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Title: Shallow forearc mantle dynamics and geochemistry: new insights from the IODP expedition 366

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Abstract: The Mariana forearc is a unique setting on Earth where serpentinite mud volcanoes exhume clasts originating from depths of 15 km and more from the forearc mantle. These peridotite clasts are variably serpentinized by interaction with slab derived fluid, and provide a record of forearc mantle dynamics and changes in geochemistry with depth. During International Oceanic Discovery Program (IODP) Expedition 366, we recovered serpentinized ultramafic clasts contained within serpentinite muds of three different mud volcanoes located at increasing distance from the Mariana trench and at increasing depth to the slab/mantle interface: Yinazao (distance to the trench: 55 km / depth to the slab/mantle interface: 13km), Fantangisña (62 km / 14 km) and Asùt Tesoru (72 km / 18 km). Four different types of ultramafic clasts were recovered: blue serpentinites, lizardite-serpentinites, antigorite/lizardite- and antigorite-serpentinites. Lizardite-serpentinites are primarily composed of orange serpentine, forming mesh and bastite textures. Raman and microprobe analyses revealed that these textures contain a mixture of Fe-rich brucite (XMg ~ 0.84) and lizardite/chrysotile. Antigorite/lizardite- and antigorite-serpentinites record the progressive recrystallization of mesh and bastite textures to antigorite, magnetite and pure Fe-poor brucite (XMg ~ 0.92). Oxygen isotope compositions of clasts and pore fluids showed that the transition from lizardite to antigorite is due to the increase in temperature from 200°C to about 400°C within the forearc area above the slab/mantle interface. Lizardite-, antigorite/lizardite- and antigorite-serpentinites displayed U-shaped chondrite normalized Rare Earth Element (REE) patterns and are characterized by high fluid mobile element concentrations (Cs, Li, Sr, As, Sb, B, Li) relative to abyssal peridotites and/or primitive mantle. The recrystallization of lizardite to antigorite is accompanied by a decrease in Cs, Li and Sr, and an increase in As and Sb concentrations in the bulk clasts, whereas B concentrations are relatively constant. Some clasts are overprinted by blue serpentine, often in association with sulfides. Most of these blue serpentinites were recovered at Yinazao and the uppermost units of Fantangisña and Asùt Tesoru suggesting alteration in the shallower portions of the forearc, possibly during exhumation of the clasts. This episode of alteration resulted in a flattening of REE spectra and an increase of Zn concentrations in serpentinites. Otherwise, no systematic changes of ultramafic clasts chemistry or mineralogy were observed with increasing depth to the slab. The samples document previously undescribed prograde metamorphic events in the shallow portions of the Mariana subduction zone, consistent with a continuous burial of the serpentinized forearc mantle during subduction. Similar processes, induced by the interaction with fluids released from the downgoing slab, likely occur in subduction zones worldwide. At greater depth, breakdown of brucite and antigorite will result in the massive transfer of fluids and fluid mobile elements, such as As, Sb and B, to the source of arc magmas.

Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given:
Data are already provided in the article and the appendixes.

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*Highlights (for review)

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- Clasts from Mariana mud volcanoes record three different stages of serpentinization
- Transition lizardite to antigorite enhanced by an increase of temperature from 200 to 400°C
- Evidences for a continuous burial of the serpentinized forearc during subduction
- Phase transitions accompanied by a modification of trace element chemistry

Shallow forearc mantle dynamics and geochemistry: new insights from the IODP expedition 366

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Abstract

The Mariana forearc is a unique setting on Earth where serpentinite mud volcanoes exhume clasts originating from depths of 15 km and more from the forearc mantle. These peridotite clasts are variably serpentinized by interaction with slab derived fluid, and provide a record of forearc mantle dynamics and changes in geochemistry with depth. During International Oceanic Discovery Program (IODP) Expedition 366, we recovered serpentinized ultramafic clasts contained within serpentinite muds of three different mud volcanoes located at increasing distance from the Mariana trench and at increasing depth to the slab/mantle interface: Yinazao (distance to the trench: 55 km / depth to the slab/mantle interface: 13km), Fantangisña (62 km / 14 km) and Asùt Tesoru (72 km / 18 km). Four different types of ultramafic clasts were recovered: blue serpentinites, lizardite-serpentinites, antigorite/lizardite- and antigorite-serpentinites. Lizardite-serpentinites are primarily composed of orange serpentine, forming mesh and bastite textures. Raman and microprobe analyses revealed that these textures contain a mixture of Fe-rich brucite (XMg ∼ 0.84) and lizardite/chrysotile. Antigorite/lizardite- and antigorite-serpentinites record the progressive recrystallization of mesh and bastite textures to antigorite, magnetite and pure Fe-poor brucite (XMg ∼ 0.92). Oxygen isotope compositions of clasts and pore fluids showed that the transition from lizardite to antigorite is due to the increase in temperature from 200°C to about 400°C within the forearc area above the slab/mantle interface. Lizardite-, antigorite/lizardite- and antigorite-serpentinites displayed U-shaped chondrite normalized Rare Earth Element (REE) patterns and are characterized by high fluid mobile element concentrations (Cs, Li, Sr, As, Sb, B, Li) relative to abyssal peridotites and/or primitive mantle. The recrystallization of lizardite to antigorite is accompanied by a decrease in Cs, Li and Sr, and an increase in As and Sb concentrations in the bulk clasts, whereas B concentrations are relatively constant. Some clasts are overprinted by blue serpentine, often in association with sulfides. Most of these blue serpentinites were recovered at Yinazao and the uppermost units of Fantangisña and Asùt Tesoru suggesting alteration in the shallower portions of the forearc, possibly during exhumation of the clasts. This episode of alteration resulted in a flattening of REE spectra and an increase of Zn concentrations in serpentinites. Otherwise, no systematic changes of ultramafic clasts chemistry or *mineralogy were observed with increasing depth to the slab. The samples document previously undescribed prograde metamorphic events in the shallow portions of the Mariana subduction zone, consistent with a continuous burial of the serpentinized forearc mantle during subduction. Similar processes, induced by the interaction with fluids released from the downgoing slab, likely occur in subduction zones worldwide. At greater depth, breakdown of brucite and antigorite will result in the massive transfer of fluids and fluid mobile elements, such as As, Sb and B, to the source of arc magmas.*

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1. Introduction

Serpentinization of the forearc mantle in subduction zones is intimately related to the devolatilization of the downgoing slab. During the onset of subduction (i.e., less than ~80 km depth) volatiles, such as H_2O, C, S, etc., are released from the slab, rise through and interact with the mantle wedge. This process influences the physical and mechanical properties of the slab/mantle wedge interface (Gerya et al., 2002; Rüpke et al., 2004; Van Keken et al., 2011), the dynamics of mantle flows (Hilairet and Reynard, 2009; Reynard, 2013; Wada et al., 2008) and controls deep volatile and redox-sensitive element cycles (Debret et al., 2018a; Deschamps et al., 2011; Hattori and Guillot, 2007; Ribeiro and Lee, 2017; Savov et al., 2007, 2005). In addition, serpentinites, either in the slab and/or the mantle wedge, have the capability to retain large amounts of water (up to 13 wt%) down to 100-200 km and up to their transformation into chlorite bearing harzburgites (e.g., Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997). However, despite its importance, relatively little is known about the extent of serpentinization, redox state and chemistry of serpentinized forearc mantle wedges worldwide.

A common way to study serpentinized forearc mantle wedges is by measuring seismic velocities (Bostock et al., 2002; Kamimura et al., 2002). Although the geometry of forearcs is highly variable and strongly controlled by the age of the slab (e.g., Van Keken et al., 2011; Reynard, 2013; Wada et al., 2008), it is widely assumed that the forearc mantle wedge is highly serpentinized, typically more than 50 % (Bostock et al., 2002; Nagaya et al., 2016), at depth ranging from 30 to 80 km. The physical properties of the mantle wedge serpentinites are often approximated by the behaviour of antigorite (i.e., the high temperature and pressure form of serpentine). Both modelling and experimental studies suggest that antigorite should be the dominant phase crystallizing in the forearc mantle (e.g., Christensen, 2004), but the importance of other serpentine varieties (lizardite and/or chrysotile) and minerals such as brucite, talc or chlorite, is poorly constrained (Reynard, 2013).

The buoyancy of serpentinized peridotites in dense anhydrous peridotites has lead several studies to propose that the serpentinized forearc mantle (or the so-called "serpentinization channel" along the slab-wedge interface) may contribute to the exhumation of high pressure terranes in active subduction zones (e.g., Chemenda et al., 1995; Guillot et al., 2000; Schwartz et al., 2001). This conclusion has been supported by the common occurrence of serpentinites with eclogitic rocks in mountain ranges. However, geochemical studies have shown that the forearc mantle wedge constitutes an essential reservoir for fluid mobile elements and water in subduction zones that must be dragged down by corner flow to contribute to the elemental and isotope budgets of subduction zone magmas (e.g. Savov et al., 2005, 2007; Hattori and Guillot, 2007; Deschamps et al., 2011; Ribeiro and Lee, 2017; Debret et al., 2018a). For example, recent mass balance calculations show that the serpentinized fore-arc mantle could provide enough water (∼7–78% of the total water injected at the trenches) to account for the water outfluxes beneath the volcanic arc (Ribeiro and Lee, 2017). Additionally, numerical models by Nagaya et al. (2016) suggest that convection could develop in serpentinized forearc mantle wedges. This result is compatible with previous numerical modelling by Honda et al. (2010) indicating that convective flow can be induced in the forearc wedge mantle when the viscosity of the wedge mantle is sufficiently low ($< \sim 4 \times 10^{19}$ Pa s^{-1}); compatible with estimates for the effective viscosity of antigorite (Hilairet et al., 2007). The discrepancies between these buoyancy and viscosity-controlled models emphasize the difficulty in assessing the dynamics of mantle flow in the serpentinized mantle wedge in subduction zones.

The Mariana forearc is a unique setting to sample and study the serpentinized mantle wedge as protrusions of hydrated mantle form serpentinite mud volcanoes on the outer forearc of the Izu–

Bonin–Mariana intra-oceanic subduction system (Fryer & Mottl, 1992; Fryer et al., 2012; Taylor & Smoot, 1984). The mud volcanoes are composed of serpentinite muds with embedded ultramafic clasts from the forearc mantle as well as mafic clasts from the subducting crust, originating from depths greater than 15 km (Fryer et al., 2000; Maekawa et al., 1993). Here we take advantage of the recent International Ocean Discovery Program (IODP) Expedition 366 to study serpentinized ultramafic clasts contained in the serpentinite muds of three mud volcanoes: Yinazao (formerly known as Blue Moon), Fantangisña (Celestial) and Asùt Tesoru (Big Blue; Fryer et al., 2018). We show that clasts from the Mariana forearc mantle are variably serpentinized and preserve various stages of lizardite recrystallization into antigorite, brucite and magnetite. Oxygen isotope chemistry and thermometry of the clasts and pore fluids show that the transition from lizardite to antigorite is likely to occur between 200 to 400°C, in good agreement with thermodynamic calculations (Evans, 2004) and field observations in alpine meta-ophiolites (Schwartz et al., 2013). No obvious correlation between the distance of the mud volcanoes to the trench and the lizardite to antigorite transition was observed. The absence of correlation suggests that complex convective flows of material occur within the mantle wedge area.

2. Geological setting

The non-accretionary Mariana subduction system, involving the subduction of the Mesozoic Pacific plate below the Philippine Sea plate, is located in the Western Pacific Ocean (Fig. 1). At the surface, the Mariana forearc is characterised by multiple horst and graben structures that developed under extensional stress caused by a rapid slab roll-back (Fryer, 1996; Harry and Ferguson, 1991). As a result, numerous serpentinite mud volcanoes are situated at varying distances from the trench (Fig. 1). They are formed by the eruption of mud flows consisting of unconsolidated serpentinite mud and containing variably serpentinized ultramafic clasts, as well as minor amounts of recycled Pacific plate and of Philippine Sea plate materials (Fryer et al., 2018; Fryer, 2012; Maekawa et al., 1993; Pabst et al., 2011). The serpentinite muds are derived from the forearc mantle where slab derived fluids interact with ultramafic lithologies and are buoyantly transported to the seafloor (Fryer, 2012 and reference therein). IODP Expedition 366 drilled at Yinazao (formerly known as Blue Moon), Fantangisña

(Celestial) and Asùt Tesoru (Big Blue) serpentinite mud volcanoes, which are located at distances of 55 km, 65 km and 70 km to the trench, respectively. Two additional serpentinites mud volcanoes, namely South Chamorro (78 km) and Conical (86 km from the trench), were previously drilled during Ocean Drilling Leg 195 and 125, respectively, and data from these sites will be incorporated here.

Yinazao is the closest to the trench. It lies at 15°43'N latitude and 147°11'E longitude (Fig. 1), at about 13 km above the subducting slab (Fryer et al., 2018; Hulme et al., 2010; Oakley, 2008). Previous studies estimated the temperature of the slab/ mantle interface below Yinazao at about 80°C (Oakley, 2008; Hulme et al., 2010). Drilling took place at the flank (Site U1491) and the summit (Site U1492) of this mud volcano (Fryer et al., 2018). The recovered cores consisted mainly of an alternation of an uppermost altered units of red-brown pelagic mud, ranging from a few cm to up to 4 m thick, and units of green and blue-grey serpentinite pebbly mud (Fig. 2). The red-brown pelagic units are interpreted as paleo-seafloor horizons altered in contact with seawater between two mud eruptions (Fryer et al., 2018). Each unit contains between 5 and 10% ultramafic clasts, most of which are fully serpentinized. Clasts recovered from the upper unit are affected by brown weathering and can display a high degree of carbonation (up to 80%, Figs 2a-b, Appendix A); whereas, clasts from the lower units are characterised by a dark blue colour (Figs 2c-d) and are frequently crosscut by mm-wide chrysotile veins with crack-seal like textures, indicative of a late-stage alteration event.

Fantangisña mud volcano is located to the north of Yinazao, at approximately 16°32'N and 147°13'E (Fig. 1). It is situated at about 14 km above the slab (Hulme et al., 2010). The temperature of the slab/ mantle interface below Fantangisña mud-volcano was estimated at about 150°C (Fryer et al., 2018; Hulme et al., 2010). During IODP Expedition 366, both the summit (Site U1497) and the flank (Site U1498) of this mud volcano were drilled (Fryer et al. 2018). The recovered cores consisted of alternating silt- or sand-rich layers containing ultramafic clasts with a brown weathering colour, and of green and/or blue-grey serpentinite pebbly mud embedding a large amount (about 20%) of dark blue ultramafic clasts (Figs 2c-d) that are predominantly harzburgites and dunites displaying a wide degree of serpentinization degree, from about 50 to 100%.

