Investigating Palaeoatmospheric Composition-Climate Interactions

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Declaration

This dissertation 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. It is not substantially the same as any that I have submitted, or, is being concurrently submitted for a degree or 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. I further state that no substantial part of my dissertation 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 60,000 words including summary/abstract, tables, and footnotes.

David Christopher Wade
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“These old... walls, I say, were not peopled with fatsams; but with men of flesh
and blood, made altogether as we are... who knows but we ourselves had
taken refuge from an evil Time, and fled to dwell here, and meditate on an
Eternity, in such fashion as we could?”

— Thomas Carlyle, Past and Present, Book II
Abstract

The composition of the atmosphere has changed substantially over Earth’s history, with important implications for past climate. A number of case studies will be presented which employ coupled climate model simulations to assess the strength of these chemical feedbacks on the climate.

The eruption of Mount Samalas in 1257 led to the largest stratospheric volcanic injection of aerosol precursor gases in the Common Era, however climate model simulations of the last millennium typically overestimate the resulting climatic cooling when compared with tree-ring proxy records. A novel configuration of the Met Office UM-UKCA climate model is presented which couples an atmosphere-ocean general circulation model to a rigorous treatment of the relevant atmospheric chemistry and microphysical aerosol processes. This permits the climate response to a particular stratospheric injection of reactive volatile gases to be quantified and for the first time to date applied to a historical volcanic eruption. This model configuration compares favourably to observational data for simulations of the 1991 Mount Pinatubo eruption. Results from an ensemble of model simulations are presented, with different assumptions about the sulfur dioxide and halogen loadings based on a recent geochemical reconstruction. These show a muted climate response, in reasonable agreement with tree ring records. Emissions of halogenated compounds lead to an increase in the sulfur dioxide lifetime, widespread ozone depletion and a prolonged climatic cooling. Strong increases in incident ultraviolet radiation at Earth’s surface also occur.

Oxygen levels may have varied from as little as 10% to as high as 35% in the Phanerozoic (541 Ma – Present). An increase in atmospheric oxygen increases atmospheric mass which leads to a reduction in incident shortwave radiation at Earth’s surface due to Rayleigh scattering. However, this is offset by an increase in the pressure broadening of greenhouse gas absorption lines. Dynamical feedbacks also lead to increased meridional heat transport, warming polar regions and cooling tropical regions. An increase in oxygen content using the HadCM3-BL and HadGEM3-AO climate models leads to a global mean
surface air temperature increase for a pre-industrial Holocene base case, in agreement with idealised 1D and 2D modeling studies. Case studies from past climates are investigated using HadCM3-BL which show that in the warmest climates, increasing oxygen may lead to a temperature decrease, as the equilibrium climate sensitivity is lower. For the Maastrichtian (72.1 – 66.0 Ma), increasing oxygen content leads to a better agreement with proxy reconstructions of surface temperature at that time irrespective of the carbon dioxide content.

There is considerable uncertainty in the timing of the rise in atmospheric oxygen content from values around 1% in the Neoproterozoic (1000 Ma – 541 Ma) to the 10-35% values inferred in the Phanerozoic with respect to two global glaciation episodes (717-635 Ma). Results of simulations with HadCM3-BL which investigate the impact of oxygen content on the Neoproterozoic Snowball Earth glaciations are presented. These demonstrate that a smaller reduction in carbon dioxide content is required to initiate a Snowball Earth at low oxygen content. Geological evidence suggests the presence of a basaltic large igneous province before the Sturtian Snowball Earth episode. This could have caused episodes of paced explosive volcanism, injecting sulfate aerosol precursors into the stratosphere. Results of simulations to investigate the impact of different volcanic aerosol emission scenarios are presented. 500 Tg SO\textsubscript{2} is investigated with a range of aerosol sizes. For aerosol size distributions consistent with the aerosol evolution in the aftermath of the Mount Pinatubo eruption, the Earth enters a Snowball Earth in between 30 and 80 years. Using a larger size of aerosols, consistent with a larger eruption, does not lead to a Snowball Earth.

These simulations show that changes to the chemical composition of the atmosphere, whether reactive gases or bulk chemical composition may have played an important role in the past climate of Earth.
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Nomenclature

Select Chemical Species

- CH$_4$  Methane
- CO$_2$  Carbon Dioxide
- H$_2$O  Water Vapour
- H$_2$SO$_4$  Sulfuric Acid
- N$_2$  Nitrogen
- N$_2$O  Nitrous Oxide
- O$_2$  Oxygen
- O$_3$  Ozone
- OH  Hydroxyl Radical
- SO$_2$  Sulfur Dioxide

Acronyms / Abbreviations

AO – GCM  Atmosphere-Ocean General Circulation Model
BDC  Brewer-Dobson Circulation
CESM – LME  Community Earth System Model - Large Millennium Ensemble
CMIP5  Coupled Model Intercomparison Project Phase 5
CRF  Cloud Radiative Forcing
EBM  Energy Balance Model
Nomenclature

ECS  Equilibrium Climate Sensitivity
ENSO  El Niño Southern Oscillation
EOF  Empirical Orthogonal Function
GCM  General Circulation Model
GMSAT  Global Mean Surface Air Temperature
GMST  Global Mean Surface Temperature
GOE  Great Oxidation Event
GPP  Gross Primary Productivity
IPCC  Intergovernmental Panel on Climate Change
ITCZ  Intertropical Convergence Zone
LIP  Large Igneous Province
MXD  MiXed wood Density
NPP  Net Primary Productivity
PFT  Plant Functional Type
PIH  Pre-Industrial Holocene
QBO  Quasi-Biennial Oscillation
sAOD  Stratospheric Aerosol Optical Depth
TRW  Tree-Ring Width
TSI  Total Spectral Irradiance
TTL  Tropical Tropopause Layer
UV  UltraViolet (radiation)
Chapter 0

A Note on Nomenclature and the Geologic Timescale

"Many who have learned from Hesiod the countless names of gods and monsters never understand that night and day are one"

— Heraclitus, Fragments

There is ongoing debate as to proper nomenclature for time periods in the Earth sciences. Time before present is indicated by ka (thousands of years ago), Ma (millions of years ago), Ga (billions of years ago) etc. while time periods are indicated by kyr (thousands of years in duration), Myr and Gyr. This is conventional in the Earth sciences community (Christie-Blick, 2011) and is employed here to avoid confusion which would be caused by employing the IUPAC standard (Holden et al., 2011). The GSA Geologic Time Scale is employed as detailed overleaf.

Throughout this thesis, aerosol refers to the particle component only of the ‘true’ aerosol, the suspension of particles in air. “Aerosol” refers to a population of similar particles and “aerosols” refers to a collection of aerosol of different compositions, e.g. sulfate aerosol, stratospheric aerosols. This is common in atmospheric aerosol science (Seinfeld and Pandis, 2006).

In the context of climate on Earth, greenhouse gas inventory is typically quoted as a volume fraction, the ratio of the number of molecules of that greenhouse gas to all molecules. For instance, 280 ppmv of CO\textsubscript{2} means that there are 280 molecules of carbon dioxide for every million molecules of air in the atmosphere. When the mass of the atmosphere changes, a constant volume mixing ratio would imply a different total mass of greenhouse gases. To maintain a constant total mass, or inventory, would therefore require
Fig. 1 The GSA Geologic Timescale ©The Geological Society of America.
altering the volume mixing ratio. As Earth's atmosphere contains two major components, oxygen and nitrogen, physical characteristics such as the molecular weight will change. These changes are relatively small as diatomic molecules with similar molecular masses will have similar physical characteristics. Throughout the text, greenhouse gas inventory is quoted as a partial pressure in Pascal unless otherwise noted as this quantity is invariant to atmospheric mass. The partial pressure, the hypothetical pressure of that gas if it alone occupied the entire volume of the original mixture at the same temperature, of any gaseous species X is given as $p_X$ throughout the text. Major gas inventory refers to the mass of that major gas in the atmosphere. A different atmospheric oxygen inventory is typically referred to as a percentage, assuming that the inventory of nitrogen and argon remain constant. Strictly, describing the atmospheric composition requires a knowledge of the surface pressure and the percentage of each constituent by volume or mass.
Chapter 1

Past Climate on Earth

Earth's history contains many examples of climatic evolution and revolution. In this chapter I will outline the key drivers of Earth's climate, examine the role that volcanic eruptions have played in the climate system and detail the rise of atmospheric oxygen on Earth. I will put forward the case that changes to the chemical composition of Earth's atmosphere have had a significant influence on the evolution of climate.

1.1 A Brief Summary of Climate on Earth

1.1.1 Atmospheric Structure

99% of Earth's atmosphere is located in the 50 km above its surface in two physically and chemically distinct layers (Seinfeld and Pandis, 2006). The troposphere contains 80% of the mass of the atmosphere and is located from the surface to around ~8 km at the poles and ~17 km in the tropics. It is characterised by a reduction in temperature with height. This positive lapse rate leads to convective instability and is important for sustaining the greenhouse effect (Pierrehumbert, 2010). Water vapour levels are also highest here. The stratosphere is heated from above by absorption of solar radiation by ozone and oxygen. This leads to vertical stability. Very cold temperatures at the tropopause, which marks the barrier between the stratosphere and troposphere, limit the concentrations of condensible gases that can enter the stratosphere. Therefore water vapour levels are much lower in the stratosphere.
1.1.2 Atmospheric Circulation

The tropospheric circulation in the zonal and annual mean is typically described as containing three circulation cells in each hemisphere (see Figure 1.1). The Hadley cells occur between the equator and 30° N/S. This circulation cell is primarily thermally driven – air rises in the tropics due to strong surface insolation. Poleward flow occurs in the upper troposphere where it is deflected by the Coriolis force leading to strong zonal jets centred on 30° N/S. Closure of the Hadley cell leads to a region of low pressure at the equator associated with heavy precipitation (inter-tropical convergence zone, ITCZ) and high pressure in the subtropics typically associated with arid land regions. Weaker Ferrel cells (30N-65N, 30S-65S) and polar cells complete the zonal and annual mean tropospheric circulation. The stratospheric circulation in the zonal mean is characterised by tropical tropospheric air rising and moving polewards, descending in the middle and high latitudes (see Figure 1.1). This ‘Brewer-Dobson Circulation’ (BDC) is a two-cell structure in the lower stratosphere with a single cell towards the winter pole at high altitudes (Plumb, 2002). This is driven by insolation and the breaking of atmospheric waves from the troposphere (Butchart, 2014). Similarly to the troposphere, there is a strong Coriolis-driven zonal jet around 50 km (polar night jet).
1.1 A Brief Summary of Climate on Earth

1.1.3 Energy Balance

For Earth, the main source of energy to warm the planet is by absorption of light from the sun. If Earth did not emit radiation to balance this ~340 Wm$^{-2}$, it would heat without bound. Earth emits radiation to balance that of the sun. The irradiance $B$ of a black body is given by

$$B(v, T_{\text{eff}}) = \frac{2h v^2}{c^2} \frac{1}{e^{hv/kT_{\text{eff}}} - 1}$$  \hspace{1cm} (1.1)

where $T_{\text{eff}}$ is the effective emission temperature of the black body (e.g. Sun or Earth), $h$ is the Planck constant, $c$ is the speed of light in a vacuum, $v$ is the radiation frequency and $k$ is the Boltzmann constant. The normalised black body spectra for Earth (255 K) and the Sun (5780 K) are shown in Figure 1.2. As a much cooler black body, Earth emits in the infrared region of the electromagnetic spectrum while the sun emits in the more energetic visible region. The effective temperature of Earth is significantly lower than its surface temperature due to the reflectivity of its surface and atmosphere and the greenhouse effect. At equilibrium, black body irradiance balances incoming solar radiation from the sun so $T_{\text{eff}}$ can be expressed as

$$\sigma T_{\text{eff}}^4 = \frac{1}{4} (1 - \alpha) L_\odot$$  \hspace{1cm} (1.2)

where $L_\odot$ is the incoming stellar radiation (1365 Wm$^{-2}$ in present-day), $\alpha$ is the planetary albedo and $\sigma$ is the Stefan-Boltzmann constant. If Earth absorbed all stellar radiation, it would radiate at an effective temperature of 278.5 K but accounting for Earth’s planetary albedo (~0.30) leads to a $T_{\text{eff}}$ of 254.8 K, significantly below its surface temperature. Neither of these calculations take into account the greenhouse effect, which raises the surface temperature ($T_s$) above $T_{\text{eff}}$.

Greenhouse gases in Earth’s atmosphere, such as carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O) and water vapour (H$_2$O), absorb infrared radiation. The strength of a particular greenhouse gas and therefore its contribution to the overall greenhouse effect depends on its abundance, its atmospheric residence time and its absorption characteristics which depend on its intrinsic molecular structure (Khalil, 1999). Carbon dioxide, water vapour, methane and nitrous oxide are the strongest greenhouse gases in Earth’s atmosphere. As the atmosphere warms, it emits more infrared radiation and some of this reaches Earth’s surface and heats it more than it would in the absence of these greenhouse gases (Arrhenius, 1897; Tyndall, 1861). 333 Wm$^{-2}$ of downwelling infrared
radiation is absorbed by Earth’s surface in the present day atmosphere (see Figure 1.3). This raises Earth’s surface temperature above the atmospheric temperature and raises the level of effective infrared emission. This is somewhat compensated by latent and sensible heat fluxes from Earth’s surface to the atmosphere. In addition, heat transport within the atmosphere causes a net increase in global mean surface temperature. This is caused by the transport by the atmosphere and ocean of heat polewards from the equator.

In the absence of water vapour, the vertical profile of temperature in the troposphere would follow the dry adiabatic lapse rate

\[ \Gamma_d = \frac{g}{c_p} = 9.8 ^{\circ} \text{C km}^{-1} \] (1.3)

where \( g \) is acceleration due to gravity and \( c_p \) is the specific heat of dry air at constant pressure. The presence of water vapour reduces this lapse rate as energy is transferred between the surface and the atmosphere by latent heat (~80 W m\(^{-2}\), see Figure 1.3). Conductive (sensible) heat fluxes are also important where surface and air temperatures differ.

In the visible spectrum, many atmospheric gases absorb radiation. Ozone and oxygen are important absorbers of ultraviolet radiation which leads to heating in the upper stratosphere and maintains this temperature stability. Molecules themselves can scatter visible radiation and aerosol particles can also scatter radiation in the Mie scattering regime (Mitchell et al., 1995). Water vapour also absorbs visible radiation, particularly in the troposphere where water vapour levels are high. Water vapour therefore plays a key role in the climate system by absorbing both visible and infrared radiation, reducing the tropospheric lapse rate, transferring heat from the surface to atmosphere and acting as a feedback on climatic changes (Held and Soden, 2000). Water vapour strongly enhances
Fig. 1.3 Earth's global energy budget. Figure reproduced from Trenberth et al. (2009), after Kiehl and Trenberth (1997).
the impact of CO$_2$ changes, assuming that relative humidity remains constant (Manabe et al., 1967).

Equation 1.2 can be extended to simply account for changes in atmospheric transmissivity and emissivity. Figure 1.4 shows a schematic for such a consideration of the equilibrium climate from a given visible transmissivity ($\tau_{\text{vis}}$) and infrared emissivity ($\epsilon_{\text{ir}} = 1 - \tau_{\text{ir}}$ as by Stefan's law transmissivity and emissivity sum to unity). Considering energy balance at the top-of-atmosphere and surface, after algebraic simplification the surface temperature can be given by

$$\sigma T_s^4 = F_{\text{solar}} \left( \frac{1 + \tau_{\text{vis}}}{2 - \epsilon_{\text{ir}}} \right)$$ (1.4)

which in the limit of no atmosphere ($\tau_{\text{vis}} = 1.0, \epsilon_{\text{ir}} = 0.0$) simplifies to equation 1.2 when $F_{\text{solar}} = \frac{1}{4}(1 - \alpha)L_\odot$. The atmospheric temperature $T_{\text{at}}$ (equivalent to $T_{\text{eff}}$) is given by

$$\sigma T_{\text{at}}^4 = F_{\text{solar}} \left( \frac{1 - \tau_{\text{vis}} + \tau_{\text{vis}} \epsilon_{\text{ir}}}{\epsilon_{\text{ir}}(2 - \epsilon_{\text{ir}})} \right)$$ (1.5)

Values for these parameters can be constrained from Figure 1.3. Using values of $\alpha = 0.299$, $\tau_{\text{vis}} = 0.674$ and $\epsilon_{\text{ir}} = 0.861$ leads to downwelling shortwave radiation of 161.2 W m$^{-2}$ and outgoing longwave radiation of 239.2 W m$^{-2}$ in reasonable agreement with Figure 1.3 but an underestimate of the surface temperature (7.5°C vs -14°C). This discrepancy is likely due to heat transport causing a net warming of the atmosphere. Changes to emissivity, transmissivity and albedo can then impact climate. For instance, a 3.0°C warming can be achieved by increasing emissivity by 0.048 from 0.861 to 0.909. Alternatively, reducing planetary albedo by 0.031 from 0.299 to 0.268 can achieve the same surface temperature increase. The surface temperature changes associated with anthropogenic climate change can then be understood as a combination of changes to longwave and shortwave contributions (Donohoe et al., 2014) by increasing atmospheric emissivity and reducing planetary albedo: a combined albedo reduction of 0.019 and increase in infrared emissivity of 0.019 would also achieve a 3.0°C surface temperature increase in the 1-layer model. While this is a useful tool for understanding broad changes to climate, it does not provide a mechanistic understanding.

