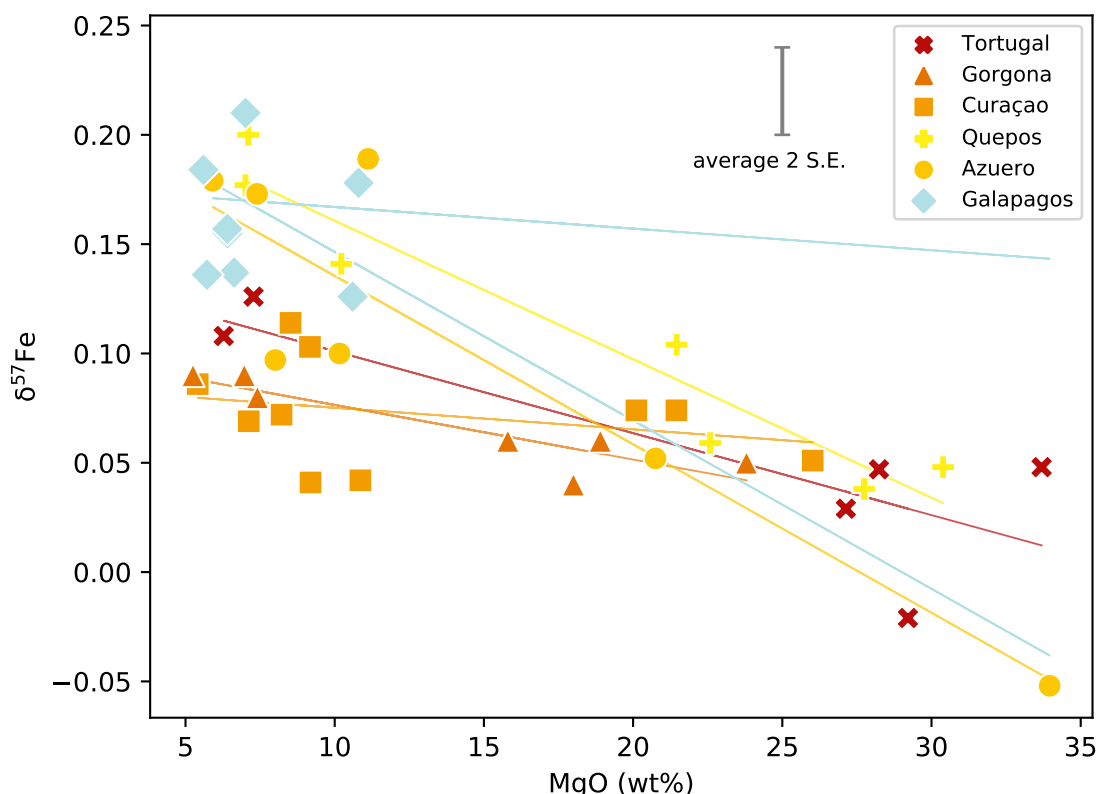
In the samples studied here,  $\delta^{57}\text{Fe}$  correlates with whole-rock MgO, as expected for fractional crystallisation and olivine accumulation trends (Teng et al., 2008; McCoy-West et al., 2018); Fig. 5.4. Low MgO samples from modern Galápagos, Azuero and Quepos show the highest  $\delta^{57}\text{Fe}$  (0.16–0.21 ‰; MgO 5.6–11.1 wt%), and high MgO samples from Tortugal and Azuero show the lowest  $\delta^{57}\text{Fe}$  (−0.05–0.03 ‰; MgO 27.1–34.0 wt%). Because fractional crystallisation/olivine accumulation produces  $\delta^{57}\text{Fe}_{\text{measured}}$  that is different from  $\delta^{57}\text{Fe}_{\text{primary}}$  (the  $\delta^{57}\text{Fe}$  of the melt prior to crystallisation), the data was first corrected back to an estimated primary liquid composition.



**Figure 5.2: Thin section and hand specimen images of a sub-section of Gorgona samples.** Samples provided by Smithsonian Institute. In the top panels, GOR-153 is shown in crossed polarised and plane polarised light.



**Figure 5.3: Thin section and hand specimen images of modern Galápagos samples.** Samples and thin sections provided by Dennis Geist.

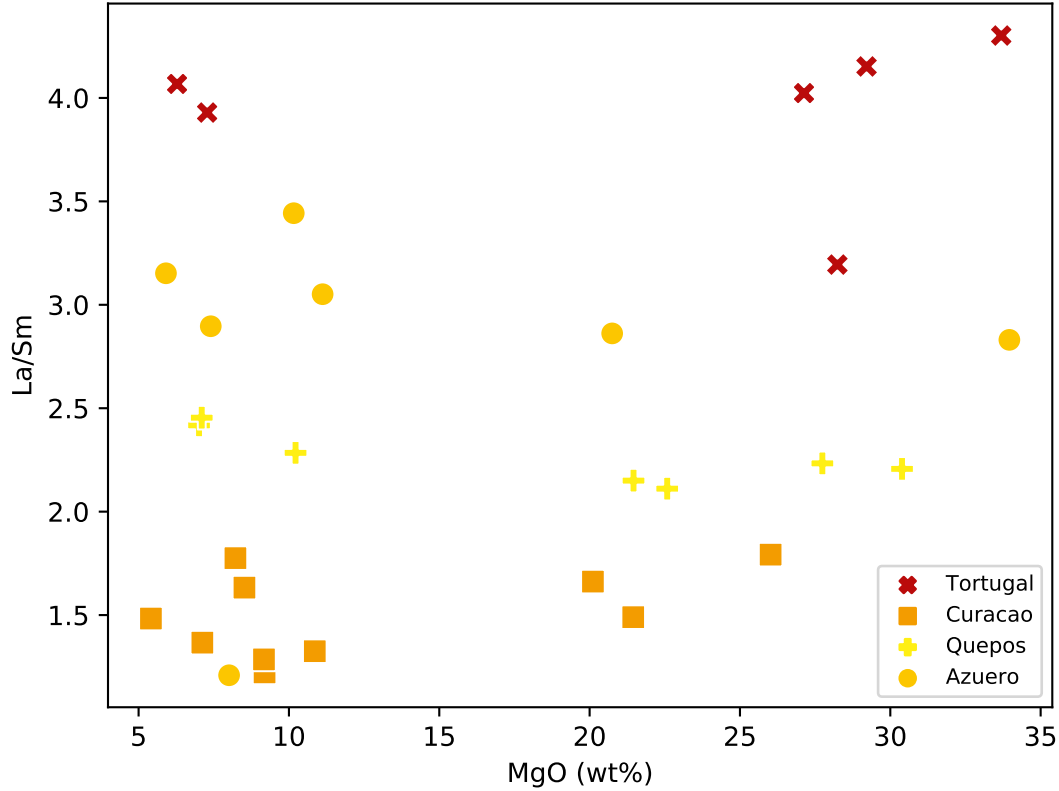


**Figure 5.4:**  $\delta^{57}\text{Fe}_{\text{measured}}$  vs MgO for Galápagos samples. Empirical  $\delta^{57}\text{Fe}_{\text{measured}}$ -MgO fits calculated for each locality using the numpy *polyfit* function are shown. For the Galápagos data, where there is insufficient MgO range to calculate an empirical fit, I have taken a mean Galápagos value of 6.94 wt% MgO,  $\delta^{57}\text{Fe} = 0.17$  ‰, and used two limits of  $\delta^{57}\text{Fe}$ -MgO behaviour from the dataset (steepest  $\delta^{57}\text{Fe}$ -MgO fit from Azuero, shallowest  $\delta^{57}\text{Fe}$ -MgO fit from Curaçao.)

### 5.3.1 Correction to primary $\delta^{57}\text{Fe}$

The correction for fractional crystallisation (or olivine accumulation) requires an estimate of primary liquid MgO, as well as an estimate of  $\Delta^{57}\text{Fe}_{\text{crystal-melt}}$ . While the latter can be theoretically calculated and estimated from natural samples, it is not generally well-constrained, with variable estimates that can have a large influence on the resulting primary  $\delta^{57}\text{Fe}$  (Sossi et al., 2016; Nebel et al., 2019; Soderman et al., 2021 [chapter 3]). Therefore, given the wide MgO range of my samples for most localities and approximately linear  $\delta^{57}\text{Fe}$ -MgO relationships, an empirical fit in MgO- $\delta^{57}\text{Fe}$  space was constructed for each locality (Fig. 5.4), and the primary  $\delta^{57}\text{Fe}$  taken along that line depending on the proposed primary MgO. These fits span low MgO samples, which have crystallised olivine  $\pm$  pyroxene (and plagioclase, but feldspar should contain very little of the Fe budget of a rock), and high MgO samples, which have accumulated olivine (e.g., Figs. 5.2, 5.3). For Galápagos, where I do not have a wide MgO range of samples (but samples have still clearly crystallised olivine  $\pm$  pyroxene, feldspar, even for samples with a glassy groundmass; Fig. 5.3), the maximum and minimum slopes from the other localities were used. The range of these slopes, at typical magmatic temperatures, approximates a  $\Delta^{57}\text{Fe}_{\text{crystal-melt}}$  between  $-0.4$  and  $-0.1 \times 10^6/T^2$ , consistent with literature estimates (Nebel et al., 2019; Soderman et al., 2021 [chapter 3]).

The approach used for Tortugal, Gorgona, Curaçao, Quepos and Azuero assumes the samples at each locality represent a single liquid line of descent, which I consider to be a suitable approximation given the constant La/Sm ratio (where the data exists) for each locality (Fig. 5.5). Removing the one Azuero and one Tortugal sample which fall off the La/Sm trend for each locality from the  $\delta^{57}\text{Fe}$ –MgO fitting results in no significant difference in the calculated primary  $\delta^{57}\text{Fe}$ .



**Figure 5.5: Published La/Sm ratios for the localities where an empirical  $\delta^{57}\text{Fe}$ –MgO fit has been used to correct to  $\delta^{57}\text{Fe}_{\text{primary}}$ , to assess the assumption of samples being related by fractional crystallisation/olivine accumulation. No data could be found for the Gorgona samples. Trace element data and sources in Table 5.6.**

For the primary MgO, values from a variety of methods were used (Table 5.2) to highlight the importance of primary MgO on the resulting primary  $\delta^{57}\text{Fe}$ . For methods involving calculation of primary MgO, compiled published whole rock data for samples from each locality were used. For calculation in equilibrium with olivine of a given forsterite content, olivine was added incrementally, calculating equilibrium liquid and olivine MgO at each step, until the desired forsterite content was reached. A  $K_{\text{d,Fe–Mg}}$  of 0.32 (Putirka, 2016) and a  $\text{Fe}^{3+}/\text{Fe}_{\text{T}}$  of 0.156 (maximum for Galápagos of 0.175 from Fisher et al., 2013; Cottrell and Kelley, 2014, corrected by a factor of 1.125 following Zhang et al., 2018a) were used, with only samples with  $\text{MgO} > 10 \text{ wt}\%$  used to avoid samples that may have crystallised pyroxene. For Tortugal, this filter was lowered to 8.5 % as no samples with higher MgO would solve for equilibrium melt compositions. The results of the primary  $\delta^{57}\text{Fe}$  calculations are in Table 5.3, and are shown in Fig. 5.6.

The range of primary  $\delta^{57}\text{Fe}$  shown in Fig. 5.6 and Table 5.3 for each approach to primary MgO calculation depends on both the range of primary MgO estimates, and the slope of the  $\delta^{57}\text{Fe}$ –MgO

**Table 5.2: Data sources for the major element chemistry required for a calculation of a primary liquid, or estimates of the primary liquid composition.** Literature estimates are given next to their reference, all other sources are compiled for the  $\text{Fo}_X$  calculations.

| Locality  | Literature data sources                                                                                                                           | Literature                     | MgO wt % range |           |          |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------|----------------|-----------|----------|
|           |                                                                                                                                                   |                                | eq. Fo91       | eq. Fo88  | eq. Fo93 |
| Tortugal  | Hauff et al. (2000b)<br>Trela et al. (2017)                                                                                                       | 23.7–27.5                      | 16.5           |           | 21.3     |
| Gorgona   | Dupré and Echeverria (1984); Walker et al. (1991)<br>Kerr et al. (1996a)<br>Herzberg and Gazel (2009)<br>Trela et al. (2017)                      | 18.0<br>19.2–22.4<br>10.1–24.5 | 11.3–19.0      |           |          |
| Curaçao   | Kerr et al. (1996b); Hauff et al. (2000a)<br>Trela et al. (2017)                                                                                  | 14.6–21.0                      | 14.2–15.2      | 10.8      |          |
| Azuero    | Hoernle et al. (2002); Wegner et al. (2011),<br>Gazel et al. (2018)                                                                               |                                | 16.1–16.5      | 11.5–11.6 |          |
| Quepos    | Frisch et al. (1992); Hauff et al. (2000b)<br>Trela et al. (2015)                                                                                 | 15.0                           | 16.0–18.6      | 11.3      |          |
| Galápagos | Naumann et al. (2002)<br>Herzberg and Gazel (2009); Geist et al. (2005),<br>Handley et al. (2011); Harpp et al. (2014b),<br>Harpp and Weis (2020) | 13.2–16.1                      | 16.4–19.7      | 11.9–14.6 |          |

fit in Fig. 5.4.

**Table 5.3:  $\delta^{57}\text{Fe}_{\text{primary}}$  for each Galápagos plume-related locality.** Values are calculated using the fits shown in Fig. 5.4 and the primary MgO ranges from Table 5.2.

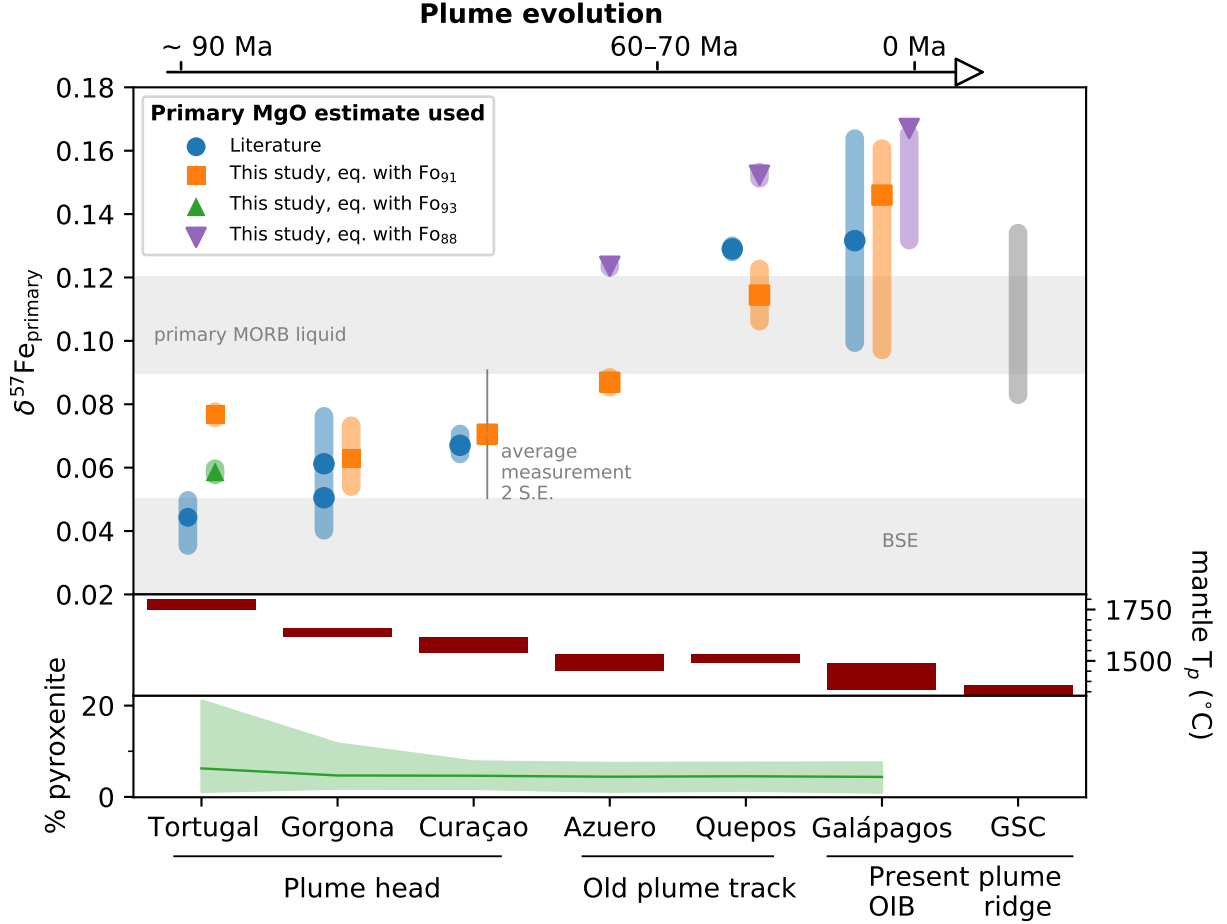
| Locality  | $\delta^{57}\text{Fe}_{\text{primary}}$ for primary MgO estimate by: |             |          |             |
|-----------|----------------------------------------------------------------------|-------------|----------|-------------|
|           | eq. Fo88                                                             | eq. Fo91    | eq. Fo93 | Literature  |
| Tortugal  |                                                                      | 0.077       | 0.059    | 0.035–0.050 |
| Gorgona   |                                                                      | 0.070–0.071 |          | 0.064–0.071 |
| Curaçao   |                                                                      | 0.053–0.073 |          | 0.040–0.076 |
| Azuero    | 0.123–0.124                                                          | 0.085–0.088 |          |             |
| Quepos    | 0.152                                                                | 0.106–0.123 |          | 0.129       |
| Galápagos | 0.132–0.165                                                          | 0.097–0.161 |          | 0.099–0.164 |

### 5.3.2 Evolution of Fe isotopic composition through plume history

As the plume ages and cools,  $\delta^{57}\text{Fe}_{\text{primary}}$  is observed to increase from plume head to tail (Fig. 5.6). Figure 5.6 also shows published Galápagos Spreading Centre samples for comparison (Gleeson et al., 2020), pooled to represent an average melt sampled at the ridge as outlined below.

#### 5.3.2.1 Calculation of pooled Galápagos Spreading Centre melts

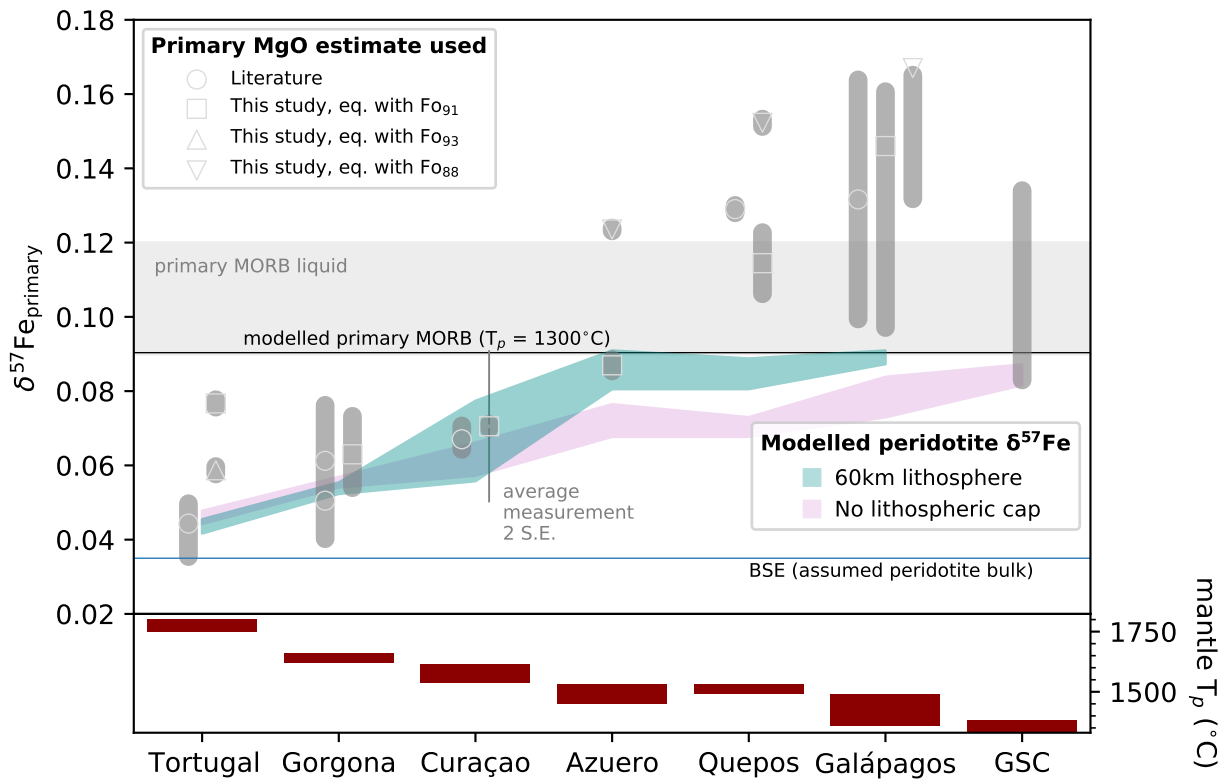
Iron isotope compositions for the Galápagos Spreading Centre (GSC) have been published by Gleeson et al. (2020), for samples taken along an E-W transect across the (approximately) N-S



**Figure 5.6: Primary  $\delta^{57}\text{Fe}$  throughout Galápagos plume evolution.** The correction to  $\delta^{57}\text{Fe}_{\text{primary}}$  from measured  $\delta^{57}\text{Fe}$  depends on how the primary liquid MgO is calculated, with an upper and lower primary MgO used for each method if appropriate (Table 5.2). The uncertainty range on each point reflects both the calculated or published range of primary MgO, and the resulting uncertainty on  $\delta^{57}\text{Fe}_{\text{primary}}$  (which depends on the slope of the  $\delta^{57}\text{Fe}$ -MgO fit), with the typical analytical error shown separately. GSC = Galápagos Spreading Centre, raw data from Gleeson et al. (2020). Primary MORB liquids from Sossi et al. (2016); Soderman et al. (2021) [chapter 3]. Mantle potential temperature ( $T_p$ ) estimates are mostly calculated from major element chemistry constraints (Table 5.1). A consideration of harzburgite in the mantle source would allow for lower  $T_p$  estimates (Matthews et al., 2021), but such estimates do not exist for all localities studied here. The bottom panel shows the calculated evolution of pyroxenite fraction (5th and 95th percentiles of accepted solutions) in the plume through time, with the minimum misfit solution shown in bold, as described in section 5.6.2.

spreading centre (Fig. 5.1). Gleeson et al. report variable  $\delta^{57}\text{Fe}$  for D, N and E-MORB samples (the classification of Teng et al., 2013), with a pyroxenite signature most apparent in E-MORB. To make a direct comparison between the spreading ridge samples (generally thought to be poorly mixed and homogenised in crustal magma chambers, (e.g., Stracke, 2021) and the OIB settings measured in this study, an aggregate GSC  $\delta^{57}\text{Fe}_{\text{primary}}$  was calculated, reflecting the contributions across the ridge. The data from Gleeson et al. (2020) was first corrected for olivine fractional crystallisation following Sossi et al. (2016); Nebel et al. (2019); Soderman et al. (2021) [chapter 3], using an upper estimate of  $\Delta^{57}\text{Fe}_{\text{ol-melt}}$  of  $-0.4 \times 10^6/T^2$  (Nebel et al., 2019) and a lower estimate of  $\Delta^{57}\text{Fe}_{\text{ol-melt}}$  of  $-0.1 \times 10^6/T^2$  (Soderman et al., 2021 [chapter 3]). Samples characterised as E-MORB by Gleeson et al. (2020) were corrected back to equilibrium with  $\text{Fo}_{88}$  olivine (typical

forsterite content for olivine in equilibrium with pyroxenite, see supplement of Soderman et al., 2021), and D- and N- MORB samples back to equilibrium with Fo<sub>91</sub> olivine, using a  $K_d$  of 0.32 Putirka (2016) and  $\text{Fe}^{3+}/\text{Fe}_T$  of 0.143 (average MORB, Zhang et al., 2018a). The aggregate melt  $\delta^{57}\text{Fe}_{\text{primary}}$  was then calculated by mass balance, using the calculated  $\delta^{57}\text{Fe}_{\text{primary}}$  and  $\text{FeO}_{\text{primary}}$  for each sample, and the range shown in Figs. 5.6 and 5.7 represents the results for  $\Delta^{57}\text{Fe}_{\text{ol-melt}} = -0.4$  and  $-0.1 \times 10^6/T^2$ .