Asùt Tesoru mud volcano lies to the north of Fantangisña, at approximately 18°06 N and 147.06 E (Fig. 1). It is located at about 18 km above the slab (Hulme et al., 2010). Temperatures at the slab/mantle interface are estimated at about 250°C (Fryer et al., 2018; Hulme et al., 2010). Three sites were drilled on the flanks (Sites U1493, U1494 and U1495) and one at the summit (Site U1496; Fryer et al., 2018). The uppermost recovered units consist of pelagic mud and fine grained sandstone or siltstone containing weathered ultramafic clasts. Lower units are mainly composed of green to blue-grey serpentinite mud with 2 to 15% lithic clasts mainly consisting of variably serpentinized harzburgites and dunites with a dark blue colour (Figs 2c-d; serpentinization degree from 30 to 100%).

3. Petrology of the ultramafic clasts

Forty three ultramafic clasts were examined for their petrography onshore (see Appendix B for sample IODP full names, locations and classification). The clasts are variably serpentinized harzburgites and dunites of several centimetres to tens of centimetres long (Fig. 2). Many clasts preserve different serpentinization stages reflecting various episodes of fluid infiltration within the mantle wedge.

3.1 Identification of serpentine varieties

The mineralogy of the ultramafic clasts was characterized by combining electron microprobe analyses and Raman spectroscopy. These methods have been used to differentiate between serpentine varieties and co-existing brucite (e.g., Debret et al., 2013; Groppo et al., 2006; Schwartz et al., 2013; Schwarzenbach et al., 2016). *In situ* major element analyses were performed with a CAMECA SX 100 electron microprobe at the Laboratoire Magmas et Volcans (Clermont-Ferrand, France). Operating conditions of 15 kV accelerating voltage, a sample current of 15 nA and a counting time of 10 s/element were used, except for Ni (20 s). Microprobe analyses are given in Appendix C. Raman spectroscopy was performed at the University of Cambridge (UK). Raman spectra were collected in the 150–1300 cm^{-1} and 3500-3800 cm^{-1} spectral ranges using a confocal Labram HR300 Raman spectrometer (Horiba Jobin Yvon) of 300 mm focal length equipped with a holographic grating of 1800 gr mm^{-1} coupled to a Peltier cooled front illuminated CCD detector, 1024×256 pixels in size. This configuration allowed for a spectral resolution of about 1.4 cm^{-1} per pixel. The excitation line at

532 nm was produced by a diode-pumped solid state laser (Laser Quantum) focused on the sample using an Olympus 50 X objective (0.42 N.A.). Spectra were corrected from a linear baseline using the fitting software Peakfit. The laser power was set at energies ranging from 5 mW to 500 µW in order to avoid degradation of serpentine or oxide minerals (Debret et al., 2013; Debret et al., 2014; Faria & Vena, 1997), and the sample surface was checked after each analysis. In order to properly define the different serpentine varieties, spectra of lizardite, chrysotile, antigorite and brucite were selected as references (Appendix D).

3.2 Serpentinization at Yinazao mud volcano

Close to the seafloor, the clasts mainly consisted of carbonated breccia made of dusty calcite and/or aragonite embedding serpentinite fragments of various sizes, from 100 µm to several centimetres (Figs 2a-b, 3a). The degree of carbonation varies from 20 to 80% in the different clasts. Serpentine minerals display pseudomorphic mesh and bastite textures that replace mantle olivines and orthopyroxenes, respectively. Large veins of chrysotile with crack seal like textures crosscut mesh and bastite textures. The rims of many clasts are affected by an episode of late alteration, consisting of brownish clay minerals, that overprints previous textures (Fig. 2b; Appendix A). This late alteration stage is in accordance with results from other studies on Conical and South Chamorro mud volcanoes drilled during previous ODP expeditions (e.g., Kahl et al., 2015).

In the deeper units, clasts consist mainly of blue serpentine, spinel and sulfides with rare hydrogrossular and relicts of mantle olivine and orthopyroxene (subsequently called 'blue serpentinites'; Figs 3b-d). Spinels are homogeneous and display euhedral shapes. They can be surrounded by ≤ 50 µm wide coronas of magnetite. Spinel cores have XCr (Cr / [Cr + Al]) of 53-54 and XMg (Mg / [Fe + Mg]) of 54-57 (Fig. 4). Serpentine forms mesh and bastite textures, replacing olivine and orthopyroxene, and display a pale blue colour in plane polarized light (Figs 3b,c). The Raman spectra of blue serpentine are characterized by peaks at 225, 381, 525, 692, 1095 and 3697 cm^{-1} characteristic of chrysotile. Brucite is intergrown with chrysotile at the microscale as indicated by additional Raman peaks at 280, 440, 3643 and 3650 cm^{-1} (Fig. 3b). Blue serpentine compositions are characterized by XMg of 0.85 to 0.94, and SiO_2 and FeO contents ranging from 17.9 to 40.3 wt% and from 4.2 to 11.3 wt%, respectively (Fig. 5). The most Si-rich analyses display a broad match to serpentine mineral stoichiometry, whereas regression analysis of the whole data set suggests variable proportions of Mg-Si-serpentine and Si-free, Fe-rich brucite endmembers (Fig. 5). The low Si analyses can be attributed to the presence of Fe-brucite at nanoscale, as this mineral has a low XMg (∼0.84 as shown by regression analyses in Fig. 5a) relative to serpentine and does not incorporate silica (see also Kahl et al., 2015; Schwarzenbach et al., 2016). Bastite textures are occasionally associated with roundish hydrogrossular crystals of about 50 µm width. Several studies have reported the presence of hydrogrossular in different serpentinization environments and this has, in most cases, been attributed to an excess in Al during the final stages of serpentine growth after pyroxene (e.g., Beard et al., 2009).

The centre of mesh and bastite textures is often associated with large opaque aggregates of ∼200 µm width (Figs 3b,c). These aggregates are composed of lamellar minerals associated with framboidal Fe-sulfides (pyrite), ranging in size from 0.5 to 2 µm, formed inside the intergranular porosity (Fig. 3d). Raman analyses of the lamellar minerals show three main peaks at 280, 440 and 3639 cm^{-1} corresponding to brucite, with four small additional peaks at 369, 521, 689 and 3689 cm^{-1} suggesting the presence of small amounts of serpentine (Fig. 3b). Occasionally, 50 to 200 µm wide veins consisting mainly of euhedral pyrite crosscut the serpentine textures (Fig. 3c).

3.3 Serpentinization at Fantangisña and Asùt Tesoru mud volcanoes

Clasts recovered from Fantangisña and Asùt-Tesoru mud volcanoes display similar textures to each other. Samples from the uppermost units are also affected by sub-surface alteration such as clay mineral crystallization and carbonation. However, in contrast to Yinazao, the formation of blue serpentine and sulfides was mainly observed close to the seafloor at Fantangisña and Asùt Tesoru. The Blue serpentine can either completely replace former textures or be limited to clast rims (Fig. 2b; Appendix A). In lower units, three different types of ultramafic clasts have been identified (Figs 2c-d; 6-8); their distribution appears to be random within the mud volcanoes (see Appendix B for more details):

(1) The first group (lizardite-rich serpentinites, referred to as Liz-serpentinites from here on) corresponds to variably serpentinized peridotites that can preserve mantle minerals (olivine, orthopyroxene, spinel and rare clinopyroxene). These Liz-serpentinite clasts were the most commonly reported during previous ODP expeditions, i.e. in South Chamorro and Conical mud volcanoes (e.g., D'Antonio and Kristensen, 2004; Savov et al., 2005, 2007; Kahl et al., 2015). Olivine XMg and NiO contents range from 0.91 to 0.93 and from 0.37 to 0.44 wt%, respectively, whereas MnO contents are below 0.1 wt%. Orthopyroxene is characterized by Cr_2O_3 and Al_2O_3 contents ranging from 0.1 to 1.88 wt% and 0.1 to 0.5 wt%, respectively. Spinel relicts have euhedral shapes with dark cores and narrow (< 100 µm) lighter rims that correspond to a compositional zoning from Mg and Al-rich cores (XMg = 0.30 - 0.59; XCr = 0.51 – 0.95) to Cr-rich rims (XMg ∼ 0; XCr ∼ 1; Fig. 4). Small magnetite crystals are present at the boundary between serpentine and spinel. The serpentinization degrees of the clasts vary from about 30 to 90%. In slightly serpentinized clasts, serpentine crystallizes as brownish veins of 20 to 300 µm width, with regular shape, crossing olivine and orthopyroxene (Fig. 6a). Raman spectra indicate mixtures of brucite and lizardite and/or chrysotile inside the veins. Serpentine fully replaces olivine and orthopyroxene by forming mesh and bastite textures where the local serpentinization degree is > 60 %. No magnetite was observed in the mesh centres. Serpentine compositions are characterized by low SiO_2 (31.8 - 40.6 wt%), XMg (0.88 – 0.95) and high FeO (3.5 – 8.1 wt%; Fig. 5) suggesting variable proportions of Fe-brucite and serpentine at microscale. Bastite is associated with amphibole minerals, which form pale green needles about 50 µm in length. Rare magnetite grains have been observed in these clasts; they crystallize mainly in the centre of brucite veins of 20 to 200 µm width crossing mantle minerals, lizardite veins, mesh or bastite textures (Fig. 6b). Towards the rims, the brucite + magnetite veins are surrounded by a corona of small antigorite lamellae, about 30 µm in length.

(2) The second group (antigorite-/lizardite-rich serpentinites, referred as Atg/Liz-serpentinites from here on) corresponds to highly serpentinized peridotites (serpentinization degree > 70%) displaying mesh and bastite textures associated with antigorite (Fig. 7). Few primary mantle spinel relicts have been observed. XMg and XCr of spinel range from 0.19 to 0.39 and from 0.63 to 0.81,

respectively. Spinel frequently displays thin, about 50 µm wide, coronas of chromite (XCr > 0.9) and magnetite toward the rim (Fig. 4). Serpentine mesh centres are often several hundred micrometres in size and characterised by a homogenous grey colour with weak birefringence and occasionally undulatory extinction. Raman spectra of the mesh and bastite textures denote mixtures between lizardite (or chrysotile) and antigorite, with pronounced peaks at 1044 and 3700 cm^{-1} and at 1100 and 3685 cm^{-1}, corresponding to antigorite and lizardite, respectively (Fig. 7a). The mesh rims are composed of antigorite needles associated with thin veinlets of pure brucite and magnetite in their centres (Fig. 7a). Chemical compositions of serpentine minerals are homogeneous throughout the samples. They are characterized by higher SiO_2 (39.8 – 45.4 wt%) and XMg (0.92-0.97) and lower FeO (1.9-5.2 wt%) relative to serpentine/brucite textures in the Liz-serpentinites (Fig. 5). This suggests the absence of brucite at microscale. The amount of antigorite is highly variable from one sample to another, varying from about 40 to 80 modal %. The serpentinites are crosscut by 200 to 500 µm wide veins of brucite and magnetite (Fig. 7b). Mesh and bastite textures in contact with these veins are recrystallized to antigorite lamellae and needles about 30 µm in length.

(3) The third group corresponds to antigorite-bearing serpentinites (Atg-serpentinites from here on) mainly made of antigorite lamellae, about 50 µm long, with interstitial brucite and magnetite (Fig. 8). The existence of antigorite bearing clasts have also been reported at Conical and South Chamorro mud volcanoes (e.g., Alt and Shanks, 2006; Murata et al., 2009). Antigorite have higher SiO_2 contents (42.2 - 44.9 wt%) and XMg (0.96-0.99) and lower FeO contents (1.2-3.2 wt%) relative to serpentine in the Liz- or Atg/Liz-serpentinites (Fig. 5). Brucite has crystallized as millimetre-sized patches containing euhedral magnetite grains about 200 µm in width (Fig. 8). Brucite has MgO and FeO contents ranging from 63.3 to 64.9 wt% and 9.7 to 9.9 wt%, respectively, and an average XMg of 0.92, which is significantly higher than that of the Fe-Brucite in Liz-serpentinites (XMg ~ 0.84, Fig. 5). The Atg-serpentinites are characterized by the presence of euhedral hydro-andradite crystals that display a diamond shape and contain numerous inclusions of magnetite. The crystallization of andradite in serpentinites has been observed in several settings (e.g. Frost, 1985) and can be attributed to a low silica activity during alteration (Frost & Beard, 2007). Magnetite is abundant throughout the samples.

4. Methods

4.1 Oxygen isotope geochemistry

4.1.1 Mineral separates

The oxygen isotope compositions of serpentine and magnetite mineral separates were measured at the University of Texas at Austin using a ThermoElectron MAT 253 mass spectrometer. Serpentinite samples were crushed and handpicked under a binocular microscope in order to visually assess mineral separate purity. In many samples, serpentine and magnetite were extensively intergrown and pure magnetite could not be separated, therefore most samples could not be confidently analysed for the $\delta^{18}O$ value of magnetite. Oxygen isotope ratios were determined on ~ 2.0 mg of mineral separates using the laser fluorination method of Sharp (1990). Standard UWG-2 ($\delta^{18}O_{garnet}$ = +5.8‰; Valley et al., 1995) and in-house standard Lausanne-1 ($\delta^{18}O_{quartz}$ = +18.1‰) were analysed to verify precision and accuracy. All $\delta^{18}O$ values are reported relative to SMOW, where the $\delta^{18}O$ value of NBS-28 is +9.7‰. The error on $\delta^{18}O$ values is ±0.1‰, based on the long-term average of standard analyses.

4.1.2 Pore fluids

Whole-round (WR) core samples were taken immediately after core sectioning on the deck for the subsequent extraction of interstitial (pore) water (IW). The length of the WR core taken for IW analyses varied from 10 cm in the upper units, to 40 cm in the deeper units where the volume of extracted IW was limited. Although this sacrificed a large amount of core material, this was the only way to get sufficient volume of pore fluids for the deeper samples, and only core sections which appeared to be highly homogenous were used. Typically one WR per section was collected between 0 and 10 mbsf, and 2 WR were selected every 10 m of depth from 10 mbsf to total depth of the core. Whole-round samples were processed in a nitrogen filled glove-bag after cooling in a refrigerator for about one hour. First the cored material was extruded from the core liner, then portions of the material that were potentially contaminated by seawater and sediment smearing were removed by scraping the core's outer surface with a spatula. For advanced piston (APC) cores about 0.5 cm of material from the outer diameter and the top and bottom faces was removed. In contrast, material recovered by extended core barrel (XCB) coring required additional removal of material, and as much as two-thirds of the sediment was removed from each WR sample. The remaining inner core of uncontaminated material (~150–300 cm^3) was placed into a titanium squeezer (modified after Manheim and Sayles, 1974) and compressed using a laboratory hydraulic press to extract pore water, using a total pressure up to 30 MPa. Fluids extracted from the compressed sediment sample were filtered through a pre-washed Whatman No. 1 filter situated above a titanium mesh screen. Approximately 10-80 mL of IW, depending on the length of the WR being processed, was collected in acid-cleaned plastic syringes attached to the squeezing assembly and filtered again through a Gelman polysulfone disposable filter (0.45 µm). After extraction, the squeezer parts were thoroughly cleaned with shipboard water, rinsed with de-ionized water, and dried. Pore fluids were syringe filtered into small, pre-cleaned (acid washed), Nalgene plastic vials, capped and then immediately flash frozen in liquid nitrogen to prevent evaporation.