There has been a long history of including these mechanistic processes into numerical or analytical models of climate. The use of radiative transfer in a 1-dimensional model framework was performed by Callendar (1938) to calculate the climate response to CO$_2$ changes while the first general circulation model (GCM) of the atmosphere was described
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by Phillips (1956). Climate models have developed in sophistication from analytical energy-balance approaches (Budyko, 1969; Sellers, 1969) to 1D models which assume radiative convective equilibrium and fixed relative humidity (Manabe et al., 1967) to include idealised ocean processes (Manabe et al., 1969). The first fully coupled climate model with realistic topography made it possible for the first time to investigate the factors which would contribute to a changing climate (Manabe et al., 1975). Since then, the increase in computational power has allowed the expansion in the number of processes and increases in model resolution. Model representation of clouds in particular has proven to be challenging and their representation in both the present atmosphere and their changes under climate forcing dominate the differences between different climate models (Bony et al., 2015; Cess et al., 1990). The radiative effects of clouds have an overall cooling effect, however this is a small residual between a larger negative shortwave term and a positive longwave term which means that small changes in cloud properties can therefore have large climate impacts. As clouds are by their nature small-scale features, changes to clouds cannot be incorporated into simpler models.

The composition of the atmosphere has changed considerably throughout Earth’s history from a CO₂-H₂O dominated atmosphere in the Hadean (Shaw, 2008) to one dominated by nitrogen (N₂) and oxygen (O₂) today. By altering the radiative balance of the atmosphere, even trace gases and particles can considerably alter the radiative balance and therefore atmospheric temperatures. I will now consider how volcanic eruptions have led to compositional and climatic changes in Earth’s history directly by the injection of sulfur species into an oxidising atmosphere and then indirectly through the impact volcanic outgassing may have had on the evolution of atmospheric oxygen.
1.2 Volcanic Eruptions & Climate

Volcanic activity on Earth is heavily correlated with plate tectonics. Figure 1.5 shows the spatial distribution of tectonic plates and active volcanoes since the beginning of 2018 – volcanic activity throughout the Holocene has been dominated by the ‘Pacific Ring of Fire’. While effusive volcanic eruptions are also important for Earth’s climate (Schmidt et al., 2012a), eruptions with single or multiple short-lived explosive phases can inject volatiles into the stratosphere. Explosive volcanic eruptions are the dominant cause of short-term climatic cooling in the instrumental and historical record. This is due to the injection of sulfur dioxide ($SO_2$) into the stratosphere and subsequently the formation of sulfate aerosols which can scatter shortwave radiation. The short-term climate response to volcanic eruptions is usually considered to be a cooling (Robock, 2000), while on long time-scales volcanism is a large net source of carbon into the atmosphere so can be considered to have a warming effect on the climate (Timmreck, 2012).
1.2 Volcanic Eruptions & Climate

1.2.1 Carbon Dioxide

Emissions of CO$_2$ from volcanoes are approximately one hundred times smaller than current anthropogenic emissions (Mörner and Etiope, 2002), however changes in volcanic sources can have large impacts on a longer timescale. Variability in continental volcanic arc emissions are well correlated with temperature over the Phanerozoic (McKenzie et al., 2016) which suggests that volcanic emissions play an important role in determining the climate state.

1.2.2 Sulfate Aerosol

Aerosols in the stratosphere are dominated by sulfate aerosol (Kremser et al., 2016) with small contributions from meteoric dust and other nonsulfate material.

The atmospheric circulation, atmospheric chemistry, microphysical aerosol processes and radiative feedbacks all play a role in governing the life cycle, distribution and climate impacts of aerosols. Volcanic eruptions can inject aerosol precursor gases directly into the stratosphere, however other transport processes are important during volcanically quiescent periods. Transport from the tropical-tropopause layer (TTL) to the tropical lower stratosphere can occur by radiative ascent ('cross-isentrope', slow transport across surfaces of constant potential temperature) or overshooting convection and transport into the extratropical lower stratosphere can occur by quasi-isentropic transport from the TTL. Strong zonal transport in the stratosphere quickly homogenises atmospheric composition while vertical and meridional transport is dominated by the BDC (see Figure 1.1). The shallow branch of the BDC (below 70 hPa) is characterised by a year-round transport in the subtropical stratosphere and the deep branch of the BDC (above 70 hPa) is characterised by a much slower transport to the winter pole. This means that particles and gases below 70 hPa can be quickly transported out of the stratosphere while those higher up have significantly longer lifetimes.

Chemical reactions control the rate of sulfate aerosol production. The rate determining step in the production of sulfate is the termolecular

$$\text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HSO}_3 + \text{M}$$

reaction. The concentration of the hydroxyl radical (OH) in the stratosphere is therefore important for the production of sulfate aerosol. Bekki (1995) describes how OH can become depleted during very large SO$_2$ injections and so can prolong the lifetime of
Fig. 1.6 “Schematic of the relevant processes that govern the stratospheric aerosol life cycle and distribution. The large blue arrows indicate the large-scale circulation, while the red arrows indicate transport processes. The black arrows indicate chemical conversions between compounds. The different chemical species are marked as either gas phase (grey triangle) or aqueous phase (blue drop). The blue thin arrows represent sedimentation of aerosol from the stratosphere to the troposphere. Note that due to its long tropospheric lifetime, carbonyl sulfide (OCS) does not necessarily require deep convection to be transported into the TTL (as shown in the figure). The red numbers represent the flux of OCS and sulfur dioxide (SO$_2$) as well as the flux of aerosol in Gg S/yr based on model simulations from Sheng et al. (2015). The approximate net flux of sulfur containing compounds across the tropopause is shown in the grey box (Sheng et al., 2015), where the 10 Gg S/yr contribution from ‘others’ can be mostly attributed to dimethyl sulfide (DMS) and hydrogen sulfide (H$_2$S). Other chemical compounds shown in this figure are carbon disulfide (CS$_2$), sulfuric acid (H$_2$SO$_4$), and black carbon (BC).” Figure and caption reproduced verbatim from (Kremser et al., 2016).
SO$_2$ with respect to OH, in an analogous way to CH$_4$ in the troposphere (Prather, 1996). However, it is still common to fix the conversion rate of SO$_2$ to H$_2$SO$_4$ to those observed in the aftermath of the eruption of Mount Pinatubo (~ 30 days) in stratospheric aerosol studies such as those investigating the impacts of geoengineering. Considering chemical impacts is also important for tropospheric eruptions, where fissure eruptions can inject SO$_2$ for long periods of time. Stevenson et al. (2003) and Highwood and Stevenson (2003) performed a pioneering study with a 3D chemical transport model to investigate the atmospheric impact of the 1783–4 eruption of Laki, Iceland. They found that SO$_2$ caused considerable OH depletion and extended its tropospheric lifetime. After subsequent reactions

\[
\text{HSO}_3 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2 \quad \text{(R1.2)}
\]

\[
\text{SO}_3 + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_2\text{SO}_4 + \text{M}. \quad \text{(R1.3)}
\]

Sulfuric acid (H$_2$SO$_4$) is highly condensible even at the low partial pressures observed in the atmosphere. H$_2$SO$_4$ can undergo binary nucleation with H$_2$O to form small particles. H$_2$SO$_4$ can also condense onto existing particles or evaporate from particles if the vapour pressure becomes very low and/or temperatures rise, such as in the upper stratosphere above ~35 km.

Aerosol particles can undergo coagulation, whereby particles stick together and become larger. Sedimentation of particles is due to gravity acting on aerosol particles. More massive particles are more easily sedimented. A particle which sediments from above 70 hPa to below will be transported out of the stratosphere more quickly. Sedimentation can therefore affect the lifetime of stratospheric aerosols. Aerosols can also be removed from the stratosphere by turbulent vertical diffusion. Once transported to the troposphere, sulfate aerosols readily undergo wet deposition by uptake to cloud droplets or collisions with precipitation. They can also be removed by dry deposition, such as over ice sheets (Marshall et al., 2018). An overview of stratospheric aerosol processes is given in Figure 1.6.

The size distribution of aerosols in Earth’s atmosphere can typically be described using lognormal distributions with different physical properties:

1. **Nucleation mode**: Very small particles which have been produced by new particle formation. Nucleation mode particles dominate aerosol when considered by number. Particles typically removed from the atmosphere by diffusive processes.
2. Accumulation mode: Intermediate particles typically 0.1-2 µm in size. Diffusive processes and gravitational settling both slow, so long atmospheric residence times. Dominates the surface area distribution of aerosol.


Stratospheric sulfate aerosol leads to changes in the radiative budget of the atmosphere (Pollack et al., 1976). A schematic for the impact of these radiative properties is shown in Figure 1.7. Stratospheric aerosols typically have effective radii of 0.2 µm for background aerosol to effective radii as high as 0.6 µm for a Pinatubo sized eruption to 1.9 µm for a 100-times Pinatubo sized eruption (English et al., 2013). These particle diameters are of the same order of magnitude as the wavelength of solar radiation. Therefore stratospheric sulfate aerosol are effective in the Mie scattering regime (Mie, 1908). Most scattering is in the forwards direction, with some backscatter. This leads to a significant reduction of direct flux to the surface while the backscattering and diffuse beam increase. The net effect is to reduce the incident solar flux at Earth's surface, a cooling effect. In the stratosphere, temperatures increase as infrared radiation is absorbed and emitted which increases the downward infrared flux, partially offsetting the surface cooling. Latent heat feedbacks serve as an additional feedback which offsets some of the cooling as less energy is transferred between the surface and the atmosphere (Jones et al., 2005) while the resultant reduction in atmospheric water vapour content enhances the cooling (Soden, 2002). This means that the cooling effect of a particular volcanic eruption depends on the size distribution of the aerosol produced. This depends sensitively on the magnitude and timescale with which the precursor gas, sulfur dioxide, is emitted. For the largest explosive eruptions which loft gases into the stratosphere the injection timescale is typically of the order of days which is much smaller than the aerosol lifetime (c.f. Laki eruption, Stevenson et al. 2003). Injection magnitude is therefore the most important factor in determining the magnitude of the climate response. As the injection magnitude increases, the quantity of sulfuric acid increases which leads to a greater rate of formation of aerosols and the growth of existing aerosol particles. As larger aerosol particles are more likely to collide, they continue to grow. These larger aerosol particles have a shorter stratospheric lifetime, as they more easily sediment. Therefore, for a larger injection of sulfur dioxide, larger aerosol particles are produced. For aerosol sizes smaller than 2.0 µm, the radiative forcing (neglecting the feedbacks mentioned above) is negative (Pinto et al., 1989). This is likely to be the case for all except for extremely rare super-eruptions. The efficiency of solar
scattering drops because larger particles are formed, while longwave feedbacks scale largely with aerosol mass. This has important implications for simulating the climate response to large volcanic eruptions (Timmreck et al., 2010).

There is observational evidence for large scale perturbations to Earth’s radiative balance in response to stratospheric sulfate aerosol. The climate response to the June 1991 eruption of Mount Pinatubo is the best quantified large Plinian eruption, so will be explored here. Analysis of changes to the longwave and shortwave top-of-atmosphere radiative fluxes shows that the perturbation to the Earth’s shortwave radiative budget peaked at the start of 1992 at around −4 to −5 W m$^{-2}$ while the perturbation to the longwave peaked in mid-1992 around +1 to +3 W m$^{-2}$ (Soden, 2002). This suggests that the largest net radiative forcing due to Pinatubo occurred at the start of 1992.

In the 1-layer atmosphere model, this can be simulated as an increase in atmospheric albedo which increased by 0.007 after the Pinatubo eruption (Wielicki et al., 2005) while absorption of longwave radiation by aerosols would increase the longwave emissivity
and water vapour feedbacks would decrease it (Soden, 2002). The equilibrium surface temperature response to albedo change alone in the 1-layer atmosphere model is $-0.7\,^\circ\text{C}$. This is stronger than the peak in observed surface temperature cooling $-0.3\,^\circ\text{C}$, due to the thermal inertia of the surface ocean (Gregory et al., 2016).

### 1.2.3 Atmospheric Chemistry

The key reactions involved in determining stratospheric ozone ($\text{O}_3$) are detailed here. Stratospheric ozone is produced by the photolysis of molecular oxygen

\[
\text{O}_2 \xrightarrow{\text{hv} \quad \lambda < 220 \text{ nm}} \text{O} + \text{O} \quad \text{(R1.4)}
\]

\[
\text{O}_3 \xrightarrow{\text{hv} \quad \lambda < 320 \text{ nm}} \text{O}^1\text{D} + \text{O}_2 \quad \text{(R1.5)}
\]

\[
\text{O}^1\text{D} + \text{M} \xrightarrow{\text{hv} \quad \lambda = 400-600 \text{ nm}} \text{O}^3\text{P} + \text{M} \quad \text{(R1.6)}
\]

\[
\text{O} + \text{O}_2 + \text{M} \xrightarrow{\text{hv}} \text{O}_3 + \text{M} \quad \text{(R1.7)}
\]

\[
\text{O} + \text{O}_3 \xrightarrow{\text{hv}} \text{O}_2 + \text{O}_2 \quad \text{(R1.8)}
\]

the so-called Chapman reactions (Chapman, 1930).

There are a number of catalytic cycles which lead to ozone destruction. NO and NO$_2$ (collectively NOx) lead to ozone destruction through the interconversion reactions (Crutzen, 1970)

\[
\text{NO} + \text{O}_3 \xrightarrow{\text{hv}} \text{NO}_2 + \text{O}_2 \quad \text{(R1.10)}
\]

\[
\text{NO}_2 + \text{O} \xrightarrow{\text{hv}} \text{NO} + \text{O}_2 \quad \text{(R1.11)}
\]

Net: $\text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2$

The major source of NOx is from N$_2$O, a naturally occurring greenhouse gas, through reaction with O$^1\text{D}$. Other natural NOx sources include soil and lightning.

HOx (OH+HO$_2$) cycles also operate (Bates and Nicolet, 1950). OH can be formed by the reaction of O$^1\text{D}$ with H$_2$O

\[
\text{O}^1\text{D} + \text{H}_2\text{O} \xrightarrow{\text{hv}} \text{OH} + \text{OH} \quad \text{(R1.12)}
\]
or CH₄

\[ \text{O}^1\text{D} + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3. \]  

\[(R1.13)\]

HOx species can interconvert by

\[ \text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H} \]  

\[(R1.14)\]

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \]  

\[(R1.15)\]

\[ \text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \]  

\[(R1.16)\]

Net: \( \text{O} + \text{O} \rightarrow \text{O}_2 \)

or alternatively

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]  

\[(R1.17)\]

\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \]  

\[(R1.18)\]

Net: \( \text{O}_3 + \text{O}_3 \rightarrow 3\text{O}_2 \).

The main source of HOx species is from water vapour which is present at low concentrations in the stratosphere.