**Figure 5.7: Primary  $\delta^{57}\text{Fe}$  for each locality in the Galápagos plume evolution, compared to modelled peridotite-only melting for a lithospheric thickness of 60 km (for the plume localities) and 0 km (to represent melting at the Galápagos Spreading Centre). The modelled primary MORB (calculated with 0 km lithospheric thickness and a  $T_p$  of 1300 °C) just overlaps with published primary MORB liquid estimates (Sossi et al., 2016; Soderman et al., 2021).**

I find that pure peridotite melting (with no lithospheric cap to the melting region, to represent the spreading centre) can explain the pooled GSC data, if  $\Delta^{57}\text{Fe}_{\text{ol-melt}} = -0.4 \times 10^6/T^2$  is used (i.e., the isotopically lightest result shown by the grey bar in Fig. 5.7). A smaller  $\Delta^{57}\text{Fe}_{\text{ol-melt}}$  would require contributions from an isotopically heavy pyroxenite-derived melt, as proposed by Gleeson et al. (2020, 2021).

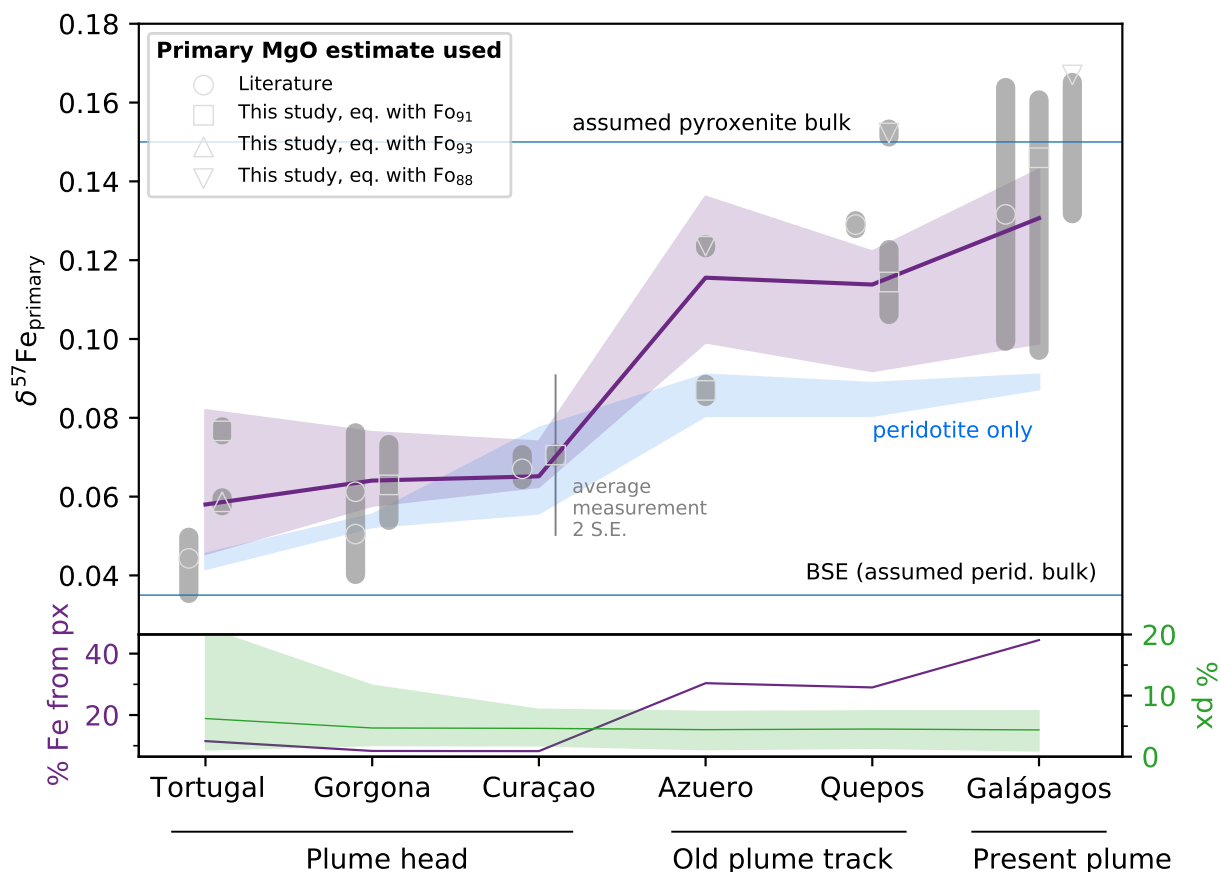
## 5.4 Relating the Fe isotope evolution of the plume to mantle lithology

### 5.4.1 Peridotite melting cannot generate observed $\delta^{57}\text{Fe}$

The increase in  $\delta^{57}\text{Fe}_{\text{primary}}$  from plume-head through to present-day coincides with  $\sim 400^\circ\text{C}$  of plume cooling ( $1800^\circ\text{C}$  to  $1400^\circ\text{C}$ ; Alvarado et al., 1997; Herzberg and Gazel, 2009; Trela et al., 2015, 2017). Smaller extents of melting from a cooler plume increase  $\Delta^{57}\text{Fe}_{\text{melt-source}}$  and create heavier iron isotopic compositions in the melt (Weyer and Ionov, 2007; Dauphas et al., 2009; Soderman et al., 2022 [chapter 4]). However, when I test this null hypothesis using my self-consistent mantle melting and equilibrium isotope fractionation model (Soderman et al., 2021, 2022 [chapters 2, 3, 4]), I find that cooling of a peridotite-only lithology cannot match the observations (Fig. 5.8, blue shading). The modelled increase in  $\delta^{57}\text{Fe}$  flattens for  $T_p$  below  $1500^\circ\text{C}$  (because the maximum mantle-melt isotopic fractionation is approached), whereas the data suggest a continuing increase in  $\delta^{57}\text{Fe}_{\text{primary}}$  from Azuero and Quepos (60–70 Ma) through to modern Galápagos (present day). The gradual increase in  $\delta^{57}\text{Fe}$  as the plume cools in this model is driven both by decreasing average melt fraction and increasing  $\text{Fe}^{3+}/\text{Fe}_T$  of the melt, as the average pressure of melting decreases with decreasing  $T_p$  (Stolper et al., 2020; Soderman et al., 2022 [chapter 4]). My model of peridotite melting can reproduce the calculated primary MORB liquid (Sossi et al., 2016) and Galápagos Spreading Centre  $\delta^{57}\text{Fe}$  (Fig. 5.7), although a contribution from pyroxenite melting is required for the isotopically heaviest GSC samples (Gleeson et al., 2020).

### 5.4.2 Evidence for a pyroxenite component in the plume

Given the poor fit of pure peridotite melting models to the data, I next test the hypothesis of a pyroxenite component in the cooling plume. Since pyroxenite lithologies are likely to have higher  $\delta^{57}\text{Fe}$  than peridotite (Williams and Bizimis, 2014; Nebel et al., 2019), the presence of pyroxenite in the plume is expected to produce higher  $\delta^{57}\text{Fe}$  melts than for pure peridotite melting. As pyroxenite is more fusible than peridotite, it is also expected that the contribution from pyroxenite-derived melts increases as the plume cools. To model the isotopic effect of pyroxenite, I have used an average of global pyroxenite lithologies observed from the mantle (MIX1G, Lambart et al., 2016, as outlined in chapter 2), taken to have a bulk  $\delta^{57}\text{Fe}$  of average MORB,  $0.15\text{‰}$  (Sossi et al., 2016). With a Monte Carlo simulation I explored the aggregate melt  $\delta^{57}\text{Fe}$  for a range of pyroxenite fractions and mantle temperatures allowed for a buoyant and progressively cooling plume (see section 5.6.2 at end of chapter). This modelling shows that the observed Fe isotope evolution of the plume is best matched by a small and approximately constant pyroxenite fraction,  $< 7\%$ , in the plume before it has undergone melting (Fig. 5.8; Table 5.4), in contrast to the larger pyroxenite



**Figure 5.8: Minimum misfit  $\delta^{57}\text{Fe}_{\text{primary}}$  of the aggregate multi-lithology melt (top, purple) and pyroxenite fraction in the source (green) from the Monte Carlo simulation.** The envelopes show the 5th and 95th percentiles of the Monte Carlo runs accepted at 95 % confidence, compared to the data and the peridotite-only case. The bottom panel also shows the fraction of Fe in the aggregate melt derived from pyroxenite.

fractions proposed for some plumes (Herzberg, 2011).

At high mantle  $T_p$  in the plume head, the Fe fraction in the bulk melt contributed from pyroxenite is small, permitting a wide range in pyroxenite fractions predicted by successful models. As the  $T_p$  decreases, there is a decrease in the fraction of the total melt coming from peridotite compared to isotopically heavy pyroxenite. This decrease is manifest in a corresponding increase in the proportion of Fe in the bulk melt originating from pyroxenite, resulting in a steeper increase of  $\delta^{57}\text{Fe}_{\text{primary}}$  with plume evolution compared to that expected for a pure peridotite source. The presence of a pyroxenite component in the modern Galápagos is consistent with published results (Vidito et al., 2013; Gleeson et al., 2020, 2021), although my results find smaller pyroxenite fractions than previously suggested (Vidito et al., 2013). These results also support the hypothesis of a pyroxenite component present throughout the history of the Galápagos plume (Trela et al., 2015; Gazel et al., 2018), but, critically, I show that plume cooling alone can generate the increase in the amount of pyroxenite-derived melt, without relying on any ad-hoc and potentially geodynamically-unlikely scenario of an increasing amount of pyroxenite in the source (Gazel et al., 2018).

The pyroxenite component used here has a bulk  $\delta^{57}\text{Fe}$  of 0.15 ‰, the composition of average

**Table 5.4: Parameters and results for the minimum misfit solution of pyroxenite and temperature evolution in the plume produced by the Monte Carlo simulation.** px. = pyroxenite. Columns, in order: (1) Plume locality; (2) Plume temperature of the best-fit solution; (3) Proportion of px in the plume in the best-fit solution; (4) Calculated plume buoyancy (section 5.5.1); (5) Percentage of Fe derived from px in the best-fit solution; (6) Calculated Fe isotope composition of the bi-lithologic melt; (7) Fraction of tungsten (W) derived from px in the best-fit solution (section 5.5.2).

| Locality  | $T_p$ (°C) | Solid px. % <sup>95th percentile</sup> <sub>5th percentile</sub> | Buoyancy (kg m <sup>3</sup> ) | % Fe from px. | $\delta^{57}\text{Fe}$ | $F_W$ from px. |
|-----------|------------|------------------------------------------------------------------|-------------------------------|---------------|------------------------|----------------|
| Tortugal  | 1752       | 6.2 <sup>21</sup> <sub>1</sub>                                   | −45                           | 12            | 0.06                   | 0.78           |
| Gorgona   | 1629       | 4.7 <sup>12</sup> <sub>2</sub>                                   | −31                           | 8             | 0.06                   | 0.66           |
| Curaçao   | 1614       | 4.6 <sup>8</sup> <sub>2</sub>                                    | −29                           | 8             | 0.07                   | 0.66           |
| Quepos    | 1498       | 4.5 <sup>8</sup> <sub>1</sub>                                    | −16                           | 29            | 0.11                   | 0.79           |
| Azuero    | 1494       | 4.4 <sup>7</sup> <sub>1</sub>                                    | −15                           | 30            | 0.12                   | 0.80           |
| Galápagos | 1459       | 4.4 <sup>8</sup> <sub>1</sub>                                    | −11                           | 44            | 0.13                   | 0.85           |

MORB (Sossi et al., 2016). If an estimate of 0.3 ‰ is used (as suggested by Nebel et al., 2019; Gleeson et al., 2020, although the processes required to form such a heavy pyroxenite remain enigmatic; Soderman et al., 2021 [chapter 3]), then the modelled trend of  $\delta^{57}\text{Fe}$  would become steeper and smaller pyroxenite fractions would reproduce the observed trend. However, the overall conclusion of plume lithology evolution would be unchanged.

Olivine trace elements are also widely used as tracers of pyroxenite in the source region of basalts, and have been taken to suggest a pyroxenite component in the Galápagos plume only becomes resolvable after the plume head stage (Trela et al., 2015, 2017; Gazel et al., 2018). I tested this hypothesis in the context of my model by estimating the equilibrium olivine trace element composition for melts from the the bi-lithologic plume, using composition-dependent olivine-melt partition coefficients (section 5.4.2.1 below). I find that an approximately constant pyroxenite fraction through plume history is also consistent with the olivine trace element contents (Fig. 5.9). I also find that when pyroxenite fractions are small, modelled Fe stable isotopes are predicted to be a more discriminating tracer of mantle source lithology than modelled trace element abundances in olivine.

#### 5.4.2.1 Olivine trace element modelling

I have compared the consistency of my model of approximately constant pyroxenite fraction in the source, as suggested by  $\delta^{57}\text{Fe}$ , with constraints from olivine trace elements. The aggregate melt composition from bi-lithologic mantle produced by my model at each locality was calculated for the best fit solution of pyroxenite fraction (major element compositions and melt fractions calculated as in section 5.6.1 at end of chapter), across the range of mantle potential temperatures covered by the model (to highlight the role of temperature). For elements not considered in THERMOCALC outputs, the partitioning behaviour during melting and bulk compositions given in Table 5.5 was used.

The equilibrium olivine trace element composition was then estimated using composition-dependent

**Table 5.5: Partitioning behaviour and bulk lithology compositions used for elements not calculated by THERMOCALC.** \*Bulk peridotite Mn is taken to be less than bulk pyroxenite MnO (Davis et al., 2009), but from Herzberg and O'Hara (2002) there is unlikely to be a uniform peridotite trace element composition in the mantle. Cpx = clinopyroxene, opx = orthopyroxene, plag = plagioclase.

| $D_{\text{min.}-\text{melt}}$ | Ni                                             |                           | Mn                                    | References                                       |
|-------------------------------|------------------------------------------------|---------------------------|---------------------------------------|--------------------------------------------------|
| Olivine                       | $\exp(4505/T - 2.075 - \ln(1/D_{\text{MgO}}))$ |                           | $0.118 + 0.214 \times D_{\text{MgO}}$ | Herzberg and O'Hara (2002), Matzen et al. (2017) |
| Garnet                        | 8                                              | 1.24 (KLB1), 4.6 (MIX1G)  |                                       | Le Roux et al. (2015)                            |
| Opx                           | 3.7                                            |                           | 0.64                                  | Le Roux et al. (2015)                            |
| Cpx                           | 22                                             | 0.77 (KLB1), 1.67 (MIX1G) |                                       | Le Roux et al. (2015)                            |
| Spinel                        | 10                                             |                           | 0.46                                  | Le Roux et al. (2015)                            |
| Plag.                         | 0.09                                           |                           | 0.03                                  | Laubier et al. (2014)                            |
| Perid. bulk                   | 1960 ppm                                       |                           | 0.11 (mol % oxide)*                   | Salter and Stracke (2004)                        |
| Pyrox. bulk                   | 1000 ppm                                       |                           | 0.13 (mol % oxide)                    | Sobolev et al. (2005)<br>Lambart et al. (2016)   |

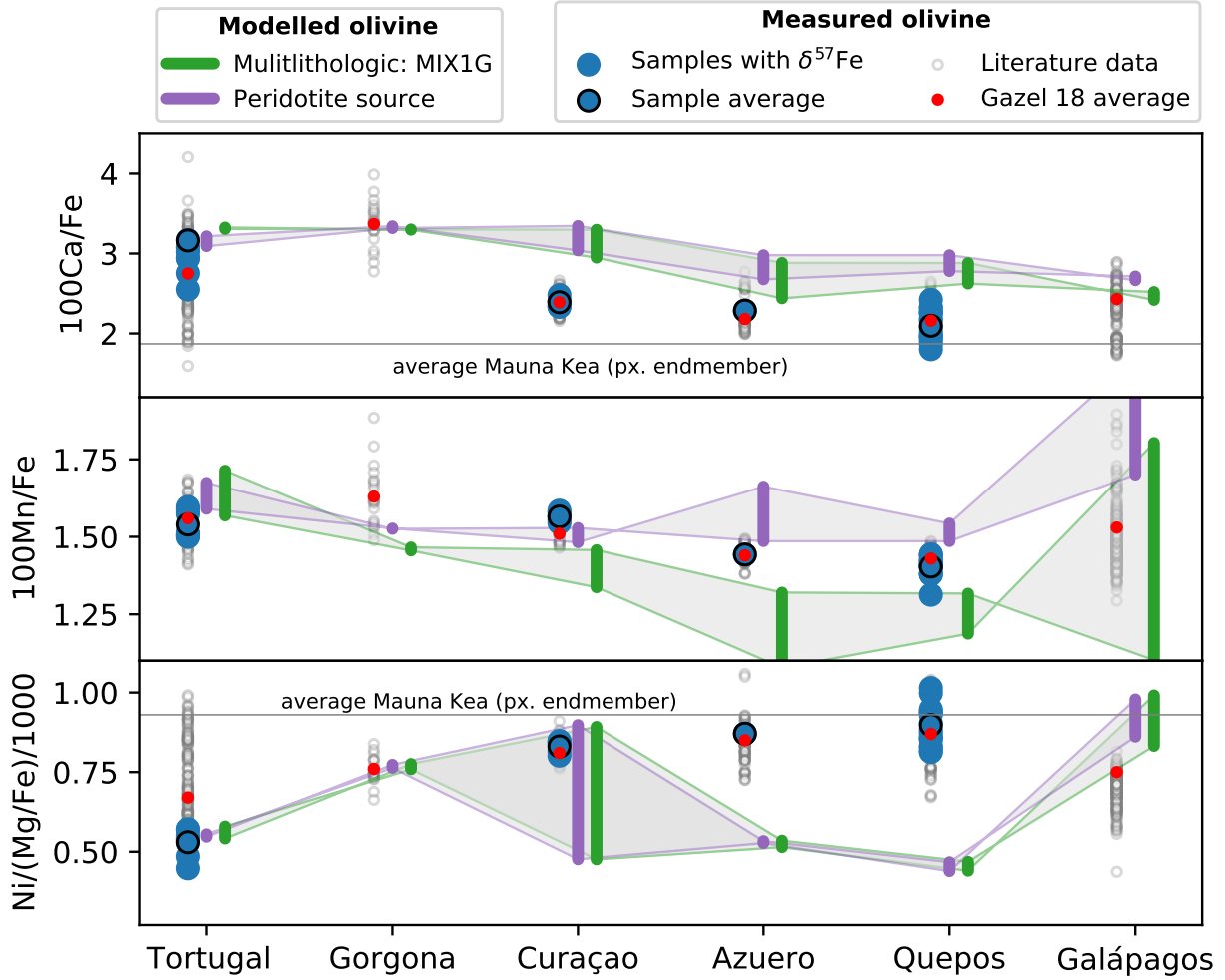
**Table 5.6: Parameterisations of partition coefficients used for olivine-melt partition coefficients for low pressure olivine crystallisation.**  $K_{\text{d,FeO/MgO}} = 0.381 - 0.790/\text{MgO (wt\%)} + 1.039/\text{MgO (wt\%)}^2$ ; Herzberg and O'Hara (2002). Partitioning behaviour for Mg, Fe, Ca, Mn from Herzberg and O'Hara (2002), for Ni from Matzen et al. (2017). Average  $T_{\text{cryst.}}$  estimates used for Ni partitioning are: Tortugal, 1590 °C; Gorgona, 1420 °C; Curaçao, 1350 °C (averages from Trela et al., 2017; Matthews et al., 2021); Azuero, 1280 °C; Quepos, 1330 °C (Gazel et al., 2019); Galápagos, 1130 °C (Stock et al., 2020).

| Partition coefficient during crystallisation | Calculation                                                    |
|----------------------------------------------|----------------------------------------------------------------|
| $D_{\text{MgO}}$                             | $(0.382 - K_{\text{d}})/0.0164$                                |
| $D_{\text{FeO}}$                             | $K_{\text{d}} \times D_{\text{MgO}}$                           |
| $D_{\text{CaO}}$                             | $-0.019 + 0.007 \times D_{\text{MgO}} + 0.063/D_{\text{MgO}}$  |
| $D_{\text{MnO}}$                             | $0.118 + 0.214 \times D_{\text{MgO}}$                          |
| $D_{\text{Ni}}$                              | $\exp(4505/T_{\text{cryst.}} - 2.075 - \ln(1/D_{\text{MgO}}))$ |

olivine-melt partition coefficients (Table 5.6; Herzberg and O'Hara, 2002; Matzen et al., 2017).

In Fig. 5.9 I compare my model results to published trace element in olivine data (filtered for Fo > 87) for the same localities (Trela et al., 2015, 2017; Gazel et al., 2018). This data has previously been used to suggest a pyroxenite component only becomes resolvable after the plume head stage.

I find that some aspects of the natural olivine data can be reproduced by my model of a cooling plume with approximately constant pyroxenite fraction throughout its history. A slight decrease in Ca/Fe in cooler plume tail localities than the plume head, as observed in natural data, can be generated by the plume cooling, regardless of lithology. My model predicts that in most cases melts from a pyroxenite-bearing source have lower Ca/Fe than pure peridotite melts, in agreement with Sobolev et al. (2007); Herzberg and Asimow (2008), but I find that there is minimal difference between the predicted olivine Ca/Fe compositions for the two source compositions. More extreme variations could be generated by a lower Ca pyroxenite. The trend of decreasing then increasing natural Mn/Fe data as the plume evolves could also be matched by a cooling plume with an approximately constant pyroxenite component; the only data not matched in this case is for Gorgona olivines, which have higher Mn/Fe than the pyroxenite-bearing model predicts. I



**Figure 5.9: Modelled olivine trace element ratios using the minimum misfit model of small, approximately constant pyroxenite fraction (green) and for a pure peridotite source (purple), compared to published olivine trace element data for these localities.** See text for details of model parameters. Olivine trace element data from Trela et al. (2015, 2017); Gazel et al. (2018), with averages from Gazel et al. (2018). The blue circles highlight the samples in the olivine trace element dataset that have been used in this  $\delta^{57}\text{Fe}$  study. Average Hawaiian Mauna Kea data (Gazel et al., 2018) is shown for reference.

note that Mn/Fe appears most sensitive to pyroxenite (with a lower Mn/Fe in olivine derived from a pyroxenite-bearing source than a peridotite source, consistent with predictions; Sobolev et al., 2007; Herzberg, 2011), but that pyroxenite and peridotite Mn concentrations are relatively poorly constrained.