Samples were measured via a Thermo Gas Bench II connected to a Thermo Delta Advantage mass spectrometer in continuous flow mode at Union College (Schenectady, New York – sample analyses are displayed in Appendix E). Three inhouse laboratory standards were used for isotopic corrections, and to assign the data to the appropriate isotopic scale using linear regression. These standards were calibrated directly to VSMOW (0.0‰) and SLAP (-55.50‰). The inhouse standards have $\delta^{18}O$ values that range from -0.6‰ to -16.52‰. The combined uncertainty (analytical uncertainty) for $\delta^{18}O$ of IW samples is ± 0.02‰ (SMOW), based on 8 internal tap water standards over two analytical sessions.

4.2 Bulk rock major and trace elements analyses

A suite of 25 representative serpentinized ultramafic clasts were analysed for major and selected trace elements by Inductively Coupled Plasma Optical Emission Spectrometry (Thermo ICP-OES Icap 6500) at the SARM (Service d'Analyses des Roches et des Minéraux Nancy, France – Appendix F). This sample set includes 5 Blue-serpentinites recovered at Yinazao (Site U1492, samples: M2, M3, M5, M6, M7), 1 Blue-serpentinite (Site U1496, sample: M24), 4 Liz-serpentinites (Site U1493, samples: TSB55, M9, M10; Site U1496, sample: M19), 2 Atg/Liz-serpentinites (Site U1495, samples: M12, M13), 4 Atg-serpentinites (Site U1495, samples: M14, M15, M16, M17) and 1 Brucitite (Site

U1496, sample: M20) recovered at Asùt Tesoru, 2 Blue-serpentinites (Site U1497, sample: M30; Site U1498, sample: M38), 2 Atg/Liz-serpentinites (Site U1497, sample: M32; Site U1498, sample: M45) and 3 Atg-serpentinites (Site U1497, samples: M50, M51, TSB102) recovered at Fantangisña. Sample digestions for major (SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K2O, TiO_2) and trace elements (Co, Cr, Ga, Ge, Ni, Sc, V, Zn, Cu) were performed on $LiBO_2$ fluxed fusions following the procedures described by Carignan et al. (2001). Boron concentrations were measured by spectrophotometric determination at the SARM. Samples were dissolved by fusion with anhydrous sodium carbonate. The reproducibility of the standard was better than 2% for major elements, 5% for Co, Cr, Ga, Ge, Ni, Sc, V, Zn, B and Li, and 10% for Cu based on repeated analyses of UB-N (serpentinite standard from the Centre de Recherches Pétrographiques et Géochimiques (CRPG) of Nancy, France). The analyses were accurate within 1-5% for SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O and within 1-10% for TiO_2 based on repeated analyses of U.S. Geological Survey, CRPG and Geological Survey of Japan standards BIR-1, UB-N and JP-1, and within 1-10% for Co, Cr, Ga, Ge, Ni, Sc, Cu, Zn, B, Li and better than 15% for V based on UB-N analyses (see Appendix F for comparison with standard preferred values).

A subset of 20 serpentinites was analysed for rare earth elements (REE), Y, Sr, Li, Rb, Cs, Cd, Pb, As, Sb, Ba, U, Th, Nb, Ta, Hf, Zr, V, Ga, Cu and Zn using a High Resolution Sector Field ICP-MS (Element XR) at the Vrije Universiteit Brussel (VUB, Belgium - Appendix F). This sample subset includes 4 Blue-serpentinites recovered at Yinazao (site U1492, samples: M2, M3, M6, M7), 1 Blue-serpentinite (site U1496, sample: M24), 3 Liz-serpentinites (site U1493, samples: TSB55, M9, M10), 2 Atg/Liz-serpentinites (site U1495, samples: M12, M13), 4 Atg-serpentinites (site U1495, samples: M14, M15, M16, M17) and 1 Brucitite (site U1496, sample: M20) recovered at Asùt Tesoru, 2 Blue-serpentinites (site U1497, sample: M30; U1498, sample: M38) and 2 Atg/Liz-serpentinites (site U1497, sample: M32; site U1498, sample: M45) recovered at Fantangisña. Samples were digested with a 1:1 mixture of HCl and HF for 4 days in par bombs. The samples were analysed in low resolution mode after dilution in 2% HNO_3 of 500 for most of trace elements and in medium resolution mode after dilution in 2% HNO_3 of 2000 for Cu, Zn, As, Ba and Pb. The external precision and accuracy were determined by analysing known ultramafic rock standards (UB-N from the CRPG Nancy, JP-1 from Geological Survey of Japan, PCC-1 and DTS-2b from US Geology Survey). One of the challenges of measuring refractory peridotites is their very low abundance of many trace elements (e.g., REE, HFSE, U, Th, Pb, As). As a consequence, there is a lack of precise and accurate data for reference materials of refractory peridotites (PCC-1, JP-1 and DTS-2b). On the basis of UB-N analysis, reproducibility is better than 10% for most of the trace elements and between 10 and 15% for Hf and Th (see Appendix F). The values obtained for rock standards UB-N, PCC-1, JP-1 and DTS-2b during this study are reported in Appendix F and are in good agreement with previously published data within a 2 standard deviation error.

5. Results and discussion of bulk rock oxygen isotope geochemistry

Results of whole rock analyses are given in Appendix F and are in good agreement with previous studies of serpentinite clasts from nearby seamounts (South Chamorro and Conical; e.g., Kodolanyi et al., 2011; Parkinson & Pearce, 1998; Savov et al., 2005, 2007; Fig. 9) and with the shipboard analyses (Fryer et al., 2018). Relatively low Al_2O_3/SiO_2 (<0.03) and high MgO/SiO_2 (>0.98) of the ultramafic clasts are consistent with a refractory protolith, i.e., dunite or pyroxene-poor harzburgite (e.g., Godard et al., 2008). The high loss on ignition values (>15 wt%) and low SiO_2 contents (<36 wt%) of some samples are in agreement with the crystallization of high amounts of sulfides (e.g. blue serpentinites) and/or brucite during peridotite serpentinization.

Chondrite-normalized REE plots are presented in Fig. 8a. Overall, the studied serpentinites are depleted in REE concentrations compared to chondrite values, and LREE (Light REE, 0.002 to 0.143 chondritic values) are more depleted than HREE (Heavy REE, 0.03 to 0.3 times chondritic values). Among the recovered clasts, two different patterns are observed. Group 1 corresponds to most of the blue serpentinite samples. They are characterized by relatively flat REE patterns with slightly higher concentrations of HREE compared to LREE (La_N/Yb_N = 0.3-0.6; Gd_N/Yb_N = 0.2-0.5; N: Chondrite normalized). This group reflects the pattern of the serpentinite mud erupted at the mud volcanoes (e.g., Savov et al., 2004; Fig. 10a) and may therefore reflect late stage re-equilibration between the mud and the ultramafic clasts.

Group 2 includes blue-, Liz-, Atg/Liz- and Atg- serpentinites. These samples display U-shape REE patterns, with depletion in the MREE (Middle Rare Earth Elements) relative to the LREE (La_N/Yb_N = 0.03-2) and HREE (Gd_N/Yb_N = 0.02-0.4; Fig. 10a), and also possess positive Eu anomalies (Eu/Eu* = $Eu_N/[(Sm_N+Gd_N)/2]$). The LREE concentrations progressively increase from the Liz-serpentinites (La_N/Yb_N = 0.04-0.13) to the Atg/Liz- (La_N/Yb_N = 0.12-2) and Atg-serpentinites (La_N/Yb_N =0.1-0.4). The Eu anomaly is more pronounced in Liz- and Atg/Liz-serpentinites (Eu/Eu* = 0.9-6.8) relative to Atg-serpentinites (Eu/Eu* = 0.7-1.8). These patterns are similar to those reported in the Conical mud volcano and have been interpreted as inherited from the peridotite protolith (Parkinson and Pearce, 1998). In Fig. 10b, Group 2 serpentinites are characterized by a strong depletion in most incompatible elements with respect to primitive mantle. The studied clasts show enrichments in Cs ($Cs_n/La_n > 21$; n: Primitive Mantle normalization) and positive anomalies in U ($U_n/Th_n > 2$), Pb ($Pb_n/La_n > 4$), Sr ($Sr_n/Pr_n > 2$), As, Sb ($As_n/Pr_n > 1500$) and Li (Li* > 60, Li* = Li / [Dy/2 + Y/2]).

Variations of fluid mobile elements (FME) and metal concentrations are observed for the different serpentinite types. The concentrations of As and Sb are lower in Liz-serpentinites (As = 0.7-1.3 ppm; Sb <0.001 ppm;) compared to Atg-serpentinites (As = 1.5-9.2 ppm; Sb = 0.03-0.21 ppm; B = 10-97 ppm), whereas Li (from 4-6 ppm to 0.4-0.8 ppm), Sr (from 1-8.5 ppm to 0.1-1 ppm) and Cs (from 0.14-0.22 ppm to <0.01-0.03 ppm) concentrations decrease from Liz- to Atg- serpentintes (Fig. 11). B and Zn concentrations are relatively constant in Liz- (B = 20-30 ppm; Zn = 35-65 ppm), Atg/Liz- (B = 48-59 ppm, Zn = 48-55 ppm) and Atg-serpentinites (B = 10-49 ppm; Zn = 36-52 ppm). It should be noted that boron (B) is highly enriched on all the studied samples relative to primitive mantle (B_{PM} = 0.19 ± 0.02 ppm, PM: Primitive Mantle; Marschall et al., 2017). Of all samples, blue serpentinites are characterized by the highest Zn (51-92 ppm), and highly variable Sr (2-28 ppm) and B (7-250 ppm) concentrations (Fig. 11c; Appendix F). It is unknown whether or not these elements are solely carried by serpentine minerals, which can incorporate these elements in its structure (e.g., Pabst et al., 2011; Debret et al., 2017), or by other accessory (micro- to nano-) phases (e.g., sulfides, spinels, hydro-garnets…).

Eight serpentine separates have $\delta^{18}O_{Srp}$ values of 5.8 to 8.3‰ (Table 1), overlapping with the range of analyses from previous Mariana mud volcano studies (6.5 to 10.8‰, reported by Alt & Shanks, 2006; 5.8 to 8.5‰ by Sakai et al., 1990; 6.1 to 10.5‰ by Kahl et al., 2015), and one magnetite separate has $\delta^{18}O_{Mgt}$ value of 1.8‰ (Table 1), in good agreement with Alt and Shanks (2006) who reported $\delta^{18}O_{Mgt}$ values of 0 to 2‰ in antigorite-rich samples. No obvious changes of $\delta^{18}O_{Srp}$ are observed with increasing distance from the trench in this study ($\delta^{18}O_{srp}$ [Yinazao] = 6.4 ‰; $\delta^{18}O_{Srp}$ [Fantangisña] = 8.3 ‰; $\delta^{18}O_{srp}$ [Asùt Tesoru] = 5.8-8.3 ‰) or in previous studies ($\delta^{18}O_{srp}$ [S. Chamorro] = 6.4-10.5 ‰; $\delta^{18}O_{srp}$ [Conical] = 6.1-10.8 ‰; Alt and Shanks, 2006; Kahl et al., 2015; Sakai et al., 1990). However, systematic variations of $\delta^{18}O_{Srp}$ relative to sample mineralogy and in pore fluids are observed. Blue serpentine displays $\delta^{18}O$ values ranging from 6.4 to 7.4‰, whereas higher $\delta^{18}O$ values are observed in Liz-serpentinites ($\delta^{18}O_{serp}$ 6.8 to 7.6‰) compared to Atg/Liz-serpentinites ($\delta^{18}O_{srp.}$ 5.8 to 6.1‰). Antigorite in the Atg-serpentinites records $\delta^{18}O_{Srp}$ values varying from 7.1 to 8.3‰, whereas associated magnetite has a $\delta^{18}O_{Mgt}$ value of 1.8 ‰. Pore fluid $\delta^{18}O$ values range from -1.39 to -0.14‰ in Yinazao, from -0.03 to 0.25‰ in Fantangisña and from 1.73 to 1.97‰ in Asùt Tesoru. Although highly variable with depth, these values suggest an increase in the $\delta^{18}O$ values of the pore fluid from shallow Yinazao (mean $\delta^{18}O_{fluid}$ = -0.90‰, n = 10) to the deeper Fantangisña (mean $\delta^{18}O_{fluid}$ = 0.11‰, n = 6) or Asùt Tesoru (mean $\delta^{18}O_{fluid}$ = 1.83‰, n = 4; Fig. 12). These values are significantly lower than those reported for South Chamorro (mean $\delta^{18}O_{fluid}$ = 2.5‰) and Conical (mean $\delta^{18}O_{fluid}$ = 4‰; Mottl et al., 2003), which are further from the trench.

6. Reconstructing forearc serpentinization conditions

Textural relationships between the different serpentine generations allow the reconstruction of a semi-quantitative temperature evolution of the serpentinization conditions within the Marianas forearc mantle wedge and thus a discussion of subduction dynamics. Forearc mantle wedge peridotites are former sub-arc peridotites that underwent extensive partial melting before being dragged into the forearc by mantle convection (e.g. Parkinson & Pearce, 1998). These peridotites are hydrated by slab-derived fluids and progressively transformed into serpentinites. The formation of early brown lizardite bearing veins crosscutting olivine and orthopyroxene in Liz-serpentinites (Fig. 6a) constitutes the first stage of the forearc mantle wedge hydration and serpentinization. These textures have been observed at the Fantangisña and Asùt Tesoru mud volcanoes as well as at the South Chamorro and Conical mud volcanoes during previous IODP expeditions (e.g. Kahl et al., 2015). The presence of significant amounts of brucite in Liz-serpentinites (Figs 5, 6a) can be attributed to the refractory composition of forearc mantle peridotites. In Mg-rich systems and at low-temperatures (e.g., Klein et al., 2014), the serpentinization of olivine results in magnesium excess allowing brucite precipitation:

$$(1)\ \ 2\ Fe_{0.15}Mg_{1.85}SiO_4 + 3\ H_2O = Fe_{0.2}Mg_{0.8}OH_2 + Fe_{0.1}Mg_{2.9}Si_2O_5(OH)_4$$

Olivine + Water = Fe-brucite + Lizardite

Here the XMg of brucite is assumed to be 0.8 based on linear regression of microprobe analyses (Fig. 5). Although lizardite and brucite can coexist over a large range of temperatures during the serpentinization process, the absence of magnetite during brown serpentine crystallization suggests rather low serpentinization temperature (< 200°C; Bonnemains et al., 2016; Klein et al., 2014). Assuming equilibria between lizardite and associated pore fluids, serpentine crystallisation temperatures (Table 1) were calculated based on the serpentine–water oxygen isotope fractionation from Saccocia et al. (2009). In agreement with petrographic observation, the temperature estimates of lizardite crystallization vary between 203 and 211°C (Table 1). It should, however, be noted that we cannot exclude an intergrowth of the serpentine separates with microscale brucite; such impurities would then lead to an overestimation of the calculated temperatures, as discussed by Alt and Shanks (2006). The crystallization temperatures estimates must therefore be considered as maxima.