Halogen species can also deplete ozone through two reaction schemes. Firstly (Stolarski and Cicerone, 1974),

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]  

\[(R1.19)\]

\[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \]  

\[(R1.20)\]

Net: \( \text{O}_3 + \text{O} \rightarrow 2\text{O}_2 \)

and the ClO dimer reactions (Molina and Molina, 1987)

\[ 2\text{Cl} + 2\text{O}_3 \rightarrow 2\text{ClO} + 2\text{O}_2 \]  

\[(R1.21)\]

\[ \text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M} \]  

\[(R1.22)\]

\[ \text{Cl}_2\text{O}_2 \overset{\text{hv}}{\rightarrow} \text{Cl} + \text{ClO}_2 \]  

\[(R1.23)\]

\[ \text{ClO}_2 + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M} \]  

\[(R1.24)\]

Net: \( 2\text{O}_3 \rightarrow 3\text{O}_2 \)
and through cross-coupling reaction (McElroy et al., 1986) schemes such as \( \text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{ClO}_2 \). Natural sources of chlorine are predominately \( \text{CH}_3\text{Cl} \) which is emitted from oceans, biomass burning and tropical wetlands (WMO, 2011). \( \text{CH}_3\text{Br} \) is a precursor for Br and has oceanic and biomass burning sources (WMO, 2011).

Important coupling and reservoir reactions include

- \( \text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2 \) \hspace{1cm} (R1.25)
- \( \text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \) \hspace{1cm} (R1.26)
- \( \text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2 \) \hspace{1cm} (R1.27)
- \( \text{CLO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M} \) \hspace{1cm} (R1.28)
- \( \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \). \hspace{1cm} (R1.29)

(Solomon, 1999). These reactions lead to longer-lived, less reactive species some of which act as a sink for the reactive species as they can be removed from the stratosphere by transport.

There has been considerable ozone depletion by anthropogenic halogen species, the first evidence for which came from measurements of column ozone in Antarctica (Figure 1.8 Column ozone (bars), CFC-11 (filled circles) and CFC-12 (unfilled circles) at October in Halley Bay, Antarctica. Raw data digitized from Farman et al. (1985)
1.2 Volcanic Eruptions & Climate

1.8, Farman et al. 1985). This suggested a strong role for heterogeneous reactions such as

\[
\begin{align*}
\text{HCl} + \text{ClONO}_2 &\rightarrow \text{HNO}_3 + \text{Cl}_2 \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O} &\rightarrow 2\text{HNO}_3 \\
\text{ClONO}_2 + \text{H}_2\text{O} &\rightarrow \text{HNO}_3 + \text{HOCl} \\
\text{HCl} + \text{HOCl} &\rightarrow \text{H}_2\text{O} + \text{Cl}_2 \\
\text{BrONO}_2 + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{O} + \text{HOBr} \\
\text{HCl} + \text{BrONO}_2 &\rightarrow \text{HNO}_3 + \text{BrCl} \\
\text{HCl} + \text{HOBr} &\rightarrow \text{H}_2\text{O} + \text{BrCl}
\end{align*}
\]

which can take place on surfaces such as polar stratospheric clouds. These reactions reduce the levels of active NOx species and increase the levels of active Cl and Br species. During volcanically active periods, sulfate aerosols can also provide a surface on which heterogeneous reactions can occur. The ozone response to volcanically-induced pulses of elevated stratospheric aerosols depends on the background chemical state. The 1991 Mount Pinatubo eruption took place during a period of high stratospheric reactive chlorine levels so reactions on sulfate aerosols lead to significant increases in reactive chlorine and therefore ozone depletion. By contrast, elevated sulfate levels before the ozone-hole era should lead to increases in ozone due to the removal of reactive nitrogen reservoirs.

In addition to SO\(_2\), other chemically active emissions from volcanic eruptions include halogenated species such as HCl which can lead to reactive Cl in the stratosphere. Henceforth, the emitted halogenated species and their highly reactive products are collectively referred to as halogens. There have been specific examples of potentially halogen-rich volcanic eruptions. Cadoux et al. (2015) performed a petrological assessment of the tephra at Mount Santorini, Crete which erupted around 1500 BC, obtaining degassing budgets for the eruption. This suggests a volatile yield of 51–675 Tg of Cl and up to 1.5 Tg of Br. Cadoux et al. (2015) then used these emissions in a 2D chemical-transport model to simulate the effects on stratospheric ozone, assuming that 2% of the halogens would reach the stratosphere which they argue to be a conservative choice based on evidence from observational (Rose et al., 2006) and plume-modelling studies (Textor et al., 2003). They simulate between 20% to >90% reductions in column ozone amounts. McConnell et al. (2017) show evidence that a series of halogen-rich volcanic eruptions in Mount Takahe, West Antarctica – 17.7 ka was coincident with an acceleration in Antarctic deglaciation at that time, consistent with warming of the Southern Ocean in response to ozone depletion.
As these eruptions were paced (i.e. there were multiple eruptions) over ~192 years this could have maintained the ozone depletion for a long period of time. Kutterolf et al. (2013) found large halogen outputs from 14 large explosive eruptions in Nicaragua over the past 70 ka, which could treble the stratospheric halogen loading assuming a 10% injection efficiency based on (Textor et al., 2003). However, the large uncertainties in the proportion of halogenated species which could reach the stratosphere should be noted as there have been few examples in the instrumental record.

In summary, the injection of volatile species from volcanoes leads to substantial perturbations to the composition of the atmosphere with important implications for the climate. This section has assumed an oxidising atmosphere with substantial O$_2$ levels, however this has not always been the case. Volcanic eruptions themselves may have had a substantial role to play in the oxidation of Earth's atmosphere, which I will now describe.

### 1.3 Rise of Atmospheric Oxygen on Earth

Figure 1.9 shows the evolution of atmospheric oxygen over Earth's history. For the first half of Earth's history, Earth's atmosphere was essentially devoid of free oxygen with less than 0.001% of present atmospheric levels (PAL, Lyons et al. 2014). The disappearance of mass-independent fractionation of sulfur isotopes in rocks suggests that oxygen levels rose from typical Archean to typical Proterozoic (0.01–10% PAL) values 2.0-2.4 Ga (Farquhar et al., 2000). However, the evolution of oxygenic photosynthesis in cyanobacteria likely happened several hundred million years before this so-called “Great Oxygenation Event” (GOE). Several theories have been proposed to explain this gap:

- Changes in volcanic outgassing associated with tectonic evolution (Holland, 2002) led to increases in CO$_2$ and SO$_2$ and reductions in H$_2$. Atmospheric oxygen sinks would therefore be reduced and sources (reduction of CO$_2$ to organic carbon) increased.

- Transition from submarine to subaerial outgassing, leading to fewer reduced gases and more oxidised gases entering the atmosphere (Kump and Barley, 2007).

- Continental oxidation and hydrogen escape (Catling et al., 2005). The photolysis of water vapour leads to the formation of O$_2$ and H$_2$, the latter can escape from the top of the atmosphere. The timescale for oxidation of the continental iron would explain the oxidation gap.
Fig. 1.9 Changes in atmospheric oxygen content over the last 3.5 billion years according to Lyons et al. 2014 (red). Note the considerable uncertainty during the Proterozoic. Widespread glaciation episodes are indicated by blue bars. There is evidence for four such glaciations in the early Paleoproterozoic and two in the late Neoproterozoic. The Sturtian glaciation (714-660 Ma) was the most protracted of these episodes. Note that these widespread glaciation episodes are coincident with rapid changes in atmospheric oxygen content. Pal: Paleozoic. Mes: Mesozoic.
• Serpentization of the seafloor (Kasting and Canfield, 2012). Higher upper mantle temperatures in Earth’s past would lead to a thicker and more mafic (higher iron content) oceanic crust. A transition to cooler mantle temperatures and less mafic seafloor would reduce the volcanic source of $H_2$.

• Banded-iron formations (BIFs, Isley and Abbott 1999). A substantial drop in BIFs around 2.4 Ga is consistent with a reduction in the sinks for atmospheric oxygen.

So the GOE required the evolution of oxygenic photosynthesis but the increase in continental growth and oxidation of both continental and seafloor rocks are likely to have been important delaying factors (Kasting, 2013). Oxygen contents in the Proterozoic (0.01-0.1 PAL) were likely sufficient to have led to oxygenation of the surface ocean but were insufficient to oxidise the deep ocean (Lenton and Daines, 2017).

The subsequent rise from typical Proterozoic values to typical Phanerozoic values (0.6–1.6 PAL) is associated with the Neoproterozoic-Paleozoic oxygenation of the deep ocean which likely occurred between 600-400 Ma. The emerging view is that oxygen levels had reached levels over 1% by the Ediacaran (635–541 Ma) as required for the complexity of the life on land and the oxygenation of the ocean (Och and Shields-Zhou, 2012), while present-day levels of oxygen were likely achieved by the colonisation of land plants ~470 Ma (Lenton et al., 2016). What caused the rise in oxygen between the Proterozoic and Phanerozoic? While the mechanistic understanding of the causes of multiple oxygen equilibria between low and high oxygen content has become increasingly advanced (Goldblatt et al., 2006) such a mechanistic understanding for why such a transition exists between Proterozoic and Phanerozoic levels is less advanced, though recent work has suggested this is likely due to phosphorus limitation (Laakso and Schrag, 2014). Snowball Earth events in the Neoproterozoic, occasions when the Earth may have been completely ice covered, bookmark this transition and may serve as a strong redox perturbation necessary to overcome strong hysteresis between stable oxygen levels (Laakso and Schrag, 2017). Alternatively, the evolution of plate tectonics may have played a key role as this would permit the growth of a large continental carbon reservoir over the Proterozoic. Release of this carbon to the atmosphere would lead to increased organic carbon burial and evolution of atmospheric oxygen through $CO_2 \rightarrow C_{org} + O_2$ (Lee et al., 2018).

The timescales for changes in atmospheric oxygen can be considered by exploring the oxygen budget. In the present day atmosphere, oxygen levels are determined by a balance between oxygen sources

• Burial of organic carbon and pyrite
1.3 Rise of Atmospheric Oxygen on Earth

Fig. 1.10 Steady-state ozone column as a function of atmospheric oxygen concentration following Ratner and Walker (1972).

- Hydrogen escape and sinks
  - Reaction with reduced volcanic gases
  - Continental weathering.

Changes in this balance can lead to changes in atmospheric oxygen content (Catling et al., 2005). Oxygen exchanges between the atmosphere and surface organic matter with a timescale of a few thousand years or between the atmosphere-ocean system and the lithosphere/asthenosphere on a timescale of ~2 million years (Catling et al., 2005). This suggests that molecules of oxygen has been cycled around 200 times during the Phanerozoic (Catling et al., 2005).

Oxygen plays a key role in the chemistry of the atmosphere. High levels of oxygen in the Phanerozoic means that the atmosphere is considered ‘oxic’, so oxidation processes
dominate, while during the Archean the atmosphere can be considered ‘reducing’ due to its very small oxidising capacity. This can be explored in a simple way by considering the ‘Chapman chemistry’ reactions, for a 1D column in chemical steady state following Ratner and Walker 1972 (see Appendix A for a full description). Figure 1.10 shows the steady state ozone column as a function of atmospheric oxygen content. Ozone in the present-day atmosphere provides a strong UV shield, which appears to be the case down to atmospheric oxygen levels below 0.1% of PAL, which is likely for the Archean. This is supported by more detailed 1D calculations (Kasting et al., 1979). Possible changes in atmospheric chemistry as $pO_2$ increased from the Archean to Proterozoic include a significant increase in OH concentrations. The oxidising capacity of the atmosphere would increase if $CH_4$ played an important role in the Archean greenhouse gas budget (as would be expected to keep the early Earth warm, Feulner 2012), the subsequent increase in methane reactivity would lead to a collapse in the strength of the greenhouse effect.

Oxygen has a direct impact on the absorption of short-wave radiation (Ladenburg et al., 1932), however this peaks in the ultraviolet region of the spectrum, therefore the climate impacts of direct absorption are quite small. However, changes in atmospheric levels of major gases have the capability to substantially alter the mass of the atmosphere and therefore the surface pressure. Atmospheric pressure has a number of roles in the radiative budget of the atmosphere. Firstly, gas molecules in the atmosphere scatter solar radiation elastically (Strutt, 1871). This is known as Rayleigh scattering, after Lord Rayleigh (John Strutt). Radiation with shorter wavelengths is more effectively scattered by this mechanism, which is the cause of the sky appearing blue (Rayleigh, 1899). As a result, an increase in atmospheric mass causes an increase in Rayleigh scattering which acts to cool the climate. Secondly, collisions between greenhouse gas molecules and other molecules cause absorption lines to become broader. As a result, an increase in atmospheric mass causes an increase in collisional broadening which acts to warm the climate. There are also collisionally induced absorptions in both the shortwave (Solomon et al., 1998) and longwave (Höpfner et al., 2012) which further contribute to the radiative forcing of $O_2$. Atmospheric mass also impacts the heat capacity of the atmosphere and therefore its ability to transport heat.

In the 1-layer atmosphere model, an increase in atmospheric mass can be considered as a simultaneous increase in planetary albedo (due to Rayleigh scattering) and increase in infrared emissivity (due to increase in pressure broadening of absorption lines). To determine the overall climate response therefore requires a mechanistic model (e.g. Payne et al. (2016)). These will be discussed in more detail in Chapter 4.
Oxygen is not the only major gas in Earth’s atmosphere (Seinfeld and Pandis, 2006). Variations in nitrogen (N\textsubscript{2}) and argon (Ar) could also have the ability to substantially impact the surface pressure. While the time-scales for variation in atmospheric oxygen are of the order of ten million years, the nitrogen cycle is substantially slower (Johnson and Goldblatt, 2015). Therefore it is likely that variations in N\textsubscript{2} will have substantially contributed to atmospheric mass variation over the last billion years. Increases in N\textsubscript{2} have been invoked for the Archean as this would help to solve the Faint Young Sun paradox. This is not consistent with palaeopycnometry measurements which reconstruct atmospheric mass from the size of fossilised rain droplet imprints (Som et al., 2016, 2012), however the uncertainty is extremely large as atmospheric mass is a secondary effect compared to rainfall rate (Kavanagh and Goldblatt, 2015). Glacial tills record a secular increase in crust nitrogen over the last 4 billion years (Johnson and Goldblatt, 2017), which suggests a reduction in pN\textsubscript{2} over this time in the absence of a change in mantle sources. Ar only constitutes around 1% of the present day atmosphere. It can be produced from the radioactive decay of \textsuperscript{40}K in the crust, hence Ar can accumulate in the atmosphere. Coltice et al. (2000) estimate \(4.5 \times 10^{16}\) kg of \textsuperscript{40}K in the crust which suggests that around \(3 \times 10^{17}\) kg of \textsuperscript{40}Ar has been released by radioactive decay. Given present levels of \(5 \times 10^{16}\) kg, this suggests the mantle is a significant sink of Ar. Regardless, Ar is unlikely to contribute significantly to atmospheric mass variation.

The molecular structures of major gases are important for climate. For a dry atmosphere which consist of grey gases (gases with a constant optical thickness across the electromagnetic spectrum), the surface temperature can be expressed as

\[
T_s = \left( \frac{1}{4} (1 - \alpha) L_{\odot} \sigma \right)^{0.25} \Gamma \left( 1 - \frac{4 R}{C_p} \right) \frac{R}{\tau_{\infty}}
\]

where \(\alpha\) is the planetary albedo, \(\sigma\) is the Stefan-Boltzmann constant, \(\Gamma\) is the Gamma function, \(\tau_{\infty}\) is the longwave optical depth and \(R/C_p\) is the dry adiabatic lapse rate (the slope of \(d\ln T / d\ln p\), Pierrehumbert (2010). Note that Equation 1.3 is the change in temperature with altitude which is often less convenient for climate calculations). For diatomic molecules, \(R/C_p\) is approximately \(2/7\). For this value, a present-day surface temperature is achieved for \(\tau_{\infty} = 0.94\). As oxygen and nitrogen are both diatomic molecules, \(R/C_p\) is approximately conserved. However, \(R/C_p\) is lower for triatomic molecules and higher for monatomic molecules (0.4). For CO\textsubscript{2}, \(R/C_p = 0.224\). Assuming the same \(\tau_{\infty}\) \(T_s\) drops by 4.8°C compared to the diatomic case. In the current atmosphere, the temperature response to replacing atmospheric nitrogen and oxygen to CO\textsubscript{2} would be dominated by
the increase in $\tau_\infty$. Changes to $R/C_p$ may be important if CO$_2$ becomes a major gas in an atmosphere where the water vapour feedback is very weak, such as the atmosphere on present-day Mars. For an atmosphere composed primarily of atomic species such as Ar the change in $R/C_p$ compared to the current atmosphere would lead to heating of some 8.8°C. This shows that major gas composition has a direct impact on atmospheric structure and surface temperatures.