The Ni content of olivines has also been proposed as a tracer of pyroxenite, with high Ni indicating pyroxenite in the melt source (e.g., Sobolev et al., 2005, 2007). The partitioning of Ni between olivine and melt is dependent on crystallisation temperature as well as melt composition (Matzen et al., 2017), which introduces uncertainty into the model where crystallisation temperatures for each locality are poorly constrained. If available, I use crystallisation temperatures from aluminium-in-olivine thermometry (Table 5.1), otherwise I use major element chemistry temperature estimates. The modelled difference in olivine  $\text{Ni}/(\text{Mg}/\text{Fe})$  contents between pure peridotite and bi-lithology source melts is small. This result arises because although the bulk melt-source

partition coefficient for olivine-free lithologies (such as MIX1G pyroxenite at depth) is lower than for olivine-bearing peridotite (Ni is compatible in olivine), the pyroxenite has a lower bulk Ni content than peridotite (Sobolev et al., 2007; Herzberg, 2011), and the model predicts that the Ni contents of the melts from peridotite and a multilithology source will be similar, reflected in the subsequently crystallising olivine. This model fits the natural olivine data for Tortugal, Gorgona, Curaçao and modern Galápagos, however has a poor fit to Azuero and Quepos, which may be in part due to uncertainties in olivine crystallisation temperature as there are only a few samples with temperature constraints.

## 5.5 Discussion

These new results provide important constraints on a number of questions regarding the composition and entrainment of material stored in or around LLSVPs by mantle plumes, given the Galápagos plume's proximity to the Pacific LLSVP and ULVZ and its proposed sampling of deep mantle material.

First, there is clear evidence for a pyroxenite lithology entrained into the mantle plume source. Given the low solidus temperature of pyroxenite relative to peridotite, pyroxenite should contribute progressively more melt as the plume temperature decreases, and the isotopically heavy component in the Galapagos plume behaves consistently with that prediction. Therefore, the lower mantle being sampled by the Galápagos plume must contain some amount of pyroxenite, either because the Pacific LLSVP is itself a pile of recycled crust (Christensen and Hofmann, 1994; Nakagawa and Tackley, 2004; Hirose et al., 2005; Ohta et al., 2008; Tackley, 2012; Mulyukova et al., 2015; Niu, 2018; Thomson et al., 2019; Huang et al., 2020b; Jones et al., 2020) or because dense recycled crust can be mixed into the LLSVP (Tackley, 2012; Li et al., 2014).

### 5.5.1 Buoyancy constraints on the fraction and density of entrained LLSVP material

Second, the source fraction of pyroxenite estimated for some plumes using trace elements in olivine can be large (Sobolev et al., 2007; Herzberg, 2011), but large pyroxenite fractions will produce a negatively buoyant plume due to their excess density relative to ambient mantle (Yasuda and Fujii, 1998; Aoki and Takahashi, 2004; Brown and Leshner, 2014; Dannberg and Sobolev, 2015; Matthews et al., 2021; Bao et al., 2022): a mantle  $T_p$  of  $\sim 1430^\circ\text{C}$  is required for a plume with 5 % recycled crust to be neutrally buoyant (not even actively upwelling) in the upper mantle (Bao et al., 2022). Hence, geodynamical modelling predicts that only small fractions of dense recycled crust should be entrained by an upwelling plume (Li et al., 2014; Jones et al., 2019). My results provide geochemical evidence directly supporting this geodynamic behaviour. In my model solution, the

Galápagos plume buoyancy (calculated following Shorttle et al., 2014; Matthews et al., 2016) decreases over time, but the plume remains positively buoyant right up to the modern day (Table 5.4). This inferred positive buoyancy of the plume is consistent with the ability of the Galápagos plume to carry deep primordial mantle material (high  $^3\text{He}/^4\text{He}$ , negative  $\mu^{182}\text{W}$ ; potentially a denser component than ambient mantle; Jackson et al., 2017) throughout its lifetime, even now at the coolest point in its history.

Geodynamic models also show that the entrainment of dense lower mantle material is dependent on the density contrast between LLSVP material and the surrounding mantle (Lin and van Keken, 2006; Jones et al., 2019). Therefore, the calculated pyroxenite fraction can be used to place constraints on the density of the material being carried by the plume (Fig. 5.10).

### 5.5.1.1 Constraining Galápagos plume buoyancy number

Without considering the presence of an ultra-low velocity zone (which affects entrainment dynamics; Jones et al., 2019), my estimate of maximum pyroxenite fraction entrained in the plume head constrains the buoyancy number,  $B$ , of the plume. Buoyancy number is the ratio of chemical density contrast of dense material to the thermal density contrast of the hot thermal boundary layer, following Jones et al. (2019), and is calculated as

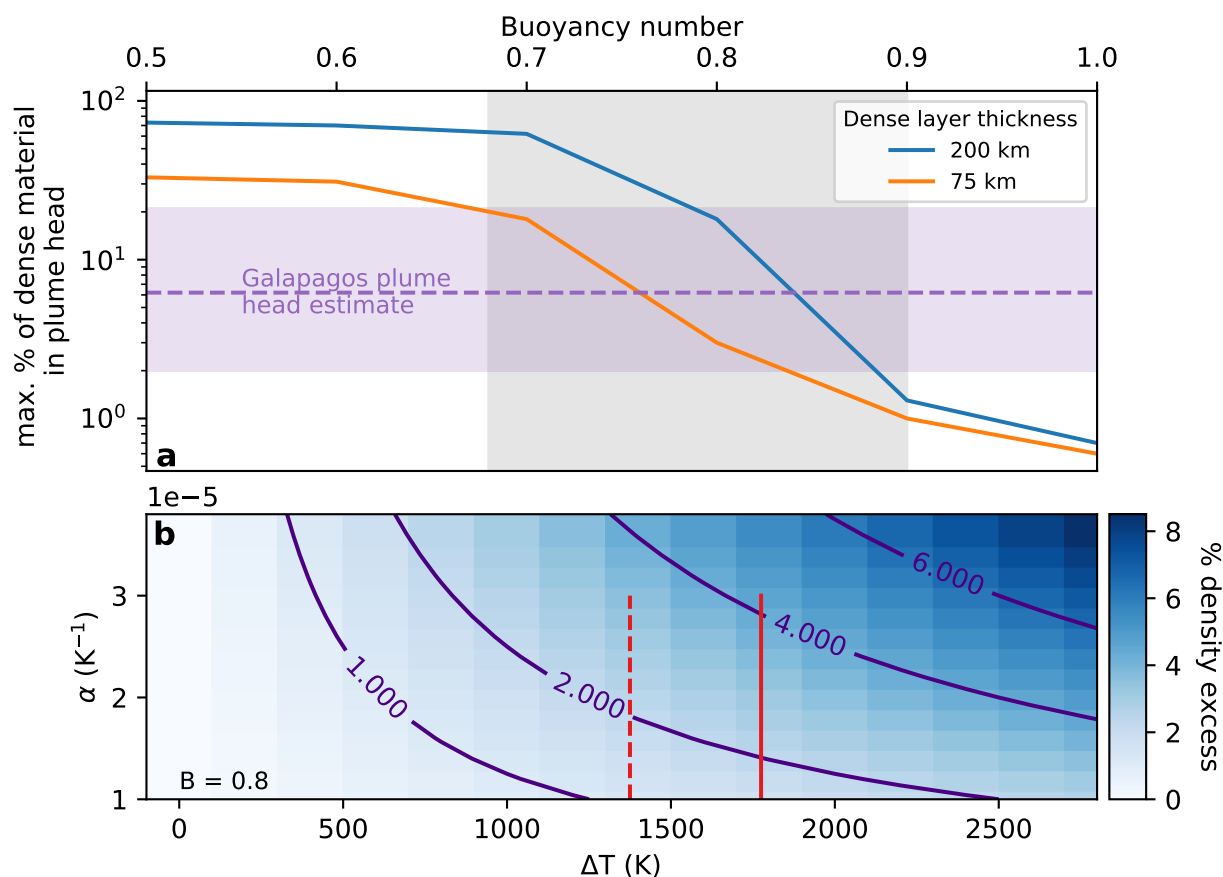
$$B = \frac{\Delta\rho_c}{\rho_0\alpha\Delta T}. \quad (5.1)$$

where  $\Delta\rho_c$  is the excess density of the lower mantle material relative to ambient mantle,  $\alpha$  is the thermal expansion coefficient,  $\rho_0$  is the reference mantle density and  $\Delta T$  is the thermal contrast across the boundary layer driving mantle plume development.

In Fig. 5.10a, I show the results from Fig. 2a in Jones et al. (2019) for the entrainment fraction of dense material in a plume head for two different thicknesses of dense layer. Fig. 5.10 shows that the maximum pyroxenite fraction in the Galápagos plume (Table 5.4) constrains the buoyancy number to be 0.7–0.9, which is consistent with estimates used in existing geodynamic mantle models (Li et al., 2014).

### 5.5.1.2 Estimating excess density of the isotopically heavy component

Given estimates of thermal expansion and the temperature contrast between the CMB and the overlying mantle that drives the upwelling plume, it is possible to use equation 5.1 to calculate the percentage excess density of the entrained component relative to ambient mantle,  $(\Delta\rho_c/\rho_0) \times 100$ . The results of this calculation are shown in Fig. 5.10b, with the red lines showing estimates of excess density given literature estimates of  $\Delta T$  and  $\alpha$ .  $\alpha$  applicable to the modelling of the lower mantle is proposed to be between  $1 \times 10^{-5}$  (Mulyukova et al., 2015) and  $3 \times 10^{-5}$  (Jones



**Figure 5.10: Constraints from pyroxenite entrainment fraction on the density of lower mantle material.** **a)** Modified from Jones et al. (2019), estimates of maximum entrainment fraction in the plume head for different boundary layer thicknesses. The grey bar shows the buoyancy number implied by the pyroxenite fraction in Tortugal (purple shading), with the latter shown by the purple bar. Buoyancy number,  $B$ , is defined as  $\Delta\rho/(\alpha\Delta T\rho_c)$ . **b)** Estimate of excess density (red lines) of entrained material in the Galápagos plume relative to ambient mantle, based on  $B = 0.8$  and using suitable estimates of thermal expansion,  $\alpha$ , and driving temperature contrast,  $\Delta T$  (see text). The contours mark density excesses in  $\alpha$ – $\Delta T$  space, as shown by the colourbar. Solid red line shows  $\Delta T$  estimate using the Tortugal  $T_p$ , dashed red line shows  $\Delta T$  estimate considering non-adiabatic cooling on the lower mantle  $T_p$  of Tortugal (see text).

et al., 2019). To estimate  $\Delta T$  ( $T_{\text{CMB}} - T_p$ , following Jones et al., 2019), I use a typical estimate of  $T_{\text{CMB}} = 3800$  K (Deschamps et al., 2015) and two estimates of  $T_p$ : 2025 K (solid line), from my  $T_p$  estimate for Tortugal (Table 5.4); 2425 K (dashed line), using the Tortugal  $T_p$  estimate but considering non-adiabatic cooling processes (e.g., diffusive heat loss) that will mean the  $T_p$  estimate in the upper mantle is lower than the plume’s  $T_p$  at depth. The 400 K estimate of these processes is taken from Fig. 2 in Albers and Christensen (1996).

These calculations estimate that the pyroxenite component has an excess density of 1.1–4.3 % relative to ambient mantle (Fig. 5.10). This excess density is in agreement with the predicted excess density of MORB stored in the lower mantle and of LLSVPs (Christensen and Hofmann, 1994; Kesson et al., 1994; Hirose et al., 2005; Ricolleau et al., 2010; Tsuchiya, 2011; Davies et al., 2015; Jones et al., 2020). Additionally, the rate of decrease in entrained dense material expected from plume head to tail is slowed if ultra-dense material is also present in the lower mantle (Jones

et al., 2019), as may be the case for the Galápagos plume with the existence of an ULVZ (Elizabeth and Fenglin, 2011; Ma et al., 2019). Therefore, the continued presence of pyroxenite entrained in the modern plume at detectable levels supports geophysical evidence for an ULVZ.

### 5.5.2 Implications for our understanding of primordial geochemical signatures

LLSVPs may also contain primordial material, which can be entrained in small proportions by an upwelling plume (e.g., Deschamps et al., 2011; Li et al., 2014; Williams et al., 2019; Harpp and Weis, 2020). Modern Galápagos shows the most negative  $\mu^{182}\text{W}$  anomalies yet measured in OIB (Mundl-Petermeier et al., 2020), consistent with a primordial lower mantle/core component entrained in the plume, despite recycled crustal material being able to overprint primordial W (and He) isotope signatures (Jackson et al., 2020a). In this study I include Fernandina volcano, the proposed current Galápagos plume location, where  $\mu^{182}\text{W}$  of  $-22$  and  $^3\text{He}/^4\text{He}$  of  $30 \text{ R/R}_A$  have been reported (Kurz et al., 2009; Mundl-Petermeier et al., 2020). A small pyroxenite component would therefore be consistent with minimal W and He overprinting of primordial material by W and  $^4\text{He}$ -rich crust, and support that both recycled and primordial material can be entrained from (or near to) the LLSVP (Li et al., 2014). The Fernandina samples themselves record  $\delta^{57}\text{Fe}_{\text{primary}}$  of  $\geq 0.06 \text{ ‰}$  (dependent on  $\Delta^{57}\text{Fe}_{\text{ol-melt}}$  used); isotopically lighter than the average modern plume shown in Fig. 5.6. Although the modern plume as a whole may have a 5–10 % pyroxenite component, individual volcanoes will record subtly different components/geochemical domains, as has been well-recorded in the Galápagos (e.g., Hoernle et al., 2000; Blichert-Toft and White, 2001; Harpp and White, 2001; Vidito et al., 2013; Harpp and Weis, 2020; Gleeson et al., 2021); it is thus likely that Fernandina records a particularly small pyroxenite fraction, producing  $\delta^{57}\text{Fe}$  most typical of peridotite melting at plume temperatures and, critically, with minimal overprinting of lower mantle primordial W and He isotope signatures. Notably, samples with the most extreme  $\mu^{182}\text{W}$  ( $\geq -17$ ) and  $^3\text{He}/^4\text{He}$  ( $\geq 25 \text{ R/R}_A$ ) recorded in Samoa (Ofu; Jackson et al., 2007b; Mundl-Petermeier et al., 2020) also have lower-than-MORB  $\delta^{57}\text{Fe}$  ( $\delta^{57}\text{Fe}_{\text{primary}} \geq 0.07 \text{ ‰}$ ) compared to other samples from different Samoan volcanoes (Soderman et al., 2021) [chapter 3]. Ofu volcano may similarly be sampling relatively less crustal material than the other volcanoes in the Samoan plumbing system.

The variation of pyroxenite-derived melt throughout plume evolution also suggests that geochemical signatures of primordial mantle may be differently diluted by recycled crustal components throughout plume history (Jackson et al., 2020a). To explore this further, I have calculated the amount of pyroxenite-derived W in the aggregate melts for the minimum misfit model, and find minimal predicted change in the fraction of W derived from pyroxenite through time (Table 5.4). Given the susceptibility of lower mantle  $\mu^{182}\text{W}$  and  $^3\text{He}/^4\text{He}$  isotope signatures to overprinting by crustal material (Jackson et al., 2020a), it could be anticipated that the earlier plume head

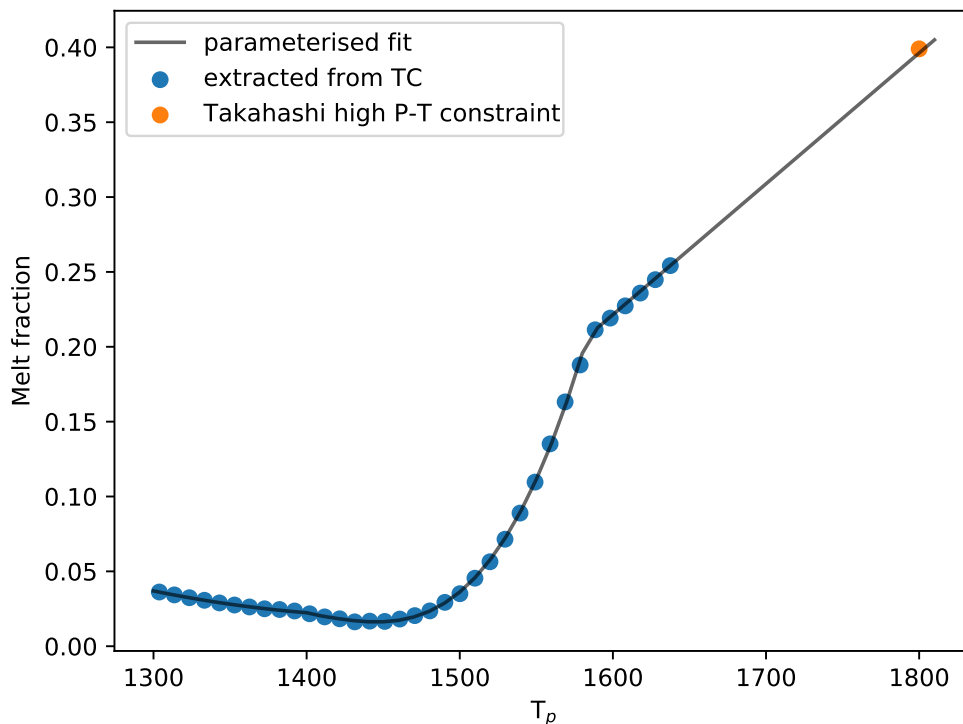
and tail localities may also show negative  $\mu^{182}\text{W}$  (and high  $^3\text{He}/^4\text{He}$ ), such as those observed in modern Galápagos samples. Confirmation of this hypothesis would provide important constraints on the dynamics of lower mantle evolution and its entrainment into the upper mantle, such as rates of mantle mixing and the extraction of volatiles from the deep Earth (e.g., Miller et al., 2019). The small pyroxenite fraction shown here for Galápagos suggests that other OIB which have also recorded large negative  $\mu^{182}\text{W}$  anomalies (such as Samoa, Hawai'i, Heard, Pitcairn; Mundl-Petermeier et al., 2020) may also have only entrained small pyroxenite fractions from their underlying LLSVPs, rather than large pyroxenite fractions previously proposed in some plumes (Sobolev et al., 2007; Herzberg, 2011). This work shows the potential of novel stable isotopes combined with self-consistent thermodynamic modelling to constrain mantle dynamics.

## **5.6 Supplement: Application of isotope fractionation and Monte Carlo models**

### **5.6.1 Extrapolation of mantle melting model to high temperatures**

I have complete isentropic decompression melting paths (i.e., no melt generated at higher pressures than the THERMOCALC results) for  $T_p = 1300^\circ\text{C}$  and  $T_p = 1400^\circ\text{C}$  (KLB1, MIX1G) and  $T_p = 1530^\circ\text{C}$  (KLB1); see Soderman et al. (2022) [chapters 2 and 4]. Following Soderman et al. (2022) [chapter 4], I calculate an average pressure of melting along each of those isentropic decompression paths, considering a lithospheric cap on the melting region of 60 km. The melt composition at the average pressure and temperature of melting is then used as an estimate of the aggregate melt composition (see Soderman et al. (2022) and section 4.10). The lithospheric thickness used is based on the modern south-western Galápagos lithospheric thickness (Gibson and Geist, 2010) and is consistent with suggestions that the Caribbean Large Igneous Province formed above relatively thick lithosphere (rather than excessively thinned due to stretching during the plume head stage; Révillon et al., 1999). Although the lithospheric thickness at the time of eruption of plume head melts is less well-constrained than the modern plume, the results for the plume head are insensitive to lithospheric thickness due to the already high degree of melting.

I then approximate the average pressure of melting for all potential temperatures (not just those with calculated isentropic decompression melting paths) by assuming a linear interpolation and extrapolation between and beyond the calculated pressures, acknowledging that this approach likely results in a slight underestimation of average melting pressure at higher  $T_p$  (Lambart et al., 2013). Using the interpolated average melting pressures and corresponding temperatures, I extract the melt composition at each point up to the P-T limits of each pseudosection, then parameterise the composition vs potential temperature behaviour. This approach allows me to extrapolate the melt composition to higher potential temperatures and pressures than covered in the pseudosection, and



**Figure 5.11: Example of the parameterisation of melt composition at average pressure of melting (here, for melt fraction of KLB1) to higher P-T conditions than the THERMOCALC model.** The parameterisation is calculated in terms of mantle potential temperature,  $T_p$ , given the assumed linear relationship between average pressure of melting and  $T_p$  (°C). The high pressure-temperature experimental constraint (orange point) is from Takahashi et al. (1993).

to conditions applicable to the localities in this study. For the parameterisation, I use an additional high pressure and temperature constraint on the melt chemistry to ensure the model produces expected behaviour, particularly for the plume head localities. For KLB1, this high P-T constraint is taken from experimental melting results (Takahashi et al., 1993). I estimate the expected melt fraction and composition from the experimental results for the average melting pressures calculated for a  $T_p$  of 1800 °C, the upper estimate for Tortugal, and use this as the extreme P-T fitting point. An example of this parameterisation is shown in Fig. 5.11. For MIX1G, I take the assumption of a linear  $T_{\text{liquidus}}$  - pressure behaviour (Lambart et al., 2013) to predict where the extrapolated  $P_{\text{average}}$  results intersect the liquidus, giving a P-T point where complete melting is expected (and therefore the melt composition to be that of the bulk system). The intersection is calculated to be at  $P = 63$  kbar,  $T = 1954$  °C, corresponding to a  $T_p$  of 1801 °C, and therefore I assume complete melting at this potential temperature to constrain the high P-T behaviour of MIX1G melts.

## 5.6.2 Monte Carlo model

I use a Monte Carlo simulation to identify the evolution of pyroxenite behaviour that can best match the calculated  $\delta^{57}\text{Fe}_{\text{primary}}$ . For each run of the model, the following steps are taken.

1. The mantle potential temperature at each locality is assigned. The temperature is a random

selection within the limits given in Table 5.1, with the added constraint that the plume must cool through time (Trela et al., 2015, 2017; Gazel et al., 2018). Based on Gazel et al. (2019), Azuero is taken to be slightly later in plume evolution than Quepos. I note that the mantle potential temperatures used here are generally calculated from major element chemistry temperatures without a consideration of lithological heterogeneity (pyroxenite and harzburgite). As shown by Matthews et al. (2021), the consideration of buoyant, low melt-production harzburgite in a plume can reduce the required  $T_p$  by 100 °C. However, mantle potential temperatures calculated in this way are only available for Tortugal, Gorgona and Curaçao, and therefore for consistency I use potential temperature estimates that have not considered harzburgite in the plume.