The crystallization of antigorite at the expense of lizardite-bearing textures has been observed at Fantangisña and Asùt Tesoru in Atg/Liz-serpentinites and has also been reported at South Chamorro and Conical mud volcanoes (e.g. Alt and Shanks, 2006). The formation of antigorite corresponds to a second stage of serpentinization that is accompanied with the precipitation of large amounts of magnetite and the crystallization of Mg-rich brucite (XMg ∼ 0.9; Figs 7 and 8). The transition of lizardite to antigorite in subduction settings is commonly interpreted to result from increasing P-T conditions during prograde metamorphism (Debret et al., 2013; Evans, 2004; Scambelluri et al., 2004; Schwartz et al., 2013; Wunder et al., 2001). The $\delta^{18}O$ values of serpentine minerals crystallizing in

Atg/Liz-serpentinites indicate crystallisation temperatures of 230-240°C if we assume equilibria between serpentine and associated pore fluids. Those estimates are however at the lower range of previous thermodynamic estimates or natural observations that predict the coexistence of lizardite and antigorite during subduction between about 250-350°C (Evans, 2004; Schwartz et al., 2013). Indeed, based on combined δD and $\delta^{18}O$ values of serpentine from Conical ultramafic clasts, Alt and Shanks (2006) propose that the serpentinizing fluids released by the subducting slab at depth are likely to increase with temperature and to be progressively enriched in ^{18}O ($\delta^{18}O_{fluid}$ ~ 5.5‰ at 250°C and ~ 9.0‰ at 400°C; Fig. 12). Similarly, Sakai et al. (1990) also suggest a slab-derived fluid with a $\delta^{18}O$ value of approximately 3.0‰ based on the oxygen and hydrogen isotope composition of Izu and Mariana forearc serpentinite clasts. In agreement with those studies, we observed a progressive increase of $\delta^{18}O$ values of pore fluids with increasing distance from the trench (Fig. 12). However, pore fluid measurements from Yinazao, Fantangisña or Asùt Tesoru (-1.39 to +1.97 ‰) are always lower than $\delta^{18}O$ estimates of slab-derived fluids suggesting that the $\delta^{18}O$ values of pore fluids are driven toward to lower values during serpentinization processes occurring within the forearc (Alt and Shanks, 2006). In agreement with this scenario, the $\delta^{18}O_{Srp}$ analyses are more or less constant and enriched in ^{18}O (5.8-10.8 ‰; e.g., Alt and Shanks, 2006; Kahl et al., 2015; Sakai et al., 1990; this study) relative to pore fluids analyses, regardless of the slab depth. Higher $\delta^{18}O$ values for pore fluids than those recorded here have been reported by Mottl et al. (2003) for the more distant South Chamorro ($\delta^{18}O_{fluid} = 2.5 \pm 0.5$ ‰) and Conical ($\delta^{18}O_{fluid} = 4 \pm 0.5$ ‰) mud volcanoes (Fig. 12). If these higher pore fluid $\delta^{18}O$ values are used, temperature estimates are somewhat higher at 243-283°C for serpentine crystallization in Atg/Liz-serpentinites and therefore in better agreement with previous estimates of the transition lizardite to antigorite in subduction zones (250-350°C; Schwartz et al., 2013).

The observation of euhedral magnetite embedded in brucite in Atg-serpentinites (Figs 6b, 7b and 8b) suggests equilibrium with brucite, which in turn formed in equilibrium with antigorite. We therefore use the $\delta^{18}O$ values of serpentine–magnetite pairs to estimates the temperature of antigorite crystallization (thermometer of Wenner & Taylor, 1971 revised by Früh-Green et al., 1996) as 322 to

409°C. These temperatures overlap or are slightly higher compared to previous estimates of 300–375°C from Alt & Shanks (2006), and suggest that the transition of lizardite to antigorite in the forearc mantle likely occurs in a temperature range of 200 to 320°C. These estimates are also in accordance with thermodynamic calculations by Evans (2004) predicting the assemblage antigorite + brucite to be more stable than lizardite and chrysotile at temperatures > 300°C.

The transition from lizardite to antigorite can follow different reactions (e.g., Evans, 2004; Vils et al., 2011). For example, in a water saturated open system, the transition can be written in a MASH system as (Evans, 2004):

$$(2)\ \ 16\ Mg_3Si_2O_5(OH)_4 + 2\ SiO_{2(aq)} = 16\ Mg_3Si_{2.125}O_{5.31}(OH)_{3.875} + H_2O_{(aq)}$$

$$\text{Lizardite} + SiO_{2(aq)} \rightarrow \text{antigorite} + H_2O_{(aq)}$$

whereby the required influx of SiO_2 could be generated by sediment dehydration (e.g. Deschamps et al., 2011; Schwartz et al., 2013). However, the absence of a SiO_2-rich phase (e.g. talc, diopside) and the high amounts of brucite (Figs 7 and 8) rather suggest a system with low SiO_2 activity. The high amounts of brucite formed during mantle wedge serpentinization are also in line with former studies of the Mariana forearc (e.g., D’Antonio & Kristensen, 2004; Murata et al., 2009) and mantle wedge relicts from the Sanbagawa Belt (southwest Japan, Kawahara et al., 2016). These observations suggest a limited transfer of SiO_2 during slab dehydration at shallow depth.

In our samples, the antigorite-forming alteration stage is accompanied by a decrease of FeO in serpentine and brucite minerals suggesting a redistribution of Fe between Fe-bearing minerals. In order to account for the production of brucite and magnetite during the recrystallization of lizardite into antigorite without the addition of SiO_2 by fluids, we propose the following equation:

$$(3)\ \ Fe_{0.2}Mg_{0.8}OH_2 + Fe_{0.1}Mg_{2.9}Si_2O_5(OH)_4 = Fe_{0.08}Mg_{0.92}(OH)_2 + Fe_{0.04}Mg_{2.78}Si_2O_5(OH)_{3.64} + 0.04\ Fe_3O_4 + 0.24\ H_2O + 0.06\ H_2$$

$$\text{Fe-Brucite} + \text{Fe-Lizardite} = \text{Brucite} + \text{Antigorite} + \text{Magnetite} + H_2O + H_2$$

with the XMg of antigorite and brucite derived from microprobe analyses. It should be noted that this equation does not take into account the potential incorporation of Fe^{3+} into serpentine minerals (Andreani et al., 2013; Debret et al., 2014), the potential mobility of Fe in slab derived fluids (Debret et al., 2016), nor the role of other redox sensitive elements (e.g., C or S). Hence the production of H_2 in the equation is speculative.

The studied samples were partly affected by late serpentinization stages characterised by the crystallization of blue serpentine and sulfides (Fig. 3). If present, this late serpentinization stage largely replaces former textures, i.e. serpentine or mantle minerals (see Appendix A). This alteration texture is highly developed in Yinazao, whereas it is limited to the uppermost units of Fantangisña and Asùt Tesoru mud volcanoes suggesting that the crystallization of blue serpentine mainly occurs as a late stage of serpentinization. Large amounts of sulfides in some of these samples may indicate ongoing reduction of sulfates to sulfides through the activity of microbial communities (e.g., Mottl et al., 2003) during this stage. These sulfides display framboidal textures that are commonly interpreted as microbe-derived textures formed during bacterially mediated sulfate reduction (e.g., Thiel et al., 1999; Wilkin and Barnes, 1997). However, based on $\delta^{18}O$ analyses, the temperature estimates of blue serpentine crystallization vary between 183 and 194°C (Table 1), higher than those considered feasible for life (~ 122°C; Kashefi and Lovley, 2003). It should be noted that these temperature estimates are maxima due to brucite/serpentine intergrowths in serpentine textures in the blue-serpentinites, as discussed above. It is thus possible that the blue serpentinites formed at temperatures lower than 122°C. In addition, recent investigations of Mariana ultramafic clasts show the possible existence of microbial ecosystems within or below the Mariana mud volcanoes (Plümper et al., 2017). Microbial activity may therefore have taken place at a similar time to the crystallization of blue-serpentine in these sub-surface environments.

The temperatures of the slab / forearc mantle interface have previously been estimated to be ~80°C below Yinazao and to be ~250°C below Asùt Tesoru (Hulme et al., 2010), in both cases using pore water chemistry. These estimates are significantly lower than ours derived from oxygen isotope thermometry (up to about 400°C) and incompatible with antigorite crystallization in a subduction setting (Evans, 2004; Schwartz et al., 2013). Although recent studies have reported the crystallization of antigorite in an oceanic setting at relatively low temperatures (e.g., Rouméjon et al., 2014), this has been attributed to Si-metasomatism, possibly following pyroxene serpentinization, and is not compatible with SiO_2 undersaturated systems. The occurrence of antigorite in our samples rather suggests a progressive increase in temperature leading to the formation of antigorite, magnetite and Fe-poor brucite at the expense of lizardite. This scenario is compatible with a progressive burial of the forearc mantle wedge during subduction.

The deep burial of forearc rocks can be due to either corner flow enhanced by the low viscosity of serpentinite (e.g. Nagaya et al., 2016) or to frictional stresses mechanically disaggregating the slab surface and eroding the mantle wedge above the décollement zone, incorporating serpentinized mantle into the aggregated subducting inventory (e.g., King et al., 2006). Both processes could potentially explain a prograde metamorphic path and the coexistence of ultramafic clasts displaying various mineralogical assemblages equilibrated at various temperatures in each of the mud volcanoes. The ultimate mechanism responsible for carrying the clasts to depth remains unclear and requires a detailed textural investigation, which is beyond the scope of this study. However, retrograde processes leading to the overprinting of high-temperature serpentine phases by lower-temperature chrysotile (± lizardite) such as those observed here are interpreted to occur during the rise of the clasts towards shallower levels in the forearc, e.g., in the mud volcano conduits. The recovered clasts display a high degree of serpentinization (most of the clasts are serpentinized to almost 100%) compared to geophysical data based on seismic velocities which suggest serpentinization ≥ 30 % in the forearc (Reynard, 2013). These conflicting observations can be reconciled if only low density material (i.e., highly serpentinized parts of the forearc) can be exhumed, probably by buoyancy (e.g. Guillot et al., 2000), during subduction.

Similar observations of prograde and retrograde metamorphism in the Mariana forearc peridotites were described by Murata et al. (2009), who recognized lower-temperature chrysotile veins in antigorite-rich clasts that both pre- and post-date high-temperature antigorite growth. The authors concluded that this reflected a complex process of tectonic cycling of shallow mantle wedge peridotites to depth and then back again to the surface. Several other studies have also noted the possibility that serpentinite formed in the shallower parts of the subduction zone may be carried deeper into the subduction zone (e.g., Kawahara et al., 2016; Kerrick & Connolly, 2001; Savov et al., 2005, 2007; Snyder et al., 2005; Tamblyn et al., 2018). This suggests that the serpentinized forearc mantle wedge can significantly contribute to arc magmas isotope and elemental budget during subduction (e.g., Ribeiro and Lee, 2017; Debret et al., 2018a).

7. Evolution of forearc mantle wedge composition during subduction

Mariana forearc mud volcanoes are formed by the interaction of slab-derived fluids and forearc peridotites. The nature of the fluids released during slab dehydration is expect to change considerably with increasing depth and associated increase of pressure and temperature at depth (Bebout, 2013 and reference therein). Previous analyses of pore water chemistry of Mariana ultramafic clasts have shown an increase in K, sulfate, carbonate alkalinity, Na/Cl, B, Mn, Fe, Co, Rb, Cs, Gd/Tb, Eu, and LREE and a decrease in Ca, Sr, and Y with depth to the slab/mantle interface (Fryer et al., 2018; Hulme et al., 2010; Mottl et al., 2003). In agreement with these observations, we observed an increase of $\delta^{18}O$ values of pore fluids from Yinazao to Asùt Tesoru and the deeper-sources South Chamorro and Conical mud volcanoes (Fig. 12). However, the bulk-rock major and trace element compositions of serpentinized clasts recovered from Yinazao, Fantangisña, Asùt Tesoru, South Chamorro and Conical mud volcanoes largely overlap and therefore do not reflect these strong variations (Fig. 9 and 11). This is in good agreement with petrographic observations showing the existence of up and down movements beneath serpentinite mud volcanoes (e.g. Kawahara et al., 2016 or this study). We do however observe modifications of clasts chemistry according to mineralogy, i.e., Blue-, Liz-, Atg/Liz- and Atg- serpentinites.

The first step of serpentinization of the forearc mantle corresponds to the formation of brown serpentine (Liz-serpentinite), a mixture of chrysotile/lizardite with Fe-rich brucite, at the expense of mantle minerals (Fig. 13). As previously documented (e.g., Kahl et al., 2015; Peters et al., 2017; Savov et al., 2005, 2007), lizardite-dominated samples are characterized by high concentrations of fluid mobile elements (FME), such as B, Li, Cs, As, Sb, relative to primitive mantle and/or abyssal serpentinite/peridotite (Fig. 11). These enrichments have been attributed to the influx of slab-derived fluids in the forearc mantle at intermediate temperatures (200-500°C). The onset of subduction is accompanied by large amounts of compaction, deformation and metamorphic reactions (e.g. clay mineral or carbonate breakdown) in the slab resulting in the release of FME-rich fluids (e.g., Barnes et al., 2014; Bebout, 2013; Cannaò et al., 2015; Debret et al., 2013, 2018a; Hattori & Guillot, 2007). The transfer of such fluids to the overlying fore-arc mantle wedge allows its serpentinization and the storage of FME in forearc serpentinites.