In summary, the rise of atmospheric oxygen on Earth is intimately linked to the emergence and evolution of life. Oxygen has a variety of roles in the Earth system including biogeochemical cycles. As a major gas in the present day atmosphere, it also plays an important role in the radiative budget of the atmosphere.

### 1.4 Thesis Aims

Geological and biological processes have co-evolved throughout Earth's history leading to changes in atmospheric composition on a wide variety of timescales. This thesis does not aim to provide a comprehensive and holistic account of all possible composition-climate interactions over the entirety of Earth's history but to provide case studies which highlight the importance of compositional variability in Earth's atmosphere:

- **Chapter 2**: A description of the methods and models employed throughout the rest of the thesis.

- **Chapter 3**: The climate and possible societal impacts of the 1257 Samalas eruption is investigated with a newly configured version of the UK Met Office climate model and previously published results with the NCAR Community Earth System Model.

- **Chapter 4**: The impacts of variability in atmospheric oxygen content in the Phanerozoic (0-541 Ma) are quantified using two structurally distinct versions of the UK Met Office climate model and compared to a previous model study.

- **Chapter 5**: The impacts of variability in atmospheric oxygen content and volcanic forcing on the initiation of Snowball Earth in the Neoproterozoic (600-700 Ma) is assessed with the UK Met Office climate model.

- **Chapter 6**: A summary of conclusions is presented along with feasibility studies and directions for future work.
Chapter 2

Methods and Model Development

This chapter describes the methods that have been used to investigate palaeoatmospheric composition-climate feedbacks. The results obtained from these methods are described in Chapters 3, 4 and 5.

2.1 Introduction

The majority of the conclusions drawn from the experiments performed in this thesis are supported by climate model experiments. While a number of important insights into past climates have been made by simpler models, a proper quantification of the range of atmospheric and oceanic feedbacks requires a fully coupled GCM.

2.2 Data Archives

Simulations performed as part of the Coupled Model Intercomparison Project Phase 5 (CMIP5) are analysed: “The fifth phase of the Coupled Model Intercomparison Project (CMIP5) will produce a state-of-the-art multimodel dataset designed to advance our knowledge of climate variability and climate change. Researchers worldwide are analyzing the model output and will produce results likely to underlie the forthcoming Fifth Assessment Report by the Intergovernmental Panel on Climate Change” (Taylor et al., 2012). The Historical simulations are a transient simulation between 1850–2005 with time-evolving climate forcing. The Past1000 simulations were conducted in collaboration with the Paleoclimate Modelling Intercomparison Project Phase 3 (PMIP3, Braconnot et al. 2012) and are transient simulations between 850–1850 based on time-evolving climate forcing.
Table 2.1 Summary of CMIP5-PMIP3 models.

<table>
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<th>Model</th>
<th>Modelling Centre</th>
<th>Citation</th>
<th>Past1000 Volcanic Forcing</th>
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<td>Beijing Climate Center</td>
<td>Xiao-Ge et al. (2013)</td>
<td>Gao et al. (2008)</td>
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<td>(BCC)</td>
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<td>Schmidt et al. (2014)</td>
<td>Crowley et al. (2008)</td>
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<td>(GISS4)</td>
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<tr>
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<tr>
<td>(MIROC)</td>
<td>Science and Technology</td>
<td></td>
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</tr>
</tbody>
</table>

Notes: Additional GISS2-ER experiments employed the Gao et al. (2008) climatology, however was not implemented correctly leading to a forcing overestimation (Atwood et al., 2016). An implementation error in IPSL led to aerosol extinction coefficients decreasing throughout the day before being updated at midnight (Atwood et al., 2016).

described by Schmidt et al. (2012b). Six CMIP5 models performed both the Historical and Past1000 simulations. These are detailed in Table 2.1. CMIP5 data was obtained from the CEDA/BADC (Centre for Environmental Data Analysis/British Atmospheric Data Centre) archive on the JASMIN post-processing system.

### 2.3 HadGEM3-ES

For the simulations performed for chapter 3, a new configuration of the HadGEM3 model was developed which extended an existing atmosphere-ocean general circulation model (AO-GCM) with interactive atmospheric chemistry to include a microphysical aerosol module. The model is integrated on the Monsoon2 system based at the UK Met Office and runs on 7 nodes (5 atmosphere, 1 ocean/sea-ice, 1 coupler) of 36 cores each. In this configuration, four model years can be integrated in 24 hours. A full model description is provided and the model is evaluated for its treatment of the main modes of climate
variability and its ability to reproduce the climate impact of the 1991 Mount Pinatubo eruption.

2.3.1 Model Description

HadGEM3-ES is a coupled atmosphere-ocean GCM with interactive atmospheric chemistry and microphysical sulfate aerosol. In this section, the physical atmosphere and ocean components will be described. Then the chemical and aerosol schemes will be described.

The atmosphere component is the UK Met Office Unified Model version 7.3 (Davies et al., 2005) in the HadGEM3-A r2.0 climate configuration (Hewitt et al., 2011). It employs a regular Cartesian grid of 3.75° longitude by 2.5° latitude (N48). In the vertical, 60 hybrid height vertical levels are employed – ‘hybrid’ indicating that the model levels are sigma levels near the surface, changing smoothly to pressure levels near the top of the atmosphere (Simmons and Strüfing, 1983). The model top is 84 km which permits a detailed treatment of stratospheric dynamics. A 20 minute timestep is used. The model employs a non-hydrostatic and fully compressible dynamical core, using a semi-implicit semi-Lagrangian advection scheme on a staggered Arakawa C-grid (Arakawa and Lamb, 1977).

A number of important sub-grid processes require parametrisation. Clouds types are modelled using the prognostic cloud fraction and condensate (PC2) scheme. For convection, a mass flux scheme is used (Hewitt et al., 2011). This employs a convective available potential energy approach to convective closure which allows convection to terminate when approaching zero mass flux or the level of neutral buoyancy (whichever is first achieved). Boundary layer processes, orographic and non-orographic gravity waves are also included in model parametrisations. Radiation is represented using the Edwards and Slingo (1996) scheme with six short-wave and nine long-wave bands, accounting for the radiative effects of water vapour, carbon dioxide, methane, nitrous oxide and ozone. A background aerosol climatology is also implemented (Cusack et al., 1998) in the stratosphere. The MOSES2 land surface scheme is used (Cox et al., 1999) which simulated atmosphere-land exchanges and hydrology. A fixed vegetation distribution of plant functional types is employed.

The ocean component of the model is OPA component of the NEMO (Nucleus for European Modelling of the Ocean, Madec 2008) model version 3.0 (Hewitt et al., 2011), run at a 96 minute timestep. In the vertical, 31 model levels are used which increase steadily between 10 m in the shallowest to 500 m in the deepest layer at 5 km in depth. NEMO
Methods and Model Development

employs a tripolar, locally anisotropic grid (ORCA2, Madec 2008) which permits a more detailed treatment of the north polar region and higher resolution in the tropics. This yields an approximate horizontal resolution of 2° in both longitude and latitude, with an increased resolution of up to 0.5° in the tropics.

The sea ice component of the model is CICE (Los Alamos Community Ice CodE) at version 4.0 (Hunke and Lipscomb, 2008), run at a 96 minute timestep. This treats sea-ice in a 5-layer model, allowing the simulation of different ice types. The atmosphere and ocean/sea-ice components exchange fields every 24 hours while NEMO and CICE exchange fields every timestep.

Atmospheric chemistry is represented by the UKCA (United Kingdom Chemistry & Aerosols) model, with updates from the model version described by Morgenstern et al. (2008). The model simulates the reactions and advection of 49 chemical tracers undergoing 187 chemical reactions. This represents a comprehensive treatment of stratospheric chemistry, including the following heterogeneous reactions on sulfate aerosols:

\[
\begin{align*}
\text{ClONO}_2 + \text{HCl} & \rightarrow 2 \text{Cl} + \text{HONO}_2 \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O} & \rightarrow \text{HONO}_2 + \text{HONO}_2 \\
\text{ClONO}_2 + \text{H}_2\text{O} & \rightarrow \text{HOCl} + \text{HONO}_2 \\
\text{HOCl} + \text{HCl} & \rightarrow 2 \text{Cl} + \text{H}_2\text{O} \\
\text{N}_2\text{O}_5 + \text{HCl} & \rightarrow \text{Cl} + \text{NO}_2 + \text{HONO}_2
\end{align*}
\]

(R2.1)  
(R2.2)  
(R2.3)  
(R2.4)  
(R2.5)

In addition, the model contains a thorough treatment of chemical Ox, NOx and ClOx catalytic cycles. Sulfur chemistry is also simulated according to Dhomse et al. (2014), which includes the rate-limiting \(\text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HSO}_3 + \text{M}\) reaction. The rate constant used is an average of the IUPAC-2004 (Atkinson and Arey, 2003) and JPL-2011 (Sander et al., 2011) recommended rates. A comparison between these approaches and a recent experimental study of the rate constant (Blitz et al., 2017) is shown in Figure 2.1 and shows that there is reasonable agreement between the different values in the lower stratosphere despite substantial differences in the troposphere. Therefore, for consistency with Dhomse et al. (2014) we maintain the merged IUPAC-JPL rate. The model treatment of tropospheric chemistry is less detailed, representing the oxidation of \(\text{CH}_4\) and \(\text{CO}\). Isoprene and other hydrocarbon species are lumped with \(\text{CO}\). This relatively simplistic scheme reflects the primary application of the model to stratospheric \(\text{SO}_2\) injections. Chemical photolysis is treated interactively for 38 chemical species by the FastJX scheme (Telford et al., 2012). Dry
deposition of tracers is calculated following Wesely 1989 while wet deposition of gas phase species is treated as Walton et al 1988, a first order loss rate depending on precipitation rate and a scavenging coefficient.

![Graph showing rate constants comparison](image)

Fig. 2.1 Comparison between IUPAC-2004, JPL-2011 and Blitz rate constants and the UKCA rate constant for the $\text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HSO}_3 + \text{M}$ reaction.

Aerosol processes for the emitted species anthropogenic sulfur, anthropogenic and biomass burning black carbon, biomass burning organic carbon and natural emissions of mineral dust are treated by CLASSIC (Coupled Large-Scale Aerosol Simulator for Studies in Climate), a bulk aerosol scheme. Aerosol microphysics tuned for stratospheric sulfate aerosol processes is treated by GLOMAP-mode. GLOMAP-mode is a two-moment aerosol scheme which tracks both number and mass (Mann et al., 2010). This allows for a 3D evolution of the size distribution, which is assumed to be modal with an evolving mean width but a fixed variance (mode width). The model treats in detail the condensation, nucleation, coagulation, cloud processing, hygroscopic growth, scavenging and dry deposition of aerosols (Mann et al., 2010). As the primary interest is stratospheric sulfate aerosol, only soluble modes are simulated by GLOMAP-mode (non-anthropogenic sulfate aerosol and sea salt). The use of a fixed modal width of 1.4 for the accumulation soluble mode, combined with preventing mode-merging between the accumulation and coarse modes was found to improve the model fidelity, compared to a more detailed sectional scheme (Dhomse et al., 2014). Interaction between aerosols and radiation is simulated by RADAER (Bellouin, 2011).

Emissions of reactive gaseous species were obtained from Lamarque et al. (2010). Due to the large uncertainty in biogenic emissions of CO (including isoprene and other lumped hydrocarbons) and NO (from soil sources) in the Pre-Industrial Holocene (PIH), their emis-
sions were set to present-day values. Similarly carbonyl sulfide is set to a lower boundary condition of 250 pptv. Dimethyl sulfide emissions are simulated interactively. These species lead to a ‘natural’ background level of stratospheric aerosol. Chlorofluorocarbons and other anthropogenic ozone depleting substances were set to zero. Natural sources of chlorine and bromine are represented by methyl bromide (5 pptv) and methyl chloride (480 pptv). Methane and nitrous oxide were set as a fixed lower boundary conditions at preindustrial Holocene levels, which are somewhat affected by human activity (Mitchell et al., 2013).

2.3.2 Model Evaluation

For the purposes of the simulations performed in Chapter 3, an evaluation of the model for key modes of climate variability and the ability of the model to simulate the climate impacts of the 1991 Mount Pinatubo volcanic eruption will be presented. The model simulates these features reasonably well and therefore is suitable for the model simulations in Chapter 3. The model is also capable of performing a wide range of other climate-change experiments, which would require further investigation beyond the scope of this evaluation.

The model was initialised from a coupled atmosphere-ocean configuration with interactive atmospheric chemistry only (Nowack et al., 2014) and iterated for 100 model years under preindustrial Holocene (PIH) condition to spin up the shallow ocean. A longer integration would be required to spin up the deep ocean, however given the short time scales (<10 years) of volcanic perturbations this is not strictly required. The following 100 year control run was analysed for its ability to represent the El Niño Southern Oscillation (ENSO) and Quasi-Biennial Oscillation (QBO) variability.

ENSO variability is assessed using the ENSO 3.4 index, which reflects temperature anomalies in the 170W–120W, 5N–5S region. This is commonly used for analysing the variability in the central Pacific (e.g. Trenberth et al. 2002) Figure 2.2A shows that the model generally captures the ENSO variability with peaks in spectral power around seven years, in reasonable agreement with the instrumental record of the ENSO index. However, the model underestimates the power of these peaks which suggests the magnitude may be underestimated. The variability in tropical 70 hPa winds was assessed in the model by comparison with the Singapore 70 hPa winds. We find a peak in the spectral power at 2.35 years in both cases, suggesting a strong agreement in the QBO frequency. However, the magnitude is underestimated. While it is challenging to comprehensively assess a
model in PIH conditions, compared to observations of climate in an anthropogenically perturbed atmosphere, it is clear that the model is capable of simulating reasonable ENSO and QBO variability.

Fig. 2.2 Power Spectrum of (A) ENSO3.4 Index simulated (dark red) and observed (light red) and (B) QBO simulated in the last 50 years of the unforced HadGEM3-ES spin-up simulation (dark red) and observed (light red). ENSO observation data source: https://www.esrl.noaa.gov/psd/gcos_wgsp/Timeseries/Data/nino34.long.data (Rayner et al., 2003). QBO observation data source: http://www.geo.fu-berlin.de/met/ag/strat/produkte/qbo/singapore.dat

The use of GLOMAP-mode for simulating the 1991 Mount Pinatubo eruption has been comprehensively validated by Dhomse et al. (2014), who found it performs similarly to other aerosol-composition climate models. However, simulations in the AO-GCM framework are required in order to assess its ability to simulate temperature changes due to large eruptions. Integrations with volcanic emissions of 10 Tg SO$_2$ and 20 Tg SO$_2$ were performed following Dhomse et al. (2014) from six different June start dates, reflecting the full range of QBO and ENSO states. For comparison to observed surface temperature changes, the Cowtan and Way surface temperature reconstruction (hereafter CW, Cowtan and Way 2014) is employed, focusing on the surface temperature product for comparison with our model simulations for the year 1992 and 1993, the years after the Mount Pinatubo eruption. An Empirical Orthogonal Function (EOF) analysis was performed to remove the signal associated with ENSO, as it has been suggested that this substantially damped
the cooling associated with the Pinatubo eruption. By inspection EOF1 (Figure 2.3a) and EOF2 (Figure 2.3b) are associated with ENSO variability, with strong gradients from the West to East Pacific. The components associated with EOFs 1 and 2 were removed from CW in CW_d+ENSO and can be compared to the pure detrended signal (CW_d, see Figure 2.3c). It should be noted that EOF1 will contain most of the anthropogenic warming trend, so removing this is desirable for this preindustrial analysis.

We also consider the CMIP5 models which performed both the Historical and Past1000 experiments (see Table 2.1) The global mean surface temperature anomaly from CWd and CWd+ENSO is compared to these six CMIP5 models and the HadGEM3-ES simulations (Figure 2.3d). Both the CMIP5 ensemble and HadGEM3-ES models simulate a –0.20 °C annually and globally-meaned cooling for 1992, in excellent agreement with the CWd+ENSO reconstruction. This shows that ENSO needs to be accounted for when assessing the CMIP5 response to large volcanic eruptions (c.f. Driscoll et al. 2012). This also shows there is a substantial role for climate variability given that the HadGEM3-ES simulations span the range of the CMIP5 simulations.