**2.** A source pyroxenite fraction is then randomly chosen for Tortugal and Galápagos, the endmembers of plume evolution in this study. I use the constraint that the plume must be buoyant to set the upper limit of pyroxenite fraction in each case, for the chosen temperature (the lower limit is 0 % pyroxenite). Plume buoyancy is calculated following Shorttle et al. (2014); Matthews et al. (2016), using the reference ambient mantle density as that of KLB1 peridotite at  $T_p = 1300$  °C, and modelling the plume as two lithology mantle (KLB1, and KG1 – the latter a silica-deficient pyroxenite to approximate MIX1G).

**3.** A pyroxenite fraction is randomly chosen for each remaining locality, between the endmember Tortugal and Galápagos values, either decreasing or increasing as the plume evolves depending on whether the fraction chosen for Galápagos is higher or lower than that for Tortugal.

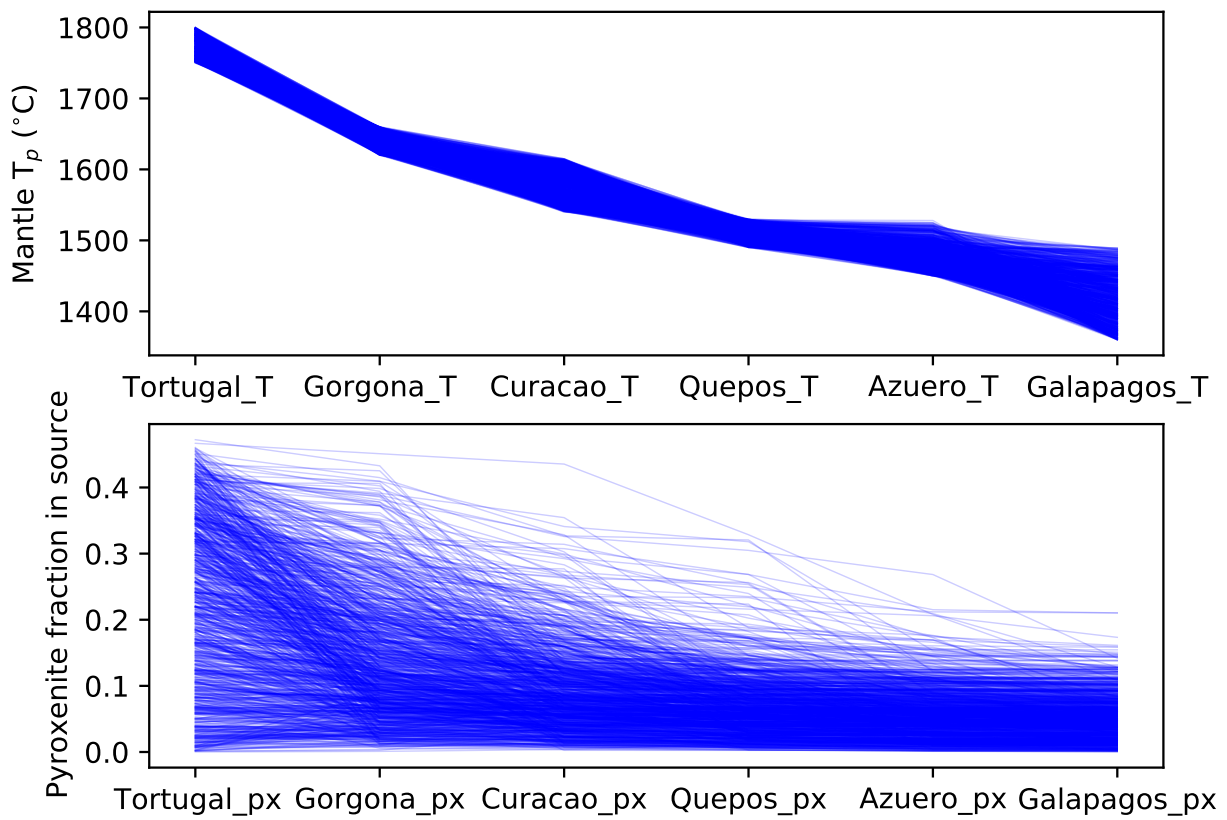
**4.** Given a mantle temperature and pyroxenite fraction for each locality, the aggregate melt  $\delta^{57}\text{Fe}$  can be then calculated, using melt fractions and FeO contents estimated as outlined in section 5.6.1.

The simulation ran the model 1000 times, covering the parameter space shown in Fig. 5.12.

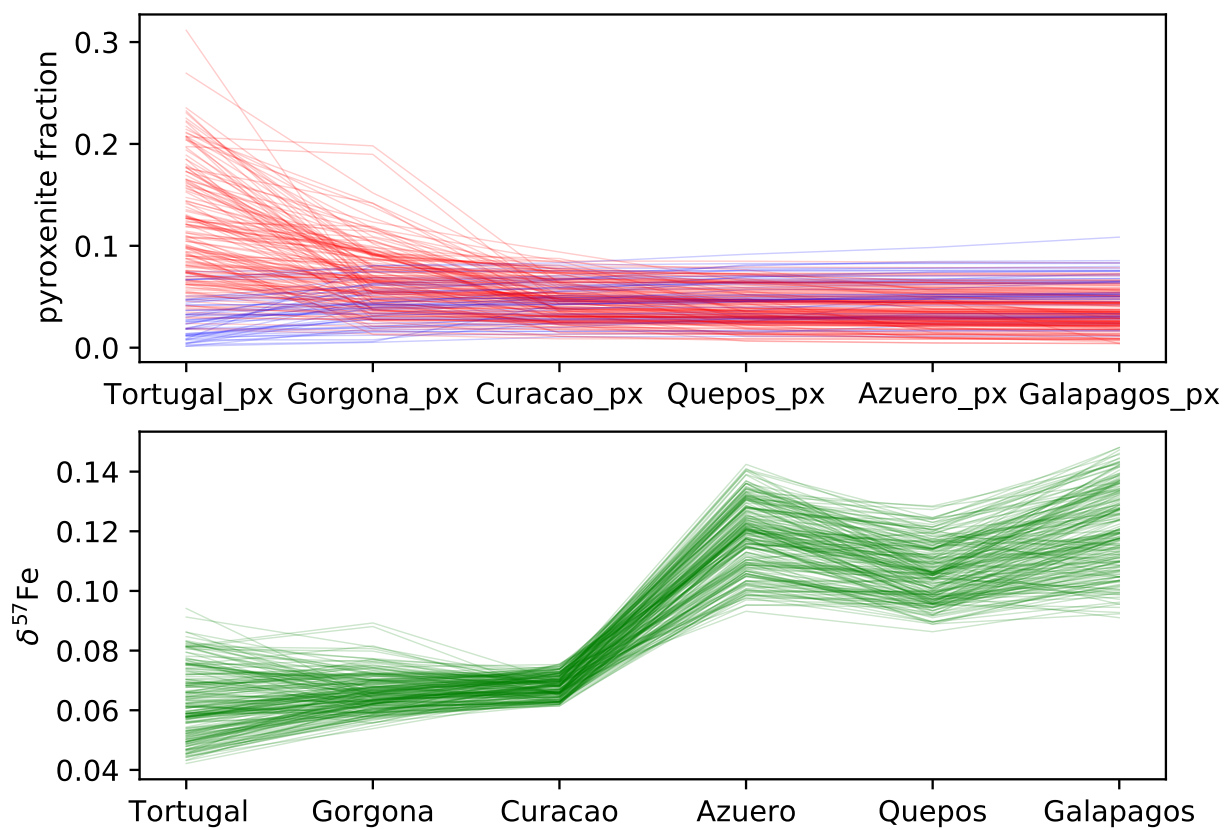
I parameterised the measured  $\delta^{57}\text{Fe}_{\text{primary}}$  at each locality by taking the median of the maximum and minimum values given by the ranges in Fig. 5.6 (regardless of primary MgO calculation method), and the difference between these maximum and minimum values. I calculated the misfit for each of the model runs as a chi-square,

$$\chi^2 = \sum \frac{(\delta^{57}\text{Fe}_{\text{model}} - \delta^{57}\text{Fe}_{\text{median of data}})^2}{\sigma^2} \quad (5.2)$$

where  $\sigma^2$  is  $0.3 \times \delta^{57}\text{Fe}_{\text{range of data}}$ . Taking a 95 % confidence interval I rejected any model runs falling above the critical  $\chi^2$  value (11.07, one-sided upper tail test), leaving approximately 200 solutions. These solutions are shown in Fig. 5.13, with < 25 % of accepted solutions recording a slightly increasing pyroxenite fraction over time, compared to > 75 % recording a decreasing pyroxenite fraction. Table 5.4 shows the results of the minimum misfit solution, and the 5th and 95th percentiles of the accepted solutions.



**Figure 5.12: Parameter space covered by the Monte Carlo simulation (1000 runs).** Top: mantle  $T_p$ , bottom: pyroxenite fraction.



**Figure 5.13: The accepted models from the Monte Carlo simulation, using the critical  $\chi^2$  at 95 % confidence.** Top: evolution of pyroxenite fraction through time, where red solutions are those with decreasing pyroxenite fraction and blue solutions are increasing pyroxenite fraction. Bottom:  $\delta^{57}\text{Fe}$  for the accepted solutions.

## 6 Summary

The heavy stable isotope dataset for basalts (MORB, OIB) is growing rapidly, and will continue to grow with improvements in mass spectrometer capabilities. Through the work presented in this thesis, I have shown how a bottom-up approach to modelling the generation of stable isotopic variability in the mantle, following Williams et al. (2021) in combining self-consistent thermodynamic modelling of mantle lithologies with isotope fractionation models, is a powerful tool to understand stable isotopic variability in erupted rocks. My approach provides a unique perspective on the ability of heavy stable isotopes to trace mantle source and process, compared to more common literature approaches. This chapter first summarises the principal results of the thesis, placing them in the context of the global questions posed in chapter 1, before discussing future work and progress that has been made since the work presented in these chapters.

### 6.1 The driver of stable isotope variation: mantle source or process?

This thesis finds that bulk source isotopic composition (e.g., the isotopic offset of MORB relative to ambient peridotite) likely dominates over mineralogical-driven fractionation (i.e., melt isotope differences driven by the presence or absence of a specific mantle source mineralogy) in determining the Fe stable isotope composition of basalts. The Fe isotope offset of MORB relative to ambient mantle is driven by the processes involved in its formation, largely partial melting and crystal fractionation, and ultimately it is these processes that are expected to drive the largest magnitude variability in basalt Fe isotope composition. By contrast, the direct role of source mineralogy in inducing Fe isotope heterogeneity in erupted basalts is minimal. This result means that Fe isotope heterogeneity in erupted basalts could be highly sensitive to isotopic heterogeneity in recycled material. Therefore there is wide scope for future studies to look at processes generating and preserving isotopic heterogeneity in recycled material, to better understand the origins of Fe isotope heterogeneity in erupted basalts. By contrast, mineralogical-driven fractionation, regardless of bulk source isotope composition, may be more dominant in systems such as Mg, Ca or Cr, providing a potential tracer of minerals such as garnet present in a basalt's mantle source.

The presence of a MORB-like recycled crustal component in the mantle can account for some, but not all, of the observed global Fe stable isotope variability in basalts. Notably, the range of MORB Fe isotope data suggests that although peridotite is the dominant melting lithology, and can

reproduce the mean MORB Fe isotope composition, a recycled crustal component with an isotopically heavy (relative to ambient mantle) composition is also melting in the MORB source mantle. This conclusion is consistent with a growing body of radiogenic isotope and major element evidence that the MORB mantle is not as homogenous on a small scale as large-scale observations may suggest (e.g., as recently reviewed by Stracke, 2021). The picture for Fe isotope behaviour in OIB is more complicated than MORB: I find that Fe isotopes in OIB reflect a variety of often poorly-understood, difficult-to-distinguish and plume-specific processes that have contributed to variable  $\delta^{57}\text{Fe}$  in the mantle and erupted melts, perhaps partly due to the more varied tectonic settings associated with OIB than MORB. Some OIB, such as Hawai'i, show no Fe isotope evidence of a recycled crustal component, whereas others, such as Pitcairn, the Azores, or rejuvenated Samoan volcanism, record heavy Fe isotope compositions relative to MORB. However, single-stage melting of a MORB-like eclogitic pyroxenite cannot generate the high  $\delta^{57}\text{Fe}$  observed in these locations, and no single additional process (e.g., hydrothermal alteration or metamorphism of downgoing material, lithospheric processing and remobilisation of small-degree melts) can clearly generate the most extreme variability seen in OIB, even after accounting for fractional crystallisation. Therefore, the observation of high  $\delta^{57}\text{Fe}$  OIB melts cannot be ascribed to a unique source or process. This ambiguity reflects the multitude of processes operating from the generation of recycled lithologies through to their mantle melting and eruption at ocean islands.

Although equilibrium Fe isotope fractionation during partial melting of pyroxenite may not be able to explain all observed OIB data, Fe isotopes may have the most sensitivity amongst the Mg-Ca-Fe-V-Cr systems, given current analytical precisions, to the presence of pyroxenite in the mantle source of a basalt. This result is largely due to the process-driven Fe isotopic variability in MORB relative to ambient mantle, compared to the other mostly source-driven systems where MORB is less isotopically distinct from BSE. As exemplified through the Galápagos case study, Fe isotopes can identify small ( $\approx 10\%$ ) pyroxenite fractions in the mantle source of basalts, and may provide more sensitivity to these small pyroxenite fractions than other tracers of mantle lithology, such as olivine trace elements. I also find that Mg and Ca stable isotopes show most sensitivity to a garnet-bearing source lithology, and Cr stable isotopes are also potentially sensitive to the presence of MORB-like pyroxenite in the mantle source. However, the behaviour of Cr isotopes is comparatively under-constrained and requires further work to be applied with confidence to mantle melts.

In some OIB, such as Samoa and Pitcairn, high  $\delta^{57}\text{Fe}$  correlates with radiogenic isotope signatures of enrichment by a crustal component, representing the EM component in radiogenic isotope space. Although previous studies have suggested that the correlations link the EM1 reservoir to an isotopically heavy, secondary reaction-zone pyroxenite (Nebel et al., 2019), the radiogenic and stable isotope composition of this EM reservoir does not seem homogenous, with radiogenic-stable isotope correlations not always existing in OIB suites, or not always trending to the same composition endmembers. This result is consistent with the view that the radiogenic isotope 'end-

members', particularly the EM components, are themselves heterogeneous, rather than a unique and distinct reservoir in the mantle (e.g., Stracke, 2012; White, 2015). Regardless of heterogeneity, the Fe stable isotope composition of the EM(1) reservoir that is required by a top-down approach to understanding stable isotope variability (e.g., Nebel et al., 2019; Gleeson et al., 2020) cannot clearly be explained by the bottom-up approach presented in this thesis. Therefore, there is as yet no clear answer to the question of whether endmember mantle reservoirs identified by radiogenic isotopes have distinct stable isotope signatures that may provide insight into their origin, providing an important category of future work.

Including for Fe isotopes, but also for aspects of the Mg-Ca-V-Cr systems, even when considering analytical uncertainty on natural sample measurements, the range in stable isotope compositions seen across the global MORB and OIB datasets suggests that kinetic isotope fractionation may be required to explain all the natural data. Disequilibrium processes have the potential to produce larger isotopic fractionations than the equilibrium case mostly discussed in this thesis, so may prove to be important in understanding the origins of MORB and particularly OIB stable isotopic variability. These processes may include melt-rock reaction, fluid metasomatism, and fractionation during melt transport and ascent, and would be a key avenue for future research.

## 6.2 Future work

This thesis has highlighted several poorly-constrained processes that could contribute to the full range of heavy stable isotope compositions in basalts. One purpose of the work in this thesis is to highlight where some of the most useful future investigations lie. Below, I outline some of the progress since these chapters were published, ongoing work and potential future projects related to the use of heavy stable isotopes as a tracer of mantle source and process. Broadly, the most pressing upcoming research areas to develop the use of heavy stable isotopes to trace mantle source and process, to complement existing mantle geochemistry tools, should focus on: (i) improving analytical precision, particularly for the Ca, V systems; (ii) a targeted analysis of carefully selected new basalt data, particularly primitive samples that do not require a significant fractional crystallisation correction, as well as those representing the endmember radiogenic mantle components; (iii) an exploration of the magnitude of disequilibrium isotope fractionation effects and their applicability to the stable isotopic composition of basalts.

### 6.2.1 New work using the framework of Soderman et al. (2022)

Earlier this year, the first Cr stable isotope data for MORB was published. Ma et al. (2022) measure the isotopic composition of primitive MORB as  $\delta^{53}\text{Cr} = -0.16 \pm 0.02\text{‰}$ , consistent with the peridotite melting and isotope fractionation results shown in Fig. 4.14. This result validates my

use of the results of the peridotite melting model to estimate the isotopic composition of subducted MORB, which represents the bulk isotopic composition of my recycled crustal endmember in my pyroxenite melting models.

New MORB and OIB Ca isotope data from Eriksen and Jacobsen (2022) also support the results of the isotope framework presented in chapter 4, highlighting the potential of Ca isotopes to trace garnet bearing mantle lithologies if analytical precision can be improved. Their use of a collision cell resulted in a long-term 2 S.D. external reproducibility of only 0.03 ‰, which is sufficiently small to test some of the hypothesis presented in chapter 4. The MORB data from Eriksen and Jacobsen (2022) overlie modelled melts from a peridotite, while some OIB samples record low  $\delta^{44}\text{Ca}$ , which could be consistent with generation from a pyroxenite lithology (Fig. 4.14). With such continued improvements in analytical capabilities, the community may find powerful new stable isotopic tracers of source mineralogy, testing the hypothesis presented in chapter 4, or even be able to distinguish kinetic from equilibrium processes (e.g., for Fe isotopes, Macris et al., 2015; McCoy-West et al., 2018; Ruttor et al., 2022). For example, it could be possible to identify accumulated/fractionated olivine that is not in equilibrium with the melt, such as achieved by McCoy-West et al. (2018), highlighting that requiring extensive fractional crystallisation or olivine addition corrections (which assume equilibrium) to data limits the reliability of resulting primary melt calculations.

## 6.2.2 Linking Fe isotopes to radiogenic isotope endmembers in the mantle

One outstanding question in using stable Fe isotopes (and other isotopic systems) to trace mantle lithology is how Fe isotopes relate to the more traditional tracers of mantle heterogeneity, long-lived radiogenic isotopes. Nebel et al. (2019) show correlations between primary  $\delta^{57}\text{Fe}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$ ,  $^{206}\text{Pb}/^{204}\text{Pb}$  in Pitcairn samples, a trend I also see in my Samoa data (Soderman et al., 2021) [Fig. 3.8, chapter 3] and seen again with the addition of more Samoa data (particularly Malu group volcanoes) from Wang et al. (2021). In these cases, the enriched component (in Nd or Pb isotope space) corresponds to the high  $\delta^{57}\text{Fe}$  component. This correlation exists despite Pitcairn and the Malu group from Samoa showing signatures of different radiogenic mantle endmembers, EM1 and EM2 respectively. By contrast, new Fe isotope data for Kea and Loa trend volcanoes from Hawai'i show no correlations with radiogenic isotope data (Ruttor et al., 2022).

An ongoing project is to collect stable Fe isotope data for a series of extreme enriched mantle component endmembers, to compare to the radiogenic isotope dataset. I will also collect Mg isotope data for the same samples building on the multi-isotope framework outlined in Soderman et al. (2022) [chapter 4]. Selected samples for this study include a dredged glass from the Mid-Atlantic Ridge with low  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$  and high  $^{87}\text{Sr}/^{86}\text{Sr}$ , thought to be tracing a Precambrian garnet-bearing continental lithospheric component (Kamenetsky et al., 2001), and a suite of Pacific seamount samples from Aitutaki, Rarotonga and Tahaa, which show strong enriched mantle (EM1

and EM2) radiogenic isotope signatures (Jackson et al., 2020b).

### 6.2.3 Alternative first-principle calculations for Fe isotope fractionation model

Last year, new first principle calculations of inter-mineral Fe isotope fractionation factors were published by Ségolène Rabin et al. (2021). Their DFT study calculated  $\beta^{\text{Fe}}$  factors for a number of relevant mantle minerals, including clino- and orthopyroxene endmembers, the olivine solid solution and spinel. They find, consistent with fractionation theory and the ionic bonding approach taken for Fe throughout this thesis, that the bonding environment of the Fe in each mineral is the main control on  $\beta^{\text{Fe}}$  factor, but highlight the importance of second atomic neighbours in controlling the isotopic properties of each mineral. Recently, in work presented at the 2022 Goldschmidt conference and in her thesis (Rabin, 2021), Rabin has extended the DFT model to include a variety of silicate melt compositions. She finds that the force constant in a melt is strongly dependent on Fe–O bond length, which relates to the composition of the melt. With this new melt data to supplement the mineral data presented in Rabin et al. (2021), these  $\beta^{\text{Fe}}$  factors could be used in my isotope fractionation model (in non-garnet bearing regions of pressure and temperature space, as garnet  $\beta^{\text{Fe}}$  factors are not yet published) to compare to the ionic bonding approach.

### 6.2.4 Experimental constraints on mineral-melt Fe isotope fractionation

Throughout the work presented in this thesis, one significant uncertainty I encountered was in the mineral-melt Fe isotope fractionations factors, both for correcting for fractional crystallisation and to predict the isotopic effect of different source mineralogies on mantle melts. First-principle calculation estimates, and measurements from natural and experimental samples exist, particularly for olivine-melt Fe isotope fractionation (e.g., Sossi et al., 2016; Prissel et al., 2018, and recent additions by Rabin et al., 2021; Rabin, 2021 as outlined above), but the pyroxene-melt fractionation factor is poorly constrained. Isotope fractionation theory suggests that the pyroxene-melt fractionation factor should be smaller than olivine-melt, because the force constant of Fe in pyroxene should be intermediate between that of olivine and silicate melt. However, ongoing work by Nicole Nie et al., presented by Anat Shahar at the 2022 Goldschmidt conference, suggests that the Fe–O force constant in clinopyroxene (as measured by NRIXS) could instead be significantly stronger than in either olivine or basalt. This result would have important implications for the calculation of primary liquid  $\delta^{57}\text{Fe}$  for samples that have crystallised pyroxene in addition to olivine, and for the ability of a pyroxene-rich mantle lithology to generate isotopic variability in its melts relative to peridotite.

Therefore, to provide a new constraint on pyroxene-melt Fe isotopic fractionation, in March–April 2022 I visited Anat Shahar’s lab at the Earth and Planets Laboratory, Carnegie Institute of Science, Washington, D.C. to perform a series of piston cylinder experiments. Using the synthetic

G2 pyroxenite composition used throughout this thesis, where clinopyroxene is the liquidus phase for a range of pressures (Fig. 2.6), I crystallised clinopyroxene up to 1.5 mm in size at 1 GPa (based on the growth method used by Rudra et al., 2021), using 1/2 inch BaCO<sub>3</sub> assemblies with a graphite capsule. To prove equilibrium (or the lack of) in the resulting data, I spiked the starting mixture with <sup>57</sup>Fe and performed a time series of experiments (allowing for the three isotope method to be used). After each experiment was chemically analysed on the electron probe, I then used a micromill to drill out co-existing pyroxene and glass (quenched melt) separates from each experiment.