The progressive burial of ultramafic material is accompanied by the recrystallization of Liz-serpentinites to antigorite, i.e., Atg/Liz- and Atg-serpentinites (Fig. 13). During this transformation, Cs, Li and Sr concentrations in serpentinites progressively decrease. Indeed, although a relatively small amount of water is released during the transition of lizardite to antigorite (e.g. Evans, 2004), this reaction can be accompanied with dissolution and leaching of C- and/or S- bearing phases (e.g. Debret et al., 2014) and FME released in fluids (e.g., Debret et al., 2013; Kodolányi & Pettke, 2011; Vils et al., 2011) suggesting that these elements are highly mobile in fluids during forearc burial. Boron concentrations remain high in Atg/Liz- and Atg-serpentinites relative to slab serpentinites (e.g., Vils et al., 2011; Debret et al., 2013) and/or abyssal peridotites/serpentinites (Andreani et al., 2009). This suggests that antigorite also crystallizes in equilibrium with B-rich slab derived fluids. *In situ* analyses of partly serpentinized forearc peridotites reveal that, in low temperature lizardite bearing serpentinites (< 200°C), serpentine textures integrate high amounts of B (up to 200 ppm, Pabst et al, 2011; Kahl et al., 2014). These values are close to those reported in antigorite bearing textures in mantle wedge settings (e.g., Deschamps et al., 2010). Hence, the absence of correlation between B concentrations and indices of prograde metamorphism suggests that, during the serpentinization of the forearc, saturation (or exchange equilibrium – e.g., Pabst et al., 2011) is rapidly reached in the serpentine, i.e., before the transition from lizardite to antigorite. In agreement with these observations, sediment pore water chemistry reveals progressive enrichments in Cs, Li and B concentrations with increasing distance to the trench (Fryer et al., 2018; Hulme et al., 2010; Mottl et al., 2003) confirming that these elements become progressively abundant in fluids during the progressive burial of the forearc (e.g., De

Hoog and Savov, 2018). In contrast to other fluid mobile elements, the concentrations of As, Sb and LREE progressively increase in whole rocks during the transition of lizardite to antigorite (Figs 9 and 10). Previous studies have shown that these elements can be incorporated in antigorite (e.g., Hattori et al., 2005). Fluids released during the early (shallow) stage of slab devolatilization are likely dominated by diagenesis and opal dehydration, whereas later (deeper) processes included decarbonation and clay mineral decomposition resulting in a modification of slab derived fluid composition (Bebout, 2013 and reference therein). As, Sb and the LREE are enriched in fluids derived from sediment decarbonation (Bebout, 2013; Debret et al., 2018a). Hence, we interpret the high As, Sb and LREE concentrations of the antigorite dominated serpentinites in terms of the onset of carbonate dissolution within the slab (e.g., carbonated altered oceanic crust). This scenario is in good agreement with high dissolved inorganic carbon concentrations of pore fluids from the furthest mud volcanoes (Asùt Tesoru, South Chamorro and Conical; Fryer et al., 2018).

During their exhumation forearc serpentinites are partly to fully recrystallized into blue serpentine. This episode is accompanied with a flattening of REE patterns (Fig. 10a – Group 1), probably linked to a high mobility of LREE in fluids (e.g., Fryer et al., 2018), and an increase in Zn concentrations (Fig. 11c). This observation suggests that the composition serpentinites recorded at depth can be partly overprinted by low-temperature reactions (< 250°C) during clast exhumation. However, the exact source of the added Zn is unclear as Zn can be mobile in fluids either at depth during serpentinite devolatilization (Pons et al., 2016), decarbonation processes (Debret et al., 2018a; Inglis et al., 2017) as well as near the seafloor through hydrothermal fluid circulation Debret et al., 2018b) and microbial activity via sulfate reduction (Kelley et al., 2009).

8. Conclusions

Our study reveals that the ultramafic clasts recovered in serpentinite mud volcanoes record three main stages of serpentinization (Fig. 13): the crystallization of brown serpentine bearing textures composed of a mixture of Fe-rich brucite and chrysotile and/or lizardite (stage 1 in Fig. 13); the formation of antigorite in equilibrium with magnetite and Fe-poor brucite at the expense of brown serpentine (stages 2 to 3 in Fig. 13); the late formation of blue serpentine associated with frambroidal sulfides during the exhumation of the ultramafic clasts (stage 4 in Fig. 13). The transition of lizardite to antigorite is enhanced by an increase of temperature from 200°C up to about 400°C within the forearc area. These estimates are in good agreement with thermodynamic calculations carried out by Evans (2004). The crystallization of antigorite at the expense of lizardite has been observed in different mud-volcanoes. Although most of the blue serpentine was observed at Yinazao, there is no evidence for a systematic serpentine phase change according to depth of the slab/mantle interface. These observations suggest the existence of complex transport mechanisms below the mud volcanoes, with the serpentinites being progressively dragged down to greater depth before their exhumation, potentially controlled by buoyancy, toward to the surface. In agreement with this scenario, no obvious changes of serpentinite clasts chemistry is observed according to depth to the slab/mantle interface (Fig. 9-11).In contrast, the crystallization of lizardite and then antigorite in serpentinites is accompanied with a decrease of Cs, Li, Sr and an increase in As, Sb and LREE concentrations in whole rock, whereas B concentrations are relatively constant. This suggests that the serpentinized mantle wedge acts as a filter for trace elements and controls the fluxes of these elements between the surface and the deep mantle. The fluid release during shallow metamorphic reactions (i.e., transition lizardite to antigorite) are likely to feed hydrothermal circulation near the surface. In contrast, the dragged down residue (Atg-serpentinites) will undergo a progressive increase in temperature, coupled to the ongoing burial, until its dehydration at greater depth. This process will release large amounts of fluid, thereby contributing to arc magmas genesis in subduction zones.

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Figure Captions

Fig. 1: Bathymetry map of the Mariana subduction system showing the locations of Yinazao, Fantangisña and Asùt Tesoru drilled during IODP Exp. 366 as well as Conical and South Chamorro that were drilled during previous ODP legs.

Fig. 2: Representative core images of the main lithostratigraphic units observed at Yinazao, Fantangisña and Asùt Tesoru flanks or summits. (a) Core image of the upper level unit recovered at the site U1492A (Yinazao summit, section 1H2-99/139cm). The uppermost units of the mud-volcano is made of red-brown pelagic mud containing carbonated serpentinite breccia and weathered serpentinites clasts (brown weathering). (b) Core image of the contact between upper and lower level units at the Site U1496A (Asùt Tesoru summit, section 1F1-1/41cm). The uppermost units of the mud-volcano is made of red-brown pelagic mud containing partly weathered serpentinite clasts. Note that the clast displays a carbonated and brown weathering crust toward to the core. The clast itself is also rimed by a halo of Blue-serpentinite while the core correspond to a Liz-serpentinite. The square indicates the localization of the macroscopic picture and thin section observations presented in Appendix A. The lower unit is made of blue-grey serpentinite mud containing serpentinite clasts of various size. (c) Core image of the lower level unit recovered at the Site 1492A (Yinazao summit, section 4F2-50/90cm). The lower unit is made of blue-grey serpentinite mud containing serpentinite clasts of various size. (d) Core image of a large clast of 40 cm long recovered at the Site 1498B (Fantangisña flank, section 3R3, 38-78cm).

Fig. 3: Photomicrographs (a: crossed polarized light; b and c: plane polarized light), back scattered electron image and Raman spectra of the carbonated (a) and blue (b-d) serpentinites recovered at the Yinazao mud volcano (photo taken by the Shipboard Scientists, 2018). (a) Carbonated breccia (shipboard sample U1491B-2H5-85/88) showing dismembered crack-seal like veins (mainly made of chrysotile, Ctl) embedded into a calcite (Cal) matrix. (b) Mesh textures with a pale blue colour (sample M7) and corresponding Raman spectra. The meshes centres are replaced by opaque aggregates composed of sulfide (pyrite) and brucite ± serpentine. Raman spectra of mesh rim (black line) and core (grey line) are mixtures between serpentine and brucite. In the high frequency region,

the core of the mesh is mainly dominated by brucite. White square: localisation of the Fig. 2s. (c) Opaque vein made of pyrite crossing mesh and bastite textures (shipboard sample U1492C-8F3-108/112). The centres of the mesh and bastite textures are associated with sulfides. (d) SEM observation of a mesh core (sample M7). The core is composed of brucite lamellae with interstitial framboidal pyrite.

Fig. 4: Plot of XCr vs. XMg of spinels in forearc ultramafic clasts from Yinazao, Fantangisña and Asùt Tesoru. Compositions broadly overlap with those of forearc peridotites and are more Fe- and Cr-rich with respect to abyssal peridotites (abyssal and forearc peridotite fields are from Dubois-Côté et al. (2005).

Fig. 5: Major element contents and normalized cations of the different serpentine phases. (a-b) Variations of XMg (= Mg / [Fe + Mg]) and FeO with SiO_2. (c-d) Variations of Mg and Fe cations per formula unit (p.f.u.) with Si + Al cations p.f.u. The decrease of XMg and SiO_2 in serpentine crystallizing in Blue serpentinites and Liz-serpentinites reflects the presence of Si-free, Fe-rich brucite at microscale. The brucite trend intercepts SiO_2 = 0 wt% value at #Mg = 0.84. Crystallization of antigorite (Atg/Liz-serpentinites and Atg-serpentinites) is associated with the disappearance of the brucite component in serpentine analyses, an increase in SiO_2 and XMg and a decrease in FeO in serpentine.

Fig. 6: Photomicrographs and corresponding Raman spectra of Liz-serpentinite recovered from Asùt Tesoru (Photomicrographs taken by the Shipboard Sci. Party, 2018). (a) Serpentine forms mesh textures with a brownish colour and preserved olivine relicts in their centres (plane polarized light, sample M19). Note the presence of euhedral and unaltered spinel on the microphotograph bottom. Mesh Raman spectra are mixed analyses of lizardite and brucite. (b) Antigorite vein with brucite and magnetite in its centre (crossed polarized light, shipboard sample U1497A-13G-CC-W 61/63). The vein crosscuts a lizardite/brucite-bearing vein.

Fig. 7: Photomicrographs (crossed polarized light) and corresponding Raman spectra of the Atg/Liz-serpentinites recovered from Fantangisña and Asùt Tesoru. (a) Antigorite crystallizes as several

hundred microns long lamellae penetrating mesh textures (sample M32). Centres of the antigorite veins are composed of magnetite and brucite. Note that the centres of the mesh textures show mixed Raman spectra between lizardite and antigorite. (b) Wide vein of brucite and magnetite crosscutting relicts of mesh textures (sample M13). The mesh texture is fully recrystallized into pure antigorite where it is in contact with the vein.

Fig. 8: Photomicrographs of Atg-serpentinites recovered from Asùt Tesoru (both in crossed polarized light). (a) Antigorite lamellae with interstitial brucite and magnetite (sample M16). (b) Brucite patch associated with euhedral grains of magnetite (sample M15).

Fig. 9: Bulk rock major element composition of Mariana ultramafic clasts illustrated in (a) Al_2O_3 vs MgO/SiO_2 and (b) MgO (wt.%) vs FeO (wt.%). South Chamorro (grey crosses) and Conical (black crosses; data from Geldmacher et al., 2008; Kodolanyi et al., 2011; Parkinson and Pearce, 1998; Pearce et al., 2000; Savov et al., 2007) are shown for comparison. On Fig. 9a, the dark line represents the silicate Earth differentiation trend and the primitive mantle ratio (PM; Godard et al., 2008). Changes in whole-rock ratios of both MgO/SiO_2 and Al_2O_3/SiO_2 accompany the transition (left to right) of depleted (e.g., dunite) to enriched (e.g., lherzolith) peridotites. On Fig. 9b, the dark line represents the stoichiometric variations of olivine Fe–Mg composition. Abyssal peridotite endmembers of dunite and lherzolite (Godard et al., 2008) are shown for comparison. Note that several samples display abnormal high MgO/SiO_2 and MgO contents, such reflect the ultra-refractory compositions of the ultramafic protoliths and/or the high amount of brucite in the samples.

Fig. 10: Whole-rock trace elemental compositions of the different ultramafic clasts (Blue-, Liz-, Atg/Liz- and Atg-serpentinites). (a) and (b) patterns are normalized to chondrite and primitive mantle (PM), respectively, using normalization values from Sun and McDonough (1989). Serpentinite mud analysis is from Kodolanyi et al. (2011). Group-1 correspond to blue serpentinites with flat patterns similar to that of serpentinite muds and Group-2 correspond to blue serpentinites, Liz-, Atg/Liz- and Atg- serpentinites with U-shaped patterns.

Fig. 11: Plots of Cs/Yb vs Li* (a), As vs Sb (b) and Sr vs Zn (c) of studied ultramafic clasts. Concentrations overlap well with those of ultramafic clasts from South Chamorro (grey crosses) and Conical (black crosses; data from Geldmacher et al., 2008; Kodolanyi et al., 2011; Parkinson and Pearce, 1998; Pearce et al., 2000; Savov et al., 2007, 2005). Abyssal peridotites (white circles; data from Andreani et al., 2014; Augustin et al., 2008; Boschi et al., 2013; Delacour et al., 2008; Jöns et al., 2010; Kodolanyi et al., 2011; Niu, 2004; Paulick et al., 2006; Rouméjon et al., 2014) have consistently lower Cs/Yb and Li* contents with respect to Liz- and Atg/Liz-serpentinites. Sr (~0.4-1000 ppm) and Zn (~30-200 ppm) concentrations of abyssal peridotites and serpentinites overlap with those of the forearc but were not presented here for sake of clarity.

Fig. 12: Plot of $\delta^{18}O$ (‰) variations in ultramafic clast pore fluids vs distance to the trench (km). The $\delta^{18}O_{fluid}$ values progressively increase passing from Yinazao to Fantangisña, Asùt Tesoru, South Chamorro and Conical. M: data from Mottl et al. (2003); A: calculated $\delta^{18}O_{fluid}$ in equilibrium with antigorite below Conical by Alt and Shanks (2006).

Fig. 13: Conceptual model illustrating serpentinisation processes in relation to fluid circulation and mantle flow within the Mariana forearc. Numbers in diagram correspond to those in the P-T diagram, where pressures have been estimated according to slab/mantle interface depth estimates below the mud volcanoes (Hulme et al., 2010). As clasts from the forearc mantle are dragged down to depth (stages 1 to 3), they undergo an increase in temperature from about 200 to 400°C and the associated transformation of lizardite into antigorite. During uplift, the clasts are variably retromorphosed into blue serpentinites (stage 4).