2.4 HadGEM3-AO

For some simulations in Chapter 3, the HadGEM3-AO model was used.

2.4.1 Model Description

The physical atmosphere, ocean and sea-ice components used are identical to the HadGEM3-ES model described in section 2.3 but does not include interactive atmospheric chemistry or microphysical stratospheric sulfate. Ozone profiles are instead fixed at a pre-industrial baseline climatology which can evolve only according to a tropopause-matching method which prevents (chemically-inconsistent) stratospheric ozone levels occurring in the troposphere.

2.4.2 Model Development: Oxygen Variability

In order to alter the atmospheric mass in HadGEM3-AO, a number of alterations were made to the code/configuration. Surface pressure, mass mixing ratios and heat capacities were altered according to Table 2.2. In addition, alterations were made to the code to adjust the oxygen content where appropriate - these are detailed in Appendix B.1.
Fig. 2.3 Time-meaned first (a) and second (b) EOFs for the Cowtan and Way surface temperature dataset. (c) GMST anomaly (purple, CW), detrended GMST anomaly (dashed red, CWd) and detrended GMST anomaly, removing the reconstructed surface temperature anomaly from EOF1 and EOF3 (red, CWd+ENSO). (d) HadGEM3 model output (mean filled circle, range indicated by vertical line) for a 10 Tg (blue-green) and a 20 Tg (red) injection. Detrended CMIP5 model output (grey) is also compared to CWd and CWd+ENSO.
Table 2.2 Code or configuration alterations for oxygen level variability. The masses of other gases including carbon dioxide are held constant. The molecular masses of air and the specific heat of air vary with composition and are adjusted to the oxygen:nitrogen ratio.

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<td>$C_{p,air}$ / J kg$^{-1}$ °C$^{-1}$</td>
<td>1005</td>
<td>1024</td>
<td>988</td>
<td>1036</td>
</tr>
</tbody>
</table>

2.5 HadCM3

In order to perform very long climate integrations, a lower-resolution model is required in order to achieve an equilibrium climate state in a computationally acceptable amount of time. In addition, for exploring other time periods in geological history it is necessary to be able to alter the continental positions and orography and the bathymetry of the ocean. This is considerably more challenging in the HadGEM framework but has been widely deployed with HadCM3. This also permits utilising existing model configurations developed by Prof. Paul Valdes (University of Bristol, hereafter PJV), which will be described below.

2.5.1 Model Description

The model employed is the HadCM3BL model (Valdes et al., 2017), a coupled Atmosphere-Ocean General Circulation Model with a vegetation model. The simulations were performed on the University of Bristol Bluecrystal Phase 3 machine. The model was run on one node of 16 cores and can integrate approximately 25 model years in 24 hours. The model was originally developed by the United Kingdom Met Office Hadley Centre (Pope et al., 2000) but has since been substantially developed further by the University of Bristol.

The atmosphere component of the model employs a regular Cartesian grid of 3.75° longitude by 2.5° latitude (N48 grid). In the vertical, 19 hybrid height vertical levels are employed – ‘hybrid’ indicating that the model levels are sigma levels near the surface, changing smoothly to pressure levels near the top of the atmosphere (Simmons and Strüfing, 1983). A 30 minute timestep is used. The primitive equation set of White and Bromley (1995) is solved to conserve energy and angular momentum, solved on a staggered Awakawa B-grid (Arakawa and Lamb, 1977) in the horizontal. The model uses Eulerian advection for tracers. Fourier filtering at high latitudes is employed in order to remove
sub-grid-scale variability. Conservation of mass angular momentum, tracers and potential temperature (mass-weighted) is ensured by a split-explicit time scheme.

A number of important sub-grid processes require parameterisations in order for their capture. Precipitation is divided into large-scale and convective schemes. Large-scale (frontal) precipitation is resolved on the grid-scale and is achieved by a simple bulk parameterisation scheme (Wilson, 1998). Convective rainfall is dealt with using a mass-flux scheme with convective downdrafts (Gregory et al., 1997). The model employs horizontal diffusion of tracers, the strength of which depends on the tracer and its location in the atmosphere (Valdes et al., 2017). Radiation is represented using the Edwards and Slingo (1996) scheme with six short-wave and eight long-wave bands, accounting for the radiative effects of water vapour, carbon dioxide and ozone, amongst other radiative active species. A background aerosol climatology is also implemented (Cusack et al., 1998). A statistical parameterisation of clouds is employed, as they are formed on scales significantly smaller than the grid-box sizes employed. Probability distribution functions of total water content parametrise the cloud amount and lifetime. Clouds can exist as water, ice or water/ice phase between 0 and -9 °C. Clouds are formed when a critical relative humidity is reached. The cloud scheme is described in more detail by Bushell (1998).

The ocean component of the model employs the same horizontal grid as the atmosphere component of the model, 3.75° longitude by 2.5° latitude. In the vertical, 20 model levels are used which increase from 10 m depth in the shallowest layer to 616 m depth in the deepest layer. A timestep of 60 minutes is employed and the ocean and atmosphere components exchange required fields once per day. The ocean component is based on the Cox (1984) model, solving the full primitive equation set in three-dimensions. A second-order numerical and centred advection schemes remove instabilities. In common with the atmosphere component, a staggered Awakawa B-grid is employed. A rigid lid is used to permit a longer timestep.

The ocean model also requires parameterisation of many physical processes. The mixed-layer model of Kraus and Turner (1967) is used with tracer and momentum mixing according to Large et al 1994 in the mixed layer and according to Pacanowski and Philander (1981) below. A background diffusion rate is used to approximate momentum mixing. Horizontal eddy mixing employs the isopycnal parametrisation of Gent and Mcwilliams (1990) and isopycnal mixing takes place according to Griffies et al. (1998). When a present-day continental configuration is employed, the Gibraltar and Hudson Straits are too small to be resolved so are modelled as a “diffusive pipe” Valdes et al. (2017). In addition, Iceland is removed to ensure an improved ocean circulation in the North Atlantic. Snow
accumulation on land is balanced by a virtual salinity flux to prevent drift in total ocean salinity.

Sea-ice is treated as a zero thickness layer on the surface of the ocean grid. Ice is assumed to form at the base at a freezing point of \(-1.8^\circ C\) but can also form from freezing in ice leads and by falling snow. A simple parameterisation of sea-ice dynamics is also employed (Gordon et al., 2000) and sea-ice formation due to convergence from drift is limited to 4 m deep. Sea-ice albedo is 0.8 for temperatures below \(-10^\circ C\), decreasing linearly to 0.5 at 0°C.

The MOSES2.1 land surface model is employed to simulate the fluxes of energy and water between the land surface and the atmosphere (Cox et al., 2000; Essery et al., 2003). TRIFFID (Top-down Representation of Interactive Foliage and Flora Including Dynamics) (Cox et al., 1998) predicts the distribution of vegetation using a plant functional type (PFT) approach. TRIFFID is run every 10 days using averaged fluxes. TRIFFID calculates vegetation properties for five PFTs: broadleaf trees, needleleaf tree, C3 grass, C4 grass and shrubs. Gridboxes can contain a mixture of PFTs based on a ‘fractional coverage co-existence approach’ Valdes et al. (2017). Net primary productivity (NPP) is also calculated, using a photosynthesis-stomatal conductance model (Cox et al., 1998) accounting for a number of factors including atmospheric oxygen content. The predicted vegetation distribution impacts the atmosphere component by altering surface albedo, evapotranspiration and surface roughness.

It is possible to alter the model topography in order to simulate past time periods. The topographies employed for the simulations in Chapter 4 are shown in Figure 2.4. The topographical reconstructions are ©Getech Ltd. The baseline simulations were set up and configured by Paul Valdes (University of Bristol). The annual average surface temperatures and annual average precipitation for these simulations are shown in Appendix Figures C.1 and C.2.

In summary, HadCM3BL is an atmosphere-ocean general circulation model with an interactive vegetation scheme (Valdes et al., 2017) suitable for performing long deep-time palaeoclimate integrations.

### 2.5.2 Model Development

In order to perform the experiments described in Chapters 4 and 5, a number of model developments were made. In addition model configurations were altered, particularly to
implement the palaeogeography required for the Marinoan (Chapter 4), however these will be described in more detailed in Chapters 4 and 5 where required.

**Oxygen Variability**

Oxygen variability was implemented similarly to Section 2.4.2. Ozone mass mixing ratios were also altered to account for the change in atmospheric molecular mass. Examples of the modsets for implementing a 35% atmospheric oxygen content are given in Appendix B.2. In addition to code changes, model start dumps require an alteration to the file header which defines the total atmospheric mass. The script to perform this was written by PJV.

**Volcanic Forcing**

For the experiments in Chapter 5, additional modsets were used to implement volcanic forcing. These were adapted from existing modsets produced by UK Met Office for simulations in Jones et al. (2005) and made available by PJV.

Stratospheric aerosol optical depths (sAOD) are taken from the extended climatology described in Sato et al. (1993). A repetitive annual cycle in sAOD, split into four equal-area latitudinal bands is selected to represent the 12 month period of the highest observed sAOD (Oct 1991 - Sep 1992) in the historical record. The aerosol optical depth is scaled to
aerosol loading assuming an aerosol size distribution consistent with the Mount Pinatubo volcanic eruption (area-weighted mean effective radius, \( R_{\text{eff}} = 0.5 \mu m \)). Finally, the aerosol loading is scaled by the required factor to simulate a large volcanic eruption.

Mie scattering calculations are performed using SOCRATES (Suite of Community RAdiative Transfer codes based on Edwards and Slingo), an offline version of the radiation code used in the Met Office Unified Model (e.g. Walters et al. (2017)) based on the original Edwards and Slingo radiation code (Edwards and Slingo, 1996). Radiative properties can be calculated for a range fixed size distributions of stratospheric sulfate aerosols. These calculated radiative properties can then included in the radiative transfer scheme in HadCM3-BL (see section 2.5.1).

2.5.3 Model Evaluation

HadCM3BL has been evaluated extensively in Valdes et al. (2017). It has also been used for a large number of simulations of deep-time palaeoclimate (Hill et al., 2013; Lunt et al., 2007, 2010; Tabor et al., 2016). HadCM3 captures well the climate response to volcanic eruptions such as winter warming post-eruption (Jones et al., 2005), despite its limited stratospheric resolution. It should be noted that we use the low resolution ocean model, which could impair this. However, as the atmosphere model is the same resolution and the short-term effects of volcanic eruptions are dominated by the radiative and dynamical processes in the atmosphere we argue that HadCM3-BL should behave similarly.

2.6 Energy Balance Decomposition

For an atmosphere which consist of grey gases (gases with a constant optical thickness across the electromagnetic spectrum), a 0D energy balance model (0D-EBM) describes the equilibrium surface temperature:

\[
\frac{S_0}{4}(1 - \alpha) = \epsilon \sigma \tau_{s,ebm}^4
\]  

(2.1)

where \( S_0 \) is the solar constant (\( L_\odot / 4 \) due to spherical geometry), \( \alpha \) is the planetary albedo, \( \epsilon \) is the effective surface emissivity, \( \sigma \) is the Steffan-Boltzmann constant and \( \tau_{s,ebm} \) is the equilibrium surface temperature for the EBM. Values for \( \alpha \) and \( \epsilon \) can be obtained from
radiative flux output from a GCM:

\[
\alpha = \frac{SW_t^\uparrow}{SW_t^\downarrow}, \quad \epsilon = \frac{LW_t^\uparrow}{LW_s^\uparrow}
\]

(2.2)

where \( SW_t^\downarrow \) and \( SW_t^\uparrow \) are the upward and downward (respectively) shortwave top-of-atmosphere fluxes. \( LW_t^\uparrow \) and \( LW_s^\uparrow \) are the upward longwave radiative fluxes at the top-of-atmosphere and surface respectively.

For simulations in Chapters 4 and 5, a 1D energy balance model (1D-EBM) has been used to deconvolve the contributions from changes in different parts of the climate system. This 1D-EBM approach has been applied to zonal mean quantities for climate simulations of the Eocene by Heinemann et al. (2009) following Budyko (1969) and Sellers (1969):

\[
SW_t^\downarrow(\phi)[1-\alpha(\phi)] - \frac{1}{2\pi R^2 \cos(\phi)} \frac{\partial F(\phi)}{\partial \phi} = \epsilon(\phi) \sigma \tau_{s,ebm}^4(\phi)
\]

(2.3)

where \( \phi \) is the latitude, \( R \) is the radius of Earth and \( SW_t^\downarrow \) is the incident shortwave radiation at the top-of-the atmosphere (Heinemann et al., 2009). \( \frac{\partial F(\phi)}{\partial \phi} \) is the divergence of total meridional heat transport and is given by

\[
\frac{\partial F(\phi)}{\partial \phi} = -2\pi R^2 \cos(\phi)(SW_t^{\text{net}}(\phi) + LW_t^{\text{net}}(\phi))
\]

(2.4)

where \( SW_t^{\text{net}} \) and \( LW_t^{\text{net}} \) are the net top-of-atmosphere shortwave and longwave radiative fluxes respectively (positive downward, Heinemann et al. 2009). Solving for \( \tau_{s,ebm} \), EBM surface temperature for each latitude can be calculated using radiative fluxes from the GCM. Where clear-sky radiative fluxes are also available, cloud radiative effects can be deconvolved from clear-sky radiative effects. The clear-sky albedo \( \alpha_c \) and clear-sky effective surface emissivity \( \epsilon_c \) can be calculated by:

\[
\alpha_c = \frac{SW_{t,c}^\uparrow}{SW_{t,c}^\downarrow}, \quad \epsilon_c = \frac{LW_{t,c}^\uparrow}{LW_s^\uparrow}
\]

(2.5)

where \( SW_{t,c}^\downarrow \) is the upward top-of-atmosphere clear-sky shortwave radiative flux and \( LW_{t,c}^\downarrow \) is the upward top-of-atmosphere clear-sky longwave radiative flux. When considering the temperature change between two experiments, the contributions from different components can be quantified by calculating \( \tau_{s,ebm} \) with different combinations of components from each experiment (Heinemann et al., 2009).
Chapter 3

Simulations of the Climate Impacts of the 1257 Eruption of Mount Samalas

The 1257 eruption of Mount Samalas (Lombok Island, Indonesia) led to the largest injection of volatile gases into the stratosphere in the last millennium. There is strong discrepancy between climate modelling studies investigating the climate response to the eruption and the climate response reconstructed by tree-ring methods. I will present integrations with the HadGEM3-ES composition-climate model to investigate the climate impact using a self-consistent treatment of aerosol microphysics. These simulations show a good agreement with tree-ring reconstructions. The CMIP5 and Community Earth System Model-Large Millennium Ensemble (CESM-LME) simulations show poorer agreement with tree-ring reconstructions. This suggests that our current understanding of chemical and physical processes is consistent with the climate response to this extremely large volcanic eruption.

3.1 Background

A detailed description of the climate impacts of volcanic eruptions generally is given in Chapter 1.

3.1.1 Common Era Climate

There are a number of factors which affect Earth's climate (see Chapter 1), however many of these have not changed appreciably over the last two millennia. For instance, Earth's orbit and global ice volume have remained relatively constant (e.g. Otto-Bliesner
et al. 2016). This means that the variability in Common Era (since 0 CE) climate is likely representative of climate variability due to natural changes to greenhouse gases, solar forcing and volcanic eruptions (Jones and Mann, 2004). In addition, the availability of proxy data for the last millennium is vast (Jones et al., 2001) and includes high fidelity tree ring archives (e.g. Wilson et al. 2016), historical records (e.g. Guillet et al. 2017) and ice cores (e.g. Sigl et al. 2014). Combined, these provide a context for the current anthropogenic warming trends – with caveats that human intervention in the Earth system started many thousands of years ago (Ruddiman, 2003). This has made the last millennium in particular a period of interest for policymakers, for instance in the last Intergovernmental Panel on Climate Change (IPCC) report (Masson-Delmotte et al., 2013; Stocker et al., 2013).