The next step of this project will be to calibrate a miniature Fe column chemistry, capable of dealing with Fe levels as low as hundreds of nanograms. The column chemistry has been designed by Peng Ni (published in Smith et al., 2021), and will allow me to process my pyroxene and glass fractions through column chemistry with sufficiently low blanks to measure the isotopic composition of each phase. I should then be able to measure the isotopic composition of pyroxene and glass from each experiment and calculate an equilibrium pyroxene-melt Fe isotope fractionation factor for conditions and compositions directly relevant to mantle melting.

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# Appendix: data tables

**Table 6.1: Fe isotope data from reference materials BIR-1, BCR-2, BHVO-2 and FeCl<sub>3</sub>.** Published literature values: BIR-1  $\delta^{56}\text{Fe} = 0.05$ ,  $\delta^{57}\text{Fe} = 0.09$ ; BCR-2  $\delta^{56}\text{Fe} = 0.09$ ,  $\delta^{57}\text{Fe} = 0.13$ ; BHVO-2  $\delta^{56}\text{Fe} = 0.11$ ,  $\delta^{57}\text{Fe} = 0.17$  (Craddock and Dauphas, 2010).

| Standard                 | Session date   | $\delta^{56}\text{Fe}$ | $\delta^{57}\text{Fe}$ | $\delta^{56}\text{Fe}_{\text{av.}}$ | 2 S.D. | $\delta^{57}\text{Fe}_{\text{av.}}$ | 2 S.D. |
|--------------------------|----------------|------------------------|------------------------|-------------------------------------|--------|-------------------------------------|--------|
| <b>2018–2019 session</b> |                |                        |                        |                                     |        |                                     |        |
| <b>BCR-2</b>             | 20/03/19       | 0.07                   | 0.15                   |                                     |        |                                     |        |
|                          |                | 0.06                   | 0.13                   |                                     |        |                                     |        |
|                          |                | 0.07                   | 0.10                   | 0.07                                | 0.01   | 0.13                                | 0.06   |
|                          | 25–28/03/19    | 0.05                   | 0.12                   |                                     |        |                                     |        |
|                          |                | 0.09                   | 0.15                   |                                     |        |                                     |        |
|                          |                | 0.07                   | 0.10                   |                                     |        |                                     |        |
|                          |                | 0.12                   | 0.19                   |                                     |        |                                     |        |
|                          | 22–25/05/19    | 0.09                   | 0.16                   | 0.08                                | 0.05   | 0.14                                | 0.07   |
|                          |                | 0.10                   | 0.15                   |                                     |        |                                     |        |
|                          |                | 0.08                   | 0.13                   |                                     |        |                                     |        |
|                          |                | 0.07                   | 0.13                   | 0.09                                | 0.03   | 0.13                                | 0.02   |
|                          | 30/07–01/08/19 | 0.08                   | 0.18                   |                                     |        |                                     |        |
|                          |                | 0.08                   | 0.11                   |                                     |        |                                     |        |
|                          |                | 0.10                   | 0.14                   |                                     |        |                                     |        |
|                          |                | 0.08                   | 0.11                   |                                     |        |                                     |        |
|                          |                | 0.06                   | 0.12                   |                                     |        |                                     |        |
|                          |                | 0.10                   | 0.11                   | 0.08                                | 0.03   | 0.13                                | 0.05   |
| <b>BHVO-2</b>            | 26–30/11/18    | 0.09                   | 0.13                   |                                     |        |                                     |        |
|                          |                | 0.09                   | 0.18                   |                                     |        |                                     |        |
|                          |                | 0.10                   | 0.15                   |                                     |        |                                     |        |
|                          |                | 0.12                   | 0.17                   |                                     |        |                                     |        |
|                          |                | 0.11                   | 0.17                   |                                     |        |                                     |        |
|                          |                | 0.10                   | 0.16                   |                                     |        |                                     |        |
|                          |                | 0.12                   | 0.16                   |                                     |        |                                     |        |
|                          |                | 0.11                   | 0.13                   |                                     |        |                                     |        |
|                          |                | 0.11                   | 0.13                   |                                     |        |                                     |        |
|                          |                | 0.12                   | 0.20                   |                                     |        |                                     |        |
|                          |                | 0.11                   | 0.19                   |                                     |        |                                     |        |
|                          |                | 0.09                   | 0.12                   |                                     |        |                                     |        |
|                          |                | 0.10                   | 0.13                   |                                     |        |                                     |        |
|                          |                | 0.13                   | 0.20                   |                                     |        |                                     |        |
|                          |                | 0.13                   | 0.16                   |                                     |        |                                     |        |
|                          |                | 0.12                   | 0.19                   |                                     |        |                                     |        |
|                          |                | 0.14                   | 0.19                   | 0.11                                | 0.03   | 0.16                                | 0.05   |
|                          | 04/12/18       | 0.11                   | 0.18                   |                                     |        |                                     |        |

**Table 6.1:** (continued)

| Standard | Session date   | $\delta^{56}\text{Fe}$ | $\delta^{57}\text{Fe}$ | $\delta^{56}\text{Fe}_{\text{av.}}$ | 2 S.D. | $\delta^{57}\text{Fe}_{\text{av.}}$ | 2 S.D. |
|----------|----------------|------------------------|------------------------|-------------------------------------|--------|-------------------------------------|--------|
|          |                | 0.11                   | 0.14                   |                                     |        |                                     |        |
|          |                | 0.14                   | 0.19                   |                                     |        |                                     |        |
|          |                | 0.11                   | 0.15                   |                                     |        |                                     |        |
|          |                | 0.14                   | 0.18                   |                                     |        |                                     |        |
|          | 25–28/03/19    | 0.12                   | 0.16                   | 0.12                                | 0.03   | 0.17                                | 0.03   |
|          |                | 0.09                   | 0.17                   |                                     |        |                                     |        |
|          |                | 0.09                   | 0.13                   |                                     |        |                                     |        |
|          |                | 0.09                   | 0.15                   |                                     |        |                                     |        |
|          |                | 0.13                   | 0.20                   |                                     |        |                                     |        |
|          |                | 0.11                   | 0.17                   |                                     |        |                                     |        |
|          |                | 0.10                   | 0.14                   |                                     |        |                                     |        |
|          |                | 0.09                   | 0.13                   |                                     |        |                                     |        |
|          |                | 0.10                   | 0.14                   |                                     |        |                                     |        |
|          |                | 0.11                   | 0.19                   |                                     |        |                                     |        |
|          |                | 0.09                   | 0.16                   |                                     |        |                                     |        |
|          | 22–25/05/19    | 0.09                   | 0.15                   | 0.10                                | 0.02   | 0.16                                | 0.04   |
|          |                | 0.13                   | 0.19                   |                                     |        |                                     |        |
|          |                | 0.15                   | 0.22                   |                                     |        |                                     |        |
|          |                | 0.12                   | 0.17                   |                                     |        |                                     |        |
|          |                | 0.13                   | 0.21                   |                                     |        |                                     |        |
|          |                | 0.13                   | 0.21                   |                                     |        |                                     |        |
|          |                | 0.09                   | 0.14                   |                                     |        |                                     |        |
|          |                | 0.12                   | 0.20                   |                                     |        |                                     |        |
|          |                | 0.12                   | 0.19                   |                                     |        |                                     |        |
|          |                | 0.10                   | 0.15                   |                                     |        |                                     |        |
|          |                | 0.13                   | 0.18                   |                                     |        |                                     |        |
|          |                | 0.07                   | 0.13                   |                                     |        |                                     |        |
|          |                | 0.10                   | 0.14                   |                                     |        |                                     |        |
|          |                | 0.13                   | 0.20                   |                                     |        |                                     |        |
|          |                | 0.13                   | 0.18                   |                                     |        |                                     |        |
|          |                | 0.13                   | 0.19                   |                                     |        |                                     |        |
|          |                | 0.11                   | 0.17                   |                                     |        |                                     |        |
|          |                | 0.10                   | 0.17                   |                                     |        |                                     |        |
|          |                | 0.13                   | 0.19                   |                                     |        |                                     |        |
|          |                | 0.12                   | 0.21                   |                                     |        |                                     |        |
|          |                | 0.15                   | 0.20                   |                                     |        |                                     |        |
|          |                | 0.14                   | 0.23                   |                                     |        |                                     |        |
|          |                | 0.13                   | 0.20                   |                                     |        |                                     |        |
|          |                | 0.11                   | 0.14                   |                                     |        |                                     |        |
|          |                | 0.14                   | 0.19                   |                                     |        |                                     |        |
|          |                | 0.12                   | 0.20                   |                                     |        |                                     |        |
|          |                | 0.11                   | 0.18                   |                                     |        |                                     |        |
|          |                | 0.12                   | 0.20                   |                                     |        |                                     |        |
|          | 30/07–01/08/19 | 0.10                   | 0.18                   | 0.12                                | 0.03   | 0.18                                | 0.05   |
|          |                | 0.09                   | 0.16                   |                                     |        |                                     |        |

**Table 6.1:** (continued)

| Standard                | Session date | $\delta^{56}\text{Fe}$ | $\delta^{57}\text{Fe}$ | $\delta^{56}\text{Fe}_{\text{av.}}$ | 2 S.D. | $\delta^{57}\text{Fe}_{\text{av.}}$ | 2 S.D. |
|-------------------------|--------------|------------------------|------------------------|-------------------------------------|--------|-------------------------------------|--------|
|                         | 13/08/19     | 0.08                   | 0.14                   |                                     |        |                                     |        |
|                         |              | 0.10                   | 0.12                   |                                     |        |                                     |        |
|                         |              | 0.11                   | 0.19                   |                                     |        |                                     |        |
|                         |              | 0.08                   | 0.10                   |                                     |        |                                     |        |
|                         |              | 0.09                   | 0.15                   |                                     |        |                                     |        |
|                         |              | 0.11                   | 0.21                   |                                     |        |                                     |        |
|                         |              | 0.11                   | 0.19                   | 0.10                                | 0.02   | 0.16                                | 0.07   |
|                         |              | 0.12                   | 0.17                   |                                     |        |                                     |        |
|                         |              | 0.10                   | 0.15                   |                                     |        |                                     |        |
|                         |              | 0.12                   | 0.19                   |                                     |        |                                     |        |
|                         |              | 0.12                   | 0.17                   | 0.11                                | 0.02   | 0.17                                | 0.03   |
|                         |              |                        |                        |                                     |        |                                     |        |
| <b>BIR-1</b>            | 26–30/11/18  | 0.04                   | 0.06                   |                                     |        |                                     |        |
|                         |              | 0.04                   | 0.05                   |                                     |        |                                     |        |
|                         |              | 0.04                   | 0.05                   |                                     |        |                                     |        |
|                         |              | 0.09                   | 0.11                   |                                     |        |                                     |        |
|                         |              | 0.05                   | 0.08                   |                                     |        |                                     |        |
|                         |              | 0.05                   | 0.09                   |                                     |        |                                     |        |
|                         |              | 0.02                   | 0.05                   |                                     |        |                                     |        |
|                         |              | 0.04                   | 0.06                   | 0.05                                | 0.04   | 0.07                                | 0.04   |
| <b>FeCl<sub>3</sub></b> | 20/03/19     | −0.73                  | −1.05                  |                                     |        |                                     |        |
|                         |              | −0.72                  | −1.05                  |                                     |        |                                     |        |
|                         |              | −0.71                  | −1.04                  |                                     |        |                                     |        |
|                         |              | −0.72                  | −1.05                  |                                     |        |                                     |        |
|                         |              | −0.71                  | −1.06                  | −0.72                               | 0.02   | −1.05                               | 0.01   |
|                         | 25–28/03/19  | −0.74                  | −1.10                  |                                     |        |                                     |        |
|                         |              | −0.71                  | −1.06                  |                                     |        |                                     |        |
|                         |              | −0.74                  | −1.07                  |                                     |        |                                     |        |
|                         |              | −0.73                  | −1.09                  |                                     |        |                                     |        |
|                         |              | −0.75                  | −1.09                  |                                     |        |                                     |        |
|                         |              | −0.75                  | −1.11                  |                                     |        |                                     |        |
|                         |              | −0.73                  | −1.10                  |                                     |        |                                     |        |
|                         |              | −0.75                  | −1.13                  |                                     |        |                                     |        |
|                         |              | −0.73                  | −1.11                  |                                     |        |                                     |        |
|                         |              | −0.74                  | −1.09                  |                                     |        |                                     |        |
|                         |              | −0.73                  | −1.10                  |                                     |        |                                     |        |
|                         |              | −0.74                  | −1.01                  |                                     |        |                                     |        |
|                         |              | −0.73                  | −1.11                  |                                     |        |                                     |        |
|                         |              | −0.75                  | −1.12                  |                                     |        |                                     |        |
|                         |              | −0.73                  | −1.04                  |                                     |        |                                     |        |
|                         |              | −0.74                  | −1.10                  |                                     |        |                                     |        |
|                         |              | −0.69                  | −1.05                  |                                     |        |                                     |        |
|                         |              | −0.69                  | −1.04                  |                                     |        |                                     |        |
|                         |              | −0.73                  | −1.06                  |                                     |        |                                     |        |
|                         |              | −0.74                  | −1.10                  |                                     |        |                                     |        |
|                         |              | −0.74                  | −1.10                  |                                     |        |                                     |        |

**Table 6.1:** (continued)

| Standard | Session date   | $\delta^{56}\text{Fe}$ | $\delta^{57}\text{Fe}$ | $\delta^{56}\text{Fe}_{\text{av.}}$ | 2 S.D. | $\delta^{57}\text{Fe}_{\text{av.}}$ | 2 S.D. |
|----------|----------------|------------------------|------------------------|-------------------------------------|--------|-------------------------------------|--------|
|          |                | -0.75                  | -1.12                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.11                  |                                     |        |                                     |        |
|          |                | -0.75                  | -1.11                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.10                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.09                  |                                     |        |                                     |        |
|          | 22-25/05/19    | -0.73                  | -1.11                  | -0.73                               | 0.03   | -1.09                               | 0.06   |
|          |                | -0.75                  | -1.10                  |                                     |        |                                     |        |
|          |                | -0.75                  | -1.10                  |                                     |        |                                     |        |
|          |                | -0.76                  | -1.09                  |                                     |        |                                     |        |
|          |                | -0.76                  | -1.09                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.08                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.08                  |                                     |        |                                     |        |
|          |                | -0.76                  | -1.10                  |                                     |        |                                     |        |
|          |                | -0.76                  | -1.10                  |                                     |        |                                     |        |
|          |                | -0.75                  | -1.08                  |                                     |        |                                     |        |
|          |                | -0.75                  | -1.11                  |                                     |        |                                     |        |
|          |                | -0.77                  | -1.10                  |                                     |        |                                     |        |
|          |                | -0.76                  | -1.12                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.06                  |                                     |        |                                     |        |
|          |                | -0.73                  | -1.09                  |                                     |        |                                     |        |
|          |                | -0.76                  | -1.12                  |                                     |        |                                     |        |
|          |                | -0.76                  | -1.12                  |                                     |        |                                     |        |
|          |                | -0.71                  | -1.07                  |                                     |        |                                     |        |
|          |                | -0.72                  | -1.07                  |                                     |        |                                     |        |
|          |                | -0.75                  | -1.10                  |                                     |        |                                     |        |
|          |                | -0.78                  | -1.11                  |                                     |        |                                     |        |
|          |                | -0.73                  | -1.04                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.09                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.10                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.09                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.11                  |                                     |        |                                     |        |
|          |                | -0.73                  | -1.08                  |                                     |        |                                     |        |
|          |                | -0.75                  | -1.07                  |                                     |        |                                     |        |
|          |                | -0.72                  | -1.05                  |                                     |        |                                     |        |
|          | 30/07-01/08/19 | -0.73                  | -1.08                  | -0.75                               | 0.03   | -1.09                               | 0.04   |
|          |                | -0.72                  | -1.05                  |                                     |        |                                     |        |
|          |                | -0.70                  | -1.08                  |                                     |        |                                     |        |
|          |                | -0.72                  | -1.09                  |                                     |        |                                     |        |
|          |                | -0.72                  | -1.12                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.15                  |                                     |        |                                     |        |
|          |                | -0.72                  | -1.05                  |                                     |        |                                     |        |
|          |                | -0.73                  | -1.08                  |                                     |        |                                     |        |
|          |                | -0.75                  | -1.10                  |                                     |        |                                     |        |
|          |                | -0.72                  | -1.06                  |                                     |        |                                     |        |
|          |                | -0.74                  | -1.10                  |                                     |        |                                     |        |

**Table 6.1:** (continued)

| Standard          | Session date   | $\delta^{56}\text{Fe}$ | $\delta^{57}\text{Fe}$ | $\delta^{56}\text{Fe}_{\text{av.}}$ | 2 S.D. | $\delta^{57}\text{Fe}_{\text{av.}}$ | 2 S.D. |
|-------------------|----------------|------------------------|------------------------|-------------------------------------|--------|-------------------------------------|--------|
|                   | 13/08/19       | −0.69                  | −1.10                  |                                     |        |                                     |        |
|                   |                | −0.73                  | −1.11                  |                                     |        |                                     |        |
|                   |                | −0.72                  | −1.08                  |                                     |        |                                     |        |
|                   |                | −0.72                  | −1.06                  |                                     |        |                                     |        |
|                   |                | −0.73                  | −1.07                  |                                     |        |                                     |        |
|                   |                | −0.74                  | −1.08                  |                                     |        |                                     |        |
|                   |                | −0.76                  | −1.08                  |                                     |        |                                     |        |
|                   |                | −0.73                  | −1.05                  | −0.73                               | 0.03   | −1.08                               | 0.05   |
|                   |                | −0.70                  | −1.06                  |                                     |        |                                     |        |
|                   |                | −0.70                  | −1.07                  |                                     |        |                                     |        |
|                   |                | −0.75                  | −1.13                  |                                     |        |                                     |        |
|                   |                | −0.73                  | −1.10                  |                                     |        |                                     |        |
|                   |                | −0.72                  | −1.07                  |                                     |        |                                     |        |
|                   |                | −0.74                  | −1.08                  |                                     |        |                                     |        |
|                   |                | −0.72                  | −1.06                  | −0.72                               | 0.04   | −1.08                               | 0.05   |
| 2021–2022 session |                |                        |                        |                                     |        |                                     |        |
| BCR-2             | 09–10/12/21    | 0.10                   | 0.13                   |                                     |        |                                     |        |
|                   |                | 0.10                   | 0.13                   |                                     |        |                                     |        |
|                   |                | 0.09                   | 0.17                   |                                     |        |                                     |        |
|                   |                | 0.10                   | 0.13                   |                                     |        |                                     |        |
|                   |                | 0.10                   | 0.14                   |                                     |        |                                     |        |
|                   | 02–04/02/22    | 0.07                   | 0.15                   | 0.09                                | 0.02   | 0.14                                | 0.03   |
|                   |                | 0.12                   | 0.19                   |                                     |        |                                     |        |
|                   |                | 0.11                   | 0.17                   |                                     |        |                                     |        |
|                   |                | 0.10                   | 0.14                   |                                     |        |                                     |        |
|                   |                | 0.10                   | 0.18                   |                                     |        |                                     |        |
|                   |                | 0.07                   | 0.14                   |                                     |        |                                     |        |
|                   |                | 0.09                   | 0.15                   |                                     |        |                                     |        |
|                   |                | 0.13                   | 0.18                   |                                     |        |                                     |        |
|                   |                | 0.11                   | 0.15                   | 0.10                                | 0.04   | 0.16                                | 0.04   |
|                   |                |                        |                        |                                     |        |                                     |        |
| BHVO-2            | 30/11–02/12/21 | 0.10                   | 0.15                   |                                     |        |                                     |        |
|                   |                | 0.09                   | 0.16                   |                                     |        |                                     |        |
|                   |                | 0.11                   | 0.15                   |                                     |        |                                     |        |
|                   |                | 0.10                   | 0.15                   |                                     |        |                                     |        |
|                   |                | 0.11                   | 0.18                   |                                     |        |                                     |        |
|                   |                | 0.12                   | 0.14                   |                                     |        |                                     |        |
|                   |                | 0.10                   | 0.14                   |                                     |        |                                     |        |
|                   |                | 0.10                   | 0.16                   |                                     |        |                                     |        |
|                   |                | 0.10                   | 0.18                   |                                     |        |                                     |        |
|                   |                | 0.09                   | 0.19                   | 0.10                                | 0.02   | 0.16                                | 0.04   |
|                   | 09–10/12/21    | 0.13                   | 0.21                   |                                     |        |                                     |        |
|                   |                | 0.11                   | 0.17                   |                                     |        |                                     |        |
|                   |                | 0.10                   | 0.15                   |                                     |        |                                     |        |
|                   |                | 0.13                   | 0.16                   |                                     |        |                                     |        |
|                   |                |                        |                        |                                     |        |                                     |        |