Figure1
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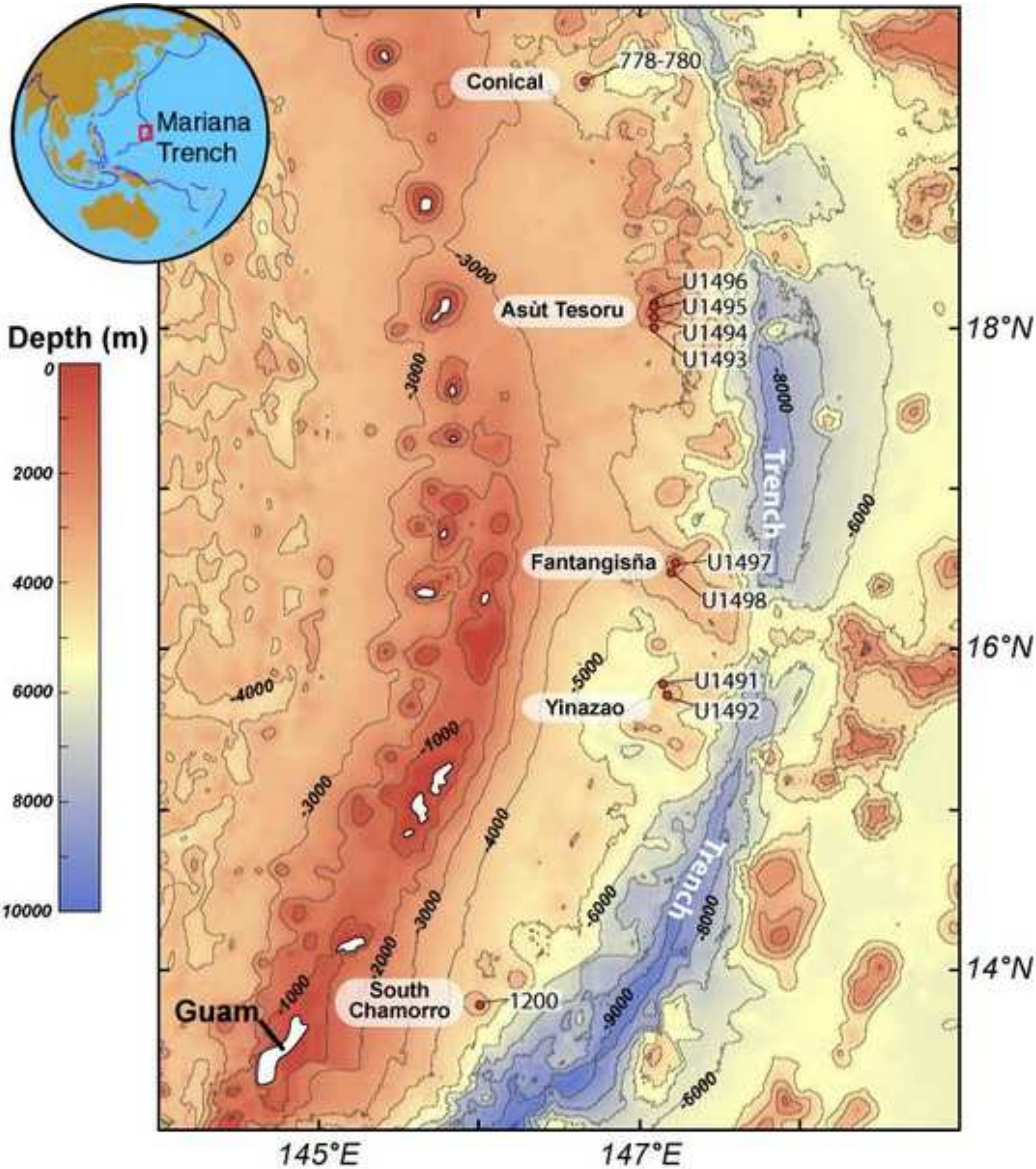

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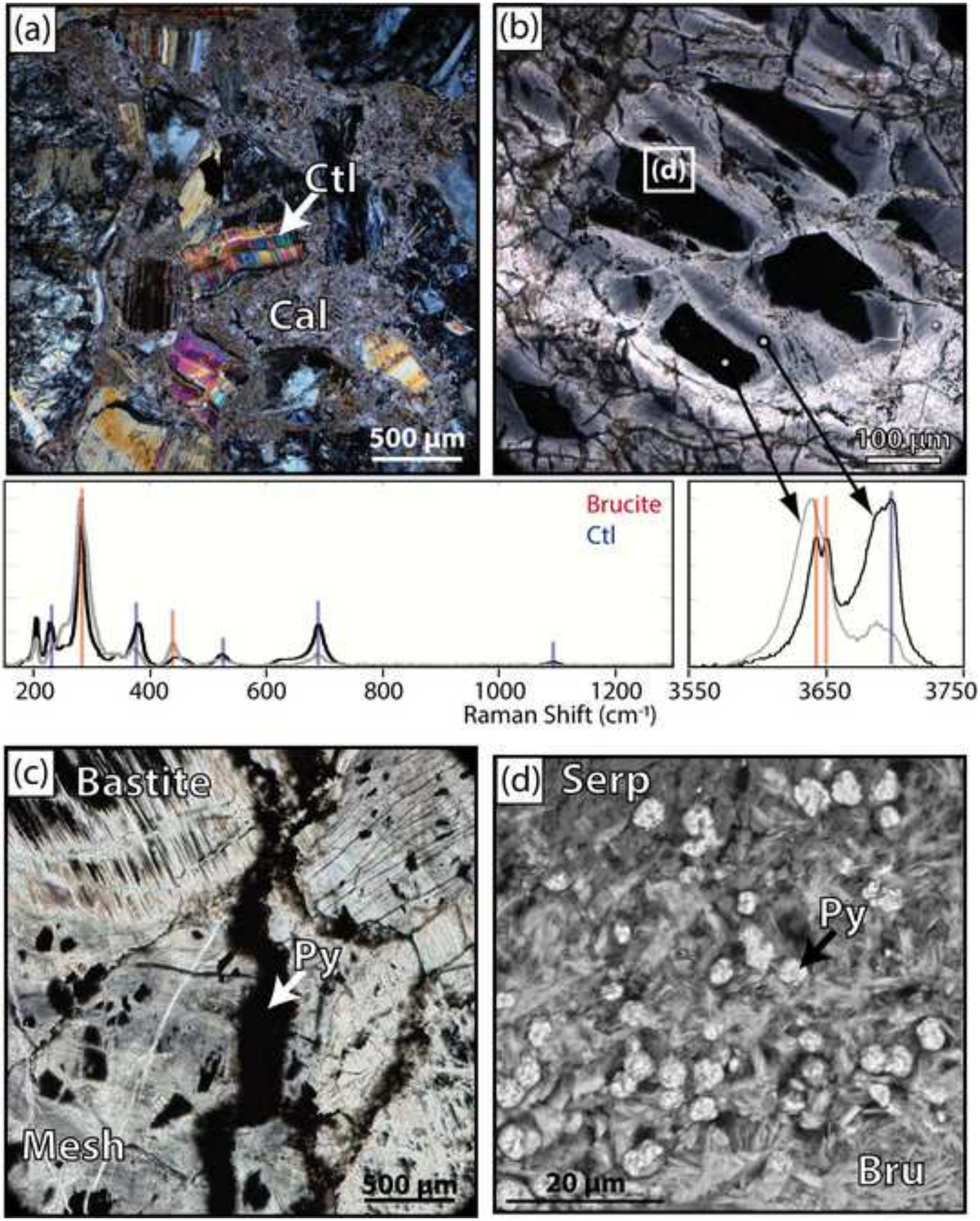

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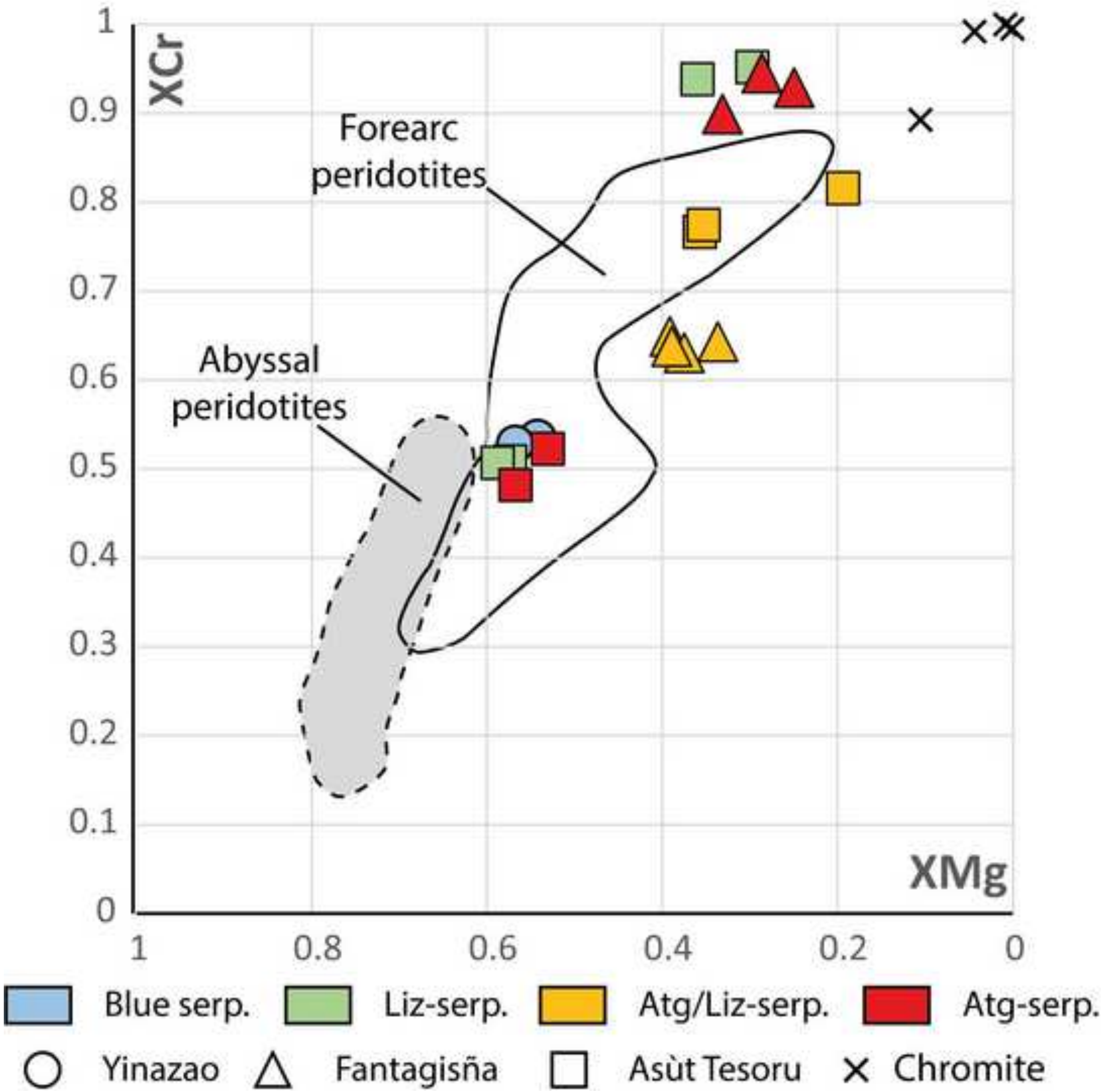

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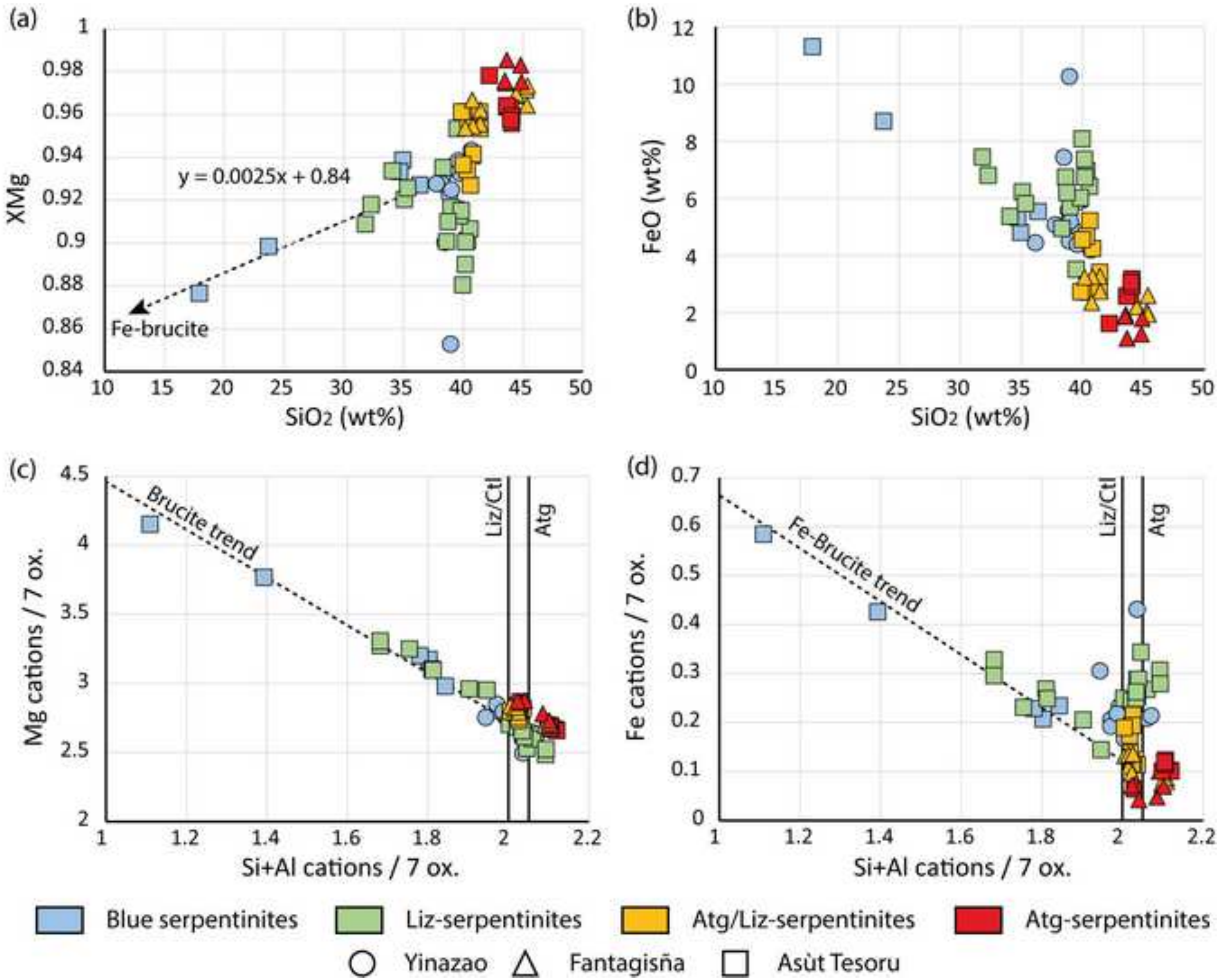