**Proxy Methods**

There are a variety of methods that have been used to reconstruct the climate variability over the common era. Biological systems are sensors for a variety of environmental indicators. Tree growth is affected by temperature, water and nutrient availability, acidity and a range of other factors. However, the growth of trees at cool, moist sites at high elevation in the mid-latitudes or northern boreal forests can be considered to be limited by temperature (Briffa et al., 1998a). Hence, records of their productivity such as tree-ring width (TRW) and maximum latewood density (MXD) are indicators of local temperature (e.g. Wilson et al. 2016). As maximum tree growth takes place during the summer, JJA temperatures are most strongly influencing the TRW and MXD in the Northern Hemisphere (Briffa et al., 1998b). This also permits annual-scale variability to be assessed (e.g. Wilson et al. 2016). Statistical techniques can be employed, correlating temperature anomalies at local sites with regional temperature changes to obtain a more holistic reconstruction of climatic changes (e.g. Guillet et al. 2017).

There are caveats to the use of tree-ring archives for reconstructions of JJA land temperature anomalies. TRW methods in particular have memory effects (Esper et al., 2015) which cause TRW to be affected many years after cooling. This has a physiological basis, caused by year-to-year food storage. MXD is not affected by this (Esper et al., 2015), however light availability may also affect MXD (Kalela-Brundin, 1997; Stine and Huybers, 2014; Tingley et al., 2014) which would suggest it is an overestimate of the climate cooling because large reductions in downward shortwave radiation at the surface would limit tree growth. Robock (2005) suggested that increases in diffuse radiation could enhance tree
ring growth as photosynthesis is enhanced by diffuse radiation. This would offset any effects of light availability changes, however modelling studies suggest that this effect is weak for boreal forests (Chen and Zhuang, 2014). This is reflected in the tree-ring record, which supports aerosol having a deleterious effect on net primary productivity for an extended period following a large volcanic eruption (Krakauer and Randerson, 2003). In addition, dissolution of sulfate aerosol into rain could occur. The occurrence of acid rain has been postulated for the 1783–4 eruption of Laki (Thordarson and Self, 2003) and could have affected tree-ring data.

Ice-cores can also provide insights into the variability of climate and forcings of climate (McKay and Kaufman, 2014). Reconstructions of CO$_2$, N$_2$O and CH$_4$ (MacFarling Meure et al., 2006) provide constraints on greenhouse gas forcing of climate over this period. Temperatures can be reconstructed using deuterium ($\delta$D) and oxygen ($\delta^{18}$O) isotopes. As isotopic signatures in ice cores are imprinted by changes in physical processes instead of biological processes, this overcomes some of the disadvantages of tree and coral-based methods. These biological proxies are affected by a wider array of environmental variables, however are more spatially variable. Stable isotope techniques can only reconstruct local temperatures. Sulfate deposition in the aftermath of volcanic eruptions can also be recovered from the ice core (e.g. Sigl et al. 2014). These can be used to estimate climate forcing associated with the eruption (e.g. Gao et al. 2008), however there is considerable uncertainty in sulfate deposition using state-of-the-art chemistry-climate models (Marshall et al., 2018).

The instrumental climate record is considered to only begin in 1850 (Brohan et al., 2006). Before this time, there are a limited number of records of climatic variables such as the Central England temperature record which has a continuous temperature record from 1659 to present. Indirect proxies of climate include grape harvest dates for wine production (García de Cortáz-Atauiri et al., 2010). More qualitative measures include observational records, however these should be used with caution. For instance, historical records of ice-skating on the Thames were thought to be characteristic of the ‘Little Ice Age’ however probably reflect changes in human management of the river around that time (Jones and Mann, 2004).

**Proxy Reconstructions**

Many attempts at reconstructing temperature variations on a global or hemispheric level utilise compilations of various proxy approaches. For instance, Ljungqvist (2010)
reconstruct northern hemisphere temperatures based on documentary, lake/river fossils and sediments, MXD, marine sediments, speleothem isotopic analysis, TRW and varved sediment thicknesses. However, temporal resolution limits the detectable climate signals to decadal timescales for most of these proxies. This prevents its use for investigating the response to volcanic eruptions. Hence, tree-ring only reconstructions may provide additional information on the annual scale. Intercomparison between multi-proxy and tree-ring-only approaches has shown general agreement (Rutherford et al., 2005), with important differences which can depend on factors such as the seasonality of the proxy data used and the statistical methodologies employed.

Figure 3.1 shows a comparison between the N-TREND2015 reconstruction of MJJA 40N-75N land temperature anomaly compared to three other tree-ring based methods (SCH2015, Schneider et al. 2015; DWJ06, D’Arrigo et al. 2008; and FRK07, Frank et al. 2007) and a variety of multi-proxy reconstructions (AMW07, Wahl and Ammann 2007; HGL07, Hegerl et al. 2007; LJN10, Ljungqvist 2010; and MANN08-EIV, Mann et al. 2008). This shows that N-TREND2015, which uses 54 sites and a mixture of TRW and MXD approaches, is broadly consistent with the multi-reconstruction mean (Figure 3.1, green line). In all reconstructions, warmer than average temperatures in the 11th Century are evident (Medieval Warm Period) and cooler than average temperature in the 17th Century (Little Ice Age). However, discrepancies between multi-model and tree-ring approaches are apparent. The N-TREND2015 reconstruction appears to reconcile many of these differences.

Shorter-term variability is also evident in tree-rings: strong volcanic eruptions lead to strong reductions in MJJA temperature anomalies, however these are stronger in MXD methods like SCH2015 (Schneider et al., 2015) than TRW methods like DWJ06 (D’Arrigo et al., 2008). N-TREND2015 appears to capture the peak temperature cooling the year after the eruption, consistent with the climate forcing profile after a volcanic eruption. However, N-TREND2015 preserves a longer-term cooling impact, consistent with TRW-only approaches. This likely reflects auto-correlation (memory) effects in the tree-ring width response to large perturbations in temperature (Krakauer and Randerson, 2003). While TRW based methods agree better with multi-proxy methods, issues with the short-term response mean that the use MXD methods is likely superior for comparing models and data. However, MXD has not been as widely assessed for confounding environmental factors as TRW (D’Arrigo et al., 2013).
Fig. 3.1 Comparison of N-TREND2015 (Anchukaitis et al., 2017; Wilson et al., 2016), DWJ06 (D’Arrigo et al., 2008), SCH2015 (Schneider et al., 2015) and FRK07 (Frank et al., 2007) tree-ring based reconstructions of NH temperature with the AMWA07 (Wahl and Ammann, 2007), HGL07 (Hegerl et al., 2007), LJN10 (Ljungqvist, 2010) and MANN08-EIV (Mann et al., 2008) multi-proxy reconstructions. For the tree-ring based methods, the correlations between that method and the average of AMW07, HGL07, LJN10 and MANN08-EIV (green line) is inset. Z-score indicates the number of standard deviations above the mean. Figure reproduced from Wilson et al. 2016.
Contributions to Radiative Forcing

There is strong heterogeneity in the temporal distribution of climatically-relevant volcanic eruptions. Figure 3.2 shows a stratospheric SO$_2$ injection reconstruction of Toohey and Sigl (2017) based on an analysis of ice core deposition records. The record shows 39 explosive volcanic eruptions greater than the Mount Pinatubo (20 Tg SO$_2$) eruption between –500 and 1900 CE. However, the relationship between SO$_2$ injection magnitude and radiative forcing is not straightforward. This is due to non-linear aerosol microphysical processes (Pinto et al., 1989; Timmreck et al., 2009) which lead to a strong fall-off in scattering efficiency as the magnitude of SO$_2$ injections become larger. However, many studies have assumed a broadly linear scaling between deposited sulfate and climate forcing (Gao et al., 2008; Otto-Bliesner et al., 2016). In addition, reconstructions of stratospheric SO$_2$ have uncertainties due to an assumed linearity between deposited sulfate and injected sulfur dioxide which is unlikely to hold (Toohey et al., 2013).

Volcanic forcing is not the only cause of climate variability in the past 2000 years. Solar variability has been suggested as a potential mediator of past climatic changes (Herschel, 1801). The sun exhibits an 11-year solar cycle, with around a 1 W m$^{-2}$ variation in peak-to-trough TSI (total spectral irradiance) (Fröhlich, 2002). This suggests a relatively weak climate forcing due to a consideration of the magnitude of the likely changes (Gray et al., 2010). Of more interest to long-term climate is any secular change in TSI, however most estimates of TSI for the last millennium (Schmidt et al., 2012b) show little variability, of the order of $\pm$1 W m$^{-2}$, similar to that associated with the 11-year solar cycle. It is therefore unsurprising that solar variability has had a small effect on the climate of the last millennium and has been confirmed using GCM studies (Schurer et al., 2014). For solar variability to contribute more substantially to climatic changes over the last millennium, climate models would have to be too insensitive to TSI changes and/or solar models underestimate the amount of change. However, the small changes in TSI simulated by solar models lead to the best agreement for GCM simulations of the last millennium (Ammann et al., 2007).

Model-Proxy Assessments of Forcing Agents

An assessment of the relative contributions of different forcing agents requires the use of climate models. This is because climate feedbacks can lead to non-linearities in the response to additional climate forcings. Meanwhile, detailed comparisons with proxy records are also important in order to assess the plausibility of model simulations (PAGES
Climate simulations of the period 850–1850 CE were performed as part of the *Past1000* experiment for CMIP5, which fed into the IPCC 5th assessment report working group 1 report considering past climate change (Vaughan et al., 2013), the detection and attribution of climate change (Bindoff et al., 2013) and the evaluation of climate models (Flato et al., 2013).

More recently, an ensemble of last millennium simulations have been performed (Otto-Bliesner et al., 2016) with the CESM model, a state-of-the-art AO-GCM which has been developed since the CMIP5 era of models. The use of an ensemble approach permits a greater understanding of the role of internal variability in last millennium climate variations. However, like the CMIP5 models, the treatment of aerosols is crude with important implications for the climate response: “The degree of volcanic cooling in the CESM-LME is generally stronger than in the reconstructions, possibly related to uncertainties in the volcanic forcing” (Otto-Bliesner et al., 2016). This interpretation has been disputed as altering the eruption season can lead to improved agreement with proxy methods, improving confidence in the atmospheric circulation response to large volcanic eruptions (Stevenson et al., 2017). However, this would not explain why the correct climatic cooling can be achieved when using an aerosol size distribution inconsistent with such a large eruption which would overestimate the shortwave scattering and underestimate the longwave absorption of the aerosols (Lacis et al., 1992; Timmreck et al., 2009). This inconsistency in the treatment of aerosols would therefore impact the circulation response simulated by Stevenson et al. (2017).

In summary, the climate of the Common Era is characterised by warmer northern hemisphere land surface temperatures in the 11th and 12th Centuries – the ‘Medieval Warm Period’ – and cooler northern hemisphere land surface temperatures in the 17th Century – the ‘Little Ice Age’. There have been a number of large, explosive volcanic eruptions which could have caused a short-term cooling of the climate and the temporal distribution of volcanic eruptions may have played a role in long-term climate variability. The annual resolution of tree-rings makes them ideal for reconstructing the climate changes associated with volcanic eruptions over the last millennium. MXD is a more robust method for assessing short-term climate variability due to memory effects in TRW data. However for long-term variability, TRW reconstructions show superior performance in comparison to multi-proxy data. The N-TREND2015 dataset was developed to ‘bridge’ between these two competing methods and performs well compared to multi-proxy data while overcoming many of the drawbacks to TRW data after volcanic eruptions. However, a consideration of confounding variables for MXD reconstructions have not
been performed, despite light limitation (Tingley et al., 2014) and acid deposition possibly being important in the aftermath of extremely large volcanic eruptions.

### 3.1.2 Samalas 1257

The eruption of Mount Samalas in 1257 (Lavigne et al., 2013) represents the largest single injection of volatile gases into the stratosphere in the Common Era (Vidal et al., 2016). A detailed geochemical study of the melt inclusions by Vidal et al. (2016) suggests $157 \pm 12$ Tg of SO$_2$ was emitted by the volcano. In addition, significant quantities of halogen species were also emitted – up to 227 Tg of Cl and 1.3 Tg of Br. The largest spikes of sulphate in ice cores in the common era occur in the years after this eruption, in both Greenland and Antarctica (Langway et al., 1988), suggesting a tropical volcanic source (Sigl et al., 2014).

Historical evidence points toward a strong cooling in the aftermath of the eruption of Samalas. Contemporary narrative sources suggest an unusually cloudy, rainy and cold summer in Europe in 1258 (Guillet et al., 2017). In addition, analysis of grape harvest dates suggest extremely poor growing conditions in 1258, with the latest grape harvest date on record: between 6 and 16 days later than in 1816 (in the aftermath of the Mount Tambora
eruption, Guillet et al. 2017). Famines also affected England and the Holy Roman Empire, with possible political implications (Guillet et al., 2017).

The climate response to the 1257 Samalas eruption is notable for its relatively muted climate cooling, compared to climate model simulations (Mann et al., 2012; Robock, 2005; Zielinski, 1995). While SO$_2$ emissions were 5-7 times the emissions from the 1991 Mount Pinatubo eruption (Toohey and Sigl, 2017), the NH temperature response reconstructed by MXD methods was only around twice as large (Mann et al., 2012). A number of modelling studies of the 1257 Samalas eruption have been performed, in the context of the Past1000 CMIP3/PMIP,CMIP5 experiment. However, most of these simulations overestimate the cooling response to Samalas as well as other large eruptions (Hartl-Meier et al., 2017). This apparent discrepancy between climate model simulations of the response to the 1257 Samalas eruption and proxy records led to the development of the ‘missing tree-ring’ hypothesis. Mann et al. (2012) posited that threshold growth effects limited the climate response response observed in the tree-ring archive. Missing tree rings would reconcile the muted climate response from Samalas with the large temperature anomalies simulated by climate models (Mann et al., 2013). However, this has since been thoroughly refuted (Anchukaitis et al., 2012; Büntgen et al., 2014; D’Arrigo et al., 2008), suggesting that the ‘muted’ climate response is not an artefact.

Climate model studies focusing on the 1257 Samalas eruptions have been performed. Timmreck et al. (2009) performed AO-GCM simulations using the Crowley et al. (2008) volcanic AOD reconstructions, using a range of aerosol effective radii. They found that aerosol effective radii between 0.7 and 1.3 $\mu$m best matched the northern-hemisphere tree ring reconstructions. However a 1$^{st}$ January eruption (1258) and an SO$_2$ injection of 260 Tg SO$_2$ (Oppenheimer 2003) is assumed. These have since been refined to a summer (1257) and ~100 Tg SO$_2$ injection since by Stoffel et al. (2015) who performed atmosphere-only GCM simulations with a microphysical aerosol module to produce aerosol fields to drive an AO-GCM to obtain the climate response. They were able to simulate a broad agreement between their AO-GCM simulations and the MXD-based reconstructions, however the response was sensitive to eruption month and the height of injection. To date, no studies which include fully interactive atmospheric chemistry and aerosol microphysics within a fully coupled AO-GCM have been performed. While ensemble methods have been used previously (e.g. Timmreck et al. 2009; Toohey et al. 2016), these studies employ the ensemble mean for comparison with tree ring records. This may be appropriate in the context of a epoch analysis when averaging over both observations and model simulations, however for individual eruptions there may be a strong impact of the initial climate state
to determining the climate response. If tree ring records record a stronger/weaker signal due to La Niña/El Niño for instance, averaging over climate model simulations would not be appropriate.

3.2 Methods & Simulations

3.2.1 Model Description

The HadGEM3-ES model (Bellouin et al., 2013; Dhomse et al., 2014; Hewitt et al., 2011; Mann et al., 2010; Morgenstern et al., 2008) is employed, as fully described in Chapter 2.

3.2.2 Model Simulations

The volcanic perturbation experiments were initialised from six different climate states, representing the range of variability in ENSO and QBO states (see Chapter 2). The volatile emissions were obtained from Vidal et al. (2016) and scaled according to Table 3.1 – between 60\% and 90\% of SO\(_2\) emitted from the volcano reaching the stratosphere spans the uncertainty in that quantity obtained from ice core records (Toohey and Sigl, 2017). Halogen emissions are much more uncertain, however as little as none (LO-SO\(_2\) and HI-SO\(_2\)) to 1\% (LO-HAL) and 20\% (HI-HAL) are plausible. We therefore construct four ensembles which span a reasonable range of uncertainties in the chemical injections.