**Table 6.1:** (continued)

| Standard                | Session date   | $\delta^{56}\text{Fe}$ | $\delta^{57}\text{Fe}$ | $\delta^{56}\text{Fe}_{\text{av.}}$ | 2 S.D. | $\delta^{57}\text{Fe}_{\text{av.}}$ | 2 S.D. |
|-------------------------|----------------|------------------------|------------------------|-------------------------------------|--------|-------------------------------------|--------|
|                         | 02–04/02/22    | 0.10                   | 0.12                   |                                     |        |                                     |        |
|                         |                | 0.11                   | 0.18                   |                                     |        |                                     |        |
|                         |                | 0.13                   | 0.15                   |                                     |        |                                     |        |
|                         |                | 0.12                   | 0.21                   |                                     |        |                                     |        |
|                         |                | 0.14                   | 0.19                   | 0.12                                | 0.03   | 0.17                                | 0.06   |
|                         |                | 0.09                   | 0.17                   |                                     |        |                                     |        |
|                         |                | 0.14                   | 0.20                   |                                     |        |                                     |        |
|                         |                | 0.11                   | 0.17                   |                                     |        |                                     |        |
|                         |                | 0.11                   | 0.17                   |                                     |        |                                     |        |
|                         |                | 0.14                   | 0.20                   |                                     |        |                                     |        |
|                         |                | 0.12                   | 0.17                   | 0.12                                | 0.04   | 0.18                                | 0.03   |
| <b>BIR-1</b>            | 30/11–02/12/21 | 0.03                   | 0.11                   |                                     |        |                                     |        |
|                         |                | 0.06                   | 0.10                   |                                     |        |                                     |        |
|                         |                | 0.07                   | 0.11                   |                                     |        |                                     |        |
|                         |                | 0.06                   | 0.09                   |                                     |        |                                     |        |
|                         | 09–10/12/21    | 0.05                   | 0.10                   | 0.05                                | 0.03   | 0.10                                | 0.02   |
|                         |                | 0.06                   | 0.12                   |                                     |        |                                     |        |
|                         |                | 0.05                   | 0.11                   |                                     |        |                                     |        |
|                         |                | 0.09                   | 0.11                   |                                     |        |                                     |        |
|                         | 02–04/02/22    | 0.06                   | 0.12                   |                                     |        |                                     |        |
|                         |                | 0.06                   | 0.07                   | 0.07                                | 0.03   | 0.11                                | 0.04   |
|                         |                | 0.04                   | 0.10                   |                                     |        |                                     |        |
|                         |                | 0.06                   | 0.09                   |                                     |        |                                     |        |
|                         |                | 0.03                   | 0.08                   |                                     |        |                                     |        |
|                         |                | 0.04                   | 0.07                   |                                     |        |                                     |        |
|                         |                | 0.05                   | 0.07                   |                                     |        |                                     |        |
|                         |                | 0.03                   | 0.06                   | 0.04                                | 0.02   | 0.08                                | 0.03   |
| <b>FeCl<sub>3</sub></b> | 30/11–02/12/21 | –0.71                  | –1.08                  |                                     |        |                                     |        |
|                         |                | –0.75                  | –1.13                  |                                     |        |                                     |        |
|                         |                | –0.75                  | –1.10                  |                                     |        |                                     |        |
|                         |                | –0.78                  | –1.16                  |                                     |        |                                     |        |
|                         |                | –0.75                  | –1.11                  |                                     |        |                                     |        |
|                         |                | –0.78                  | –1.14                  |                                     |        |                                     |        |
|                         |                | –0.77                  | –1.13                  |                                     |        |                                     |        |
|                         |                | –0.72                  | –1.10                  |                                     |        |                                     |        |
|                         |                | –0.74                  | –1.11                  |                                     |        |                                     |        |
|                         |                | –0.74                  | –1.12                  |                                     |        |                                     |        |
|                         |                | –0.74                  | –1.12                  |                                     |        |                                     |        |
|                         |                | –0.71                  | –1.06                  |                                     |        |                                     |        |
|                         |                | –0.75                  | –1.14                  |                                     |        |                                     |        |
|                         | 09–10/12/21    | –0.74                  | –1.11                  | –0.75                               | 0.04   | –1.12                               | 0.05   |
|                         |                | –0.77                  | –1.11                  |                                     |        |                                     |        |
|                         |                | –0.75                  | –1.12                  |                                     |        |                                     |        |
|                         |                | –0.73                  | –1.10                  |                                     |        |                                     |        |
|                         |                | –0.76                  | –1.14                  |                                     |        |                                     |        |

**Table 6.1:** (continued)

| Standard | Session date | $\delta^{56}\text{Fe}$ | $\delta^{57}\text{Fe}$ | $\delta^{56}\text{Fe}_{\text{av.}}$ | 2 S.D. | $\delta^{57}\text{Fe}_{\text{av.}}$ | 2 S.D. |
|----------|--------------|------------------------|------------------------|-------------------------------------|--------|-------------------------------------|--------|
|          |              | -0.75                  | -1.08                  |                                     |        |                                     |        |
|          |              | -0.76                  | -1.12                  |                                     |        |                                     |        |
|          |              | -0.76                  | -1.10                  |                                     |        |                                     |        |
|          |              | -0.77                  | -1.13                  |                                     |        |                                     |        |
|          |              | -0.76                  | -1.09                  | -0.76                               | 0.03   | -1.11                               | 0.04   |
|          | 02-04/02/22  | -0.71                  | -1.08                  |                                     |        |                                     |        |
|          |              | -0.73                  | -1.06                  |                                     |        |                                     |        |
|          |              | -0.73                  | -1.10                  |                                     |        |                                     |        |
|          |              | -0.74                  | -1.09                  |                                     |        |                                     |        |
|          |              | -0.73                  | -1.15                  |                                     |        |                                     |        |
|          |              | -0.76                  | -1.16                  |                                     |        |                                     |        |
|          |              | -0.68                  | -1.06                  |                                     |        |                                     |        |
|          |              | -0.67                  | -1.02                  |                                     |        |                                     |        |
|          |              | -0.76                  | -1.13                  |                                     |        |                                     |        |
|          |              | -0.77                  | -1.15                  |                                     |        |                                     |        |
|          |              | -0.75                  | -1.09                  |                                     |        |                                     |        |
|          |              | -0.75                  | -1.12                  |                                     |        |                                     |        |
|          |              | -0.73                  | -1.09                  |                                     |        |                                     |        |
|          |              | -0.74                  | -1.08                  |                                     |        |                                     |        |
|          |              | -0.77                  | -1.13                  |                                     |        |                                     |        |
|          |              | -0.73                  | -1.12                  |                                     |        |                                     |        |
|          |              | -0.75                  | -1.11                  |                                     |        |                                     |        |
|          |              | -0.72                  | -1.06                  |                                     |        |                                     |        |
|          |              | -0.75                  | -1.04                  |                                     |        |                                     |        |
|          |              | -0.74                  | -1.07                  | -0.74                               | 0.05   | -1.10                               | 0.07   |

**Table 6.2: Fe isotope data for chapter 3.** Azores Fe isotope data collected by Saskia Rutter at Monash University (†) and by Helen Williams at Durham University (§); Samoa Fe isotope data collected by me. Also shown, for reference, are measured Fe/Mn collected by Munir Humayan, and published selected major element and radiogenic isotope data used in the analysis throughout the chapter. Samoa literature data: Workman et al. (2004); Jackson et al. (2007a); Hart and Jackson (2014). Azores literature data: Turner et al. (1997); Beier et al. (2008); Millet et al. (2009); Watanabe (2010); Yu (2011); Beier et al. (2012); Béguélin et al. (2017); Waters et al. (2020). S.E. calculated as  $S.D./\sqrt{n}$ . n = number of repeat analyses. 'rep' represents duplicate dissolution of sample.

| Sample           | Volcano   | $\delta^{56}\text{Fe}$ | 2 S.D. | $\delta^{57}\text{Fe}$ | 2 S.D. | 2 S.E. | n  | MgO   | FeO <sub>T</sub> | Fe/Mn | $^{143}\text{Nd}/^{144}\text{Nd}$ | $^{87}\text{Sr}/^{86}\text{Sr}$ | $^{206}\text{Pb}/^{204}\text{Pb}$ |
|------------------|-----------|------------------------|--------|------------------------|--------|--------|----|-------|------------------|-------|-----------------------------------|---------------------------------|-----------------------------------|
| <b>Samoa</b>     |           |                        |        |                        |        |        |    |       |                  |       |                                   |                                 |                                   |
| ALIA115-18       | Savai'i   | 0.12                   | 0.05   | 0.19                   | 0.05   | 0.02   | 7  | 5.09  | 7.09             |       | 0.51231                           | 0.71859                         | 18.957                            |
| ALIA115-18 rep   | Savai'i   | 0.12                   | 0.04   | 0.21                   | 0.01   | 0.01   | 3  |       |                  |       |                                   |                                 |                                   |
| AVON-3-77-1      | Malumalu  | 0.14                   | 0.03   | 0.21                   | 0.05   | 0.02   | 4  | 7.62  | 12.17            |       | 0.51266                           | 0.70693                         | 19.268                            |
| AVON-3-77-9      | Malumalu  | 0.13                   | 0.06   | 0.19                   | 0.08   | 0.03   | 5  | 8.45  | 11.08            |       | 0.51258                           | 0.70726                         | 19.331                            |
| ALIA106-03       | Malumalu  | 0.14                   | 0.03   | 0.21                   | 0.04   | 0.01   | 8  | 6.56  | 12.97            |       | 0.51265                           | 0.70689                         | 19.291                            |
| AVON-3-78-1      | Malumalu  | 0.10                   | 0.03   | 0.15                   | 0.05   | 0.02   | 9  | 19.68 | 11.89            |       | 0.51252                           | 0.7089                          | 19.237                            |
| ALIA112-02       | Tutuila   | 0.10                   | 0.04   | 0.15                   | 0.07   | 0.02   | 5  | 6.68  | 11.11            |       | 0.51262                           |                                 | 19.264                            |
| AVON-3-76-8      | Malumalu  | 0.12                   | 0.04   | 0.19                   | 0.04   | 0.03   | 6  | 6.27  | 11.93            |       | 0.51267                           | 0.70637                         | 19.294                            |
| OFU-04-14        | Ofu       | 0.07                   | 0.04   | 0.12                   | 0.02   | 0.01   | 8  | 16.02 | 12.7             |       | 0.51282                           | 0.70452                         | 19.126                            |
| AVON-3-73-1      | Vailulu'u | 0.11                   | 0.02   | 0.15                   | 0.04   | 0.01   | 11 | 7.52  | 11.26            |       | 0.51267                           | 0.70672                         | 19.230                            |
| T33              | Ta'u      | 0.12                   | 0.01   | 0.21                   | 0.03   | 0.02   | 5  | 12.4  | 11.61            |       | 0.51278                           | 0.70474                         | 19.284                            |
| OFU-05-18        | Ofu       | 0.07                   | 0.04   | 0.12                   | 0.05   | 0.01   | 6  | 9.81  | 12.78            |       | 0.51283                           | 0.70458                         | 19.189                            |
| AVON-3-70-9      | Vailulu'u | 0.10                   | 0.03   | 0.16                   | 0.04   | 0.02   | 5  | 6.47  | 11.65            |       | 0.51275                           | 0.70535                         | 19.396                            |
| AVON-3-63-2      | Vailulu'u | 0.08                   | 0.06   | 0.13                   | 0.07   | 0.02   | 11 | 23.87 | 10.39            |       | 0.51272                           | 0.70539                         | 19.358                            |
| AVON-3-71-22     | Vailulu'u | 0.05                   | 0.01   | 0.07                   | 0.04   | 0.02   | 2  | 21.79 | 10.77            |       | 0.51275                           | 0.70547                         | 19.358                            |
| AVON-3-71-22 rep | Vailulu'u | 0.08                   | 0.03   | 0.13                   | 0.03   | 0.02   | 3  |       |                  |       |                                   |                                 |                                   |
| <b>Azores</b>    |           |                        |        |                        |        |        |    |       |                  |       |                                   |                                 |                                   |
| SJ01†            | São Jorge | 0.20                   | 0.02   | 0.34                   | 0.05   | 0.02   | 5  | 8.24  | 10.43            | 63.1  | 0.512900                          | 0.703743                        | 19.347                            |
| SJ05 †           | São Jorge | 0.13                   | 0.06   | 0.24                   | 0.05   | 0.03   | 4  | 8.95  | 12.05            |       | 0.512983                          | 0.703715                        | 20.047                            |
| SJ07†            | São Jorge | 0.14                   | 0.02   | 0.24                   | 0.08   | 0.03   | 6  | 8.45  | 11.56            |       | 0.512959                          | 0.703752                        | 20.511                            |
| SJ50†            | São Jorge | 0.14                   | 0.04   | 0.22                   | 0.06   | 0.03   | 3  | 8.84  | 10.70            |       | 0.512956                          | 0.703761                        | 20.177                            |
| SJ51†            | São Jorge | 0.18                   | 0.04   | 0.23                   | 0.03   | 0.02   | 5  | 11.99 | 11.18            |       | 0.512980                          | 0.703742                        | 20.127                            |
| SJ52 †           | São Jorge | 0.14                   | 0.02   | 0.23                   | 0.03   | 0.01   | 6  | 8.20  | 11.59            |       | 0.512955                          | 0.703745                        | 20.507                            |
| SJ30 †           | São Jorge | 0.17                   | 0.05   | 0.28                   | 0.07   | 0.04   | 3  | 9.70  | 11.32            | 68.5  | 0.512831                          | 0.703502                        | 19.631                            |

Table 6.2: (continued)

| Sample                 | Volcano        | $\delta^{56}\text{Fe}$ | 2 S.D. | $\delta^{57}\text{Fe}$ | 2 S.D. | 2 S.E. | n | MgO   | FeO <sub>T</sub> | Fe/Mn | $^{143}\text{Nd}/^{144}\text{Nd}$ | $^{87}\text{Sr}/^{86}\text{Sr}$ | $^{206}\text{Pb}/^{204}\text{Pb}$ |
|------------------------|----------------|------------------------|--------|------------------------|--------|--------|---|-------|------------------|-------|-----------------------------------|---------------------------------|-----------------------------------|
| SJ31b <sup>†</sup>     | São Jorge      | 0.25                   | 0.09   | 0.28                   | 0.04   | 0.02   | 3 | 8.91  | 12.40            | 72.6  | 0.512835                          | 0.703481                        | 19.823                            |
| WASJ18 <sup>†</sup>    | São Jorge      | 0.20                   | 0.06   | 0.28                   | 0.06   | 0.02   | 6 | 9.72  | 10.35            | 64.9  | 0.512916                          | 0.70350                         | 19.691                            |
| T2 <sup>†</sup>        | Terceira       | 0.12                   | 0.03   | 0.14                   | 0.03   | 0.02   | 3 | 5.54  | 10.53            | 51.6  | 0.51296                           | 0.70352                         | 19.883                            |
| T6 <sup>†</sup>        | Terceira       | 0.14                   | 0.05   | 0.16                   | 0.04   | 0.02   | 3 | 8.70  | 11.03            | 59.8  | 0.51292                           | 0.70348                         | 19.381                            |
| T18 <sup>†</sup>       | Terceira       | 0.16                   | 0.04   | 0.22                   | 0.02   | 0.01   | 5 | 7.94  | 10.48            | 58.0  | 0.51290                           | 0.70355                         | 19.736                            |
| WAT3 <sup>†</sup>      | Terceira       | 0.15                   | 0.02   | 0.20                   | 0.02   | 0.01   | 4 | 11.80 | 8.72             | 58.4  | 0.51291                           | 0.70344                         | 19.768                            |
| AZT-03-12 <sup>§</sup> | Terceira       | 0.02                   | 0.00   | 0.05                   | 0.03   | 0.02   | 3 | 5.45  | 12.44            |       | 0.512981                          | 0.703420                        | 19.640                            |
| AZT-03-16 <sup>§</sup> | Terceira       | 0.07                   | 0.04   | 0.13                   | 0.03   | 0.02   | 3 | 5.67  | 10.88            |       | 0.512993                          | 0.703491                        | 20.020                            |
| P4 <sup>†</sup>        | Pico           | 0.14                   | 0.04   | 0.18                   | 0.03   | 0.02   | 2 | 10.36 | 9.94             | 61.2  | 0.512818                          | 0.703788                        | 19.589                            |
| P5 <sup>†</sup>        | Pico           | 0.20                   | 0.06   | 0.24                   | 0.02   | 0.02   | 2 | 9.63  | 9.80             | 60.8  | 0.512887                          | 0.703756                        | 19.538                            |
| P25 <sup>†</sup>       | Pico           | 0.18                   | 0.05   | 0.22                   | 0.05   | 0.02   | 5 | 8.24  | 9.99             | 60.9  | 0.51290                           | 0.70379                         | 19.614                            |
| P26 <sup>†</sup>       | Pico           | 0.16                   | 0.03   | 0.24                   | 0.05   | 0.02   | 6 | 10.83 | 10.28            | 61.8  | 0.512813                          | 0.70380                         | 19.653                            |
| P29 <sup>†</sup>       | Pico           | 0.22                   | 0.08   | 0.28                   | 0.05   | 0.02   | 4 | 8.16  | 9.31             | 53.9  | 0.512813                          | 0.70377                         | 19.711                            |
| WAP9 <sup>†</sup>      | Pico           | 0.15                   | 0.03   | 0.17                   | 0.06   | 0.04   | 2 | 13.21 | 9.14             | 62.0  | 0.51287                           | 0.70393                         | 19.476                            |
| AZP-03-10 <sup>§</sup> | Pico           | 0.16                   | 0.03   | 0.24                   | 0.03   | 0.02   | 3 | 6.60  | 10.86            |       | 0.512963                          | 0.703535                        | 20.010                            |
| AZP-03-23 <sup>§</sup> | Pico           | 0.17                   | 0.04   | 0.25                   | 0.05   | 0.03   | 3 | 5.79  | 11.44            |       | 0.512976                          | 0.703500                        | 19.870                            |
| AZP-03-50 <sup>§</sup> | Pico           | 0.17                   | 0.02   | 0.27                   | 0.00   | 0.00   | 3 | 6.00  | 10.56            |       | 0.512916                          | 0.703716                        | 19.910                            |
| F/FG-28 <sup>†</sup>   | Faial          | 0.18                   | 0.06   | 0.26                   | 0.03   | 0.01   | 5 | 8.13  | 9.75             |       | 0.51284                           | 0.70385                         | 19.011                            |
| F/CP-18 <sup>†</sup>   | Faial          | 0.20                   | 0.03   | 0.27                   | 0.02   | 0.01   | 6 | 7.83  | 9.32             | 60.8  | 0.51287                           | 0.70398                         | 19.107                            |
| F/CA-6 <sup>†</sup>    | Faial          | 0.20                   | 0.03   | 0.26                   | 0.04   | 0.02   | 5 | 9.73  | 9.66             | 63.3  | 0.51293                           | 0.70377                         | 19.117                            |
| F/CA-24 <sup>†</sup>   | Faial          | 0.15                   | 0.07   | 0.19                   | 0.03   | 0.02   | 4 | 13.99 | 10.21            | 62.0  | 0.512864                          | 0.703908                        | 19.560                            |
| WAF1a <sup>†</sup>     | Faial          | 0.14                   | 0.08   | 0.26                   | 0.05   | 0.03   | 4 | 13.51 | 9.77             | 63.8  | 0.51286                           | 0.70388                         | 19.579                            |
| AZF-03-11 <sup>§</sup> | Faial          | 0.23                   | 0.01   | 0.34                   | 0.03   | 0.02   | 3 | 5.47  | 9.73             |       | 0.512881                          | 0.703840                        | 19.620                            |
| 525DS2 <sup>§</sup>    | João de Castro | 0.14                   | 0.02   | 0.27                   | 0.00   | 0.00   | 3 | 15.78 | 10.74            |       | 0.512873                          | 0.703361                        | 19.180                            |
| 523DS2 <sup>§</sup>    | João de Castro | 0.15                   | 0.01   | 0.21                   | 0.05   | 0.03   | 2 | 6.25  | 9.34             |       | 0.512827                          | 0.703784                        | 18.999                            |
| AZG-03-07 <sup>§</sup> | Graciosa       | 0.26                   | 0.04   | 0.37                   | 0.02   | 0.01   | 2 | 8.17  | 10.36            |       | 0.512897                          | 0.703647                        | 19.300                            |
| AZG-03-28 <sup>§</sup> | Graciosa       | 0.18                   | 0.02   | 0.27                   | 0.08   | 0.04   | 3 | 7.02  | 9.52             |       | 0.512962                          | 0.703373                        | 19.880                            |

**Table 6.3: Fe isotope data for chapter 5.** Also shown are reference major and trace element data from the literature used in analyses throughout the chapter: Tortugal from Trela et al. (2017); Gorgona from Echeverría (1980); Aitken and Echeverría (1984); Ludwig (2017); Curaçao from Trela et al. (2017); Azuero from Gazel et al. (2018); Quepos from Trela et al. (2015); Galápagos from Geist et al. (1998); Naumann et al. (2002); Geist et al. (2005); Handley et al. (2011); Harpp et al. (2014b); Harpp and Weis (2020) and Dennis Geist (pers. comm.) for sample FLO3-128. For Gorgona samples, the Smithsonian catalogue's reference numbers are given in column 1. The lithological classification of Tortugal, Azuero, Quepos, and Curaçao samples by E. Gazel, and of Gorgona samples by L. Echeverría is also given.

| Locality                     | Sample       | Lithology | Measured in    | $\delta^{56}\text{Fe}$ | 2 S.D. | $\delta^{57}\text{Fe}$ | 2 S.D. | n  | 2 S.E. ( $\delta^{57}\text{Fe}$ ) | MgO   | FeO <sub>T</sub> | La    | Sm   |
|------------------------------|--------------|-----------|----------------|------------------------|--------|------------------------|--------|----|-----------------------------------|-------|------------------|-------|------|
| <b>Tortugal</b>              | TO-010513-1  | Picrite   | 2019           | 0.02                   | 0.02   | 0.05                   | 0.02   | 6  | 0.01                              | 28.24 | 11.77            | 5.75  | 1.8  |
|                              | TO-010513-3  | Basalt    | 2019           | 0.07                   | 0.03   | 0.13                   | 0.06   | 6  | 0.03                              | 7.28  | 10.94            | 23.93 | 6.09 |
|                              | TO-010513-4  | Basalt    | 2019           | 0.06                   | 0.04   | 0.11                   | 0.05   | 8  | 0.02                              | 6.28  | 10.98            | 25.79 | 6.34 |
|                              | TO-010513-7  | Picrite   | 2019           | -0.01                  | 0.02   | -0.02                  | 0.04   | 7  | 0.01                              | 29.21 | 11.89            | 12    | 2.89 |
|                              | TO-010613-10 | Picrite   | 2019           | 0.02                   | 0.04   | 0.03                   | 0.04   | 8  | 0.01                              | 27.13 | 12.02            | 10.3  | 2.56 |
| <b>Gorgona NMNH 118183-4</b> | TO-080514-1  | Picrite   | 2021           | 0.02                   | 0.03   | 0.05                   | 0.04   | 5  | 0.02                              | 33.69 | 11.75            | 9.98  | 2.32 |
|                              | GOR 2P       | Komatiite | 2019           | 0.03                   | 0.04   | 0.06                   | 0.05   | 9  | 0.02                              | 18.9  | 10.60            |       | 1.35 |
|                              | GOR 6A       | Basalt    | 2019           | 0.04                   | 0.02   | 0.08                   | 0.02   | 6  | 0.01                              | 7.41  | 13.10            |       | 2.58 |
|                              | GOR 23A      | Basalt    | 2019           | 0.06                   | 0.03   | 0.09                   | 0.07   | 8  | 0.02                              | 5.25  | 13.40            |       | 3.01 |
|                              | GOR 23B      | Komatiite | 2019           | 0.01                   | 0.03   | 0.03                   | 0.07   | 9  | 0.02                              | 18    | 12.50            |       |      |
| <b>NMNH 118183-103</b>       | GOR 111      | Basalt    | 2019           | 0.05                   | 0.03   | 0.09                   | 0.02   | 6  | 0.01                              | 6.97  | 12.46            |       | 2.78 |
|                              | GOR 38       | Komatiite | 2019           | 0.04                   | 0.03   | 0.07                   | 0.05   | 6  | 0.02                              | 15.8  | 11.30            |       | 1.3  |
|                              | PC5          | Komatiite | 2019           | 0.03                   | 0.04   | 0.05                   | 0.07   | 9  | 0.03                              |       |                  |       |      |
|                              | GOR 42D      | Komatiite | 2019           | -0.02                  | 0.04   | -0.02                  | 0.08   | 9  | 0.03                              |       |                  |       |      |
|                              | GOR 153      | Komatiite | 2019           | 0.03                   | 0.02   | 0.05                   | 0.03   | 6  | 0.01                              | 23.8  | 12.22            |       |      |
| <b>Curaçao</b>               | CUR-13       | Picrite   | 2019           | 0.03                   | 0.03   | 0.04                   | 0.05   | 7  | 0.02                              | 10.86 | 9.07             | 1.67  | 1.26 |
|                              | CUR-14       | Basalt    | 2019           | 0.02                   | 0.06   | 0.03                   | 0.09   | 5  |                                   |       |                  |       |      |
|                              | CUR-14       |           | 2021           | 0.04                   | 0.03   | 0.06                   | 0.05   | 5  |                                   |       |                  |       |      |
|                              |              |           | <i>average</i> | 0.03                   | 0.05   | 0.04                   | 0.07   | 10 | 0.02                              | 9.19  | 9.25             | 1.81  | 1.48 |
|                              | CUR-19       | Basalt    | 2019           | 0.05                   | 0.04   | 0.09                   | 0.05   | 9  | 0.02                              | 5.41  | 13.44            | 4.42  | 2.98 |
| <b>NMNH 118183-72</b>        | CUR-20       | Basalt    | 2019           | 0.03                   | 0.03   | 0.07                   | 0.03   | 9  | 0.01                              | 7.12  | 11.50            | 3.28  | 2.4  |
|                              | CUR-11       | Picrite   | 2021           | 0.02                   | 0.01   | 0.05                   | 0.02   | 4  | 0.01                              | 26.02 | 11.18            | 1.81  | 1.01 |
|                              | CUR-02       | Picrite   | 2021           | 0.06                   | 0.04   | 0.07                   | 0.01   | 4  | 0.01                              | 21.45 | 11.04            | 2.22  | 1.49 |
|                              | CUR-04       | Picrite   | 2021           | 0.05                   | 0.02   | 0.07                   | 0.03   | 6  | 0.01                              | 20.11 | 10.67            | 2.31  | 1.39 |
|                              | CUR-09       | Basalt    | 2021           | 0.06                   | 0.03   | 0.11                   | 0.05   | 6  | 0.02                              | 8.52  | 10.12            | 3.2   | 1.96 |