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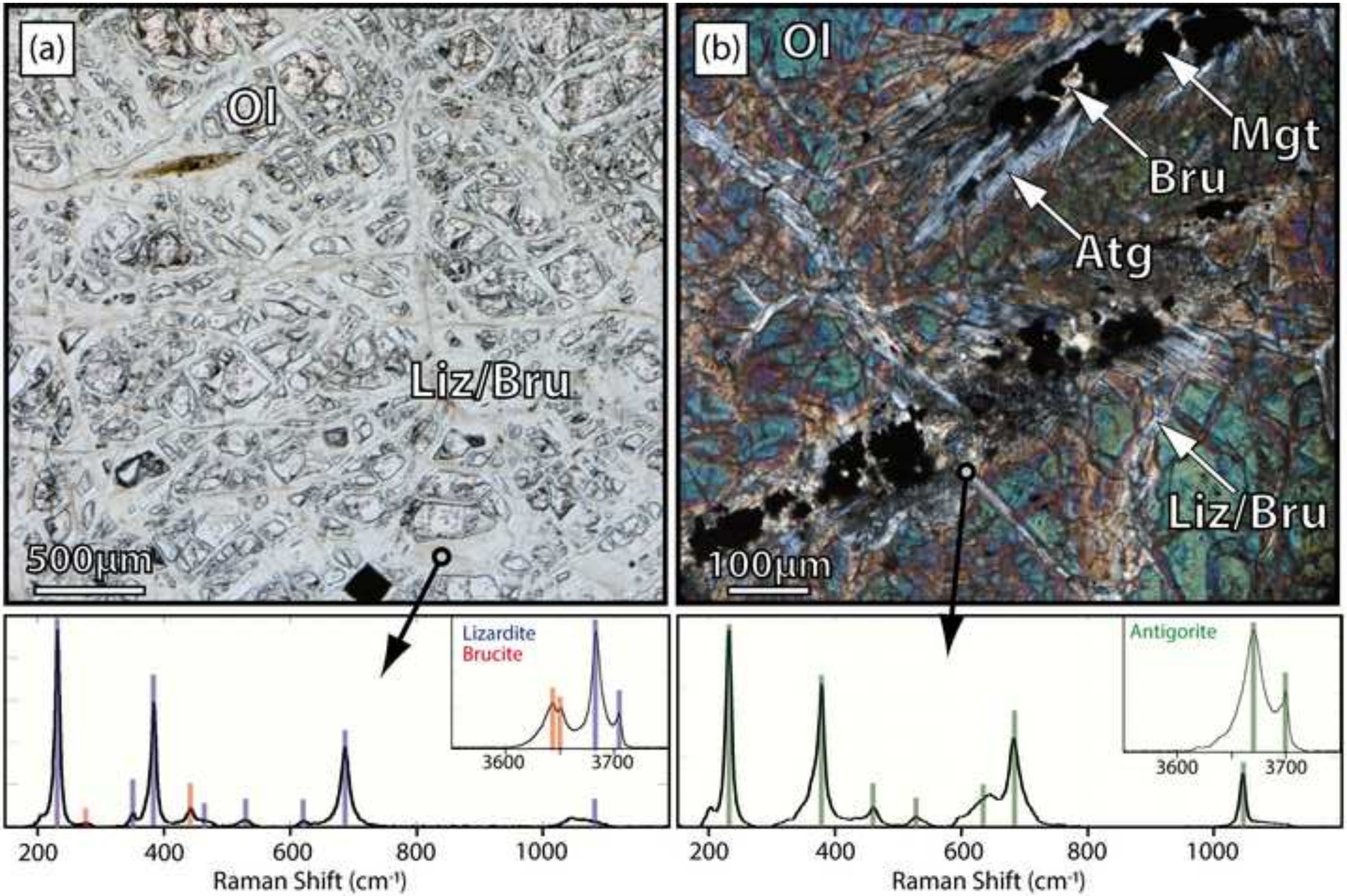

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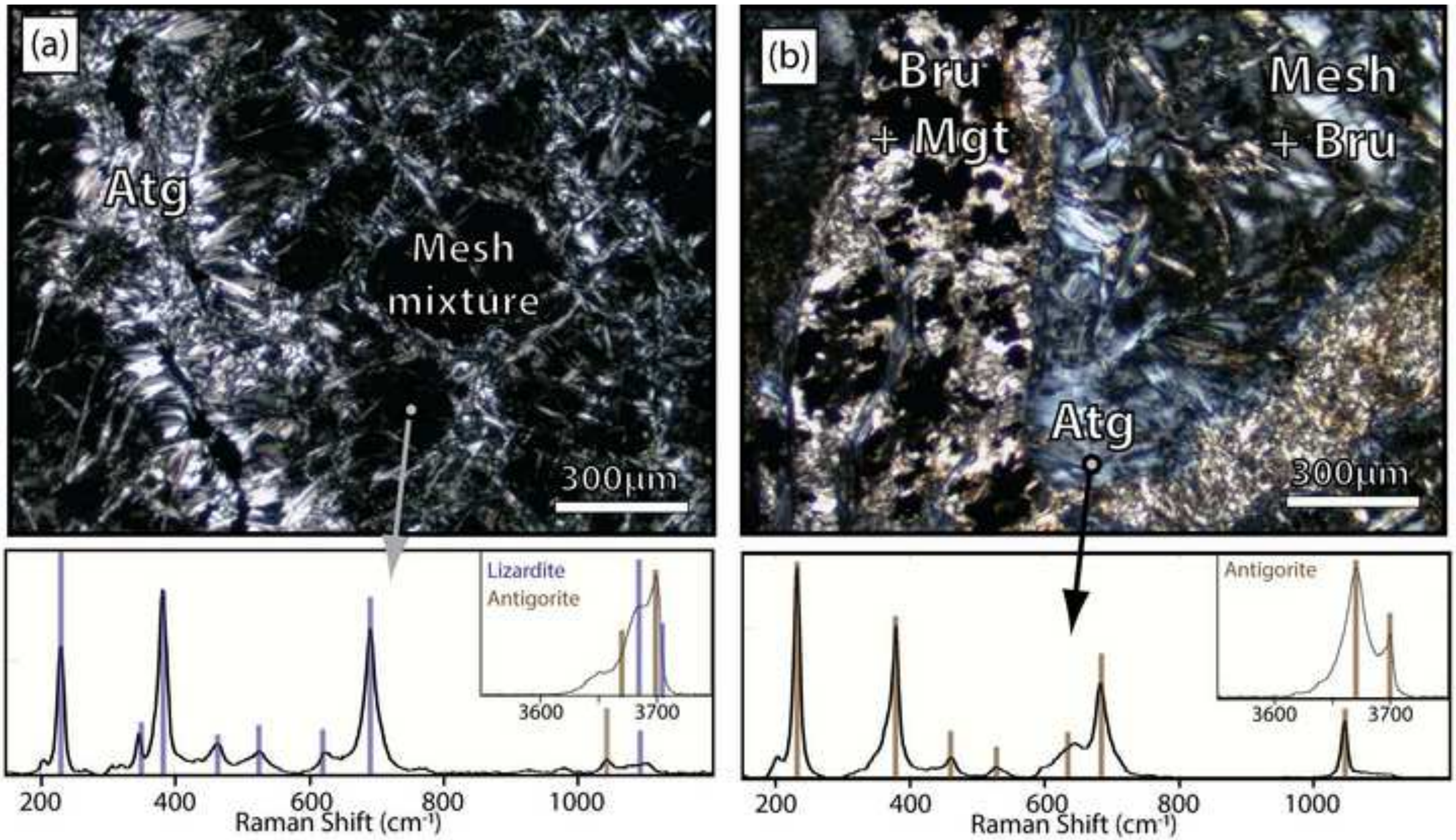

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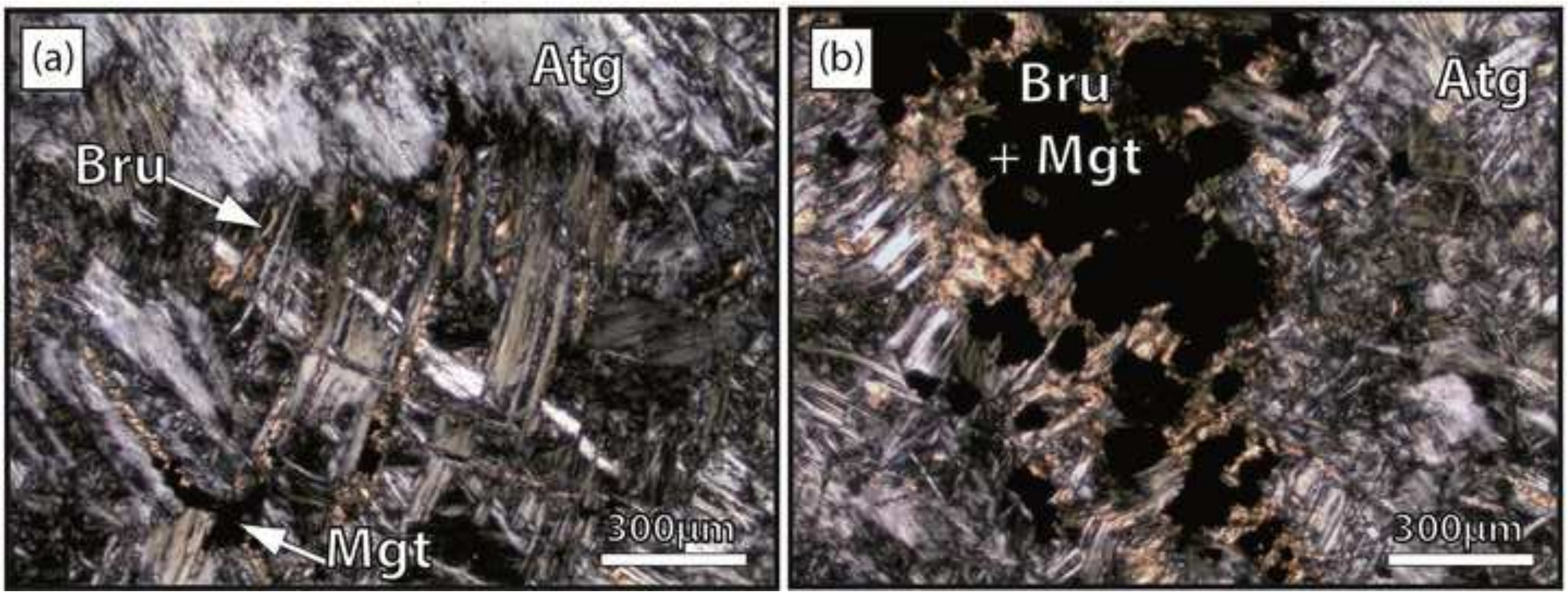

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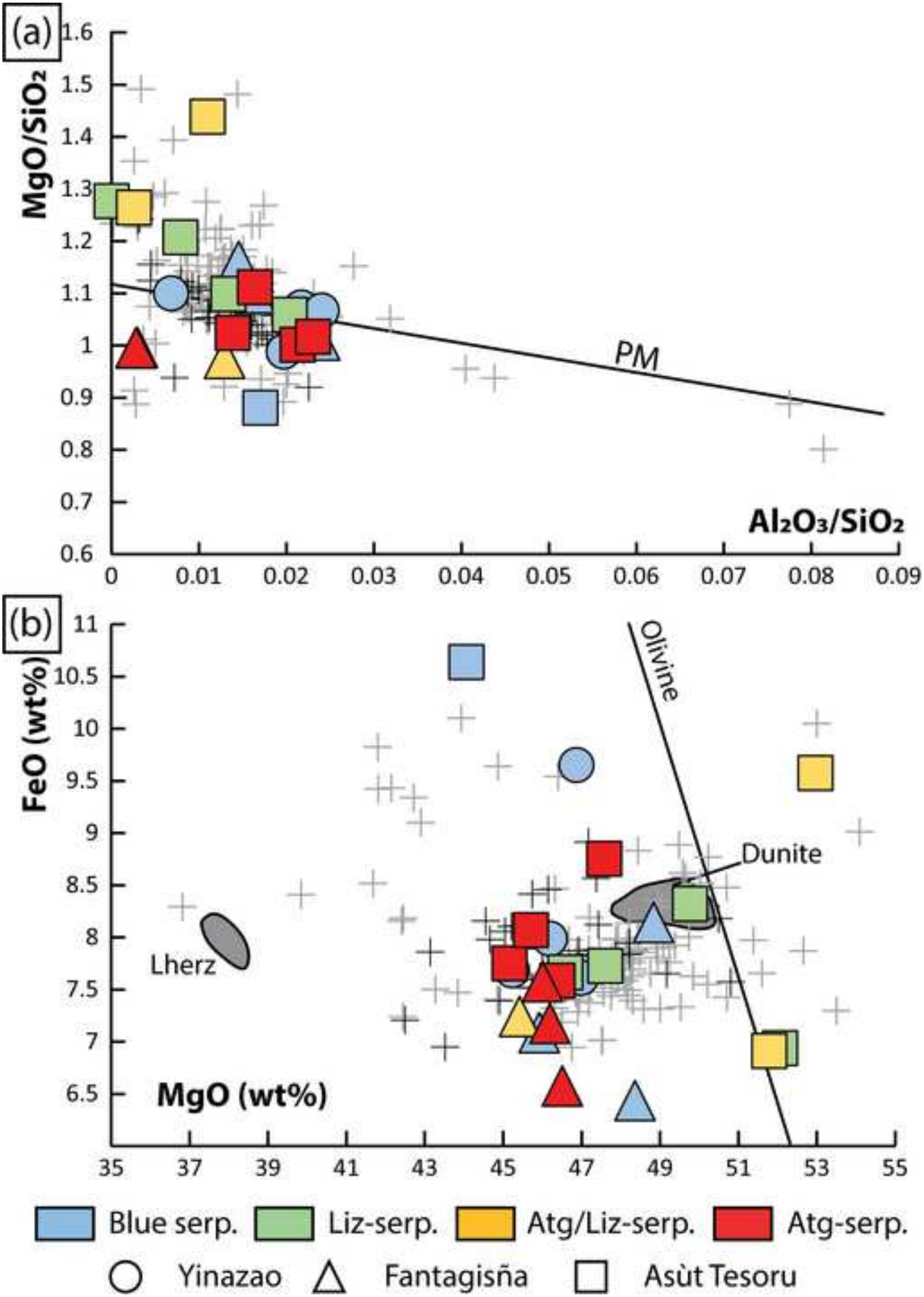

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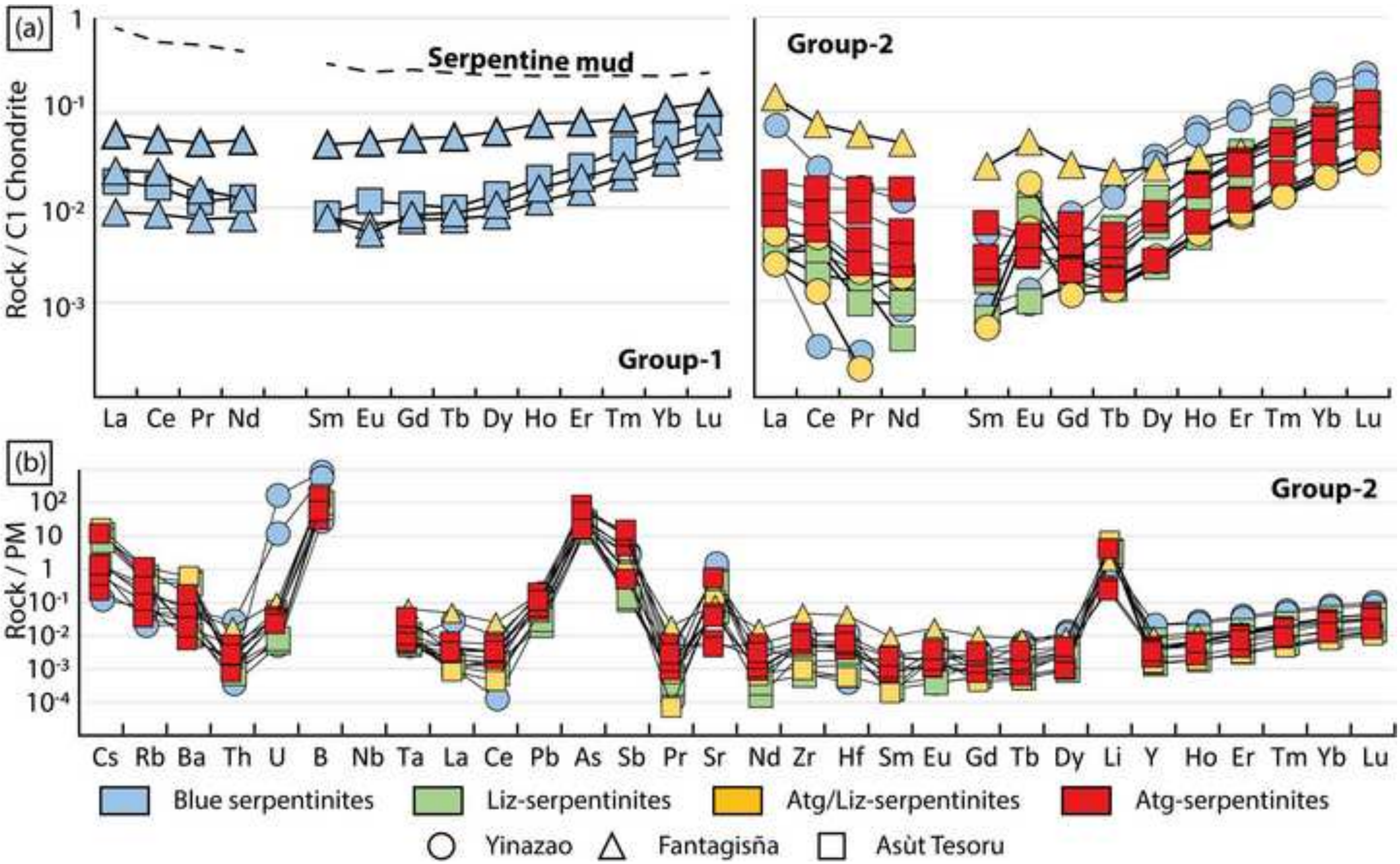