Injection heights and timing are also uncertain and challenging to quantify. Stoffel et al. (2015) showed best model agreement with May and July eruptions, therefore we selected a June eruption. Injection heights are another source of uncertainty, Vidal et al. (2016) suggest an injection height peak of 40 km, however this is substantially above the height of the Junge layer. In this region of the atmosphere, the role of meteoric smoke particles could become important. However, large discrepancies between models and observations in global climate models (Brooke et al., 2017) suggests that a naive application to past climates would not be appropriate as the input of meteoric smoke particles in past climates could not be well constrained from the ice core record. The top of the injection height was increased from 27 km (for Pinatubo) to 34 km to reflect the more explosive volcanic eruption.
Table 3.1 Summary of Samalas Experiments

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>Experiments</th>
<th>Initialised</th>
<th>SO$_2$ Emission / Tg</th>
<th>HCl Emission / Tg</th>
<th>HBr Emission / Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>HI-HAL</td>
<td>S1-6</td>
<td>DA1-6</td>
<td>142.2</td>
<td>46.68</td>
<td>0.263</td>
</tr>
<tr>
<td>LO-HAL</td>
<td>S7-12</td>
<td>DA1-6</td>
<td>94.8</td>
<td>2.33</td>
<td>0.013</td>
</tr>
<tr>
<td>HI-SO2</td>
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<td>DA1-6</td>
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<td>0.000</td>
</tr>
<tr>
<td>LO-SO2</td>
<td>S19-24</td>
<td>DA1-6</td>
<td>94.8</td>
<td>0.00</td>
<td>0.000</td>
</tr>
</tbody>
</table>

### 3.2.3 Proxy Data

Climate model simulations are compared to publicly available tree-ring reconstructions. The MXD-based reconstructions of Guillet et al. 2017 (hereafter SG17) and Schneider et al. 2015 (hereafter SCH15) are employed. The mixed TRW-MXD reconstruction N-TREND2015 is also used (Wilson et al., 2016), as described in section 3.1.1. In all cases, the temperature anomaly is taken as the anomaly against a 30-year running mean.

### 3.2.4 CMIP5 and CESM-LME

The CMIP5 models which contributed to the Past1000 experiment for CMIP5-PMIP are detailed in Table 2.1. CMIP5 data was accessed on the JASMIN analysis platform. In addition, results of CESM-LME simulations are also presented (Otto-Bliesner et al., 2016), as described in section 3.1.1. CESM-LME data was obtained from https://www.earthsystemgrid.org/.

### 3.3 Results - Composition and Forcing in HadGEM3

In this section, the evolution of atmospheric composition in the HadGEM3-ES simulations is presented. The differences in response between the different emissions scenarios is described and potential mechanisms to explain the differences are put forward.
Fig. 3.3 Top: Ensemble mean simulated zonal mean ozone column for (A) HI-HAL, (B) LO-HAL and (C) BOTH-SO2. The black contour indicates the 220 DU isoline. Bottom: Ensemble mean simulated zonal mean ozone column change for (A) HI-HAL, (B) LO-HAL and (C) BOTH-SO2. Differences that are not significant at the 95% confidence interval according to a Kolmogorov-Smirnov test are indicated with stipples.
3.3 Results - Composition and Forcing in HadGEM3

3.3.1 Impacts on Ozone

The ozone response to the injection of stratospheric SO$_2$ is expected to depend on the background chemical state and the magnitude of the halogen injection. Figure 3.3 shows the zonal mean ozone column for the HI-HAL, LO-HAL and mean of the HI- and LO-SO$_2$ ensembles (hereafter BOTH-SO$_2$). Ozone differences from the climatological mean for the unperturbed Base are also shown in Figure 3.3. For the HI-HAL case, the global mean ozone column amounts drops by 242 DU, a 75% decrease from the unperturbed case. This represents near-total stratospheric ozone loss. Tropical ozone depletion remains for around 4 years after the eruption, where tropical column ozone drop below 180 DU. At high latitudes, the ozone loss is greater and persists for longer, particularly in the Southern Hemisphere where ozone depletion, according to the US National Aeronautics and Space Agency definition of 220 DU, takes place up to a decade later. In the more conservative LO-HAL scenario, tropical ozone depletion occurs only in the year following the eruption, with more limited Northern hemisphere ozone loss. However, global mean ozone columns reduce by 25% two years after the eruption representing a peak of 81 DU reduction. Declines in ozone are more persistent in the Southern hemisphere, where ozone depletion still takes place up to six years after the injection. Meanwhile, global mean column ozone increases in BOTH-SO$_2$ by 4% at the peak, 12 months after the eruption. There is a latitudinal dependence with decreases in the tropics and increases in the extratropical midlatitudes.

The latitudinal dependence of the ozone changes in the BOTH-SO$_2$ scenario suggests a dynamical response to the aerosol heating. Figure 3.4 shows the change in residual mean meridional circulation, $\overline{w}^*$ at 70 hPa. $\overline{w}^*$ increases in the tropics (in a region of upwelling) and decreases in the extratropics (in a region of downwelling). This suggests a more vigorous Brewer-Dobson circulation in response to the injections of SO$_2$ which brings more ozone poor air from the troposphere and increases transport of air masses away from ozone producing regions. Ozone column would otherwise be expected to increase in BOTH-SO$_2$ due to chemical feedbacks – heterogeneous reaction of N$_2$O$_5$ on sulfate aerosol leads to a reduction in reactive N which reduces ozone depletion. By contrast the sharp decreases in ozone column evident in HI-HAL and LO-HAL are indicative of chemical changes. The injection of HCl and HBr leads to reactive halogen species which can deplete ozone.
Table 3.2 Simulated SO$_2$ Lifetime

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>SO$_2$ Lifetime / days</th>
</tr>
</thead>
<tbody>
<tr>
<td>HI-HAL</td>
<td>102</td>
</tr>
<tr>
<td>LO-HAL</td>
<td>68</td>
</tr>
<tr>
<td>HI-SO2</td>
<td>68</td>
</tr>
<tr>
<td>LO-SO2</td>
<td>62</td>
</tr>
</tbody>
</table>
3.3 Results - Composition and Forcing in HadGEM3

3.3.2 Impacts on Sulfate Burden

As the initial oxidation of SO$_2$ by OH is the rate determining step in the production of stratospheric sulfate aerosols, the lifetime of SO$_2$ is a proxy for the rate of aerosol production. The e-folding time of SO$_2$ is employed here – the time taken to reach $1/e$ of the initial injection of SO$_2$, as the decay of SO$_2$ is not exponential. The ensemble average SO$_2$ lifetimes are shown in Table 3.2. The additional injection of SO$_2$ from LO-SO2 to HI-SO2 leads to an increase in SO$_2$ lifetime of 6 days, around the same as the injection of 1% halogens from LO-SO2 to LO-HAL. The 20% halogen emission however leads to the most substantial increase in SO$_2$ lifetime, from 68 to 102 days in HI-HAL. An increase in SO$_2$ lifetime with the co-emission of HCl is supported by model simulations of the Sarychev Peak volcano in 2009 (Lurton et al., 2018). This is due to ozone depletion leading to less stratospheric OH, extending the SO$_2$ lifetime.

Figure 3.5 shows the evolution of global sulfate burden and aerosol effective radius for the four ensembles. The largest aerosol burden simulated is for the HI-SO2 case, where the maximum in sulfate burden is simulated in November. For the LO-SO2 case, the peak in sulfate burden is simulated in December and is consistent with a 33% smaller injection magnitude. The simulated peak effective radius is larger in the HI-SO2 case than the LO-SO2 case, 1.09 vs 0.94 $\mu$m, which is consistent with a larger magnitude of SO$_2$ injection and an earlier peak in aerosol burden as larger aerosols sediment from the stratosphere more quickly. The additional halogens injected in the LO-HAL case compared to the LO-SO2 case lead to a small reduction in peak sulfate burden from 105 to 100 Tg while the aerosol effective radius is slightly reduced from 0.94 to 0.93 $\mu$m, however is within the variability between simulations. In the HI-HAL case the peak aerosol burden is substantially reduced to 80 Tg from 180 Tg, while effective particle radius drops to 0.90 $\mu$m on the addition of 20% yield of halogen species. These aerosol size distributions are consistent with the 0.7-1.3 $\mu$m that Timmreck et al. (2009) employ to simulate a reasonable climate response to Samalas.

3.3.3 Atmospheric Radiative Balance

Stratospheric sulfate aerosols lead to a perturbation to Earth's radiative budget. Figure 3.6A shows the decomposition of the top-of-atmosphere (top) and surface (bottom) radiative budgets for the HI-SO2 ensemble. The presence of sulfate aerosols leads to a substantial increase in top-of-atmosphere outgoing shortwave radiation, peaking around 20 Wm$^{-2}$. This is counteracted by a large reduction in outgoing longwave radiation, peaking around
Fig. 3.5 Evolution of total sulfate aerosol burden (top) and aerosol effective radius (bottom) for the HadGEM3-ES ensembles. Individual simulations (dotted lines) and ensemble means (solid lines) are indicated.
Fig. 3.6 Radiative budget anomalies for the top-of-atmosphere (left) and surface (right) for (A) the HI-SO2 ensemble mean, decomposed into its components, (B) the change in shortwave component only for HI-HAL, LO-HAL, HI-SO2 and LO-SO2 ensemble means and (C) the net change for HI-HAL, LO-HAL, HI-SO2 and LO-SO2 ensemble means.
17 Wm\(^{-2}\). This is due to the scattering of shortwave radiation and the absorption of longwave radiation in the stratosphere. The shortwave and longwave contributions to the surface heat budget behave similarly. The surface heat budget also accounts for changes to sensible and latent heat fluxes, both positive (in the downward sense) in response to stratospheric aerosol. Sensible heat fluxes reduce in the upwards direction in response to a cooler surface with respect to the troposphere and latent heat fluxes reduce in the upwards direction as less water vapour is evaporated from the surface.

It is common to quote the “volcanic forcing” of a particular eruption as the change to the net shortwave radiation balance at Earth’s surface (e.g. Slawinska et al 2017). As shown in Figure 3.6A, this does not account for the complex changes to the radiative budget that result from changing both the balance of longwave and shortwave radiation in the atmosphere. However, for the purposes of intercomparison this quantity is shown in Figure 3.6B (right) for the mean of the HI-HAL, LO-HAL, HI-SO2 and LO-SO2 ensembles. These show the largest deviation in net surface shortwave occurs for the HI-SO2 case, which is expected as it is a larger volcanic eruption. On the basis of this metric alone, we would expect the largest climatic cooling to be achieved with the HI-SO2 case and for HI-HAL to have the weakest climatic cooling response. The top-of-atmosphere budgets (Figure 3.6 left) show that while HI-HAL has a lower peak in the top-of-atmosphere shortwave imbalance, the atmospheric cooling impact is extended compared to the HI-SO2 ensemble.

As a more holistic measure of the perturbation to Earth’s radiative budget, Figure 3.6C shows the change to top-of-atmosphere (left) net and surface (right) net radiative budget change. This shows that the surface-shortwave metric is insufficient to describe the changes to the surface radiative budget. When accounting for changes to longwave, sensible and latent heat fluxes it is clear that all ensembles show a similar change to the surface radiative heat budget in the first year after the eruption. HI-HAL also shows an extended cooling, with negative net surface heat anomalies up to 4 years after the eruption. This would suggest that the short-term climate response to the different emissions scenarios should be similar.

### 3.4 Results - Surface Climate

In this section, the climate response from the HadGEM3-ES scenarios is described. Comparisons between the HadGEM3-ES simulations, the CESM-LME, the CMIP5 Past1000 simulations and tree-ring data from SG17 and N-TREND2015 are presented.
3.4 Results - Surface Climate

3.4.1 CESM-LME

An ensemble of 13 simulations of the last millennium was performed for the CESM-LME (Otto-Bliesner et al., 2016). Figure 3.7 shows the JJA surface temperature anomaly in 1258 against a 30-year running-mean for each ensemble member (1-13), the ensemble mean (M) and the SG17 MXD reconstruction (T). The forced climate response, the ensemble mean, simulated by CESM is –1.25 °C for the 40-90N land mean (NHLAND) surface temperature compared to –0.71 °C in SG17. While there is a wide spread in response between the different ensemble members, all overestimate the cooling compared to the tree-ring reconstruction (–0.97 to –1.72 °C). However, the uncertainty in the SG17 reconstruction is large – between –1.39 and –0.08 °C which means 9 of the 13 ensemble members plausibly simulate the NHLAND surface temperature anomaly. These ‘plausible’ ensemble members generally capture patterns of both warmer and cooler conditions which are evident in the tree-ring reconstruction while the forced climate response is a cooling.

Figure 3.8 shows the JJA surface temperature anomaly in 1259 against a 30-year running-mean for each ensemble member (1-13), the ensemble mean (M) and the SG17 MXD reconstruction (T). The forced climate response, the ensemble mean, simulated by CESM is –2.77 °C for the 40-90N land surface mean surface temperature compared to –1.19 °C (–1.73/–0.56 min/max) in SG17. For 1259, no ensemble member simulates plausible NHLAND temperature anomalies (range of –2.32 to –3.32).

This suggests that the CESM-LME substantially overestimates the cooling associated with the eruption of Mount Samalas in 1257. CESM-LME performs more favourably for the c1452-3 eruption (Appendix Figures C.8 and C.9), 1600 eruption of Huapyutina (Appendix Figures C.10 and C.11) and 1815 eruption of Tambora (Appendix Figures C.12 and C.13) compared to the SG17 reconstruction.

3.4.2 HadGEM3-ES

Based on the analysis of the radiative balance changes in HadGEM3-ES (section 3.3.3), it would be expected that the peak surface cooling in each ensemble would be similar. An analysis of the change to surface air temperature in Figure 3.9 supports this. All ensembles show a short-term global mean cooling peaking around 0.5 °C. The peak in northern-hemisphere cooling is stronger, around 1.0 °C of peak cooling (Figure 3.9 centre). This reflects the larger land surface in the NH. A stronger cooling is observed for the Northern Hemisphere extratropical (>40 N) land, hereafter referred to as NHLAND (Figure 3.9 right, note change of scale). A peak cooling between 1 and 2 °C represents a strong regional
Fig. 3.7 1258 JJA surface air temperature anomaly against a 30 year running-mean for the CESM-LME simulations (1-13), the ensemble mean (M) and the Guillet et al. (2017) MXD reconstruction. 40-90N land surface averaged temperature anomalies are inset right. For each ensemble member (1-13), green (red) anomalies indicates the ensemble response is (not) within the range reported by Guillet et al. (2017).
Fig. 3.8 As Figure 3.7 for 1259.
cooling in the ensemble mean. However, this region shows particularly strong variability in the mean response (see light lines).

Figure 3.9 also shows estimated time for recovery for each ensemble. The climate is considered to have recovered when a positive anomaly is recorded for the 12 subsequent months. The injections of halogens is associated with an increase in the time for recovery, even with only a 1% halogen injection efficiency. Northern hemisphere mean temperatures remain below their pre-eruption values for 6 years after the eruption in LO-HAL, compared to 4 years for LO-SO2. For HI-HAL, global and northern hemisphere mean surface temperatures remain below their pre-eruption values for over a decade. This suggests that the co-emission of volcanic halogens prolongs the climatic cooling of a single volcanic eruption. This is consistent with the prolonged negative anomalies in top-of-atmosphere and surface net radiative heat imbalance (Figure 3.6C) due to the substantial depletion in atmospheric ozone.

Considering each ensemble member, the JJA surface air temperature anomalies for each simulation compared to a non-volcanic baseline are shown in Figure 3.10 for 1258 and Figure 3.11 for 1259. Widespread cooling of extratropical northern hemisphere land in 1258 is evident in all simulations except for LO-SO2(ENS1) and HI-HAL(ENS6). All other simulations show surface air temperature anomalies broadly consistent with the reconstructed values of SG17 with patterns of warming and cooling. For 1259, most simulations show too weak a cooling compared to the SG17 NHLAND averages and four simulations exhibit an NHLAND warming. However, most simulations show patterns of warming and cooling particularly the deep cooling of NW Russia evident in the SG17 record.