Table 6.3: (continued)

| Locality                 | Sample       | Lithology | Measured in | $\delta^{56}\text{Fe}$ | 2 S.D. | $\delta^{57}\text{Fe}$ | 2 S.D. | n  | 2 S.E. ( $\delta^{57}\text{Fe}$ ) | MgO   | FeO <sub>T</sub>                        | La    | Sm   |
|--------------------------|--------------|-----------|-------------|------------------------|--------|------------------------|--------|----|-----------------------------------|-------|-----------------------------------------|-------|------|
| Azuero                   | CUR-06       | Basalt    | 2021        | 0.05                   | 0.03   | 0.07                   | 0.03   | 8  | 0.01                              | 8.22  | 10.17                                   | 4.03  | 2.27 |
|                          | CUR-12       | Basalt    | 2021        | 0.06                   | 0.04   | 0.1                    | 0.02   | 4  | 0.01                              | 9.17  | 9.73                                    | 2.16  | 1.68 |
|                          | AZ-090913-2  | Basalt    | 2019        | 0.06                   | 0.01   | 0.10                   | 0.03   | 6  | 0.01                              | 10.16 | 10.35                                   | 13.79 | 6.91 |
|                          | AZ-091613-12 | Picrite   | 2019        | -0.03                  | 0.02   | -0.05                  | 0.08   | 8  | 0.03                              | 33.96 | 12.20                                   | 8.35  | 2.95 |
|                          | AZ-091613-15 | Basalt    | 2019        | 0.07                   | 0.02   | 0.10                   | 0.06   | 3  | 0.03                              | 8.01  | 11.42                                   | 3.47  | 2.87 |
|                          | AZ-091713-18 | Basalt    | 2019        | 0.13                   | 0.02   | 0.18                   | 0.05   | 6  | 0.02                              | 5.91  | 12.19                                   | 27.93 | 8.86 |
|                          | AZ-091713-19 | Picrite   | 2019        | 0.02                   | 0.03   | 0.05                   | 0.04   | 12 | 0.01                              | 20.75 | 11.66                                   | 14.28 | 4.99 |
|                          | AZ-091613-13 | Basalt    | 2021        | 0.12                   | 0.03   | 0.17                   | 0.03   | 6  | 0.01                              | 7.40  | 10.98                                   | 19.55 | 6.75 |
|                          | AZ-091713-17 | Basalt    | 2021        | 0.12                   | 0.03   | 0.19                   | 0.05   | 8  | 0.02                              | 11.12 | 10.29                                   | 19.07 | 6.25 |
| Quepos                   | QP-121211-6  | Basalt    | 2019        | 0.12                   | 0.03   | 0.18                   | 0.04   | 6  | 0.02                              | 7.01  | 11.19                                   | 13.9  | 5.75 |
|                          | QP-121211-7  | Picrite   | 2019        | 0.02                   | 0.04   | 0.04                   | 0.05   | 5  | 0.02                              | 27.74 | 11.58                                   | 5.74  | 2.57 |
|                          | QP-121211-8  | Basalt    | 2019        | 0.13                   | 0.02   | 0.20                   | 0.06   | 5  | 0.03                              | 7.10  | 10.46                                   | 15.02 | 6.12 |
|                          | QP-121211-9  | Picrite   | 2019        | 0.06                   | 0.02   | 0.10                   | 0.04   | 5  | 0.03                              | 21.46 | 11.06                                   | 6.88  | 3.2  |
|                          | QP-121211-10 | Picrite   | 2019        | 0.02                   | 0.05   | 0.05                   | 0.04   | 6  | 0.02                              | 30.39 | 11.45                                   | 5.23  | 2.37 |
|                          | QP-121311-11 | Diabase   | 2019        | 0.11                   | 0.03   | 0.14                   | 0.06   | 6  | 0.02                              | 10.22 | 9.96                                    | 10.69 | 4.68 |
|                          | QP-121311-12 | Picrite   | 2019        | 0.03                   | 0.02   | 0.06                   | 0.05   | 6  | 0.02                              | 22.58 | 11.45                                   | 7.79  | 3.69 |
|                          | CA37         |           | 2019        | 0.13                   | 0.04   | 0.21                   | 0.07   | 9  | 0.02                              | 7.01  | 10.99                                   | 22.46 | 6.88 |
|                          | Fe06-02      |           | 2019        | 0.1                    | 0.03   | 0.16                   | 0.04   | 6  | 0.02                              | 6.41  | 13.25 (Fe <sub>2</sub> O <sub>3</sub> ) | 16.4  | 6.25 |
| Galápagos (Cerro Azul)   |              |           |             |                        |        |                        |        |    |                                   |       |                                         |       |      |
| Galápagos (Fernandina)   |              |           |             |                        |        |                        |        |    |                                   |       |                                         |       |      |
| Galápagos (Fernandina)   | Fe15-13      |           | 2019        | 0.08                   | 0.03   | 0.14                   | 0.04   | 4  | 0.02                              | 6.63  | 11.04                                   | 14.19 |      |
| Galápagos (Floreana)     | FLO3-32      |           | 2019        | 0.12                   | 0.04   | 0.18                   | 0.07   | 8  | 0.02                              | 10.80 | 10.49                                   | 35.1  | 4.52 |
| Galápagos (Floreana)     | FLO3-128     |           | 2019        | 0.09                   | 0.06   | 0.13                   | 0.08   | 10 | 0.03                              | 10.60 | 9.45                                    |       |      |
| Galápagos (Sierra Negra) | SN91-31      |           | 2019        | 0.11                   | 0.07   | 0.18                   | 0.07   | 6  | 0.03                              | 5.60  |                                         |       |      |
| Galápagos (Wolf Volcano) | W95-3        |           | 2019        | 0.10                   | 0.03   | 0.16                   | 0.05   | 8  | 0.02                              | 6.40  | 10.47                                   | 13.1  | 5.89 |
| Galápagos (Wolf Volcano) | W95-65       |           | 2019        | 0.09                   | 0.03   | 0.14                   | 0.04   | 6  | 0.02                              | 5.72  | 12.06                                   |       |      |

**Table 6.4: Melt isotope compositions along isentropic decompression paths, KLB1. Isentropes are calculated for peridotite.**

| Pressure (kbar) | $T_{T_p=X}$ ( $^{\circ}\text{C}$ ) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ | $T_{T_p=X}$ ( $^{\circ}\text{C}$ ) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ |
|-----------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
|                 | $T_p = 1300$                       |                                     |                                     |                                     |                                    |                                     |                                    |                                     |                                     |                                     |                                    |                                     |
| 5               | 1256                               | -0.012                              | -0.074                              | 0.055                               | 0.020                              | -0.013                              | $T_p = 1400$                       |                                     |                                     |                                     |                                    |                                     |
| 5.5             | 1260                               | -0.013                              | -0.077                              | 0.055                               | 0.022                              | -0.015                              | 1337                               | -0.007                              | -0.032                              | 0.045                               | 0.009                              | -0.003                              |
| 6               | 1263                               | -0.014                              | -0.079                              | 0.054                               | 0.025                              | -0.017                              | 1339                               | -0.008                              | -0.035                              | 0.045                               | 0.010                              | -0.005                              |
| 6.5             | 1266                               | -0.014                              | -0.081                              | 0.054                               | 0.027                              | -0.019                              | 1341                               | -0.009                              | -0.038                              | 0.045                               | 0.010                              | -0.006                              |
| 7               | 1269                               | -0.015                              | -0.083                              | 0.054                               | 0.029                              | -0.020                              | 1343                               | -0.009                              | -0.041                              | 0.044                               | 0.011                              | -0.007                              |
| 7.5             | 1272                               | -0.015                              | -0.085                              | 0.054                               | 0.031                              | -0.021                              | 1345                               | -0.010                              | -0.044                              | 0.044                               | 0.012                              | -0.008                              |
| 8               | 1275                               | -0.015                              | -0.086                              | 0.054                               | 0.034                              | -0.023                              | 1347                               | -0.010                              | -0.047                              | 0.044                               | 0.012                              | -0.009                              |
| 8.5             | 1278                               | -0.016                              | -0.087                              | 0.054                               | 0.036                              | -0.023                              | 1348                               | -0.011                              | -0.050                              | 0.043                               | 0.013                              | -0.010                              |
| 9               | 1281                               | -0.016                              | -0.088                              | 0.054                               | 0.038                              | -0.024                              | 1350                               | -0.011                              | -0.053                              | 0.043                               | 0.014                              | -0.010                              |
| 9.5             | 1284                               | -0.016                              | -0.089                              | 0.054                               | 0.041                              | -0.025                              | 1352                               | -0.011                              | -0.056                              | 0.043                               | 0.014                              | -0.011                              |
| 10              | 1287                               | -0.016                              | -0.090                              | 0.054                               | 0.043                              | -0.026                              | 1354                               | -0.012                              | -0.059                              | 0.042                               | 0.015                              | -0.011                              |
| 10.5            | 1290                               | -0.017                              | -0.091                              | 0.054                               | 0.046                              | -0.026                              | 1356                               | -0.012                              | -0.063                              | 0.042                               | 0.015                              | -0.012                              |
| 11              | 1293                               | -0.017                              | -0.091                              | 0.055                               | 0.048                              | -0.027                              | 1358                               | -0.012                              | -0.066                              | 0.042                               | 0.016                              | -0.012                              |
| 11.5            | 1296                               | -0.017                              | -0.091                              | 0.055                               | 0.051                              | -0.027                              | 1360                               | -0.013                              | -0.069                              | 0.042                               | 0.016                              | -0.013                              |
| 12              | 1299                               | -0.017                              | -0.092                              | 0.055                               | 0.054                              | -0.028                              | 1361                               | -0.013                              | -0.073                              | 0.041                               | 0.017                              | -0.013                              |
| 12.5            | 1302                               | -0.017                              | -0.092                              | 0.055                               | 0.056                              | -0.028                              | 1364                               | -0.013                              | -0.074                              | 0.041                               | 0.018                              | -0.014                              |
| 13              | 1305                               | -0.017                              | -0.092                              | 0.055                               | 0.059                              | -0.029                              | 1367                               | -0.013                              | -0.077                              | 0.041                               | 0.018                              | -0.014                              |
| 13.5            | 1308                               | -0.017                              | -0.091                              | 0.055                               | 0.063                              | -0.029                              | 1370                               | -0.013                              | -0.077                              | 0.041                               | 0.020                              | -0.016                              |
| 14              | 1311                               | -0.017                              | -0.091                              | 0.056                               | 0.066                              | -0.030                              | 1374                               | -0.014                              | -0.078                              | 0.041                               | 0.021                              | -0.017                              |
| 14.5            | 1314                               | -0.017                              | -0.091                              | 0.056                               | 0.070                              | -0.030                              | 1377                               | -0.014                              | -0.079                              | 0.042                               | 0.022                              | -0.018                              |
| 15              | 1317                               | -0.018                              | -0.090                              | 0.057                               | 0.075                              | -0.030                              | 1380                               | -0.014                              | -0.079                              | 0.042                               | 0.024                              | -0.019                              |
| 15.5            | 1320                               | -0.018                              | -0.089                              | 0.057                               | 0.080                              | -0.031                              | 1383                               | -0.014                              | -0.080                              | 0.042                               | 0.025                              | -0.019                              |
| 16              | 1323                               | -0.018                              | -0.088                              | 0.058                               | 0.086                              | -0.031                              | 1386                               | -0.014                              | -0.080                              | 0.042                               | 0.027                              | -0.020                              |
| 16.5            | 1326                               | -0.019                              | -0.087                              | 0.058                               | 0.086                              | -0.031                              | 1389                               | -0.014                              | -0.081                              | 0.043                               | 0.028                              | -0.021                              |
| 17              | 1329                               |                                     |                                     |                                     | 0.092                              | -0.031                              | 1392                               | -0.014                              | -0.081                              | 0.043                               | 0.030                              | -0.022                              |
| 17.5            | 1329                               |                                     |                                     |                                     |                                    |                                     | 1395                               | -0.015                              | -0.081                              | 0.044                               | 0.032                              | -0.022                              |
| 18              | 1330                               |                                     |                                     |                                     |                                    |                                     | 1398                               | -0.015                              | -0.081                              | 0.044                               | 0.034                              | -0.023                              |
|                 |                                    |                                     |                                     |                                     |                                    |                                     | 1401                               | -0.015                              | -0.081                              | 0.045                               | 0.036                              | -0.024                              |

Table 6.4: (KLB1, continued)

| Pressure (kbar) | $T_{T_p=X}$ (°C) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ | $T_{T_p=X}$ (°C) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ |
|-----------------|------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| 18.5            | 1331             |                                     |                                     |                                     |                                    |                                     | 1404             | -0.015                              | -0.080                              | 0.045                               | 0.039                              | -0.025                              |
| 19              | 1332             |                                     |                                     |                                     |                                    |                                     | 1407             | -0.015                              | -0.080                              | 0.046                               | 0.042                              | -0.025                              |
| 19.5            | 1333             |                                     |                                     |                                     |                                    |                                     | 1410             | -0.015                              | -0.080                              | 0.047                               | 0.045                              | -0.026                              |
| 20              | 1333             |                                     |                                     |                                     |                                    |                                     | 1413             | -0.015                              | -0.079                              | 0.048                               | 0.049                              | -0.027                              |
| 20.5            | 1334             |                                     |                                     |                                     |                                    |                                     | 1416             | -0.015                              | -0.078                              | 0.049                               | 0.053                              | -0.028                              |
| 21              | 1335             |                                     |                                     |                                     |                                    |                                     | 1419             | -0.015                              | -0.078                              | 0.050                               | 0.057                              | -0.028                              |
| 21.5            | 1336             |                                     |                                     |                                     |                                    |                                     | 1422             | -0.015                              | -0.077                              | 0.051                               | 0.062                              | -0.029                              |
| 22              | 1337             |                                     |                                     |                                     |                                    |                                     | 1426             | -0.014                              | -0.077                              | 0.052                               | 0.066                              | -0.029                              |
| 22.5            | 1338             |                                     |                                     |                                     |                                    |                                     | 1431             | -0.013                              | -0.079                              | 0.054                               | 0.071                              | -0.029                              |
| 23              | 1338             |                                     |                                     |                                     |                                    |                                     | 1435             | -0.011                              | -0.081                              | 0.056                               | 0.075                              | -0.029                              |
| 23.5            | 1339             |                                     |                                     |                                     |                                    |                                     | 1439             | -0.009                              | -0.083                              | 0.058                               | 0.078                              | -0.029                              |
| 24              | 1340             |                                     |                                     |                                     |                                    |                                     | 1440             |                                     |                                     |                                     |                                    |                                     |
| $T_{T_p=1530}$  |                  |                                     |                                     |                                     |                                    |                                     |                  |                                     |                                     |                                     |                                    |                                     |
| 5               | 1436             | -0.001                              | -0.011                              | 0.034                               | 0.002                              | 0.009                               |                  |                                     |                                     |                                     |                                    |                                     |
| 5.5             | 1438             | -0.002                              | -0.012                              | 0.034                               | 0.003                              | 0.007                               |                  |                                     |                                     |                                     |                                    |                                     |
| 6               | 1440             | -0.002                              | -0.013                              | 0.034                               | 0.003                              | 0.005                               |                  |                                     |                                     |                                     |                                    |                                     |
| 6.5             | 1442             | -0.003                              | -0.014                              | 0.034                               | 0.004                              | 0.003                               |                  |                                     |                                     |                                     |                                    |                                     |
| 7               | 1443             | -0.004                              | -0.015                              | 0.034                               | 0.004                              | 0.002                               |                  |                                     |                                     |                                     |                                    |                                     |
| 7.5             | 1445             | -0.004                              | -0.017                              | 0.033                               | 0.005                              | 0.000                               |                  |                                     |                                     |                                     |                                    |                                     |
| 8               | 1447             | -0.005                              | -0.018                              | 0.033                               | 0.005                              | -0.001                              |                  |                                     |                                     |                                     |                                    |                                     |
| 8.5             | 1449             | -0.006                              | -0.019                              | 0.033                               | 0.006                              | -0.002                              |                  |                                     |                                     |                                     |                                    |                                     |
| 9               | 1451             | -0.006                              | -0.020                              | 0.033                               | 0.006                              | -0.003                              |                  |                                     |                                     |                                     |                                    |                                     |
| 9.5             | 1453             | -0.007                              | -0.022                              | 0.033                               | 0.006                              | -0.004                              |                  |                                     |                                     |                                     |                                    |                                     |
| 10              | 1455             | -0.007                              | -0.023                              | 0.032                               | 0.007                              | -0.005                              |                  |                                     |                                     |                                     |                                    |                                     |
| 10.5            | 1456             | -0.007                              | -0.024                              | 0.032                               | 0.007                              | -0.006                              |                  |                                     |                                     |                                     |                                    |                                     |
| 11              | 1458             | -0.008                              | -0.026                              | 0.032                               | 0.007                              | -0.006                              |                  |                                     |                                     |                                     |                                    |                                     |
| 11.5            | 1460             | -0.008                              | -0.027                              | 0.032                               | 0.008                              | -0.007                              |                  |                                     |                                     |                                     |                                    |                                     |
| 12              | 1462             | -0.009                              | -0.028                              | 0.032                               | 0.008                              | -0.007                              |                  |                                     |                                     |                                     |                                    |                                     |
| 12.5            | 1464             | -0.009                              | -0.030                              | 0.032                               | 0.008                              | -0.008                              |                  |                                     |                                     |                                     |                                    |                                     |

Table 6.4: (KLB1, continued)

| Pressure (kbar) | $T_{T_p=X}$ ( $^{\circ}\text{C}$ ) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ | $T_{T_p=X}$ ( $^{\circ}\text{C}$ ) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ |
|-----------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| 13              | 1466                               | -0.009                              | -0.031                              | 0.031                               | 0.009                              | -0.008                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 13.5            | 1467                               | -0.009                              | -0.032                              | 0.031                               | 0.009                              | -0.009                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 14              | 1469                               | -0.010                              | -0.033                              | 0.031                               | 0.009                              | -0.009                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 14.5            | 1471                               | -0.010                              | -0.035                              | 0.031                               | 0.009                              | -0.009                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 15              | 1473                               | -0.010                              | -0.036                              | 0.031                               | 0.010                              | -0.010                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 15.5            | 1475                               | -0.010                              | -0.037                              | 0.031                               | 0.010                              | -0.010                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 16              | 1477                               | -0.010                              | -0.038                              | 0.031                               | 0.010                              | -0.010                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 16.5            | 1478                               | -0.011                              | -0.040                              | 0.031                               | 0.010                              | -0.011                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 17              | 1480                               | -0.011                              | -0.041                              | 0.031                               | 0.011                              | -0.011                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 17.5            | 1482                               | -0.011                              | -0.042                              | 0.030                               | 0.011                              | -0.011                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 18              | 1484                               | -0.011                              | -0.043                              | 0.030                               | 0.011                              | -0.011                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 18.5            | 1486                               | -0.011                              | -0.045                              | 0.030                               | 0.011                              | -0.011                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 19              | 1488                               | -0.011                              | -0.046                              | 0.030                               | 0.011                              | -0.012                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 19.5            | 1490                               | -0.011                              | -0.047                              | 0.030                               | 0.011                              | -0.012                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 20              | 1491                               | -0.011                              | -0.049                              | 0.030                               | 0.012                              | -0.012                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 20.5            | 1493                               | -0.012                              | -0.050                              | 0.030                               | 0.012                              | -0.012                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 21              | 1495                               | -0.012                              | -0.051                              | 0.030                               | 0.012                              | -0.012                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 21.5            | 1497                               | -0.012                              | -0.053                              | 0.030                               | 0.012                              | -0.012                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 22              | 1499                               | -0.012                              | -0.054                              | 0.030                               | 0.012                              | -0.012                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 22.5            | 1501                               | -0.012                              | -0.056                              | 0.030                               | 0.012                              | -0.012                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 23              | 1502                               | -0.012                              | -0.057                              | 0.029                               | 0.012                              | -0.012                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 23.5            | 1504                               | -0.012                              | -0.059                              | 0.029                               | 0.013                              | -0.012                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 24              | 1506                               | -0.012                              | -0.060                              | 0.029                               | 0.013                              | -0.013                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 24.5            | 1508                               | -0.012                              | -0.061                              | 0.030                               | 0.013                              | -0.013                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 25              | 1510                               | -0.012                              | -0.063                              | 0.029                               | 0.013                              | -0.013                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 25.5            | 1513                               | -0.012                              | -0.062                              | 0.030                               | 0.014                              | -0.015                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 26              | 1516                               | -0.012                              | -0.062                              | 0.030                               | 0.015                              | -0.015                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 26.5            | 1520                               | -0.012                              | -0.062                              | 0.030                               | 0.015                              | -0.016                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 27              | 1523                               | -0.012                              | -0.061                              | 0.031                               | 0.017                              | -0.017                              |                                    |                                     |                                     |                                     |                                    |                                     |