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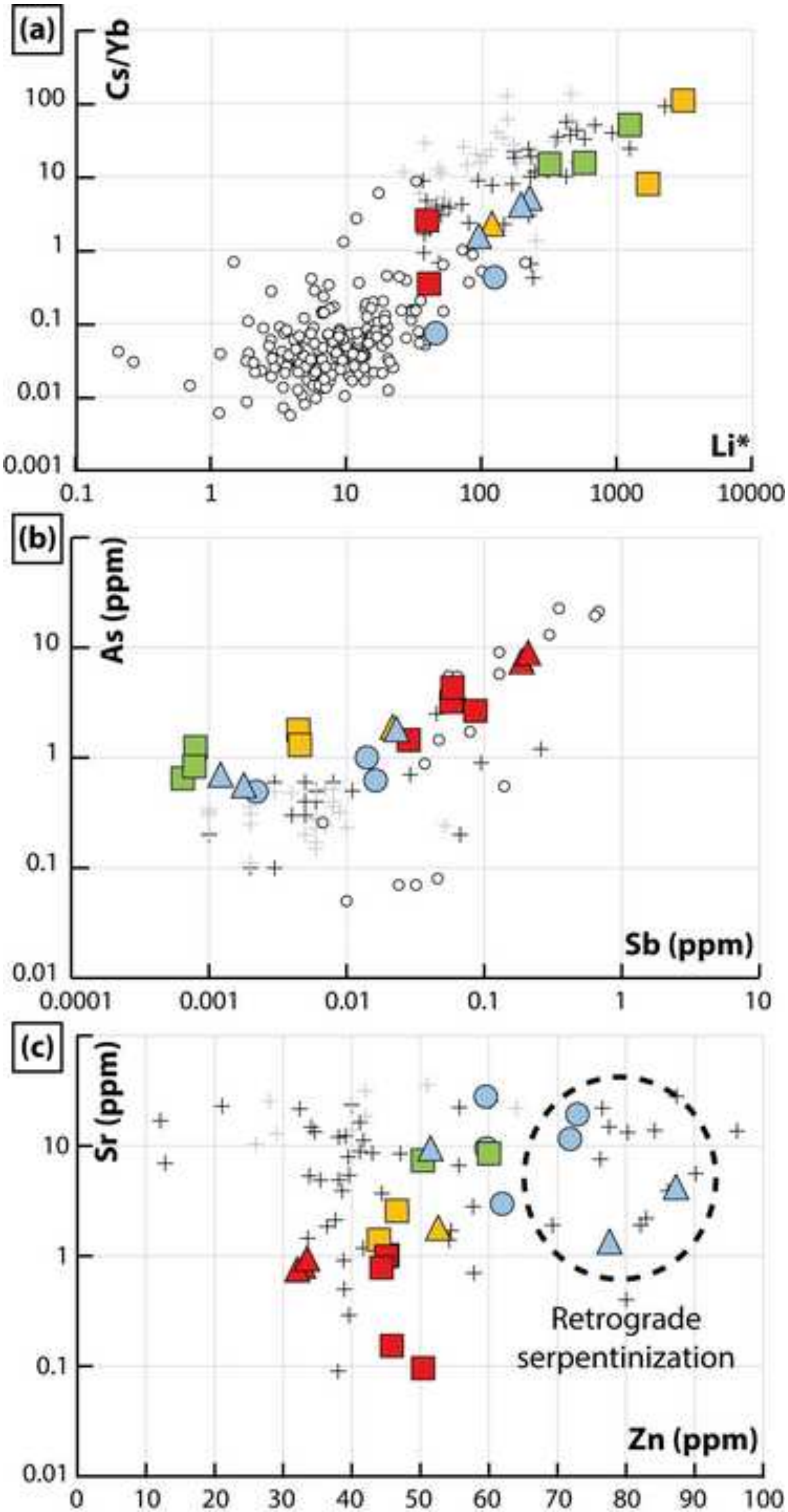

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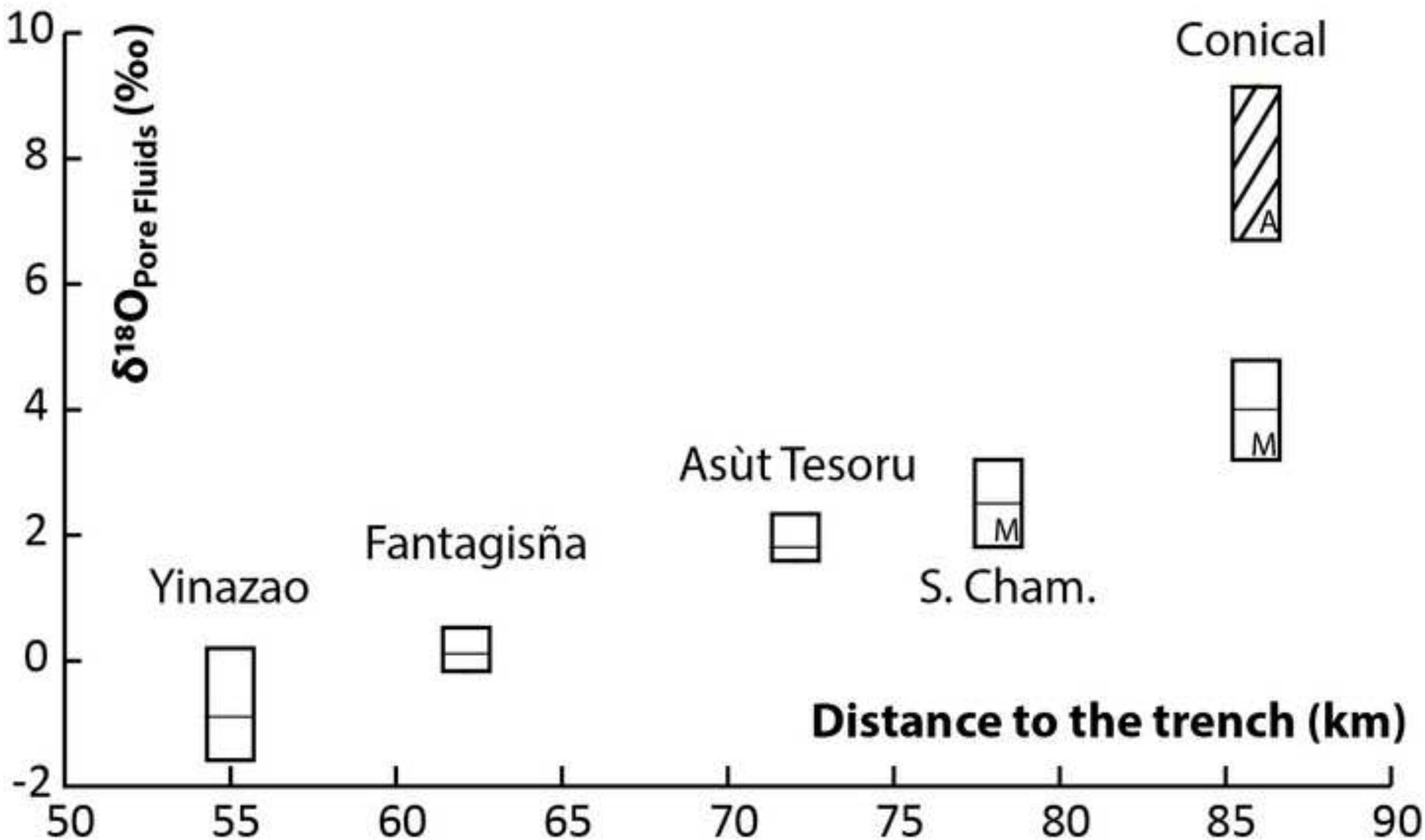

Figure13

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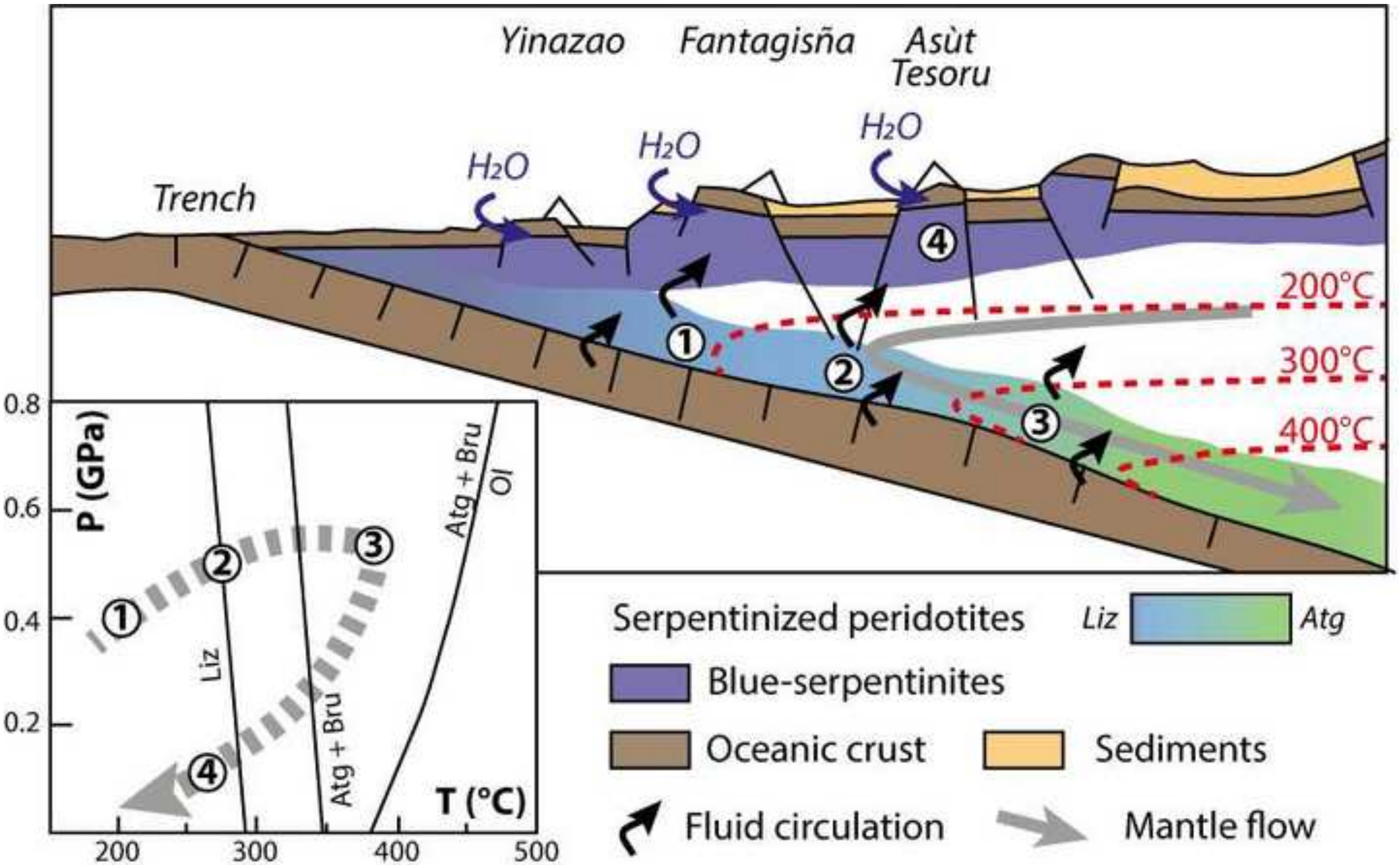

Table 1: Oxygen isotope data and resultant temperature estimates for selected samples. Pore fluid $\delta^{18}O$ are minimum, maximum and average values.

Reference	**$\delta^{18}O_{Srp}$ (‰)**	**$\delta^{18}O_{fluid}$(‰)**			**T (°C)[1]**			**$\delta 18O_{fluid}$* (‰)**	**T(°C)[1]**	**$\delta^{18}O_{Mgt}$ (‰)**	**T(°C)[2]**
		mean	min	max	mean	min	max				
Blue serpentinite											
M3	6.4	-0.9	-1.4	-0.1	183	176	194	-	-	-	-
M30	7.4 *(7.3)*	0.1	0.0	0.3	183	181	184	-	-	-	-
Liz-serpentinite											
M9	7.6	1.8	1.7	2.0	205	203	206	-	-	-	-
M10	6.8	1.8	1.7	2.0	220	218	222	-	-	-	-
Atg/Liz-serpentinite											
M12	6.1	1.8	1.7	2.0	232	230	234	4.0	276	-	-
M13	5.8	1.8	1.7	2.0	238	236	240	4.0	283	-	-
Atg-serpentinite											
M14	8.0	-	-	-	-	-	-	-	-	1.8	340
M15	7.1	-	-	-	-	-	-	-	-	1.8	409
M51	8.3	-	-	-	-	-	-	-	-	1.8	322

All $\delta^{18}O$ values are given in SMOW. (*value*): duplicate; 1: thermometer serpentine/fluid of Saccocia et al (2009); 2: thermometer serpentine/magnetite of Wenner and Taylor (1971) revised by Früh-Green et al. (1996); *fluid value from Mottl et al. (2003).

AppendixA

AppendixB
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AppendixC

AppendixE

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AppendixF

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