Table 6.5: (MIX1G, continued)

| Pressure (kbar) | $T_{T_p=X}$ (°C) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ | $T_{T_p=X}$ (°C) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ |
|-----------------|------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| 18.5            | 1331             | -0.032                              | -0.067                              | 0.047                               | 0.064                              | -0.057                              | 1404             | -0.024                              | -0.011                              | 0.007                               | 0.007                              | -0.027                              |
| 19              | 1332             | -0.027                              | -0.072                              | 0.048                               | 0.072                              | -0.058                              | 1407             | -0.018                              | -0.015                              | 0.011                               | 0.009                              | -0.030                              |
| 19.5            | 1333             | -0.023                              | -0.076                              | 0.049                               | 0.082                              | -0.058                              | 1410             | 0.002                               | -0.023                              | 0.017                               | 0.012                              | -0.033                              |
| 20              | 1333             | -0.020                              | -0.080                              | 0.050                               | 0.093                              | -0.058                              | 1413             | 0.016                               | -0.031                              | 0.019                               | 0.013                              | -0.033                              |
| 20.5            | 1334             | -0.016                              | -0.081                              | 0.049                               | 0.092                              | -0.058                              | 1416             | 0.028                               | -0.037                              | 0.021                               | 0.015                              | -0.033                              |
| 21              | 1335             |                                     |                                     |                                     |                                    |                                     | 1419             | 0.038                               | -0.044                              | 0.022                               | 0.016                              | -0.034                              |
| 21.5            | 1336             |                                     |                                     |                                     |                                    |                                     | 1422             | 0.047                               | -0.049                              | 0.024                               | 0.018                              | -0.035                              |
| 22              | 1337             |                                     |                                     |                                     |                                    |                                     | 1426             | 0.054                               | -0.053                              | 0.025                               | 0.018                              | -0.035                              |
| 22.5            | 1338             |                                     |                                     |                                     |                                    |                                     | 1431             | 0.060                               | -0.057                              | 0.026                               | 0.019                              | -0.035                              |
| 23              | 1338             |                                     |                                     |                                     |                                    |                                     | 1435             | 0.064                               | -0.060                              | 0.026                               | 0.020                              | -0.035                              |
| 23.5            | 1339             |                                     |                                     |                                     |                                    |                                     | 1439             | 0.069                               | -0.063                              | 0.027                               | 0.021                              | -0.036                              |
| 24              | 1340             |                                     |                                     |                                     |                                    |                                     | 1440             | 0.077                               | -0.070                              | 0.028                               | 0.022                              | -0.037                              |
| 24.5            | 1341             |                                     |                                     |                                     |                                    |                                     | 1441             | 0.083                               | -0.076                              | 0.030                               | 0.024                              | -0.038                              |
| 25              | 1342             |                                     |                                     |                                     |                                    |                                     | 1442             | 0.088                               | -0.081                              | 0.031                               | 0.025                              | -0.039                              |
| 25.5            | 1343             |                                     |                                     |                                     |                                    |                                     | 1443             | 0.093                               | -0.086                              | 0.032                               | 0.027                              | -0.040                              |
| 26              | 1343             |                                     |                                     |                                     |                                    |                                     | 1443             | 0.097                               | -0.090                              | 0.032                               | 0.028                              | -0.041                              |
| 26.5            | 1344             |                                     |                                     |                                     |                                    |                                     | 1444             | 0.101                               | -0.095                              | 0.033                               | 0.029                              | -0.042                              |
| 27              | 1345             |                                     |                                     |                                     |                                    |                                     | 1445             | 0.104                               | -0.099                              | 0.034                               | 0.031                              | -0.042                              |
| 27.5            | 1346             |                                     |                                     |                                     |                                    |                                     | 1446             | 0.107                               | -0.103                              | 0.035                               | 0.032                              | -0.043                              |
| 28              | 1347             |                                     |                                     |                                     |                                    |                                     | 1447             | 0.107                               | -0.107                              | 0.036                               | 0.034                              | -0.044                              |
| 28.5            | 1348             |                                     |                                     |                                     |                                    |                                     | 1448             | 0.108                               | -0.111                              | 0.037                               | 0.037                              | -0.045                              |
| 29              | 1348             |                                     |                                     |                                     |                                    |                                     | 1448             | 0.109                               | -0.115                              | 0.038                               | 0.039                              | -0.046                              |
| 29.5            | 1349             |                                     |                                     |                                     |                                    |                                     | 1449             | 0.107                               | -0.118                              | 0.039                               | 0.042                              | -0.047                              |
| 30              | 1350             |                                     |                                     |                                     |                                    |                                     | 1450             | 0.102                               | -0.120                              | 0.039                               | 0.047                              | -0.048                              |
| 30.5            | 1351             |                                     |                                     |                                     |                                    |                                     | 1451             | 0.098                               | -0.122                              | 0.040                               | 0.052                              | -0.048                              |
| 31              | 1352             |                                     |                                     |                                     |                                    |                                     | 1452             | 0.094                               | -0.124                              | 0.041                               | 0.059                              | -0.049                              |
| 31.5            | 1353             |                                     |                                     |                                     |                                    |                                     | 1453             | 0.092                               | -0.126                              | 0.042                               | 0.066                              | -0.049                              |
| 32              | 1353             |                                     |                                     |                                     |                                    |                                     | 1453             | 0.092                               | -0.129                              | 0.043                               | 0.074                              | -0.049                              |
| 32.5            | 1354             |                                     |                                     |                                     |                                    |                                     | 1454             | 0.092                               | -0.132                              | 0.044                               | 0.080                              | -0.048                              |

Table 6.5: (MIX1G, continued)

| Pressure (kbar) | $T_{T_p=X}$ ( $^{\circ}\text{C}$ ) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ | $T_{T_p=X}$ ( $^{\circ}\text{C}$ ) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ |
|-----------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| 33              | 1355                               |                                     |                                     |                                     |                                    |                                     | 1455                               | 0.094                               | -0.135                              | 0.045                               | 0.086                              | -0.048                              |
| 33.5            | 1356                               |                                     |                                     |                                     |                                    |                                     | 1456                               | 0.097                               | -0.137                              | 0.045                               | 0.090                              | -0.048                              |
| 34              | 1357                               |                                     |                                     |                                     |                                    |                                     | 1457                               |                                     |                                     |                                     |                                    |                                     |
| $T_{T_p=1530}$  |                                    |                                     |                                     |                                     |                                    |                                     |                                    |                                     |                                     |                                     |                                    |                                     |
| 5               | 1436                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 5.5             | 1438                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 6               | 1440                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 6.5             | 1442                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 7               | 1443                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 7.5             | 1445                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 8               | 1447                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 8.5             | 1449                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 9               | 1451                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 9.5             | 1453                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 10              | 1455                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 10.5            | 1456                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 11              | 1458                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 11.5            | 1460                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 12              | 1462                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 12.5            | 1464                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 13              | 1466                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 13.5            | 1467                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 14              | 1469                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 14.5            | 1471                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 15              | 1473                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 15.5            | 1475                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 16              | 1477                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 16.5            | 1478                               | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |                                    |                                     |                                     |                                     |                                    |                                     |
| 17              | 1480                               | -0.001                              | 0.000                               | 0.000                               | 0.000                              | -0.001                              |                                    |                                     |                                     |                                     |                                    |                                     |

Table 6.5: (MIX1G, continued)

| Pressure (kbar) | $T_{T_p=X}$ ( $^{\circ}\text{C}$ ) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ | $T_{T_p=X}$ ( $^{\circ}\text{C}$ ) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ |
|-----------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| 17.5            | 1482                               | -0.002                              | 0.000                               | 0.000                               | 0.000                              | -0.001                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 18              | 1484                               | -0.002                              | -0.001                              | 0.000                               | 0.000                              | -0.002                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 18.5            | 1486                               | -0.003                              | -0.001                              | 0.000                               | 0.000                              | -0.002                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 19              | 1488                               | -0.003                              | -0.001                              | 0.000                               | 0.000                              | -0.003                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 19.5            | 1490                               | -0.004                              | -0.001                              | 0.000                               | 0.000                              | -0.003                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 20              | 1491                               | -0.005                              | -0.001                              | 0.000                               | 0.001                              | -0.004                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 20.5            | 1493                               | -0.005                              | -0.002                              | 0.000                               | 0.001                              | -0.004                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 21              | 1495                               | -0.006                              | -0.002                              | 0.000                               | 0.001                              | -0.005                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 21.5            | 1497                               | -0.006                              | -0.002                              | 0.000                               | 0.001                              | -0.005                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 22              | 1499                               | -0.007                              | -0.002                              | 0.000                               | 0.001                              | -0.006                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 22.5            | 1501                               | -0.007                              | -0.002                              | 0.000                               | 0.001                              | -0.006                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 23              | 1502                               | -0.008                              | -0.003                              | 0.000                               | 0.001                              | -0.006                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 23.5            | 1504                               | -0.008                              | -0.003                              | 0.000                               | 0.001                              | -0.007                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 24              | 1506                               | -0.009                              | -0.003                              | 0.000                               | 0.001                              | -0.007                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 24.5            | 1508                               | -0.008                              | -0.004                              | 0.000                               | 0.001                              | -0.007                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 25              | 1510                               | -0.002                              | -0.006                              | 0.001                               | 0.002                              | -0.007                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 25.5            | 1513                               | 0.011                               | -0.011                              | 0.006                               | 0.004                              | -0.014                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 26              | 1516                               | 0.017                               | -0.013                              | 0.005                               | 0.004                              | -0.011                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 26.5            | 1520                               | 0.027                               | -0.017                              | 0.009                               | 0.006                              | -0.017                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 27              | 1523                               | 0.033                               | -0.021                              | 0.010                               | 0.006                              | -0.018                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 27.5            | 1527                               | 0.039                               | -0.024                              | 0.011                               | 0.007                              | -0.019                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 28              | 1530                               | 0.044                               | -0.028                              | 0.012                               | 0.008                              | -0.019                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 28.5            | 1533                               | 0.049                               | -0.032                              | 0.013                               | 0.009                              | -0.020                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 29              | 1537                               | 0.053                               | -0.034                              | 0.014                               | 0.009                              | -0.021                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 29.5            | 1542                               | 0.057                               | -0.037                              | 0.015                               | 0.010                              | -0.021                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 30              | 1546                               | 0.060                               | -0.039                              | 0.015                               | 0.010                              | -0.022                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 30.5            | 1550                               | 0.063                               | -0.041                              | 0.016                               | 0.011                              | -0.022                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 31              | 1555                               | 0.066                               | -0.044                              | 0.017                               | 0.011                              | -0.023                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 31.5            | 1559                               | 0.068                               | -0.046                              | 0.017                               | 0.012                              | -0.024                              |                                    |                                     |                                     |                                     |                                    |                                     |

Table 6.5: (MIX1G, continued)

| Pressure (kbar) | $T_{T_p=X}$ ( $^{\circ}\text{C}$ ) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ | $T_{T_p=X}$ ( $^{\circ}\text{C}$ ) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ |
|-----------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| 32              | 1563                               | 0.070                               | -0.048                              | 0.018                               | 0.012                              | -0.024                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 32.5            | 1567                               | 0.073                               | -0.050                              | 0.018                               | 0.013                              | -0.025                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 33              | 1572                               | 0.075                               | -0.052                              | 0.019                               | 0.013                              | -0.025                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 33.5            | 1576                               | 0.076                               | -0.054                              | 0.019                               | 0.013                              | -0.026                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 34              | 1580                               | 0.078                               | -0.056                              | 0.019                               | 0.014                              | -0.027                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 34.5            | 1584                               | 0.080                               | -0.058                              | 0.020                               | 0.014                              | -0.027                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 35              | 1587                               | 0.082                               | -0.061                              | 0.021                               | 0.015                              | -0.028                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 35.5            | 1590                               | 0.085                               | -0.065                              | 0.022                               | 0.016                              | -0.030                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 36              | 1592                               | 0.087                               | -0.068                              | 0.022                               | 0.017                              | -0.031                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 36.5            | 1595                               | 0.089                               | -0.071                              | 0.023                               | 0.018                              | -0.032                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 37              | 1598                               | 0.091                               | -0.074                              | 0.024                               | 0.019                              | -0.033                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 37.5            | 1601                               | 0.093                               | -0.076                              | 0.024                               | 0.019                              | -0.033                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 38              | 1603                               | 0.094                               | -0.079                              | 0.025                               | 0.020                              | -0.034                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 38.5            | 1606                               | 0.096                               | -0.081                              | 0.025                               | 0.021                              | -0.035                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 39              | 1609                               | 0.097                               | -0.083                              | 0.025                               | 0.021                              | -0.035                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 39.5            | 1611                               | 0.098                               | -0.086                              | 0.026                               | 0.022                              | -0.036                              |                                    |                                     |                                     |                                     |                                    |                                     |
| 40              | 1614                               | 0.099                               | -0.087                              | 0.026                               | 0.022                              | -0.036                              |                                    |                                     |                                     |                                     |                                    |                                     |

**Table 6.6: Melt isotope compositions along isentropic decompression paths, G2.** Isentropes are calculated for peridotite.

| Pressure (kbar) | $T_{T_p=1300}$ (°C) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ | $T_{T_p=1400}$ (°C) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ |
|-----------------|---------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|---------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| 5               | 1256                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1337                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 5.5             | 1260                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1339                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 6               | 1263                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1341                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 6.5             | 1266                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1343                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 7               | 1269                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1345                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 7.5             | 1272                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1347                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 8               | 1275                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1348                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 8.5             | 1278                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1350                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 9               | 1281                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1352                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 9.5             | 1284                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1354                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 10              | 1287                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1356                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 10.5            | 1290                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1358                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 11              | 1293                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1360                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 11.5            | 1296                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               | 1361                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 12              | 1299                | -0.001                              | -0.001                              | 0.000                               | 0.000                              | -0.003                              | 1364                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 12.5            | 1302                | -0.002                              | -0.001                              | 0.000                               | 0.001                              | -0.006                              | 1367                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 13              | 1305                | -0.004                              | -0.002                              | 0.000                               | 0.001                              | -0.009                              | 1370                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 13.5            | 1308                | -0.005                              | -0.003                              | 0.000                               | 0.001                              | -0.011                              | 1374                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 14              | 1311                | -0.006                              | -0.004                              | 0.001                               | 0.002                              | -0.013                              | 1377                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 14.5            | 1314                | -0.008                              | -0.005                              | 0.001                               | 0.002                              | -0.015                              | 1380                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 15              | 1317                | -0.009                              | -0.005                              | 0.001                               | 0.003                              | -0.016                              | 1383                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 15.5            | 1320                | -0.010                              | -0.006                              | 0.001                               | 0.003                              | -0.018                              | 1386                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 16              | 1323                | -0.012                              | -0.007                              | 0.001                               | 0.003                              | -0.019                              | 1389                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 16.5            | 1326                | -0.013                              | -0.008                              | 0.001                               | 0.004                              | -0.020                              | 1392                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 17              | 1329                | -0.014                              | -0.009                              | 0.001                               | 0.004                              | -0.021                              | 1395                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 17.5            | 1329                | -0.017                              | -0.010                              | 0.001                               | 0.005                              | -0.023                              | 1398                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 18              | 1330                | -0.019                              | -0.012                              | 0.002                               | 0.006                              | -0.024                              | 1401                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 18.5            | 1331                | -0.021                              | -0.013                              | 0.002                               | 0.007                              | -0.025                              | 1404                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |

Table 6.6: (G2, continued)

| Pressure (kbar) | $T_{T_p=1300}$ (°C) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ | $T_{T_p=1400}$ (°C) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ |
|-----------------|---------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|---------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| 19              | 1332                | -0.023                              | -0.014                              | 0.002                               | 0.008                              | -0.026                              | 1407                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 19.5            | 1333                | -0.025                              | -0.016                              | 0.003                               | 0.008                              | -0.027                              | 1410                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 20              | 1333                | -0.027                              | -0.017                              | 0.003                               | 0.009                              | -0.028                              | 1413                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 20.5            | 1334                | -0.029                              | -0.019                              | 0.003                               | 0.010                              | -0.029                              | 1416                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 21              | 1335                | -0.017                              | -0.024                              | 0.006                               | 0.011                              | -0.029                              | 1419                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 21.5            | 1336                | -0.006                              | -0.030                              | 0.008                               | 0.013                              | -0.028                              | 1422                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 22              | 1337                | 0.004                               | -0.035                              | 0.011                               | 0.014                              | -0.028                              | 1426                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 22.5            | 1338                | 0.013                               | -0.041                              | 0.013                               | 0.015                              | -0.028                              | 1431                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 23              | 1338                | 0.022                               | -0.046                              | 0.016                               | 0.017                              | -0.028                              | 1435                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | 0.000                               |
| 23.5            | 1339                | 0.029                               | -0.051                              | 0.018                               | 0.018                              | -0.028                              | 1439                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | -0.007                              |
| 24              | 1340                | 0.036                               | -0.056                              | 0.020                               | 0.019                              | -0.028                              | 1440                | 0.000                               | 0.000                               | 0.000                               | 0.000                              | -0.001                              |
| 24.5            | 1341                | 0.042                               | -0.061                              | 0.022                               | 0.020                              | -0.028                              | 1441                | -0.003                              | -0.002                              | 0.000                               | 0.001                              | -0.007                              |
| 25              | 1342                | 0.047                               | -0.066                              | 0.024                               | 0.021                              | -0.028                              | 1442                | -0.005                              | -0.003                              | 0.000                               | 0.001                              | -0.010                              |
| 25.5            | 1343                | 0.052                               | -0.070                              | 0.026                               | 0.022                              | -0.028                              | 1443                | -0.007                              | -0.004                              | 0.000                               | 0.002                              | -0.013                              |
| 26              | 1343                | 0.057                               | -0.075                              | 0.027                               | 0.024                              | -0.029                              | 1443                | -0.009                              | -0.005                              | 0.000                               | 0.003                              | -0.016                              |
| 26.5            | 1344                | 0.061                               | -0.079                              | 0.029                               | 0.025                              | -0.029                              | 1444                | -0.011                              | -0.007                              | 0.000                               | 0.004                              | -0.018                              |
| 27              | 1345                | 0.064                               | -0.083                              | 0.030                               | 0.026                              | -0.029                              | 1445                | -0.010                              | -0.016                              | 0.001                               | 0.004                              | -0.019                              |
| 27.5            | 1346                | 0.068                               | -0.086                              | 0.032                               | 0.027                              | -0.029                              | 1446                | -0.004                              | -0.013                              | 0.002                               | 0.005                              | -0.019                              |
| 28              | 1347                | 0.071                               | -0.090                              | 0.033                               | 0.028                              | -0.030                              | 1447                | 0.004                               | -0.018                              | 0.003                               | 0.007                              | -0.019                              |
| 28.5            | 1348                | 0.073                               | -0.093                              | 0.034                               | 0.029                              | -0.030                              | 1448                | 0.013                               | -0.023                              | 0.005                               | 0.008                              | -0.019                              |
| 29              | 1348                | 0.076                               | -0.096                              | 0.035                               | 0.030                              | -0.030                              | 1448                | 0.020                               | -0.028                              | 0.007                               | 0.009                              | -0.020                              |
| 29.5            | 1349                | 0.079                               | -0.100                              | 0.036                               | 0.031                              | -0.030                              | 1449                | 0.027                               | -0.033                              | 0.009                               | 0.010                              | -0.020                              |
| 30              | 1350                | 0.081                               | -0.103                              | 0.037                               | 0.032                              | -0.031                              | 1450                | 0.033                               | -0.038                              | 0.010                               | 0.011                              | -0.021                              |
| 30.5            | 1351                | 0.083                               | -0.106                              | 0.038                               | 0.033                              | -0.031                              | 1451                | 0.039                               | -0.043                              | 0.012                               | 0.012                              | -0.021                              |
| 31              | 1352                | 0.085                               | -0.110                              | 0.040                               | 0.036                              | -0.037                              | 1452                | 0.044                               | -0.048                              | 0.014                               | 0.013                              | -0.022                              |
| 31.5            | 1353                | 0.087                               | -0.114                              | 0.042                               | 0.040                              | -0.044                              | 1453                | 0.048                               | -0.052                              | 0.015                               | 0.014                              | -0.022                              |
| 32              | 1353                | 0.088                               | -0.117                              | 0.045                               | 0.044                              | -0.050                              | 1453                | 0.052                               | -0.057                              | 0.016                               | 0.015                              | -0.023                              |
| 32.5            | 1354                | 0.087                               | -0.119                              | 0.046                               | 0.048                              | -0.056                              | 1454                | 0.056                               | -0.061                              | 0.018                               | 0.016                              | -0.023                              |
| 33              | 1355                | 0.084                               | -0.121                              | 0.048                               | 0.051                              | -0.063                              | 1455                | 0.059                               | -0.065                              | 0.019                               | 0.017                              | -0.024                              |

**Table 6.6:** (G2, continued)

| Pressure (kbar) | $T_{T_p=1300}$ (°C) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ | $T_{T_p=1400}$ (°C) | $\delta^{26}\text{Mg}_{\text{liq}}$ | $\delta^{44}\text{Ca}_{\text{liq}}$ | $\delta^{57}\text{Fe}_{\text{liq}}$ | $\delta^{51}\text{V}_{\text{liq}}$ | $\delta^{53}\text{Cr}_{\text{liq}}$ |
|-----------------|---------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|---------------------|-------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| 33.5            | 1356                | 0.073                               | - 0.123                             | 0.047                               | 0.069                              | - 0.089                             | 1456                | 0.062                               | - 0.068                             | 0.020                               | 0.018                              | - 0.025                             |
| 34              | 1357                | 0.072                               | - 0.125                             | 0.048                               | 0.074                              | - 0.095                             | 1457                | 0.065                               | - 0.072                             | 0.021                               | 0.019                              | - 0.025                             |
| 34.5            | 1358                |                                     |                                     |                                     |                                    |                                     | 1458                | 0.067                               | - 0.075                             | 0.022                               | 0.020                              | - 0.026                             |
| 35              | 1358                |                                     |                                     |                                     |                                    |                                     | 1458                | 0.069                               | - 0.079                             | 0.023                               | 0.021                              | - 0.027                             |
| 35.5            | 1359                |                                     |                                     |                                     |                                    |                                     | 1459                | 0.071                               | - 0.082                             | 0.024                               | 0.022                              | - 0.027                             |
| 36              | 1360                |                                     |                                     |                                     |                                    |                                     | 1460                | 0.073                               | - 0.085                             | 0.025                               | 0.023                              | - 0.028                             |
| 36.5            | 1361                |                                     |                                     |                                     |                                    |                                     | 1461                | 0.075                               | - 0.088                             | 0.026                               | 0.024                              | - 0.029                             |
| 37              | 1362                |                                     |                                     |                                     |                                    |                                     | 1462                | 0.076                               | - 0.090                             | 0.026                               | 0.025                              | - 0.029                             |
| 37.5            | 1363                |                                     |                                     |                                     |                                    |                                     | 1463                | 0.078                               | - 0.093                             | 0.027                               | 0.026                              | - 0.030                             |
| 38              | 1363                |                                     |                                     |                                     |                                    |                                     | 1463                | 0.079                               | - 0.096                             | 0.028                               | 0.027                              | - 0.030                             |
| 38.5            | 1364                |                                     |                                     |                                     |                                    |                                     | 1464                | 0.081                               | - 0.099                             | 0.029                               | 0.029                              | - 0.034                             |
| 39              | 1365                |                                     |                                     |                                     |                                    |                                     | 1465                | 0.083                               | - 0.104                             | 0.031                               | 0.032                              | - 0.040                             |
| 39.5            | 1366                |                                     |                                     |                                     |                                    |                                     | 1466                | 0.086                               | - 0.109                             | 0.034                               | 0.037                              | - 0.048                             |
| 40              | 1367                |                                     |                                     |                                     |                                    |                                     | 1467                | 0.088                               | - 0.113                             | 0.036                               | 0.041                              | - 0.054                             |