### 3.4.3 Comparing HadGEM3-ES, CESM-LME & CMIP5

A comparison between the CMIP5, CESM-LME and HadGEM3-ES ensembles and the tree-ring reconstructions is shown in Figure 3.12. The HadGEM3-ES ensemble is in excellent agreement with the temperature reconstructions for 1258, however fails to capture the reduction in surface air temperatures reconstructed between 1258 and 1259. The simulated temperature anomaly was still within the error for some ensemble members. The CMIP5 and CESM-LME all simulate cooler temperatures in 1259, however in both cases the mean across all models is cooler than the reconstructed temperatures. However, given the limited spatial area which the tree-ring areas cover, there is substantial uncertainty in JJA NHLAND. By placing an upper bar on cooling it permits excluding many of the
Fig. 3.9 Global (left), Northern Hemisphere (centre) and 40-90N land (right) mean JJA surface air temperature anomalies simulated for each HadGEM3-ES simulation (light) and ensemble mean (dark). Return dates are indicated for each ensemble mean (red dashed lines). Note the expanded scale for >40N land, indicated in blue.
Fig. 3.10 1258 JJA surface air temperature anomaly for the HadGEM3-ES simulations. The 40-90N land mean anomalies are inset right. For each simulation, green (red) anomalies indicates the ensemble response is (not) within the range reported by Guillet et al. (2017).
3.4 Results - Surface Climate

Fig. 3.11 As Figure 3.10 for 1259.
Fig. 3.12 Reconstructed 40N-90N land surface air temperature for N-TREND2015, Schneider et al. (2015) and Guillet et al. (2017). Mean values indicated with solid lines with uncertainty range shaded. Ranges of simulated 40-90N land surface temperature for CMIP5, CESM-LME and HadGEM3-ES (BOTH-SO2 and HI-HAL) ensembles are indicated.
CMIP5 model simulations and all of the CESM-LME simulations as lying outside both the N-TREND2015 and SG17 reconstructed anomalies. None of the HadGEM3-ES simulations can be excluded by this generous metric. Simulations of warmer temperatures in 1258 and 1259 in particular could probably be excluded as not representing an appropriate climate response.

The different HadGEM3-ES ensembles show variability in the climate response simulated. BOTH-SO2 show a rapid recovery in most cases, between a peak in 0.4-1.2 drop in NHLAND, which reduces to 0-0.4 in 1259. HI-SO2-S1 and LO-SO2-S1 for example exhibit a strong cooling of NW Russia and Labrador and captures the warming in Alaska. While for LO-HAL, HI-SO2 and LO-SO2 only one of six simulations exhibits a NHLAND cooling consistent with the SG17 reconstruction, HI-HAL shows 4 out of 6. However, all simulations fall short of the SG17 mean response of $-1.19^\circ C$.

In this section, the temperature response from HadGEM3-ES, CESM-LME and CMIP5 have been compared. HadGEM3-ES simulates a more muted climatic cooling than CESM-LME and the CMIP5 ensemble averages. However, there is variability within each ensemble. BCC shows the weakest cooling from the CMIP5 archive while CCSM4 simulates the strongest cooling despite apparently using the same volcanic dataset (Hartl-Meier et al., 2017). CESM-LME is cooler still than the CMIP5 ensemble, closer to the CCSM4 simulation (CESM is an updated version of CCSM4). However, there is considerable variability in the climate response between ensemble members of both CESM-LME and the HadGEM3-ES ensembles. This shows that initial conditions play a large role modulating the climate response to volcanic forcing.

### 3.5 Results - Societal Impacts

The changes to atmospheric composition and climate in the aftermath of the 1257 Samalas eruption may have had a number of impacts on society. This section will address some of these.

#### 3.5.1 UV Index

Ozone depletion can lead to an increase in surface ultraviolet (UV) light which could cause DNA damage to animals and plants. The clear-sky UV index is given by

$$UVI = 12.5 \mu_0^{2.42} (\Omega/300)^{-1.23}$$  \hspace{1cm} (3.1)
Fig. 3.13 Daytime-mean clear-sky ultraviolet index for (A) HI-HAL, (B) LO-HAL and (C) BOTH-SO2.
3.5 Results - Societal Impacts

Fig. 3.14 Change in Huglin Index (HI) to a particular year from the mean of the ten prior years for CESM-LME for the France region (yellow square on right). Left: Frequency of HI changes simulated for the 1000 year unforced 850 CE simulation (yellow). Values for 1258 (red) and 1259 (black) for forced ensemble members 2-13 are indicated (crosses) and for the ensemble mean (vertical lines). Right: HI change for forced ensemble member 2 for 1258. Sites with historical records of a poor grape harvest in Guillet et al. (2017) are indicated (black circles).

... according to Madronich (2007), where $\mu_0$ is the cosine of the solar zenith angle and $\Omega$ is the total vertical ozone column (in Dobson units). 12.5 is a unitless scaling factor. Note that this equation only accounts for changes to ozone column and neglect aerosol and cloud changes. The daily-mean average UV index coloured by World Health Organization categories (Low, Medium, High and Extreme) is show in Figure 3.13. This shows that in the HI-HAL scenario, high or extreme UV levels would be expected for much of the extratropics in the three-four summers after the eruption. Assessment of changes to surface UV is made more challenging by the presence of volcanic aerosols, which also scatter UV radiation. However, it is worth noting that similarly to the case for visible light, scattering peaks when the diameter of the particle is of the order of the wavelength of radiation. Damaging UVB and UVC radiation will then be scattered even less effectively than visible light for the larger aerosol size distributions.

3.5.2 Viticulture Impacts

1257-8 is associated with a considerable number of impacts on agriculture. Famines in England in 1257 are associated with subsequent political upheavals that led to King John being deposed (Guillet et al., 2017). However, there is limited quantitative data with which
to challenge model simulations. Guillet et al. (2017) showed the wine harvest in 1258 was particularly poor, with a grape harvest date later than any since recorded. Cool, wet summers lead to a poor grape harvest.

The effects of temperature alone can also be considered using the Huglin index ($HI$)

\[
HI = K \cdot \sum_{1 \text{ Apr}}^{30 \text{ Sep}} \left( \frac{T_{\text{mean}} + T_{\text{max}}}{2} - 10 \right)
\]  

(3.2)

where $K$ is a factor accounting for the length of day following Hall and Jones (2010), $T_{\text{mean}}$ is the daily mean temperature and $T_{\text{max}}$ is the daily maximum temperature. A particular range of $H$ corresponds to a growing environment which is ideal for the particular variety of grape in bands of 100. Therefore, significant changes in $HI$ can lead to a region becoming unsuitable for that particular grape variety. Figure 3.14 shows the change in Huglin Index for a particular year compared to the mean of the previous ten years simulated by the CESM-LME for 1258 (red crosses) and 1259 (purple crosses) for the France region (Figure 3.14 right, yellow box) compared to a 1000 year 850 forcing simulation. The change in Huglin index simulated by CESM-LME for 1258 varies from -80 to -410. Ensemble member 2 shows the largest change and this is shown in Figure 3.14 (right). Changes to the Huglin Index of over 200 are simulated for all sites which recorded a poor grape harvest in SG17 (black circles). Simulations and the historical record both show that there is considerable variability in societally-relevant climate effects. Note that only the temperature effects are considered in $HI$, there is no accounting for changes to the downwelling solar radiation or the changes in partitioning of direct and scattered solar fluxes. In addition, possible UV changes have not been accounted for. UV has been shown to alter the level of flavonols in the skins of grapes in New Zealand (Gregan et al., 2012). Also, it should be noted that as CESM appeared to overestimate the cooling in 1259, caution should be exercised in interpreting the $HI$ changes for that year.

3.6 Discussion & Conclusions

In this section the results will be discussed in the context of last millennium climate. Evidence (or lack thereof) for ozone depletion from Samalas will be discussed.
3.6 Discussion & Conclusions

3.6.1 Evidence for Ozone Depletion

Ozone depletion in the stratosphere would be expected in increasing tropospheric OH and therefore lead to faster removal of CH$_4$ and N$_2$O (Bekki et al., 1994). Combined with cooler global temperatures, which would reduce biological emissions of CH$_4$ and N$_2$O, levels of these chemical constituents would be expected to drop further. In addition, deposition of sulfate has been shown to reduce CH$_4$ emissions from wetland sources (Gauci et al., 2004). In the modelling set-up used, CH$_4$ and N$_2$O were held at lower boundary conditions, so are heavily constrained. This is due to the large uncertainty in pre-industrial emissions of these compounds and the long chemical timescales associated with CH$_4$ (10 years) and N$_2$O (100 years). Including CH$_4$, and particularly N$_2$O, emissions would be too computationally intensive. However, records of these greenhouse gases in the ice core record could yield some insights into the chemical perturbation associated with the eruption. The best candidate for an ozone-depletion signal is from high-resolution continuous flow CH$_4$ measurements and this has been performed for the NEEM ice core (Rhodes et al., 2013) based on the age model of Sigl et al. (2013). These measurements are shown in Figure 3.15: 1258 is associated with the lowest CH$_4$ concentrations since the 1230s and no lower concentrations were measured until the very end of the 14th Century. As the age model uncertainty is less than ±1 year this gives some confidence in the timing of the response. However, this reduction is short lived and CH$_4$ concentrations subsequently rise into the mid 1260s, which is not consistent with ongoing ozone depletion. In addition, methane sources and the OH source from H$_2$O would be affected by environmental changes associated with the eruption. In order to better constrain source/sink relationships, continuous flow measurements from Antarctica would be needed and to date the only measurements obtained are for the WAIS which ends 9.8 ka (Rhodes et al., 2017). Shorter-lived trace gases may also give some insights into tropospheric changes. Increases in OH could lead to increases in hydrogen peroxide (H$_2$O$_2$), however analysis of the Tunu (Greenland) record do not show increases in H$_2$O$_2$ at this time (see Figure 3.16).

Changes in surface UV, which were particular marked in the HI-SO2 scenario would be expected to lead to an increase in the incidence of cataracts or skin cancer. No evidence for such an increase in skin-cancer incidence exists to date, however longevity was much lower in the 13th Century. While UK aristocrats who reached 21 years of age could be expected to reach 64 years of age in the 13th Century (Lancaster, 1990), life expectancy for the working classes would be much lower. UV increases would also most adversely affect
Fig. 3.15 Continuous CH$_4$ measurements from the NEEM ice core (Greenland, Rhodes et al. 2013).

Fig. 3.16 Selected ice core composition measurements from Tunu ice core (Greenland, Joseph McConnell. 2016 doi:10.18739/A2ZQ1G)
those whose occupations were outdoors, such as farm labourers, many of whom perished in the famines at this time in Europe.

In conclusion, ozone depletion would be expected to cause a number of changes to atmospheric composition or manifest itself through the increase in incident UV at Earth's surface. However, no conclusive signal in these metrics can be determined which does not permit the occurrence of ozone depletion to be conclusively proved or disproved.

### 3.6.2 Muted climate cooling

Hartl-Meier et al. (2017) showed that many CMIP5 simulations simulated too strong a cooling response to the 1257 Samalas eruption. This is also the case for CESM-LME (Section 3.4.1). By contrast, HadGEM3-ES generally agrees with the SG17 and N-TREND2015 temperature anomalies for 1258. For 1259, the HadGEM3-ES simulations fall closer to the N-TREND2015 and SCH15 reconstructions, underestimating compared to the SG17 reconstruction. While CESM-LME and CMIP5 models simulated this drop between 1258 and 1259, this could be due to the imposed radiative forcing, which is stronger in 1259 in the Gao et al. (2008) reconstruction. Cooler NHLAND in 1259 than 1258 were simulated in four of the 24 simulations which suggests that there may be a role for climate variability in determining this response. It should be noted that Stoffel et al. (2015) were also unable to simulate cooler temperatures in 1259 than 1258 in the ensemble mean, forcing a coupled climate model with aerosol climatologies produced by a 2D aerosol scheme. This is consistent with radiative forcing peaking the year after the eruption before dropping off after aerosols sediment and are transported out of the stratosphere. This supports the climate response in the SCH15 MXD reconstruction, as this is weaker in 1259 than 1258.

These simulations show that there is a general agreement between the magnitude of cooling in tree-ring records and climate models, using an appropriate choice for SO$_2$ loading. The use of a climate forcing scaled linearly from ice core deposition (Gao et al., 2008) in a large number of studies (e.g. Otto-Bliesner et al. 2016) is clearly inappropriate due to long-known self-limiting processes associated with larger magnitude of sulfur dioxide injection leading to larger aerosol sizes Pinto et al. (1989); Timmreck et al. (2010), see also Section 1.2.2). This leads to an overestimation of climatic cooling response to Samalas in the CESM-LME simulations, and possibly other large volcanic eruptions (Schneider et al., 2017). While the forcing can be adjusted temporally to match the tree ring data (Stevenson et al., 2017), this just suggests that CESM can simulate the correct climate response for an inappropriately large forcing.
In particular, Zhong et al. (2011) found a strong sea-ice–ocean feedback response to volcanism in the 13th Century, using the CCSM3 climate model. This has also been simulated in CCSM4 (Miller et al., 2012), which simulated the strongest climate response to the Samalas eruption in the CMIP5 archive. This mechanism was not found in all simulations however and if it requires reaching some threshold sea-ice cover to operate this would suggest that it is very unlikely to have occurred in the aftermath of Samalas, due to the severe overestimation of the cooling in CCSM4 (Hartl-Meier et al., 2017). Slawinska and Robock (2018) have recently shown that such a response occurs in the CESM model by investigating the CESM-LME ensemble. Unfortunately, Slawinska and Robock (2018) failed to assess the ability of the model to simulate the correct climate response to the Samalas eruption, compared to tree-ring data. While CESM may have an excellent representation of Arctic climate in the present-day, vastly overestimating the forcing may lead to false conclusions when assessing the role of volcanic forcing compared to solar variability, greenhouse gas changes etc. Accounting for these model biases is challenging as the kind of sea-ice–ocean feedbacks that have been invoked by Zhong et al. (2011), Miller et al. (2012) and Slawinska and Robock (2018) are highly non-linear and may depend on background climate. This suggests that extreme caution should be used when using CESM-LME to assess the role of volcanic forcing in 13th Century climate change.

Looking to the future, many models which contribute to the sixth phase of the Coupled Model Intercomparison Project – CMIP6 (Eyring et al., 2016) – will perform Past1000 experiments (Jungclaus et al., 2017) employing the Toohey and Sigl (2017) eVol2k reconstruction for volcanic forcing. This is a major step forwards from CMIP5, where the option to use either the Gao et al. (2008) or Crowley et al. (2008) reconstructions and lack of clarity in model implementation makes a quantitative comparison between models challenging (Atwood et al., 2016; Schneider et al., 2017). Regardless, a detailed description of the implementation of volcanic forcing is still required – Jungclaus et al. (2017) compare the ‘volcanic forcing’ of Gao et al. (2008), Crowley et al. (2008) and Toohey and Sigl (2017) by comparing AOD at 500 nm which is insufficient to quantify the radiative forcing. If models account for the impacts of aerosol size on the radiative forcing in different ways or neglect these important effects entirely, this may make quantitative comparisons of the CMIP6 Past1000 experiment more challenging.

That the climate response was similar in HI-SO2 and LO-SO2 suggests that in HadGEM3-ES these SO2 loadings are near the peak in cooling for a single volcanic eruption.

There must be a peak cooling due to a single volcanic eruption somewhere between 0.2 µm (background) and 2.0 µm effective radius as even relatively small eruptions cause a
measurable global cooling and above 2.0 $\mu$m, the longwave warming component begins to dominate over the shortwave cooling component. This suggests that cooling saturates as the magnitude of the sulfur dioxide injection increases. However, previous climate model simulations have suggested a very strong cooling response to the eruption of Toba (~75 ka). Jones et al. (2005) simulated a 11 $^\circ$C peak in global mean surface air temperature cooling in response to an idealised 100-times Pinatubo eruption with the HadCM3 model by scaling up stratospheric aerosol loadings observed in the aftermath of the 1991 Mount Pinatubo eruption. Robock et al. (2009a) simulated a 10 $^\circ$C peak cooling for a similar simulation with the CCSM3.0 model and 8-17$^\circ$C with GISS ModelE. Simulations with interactive chemistry in GISS ModelE showed a substantial moistening of the UTLS, maintaining the oxidising capacity of the stratosphere. However, the ModelE simulations did not account for microphysical aerosol processes which would suggest that the aerosol produced by ModelE would be too long-lived due to sedimentation effects. More recently, a state-of-the-art sectional aerosol model simulation of a 100-$\times$ Pinatubo scenario (English et al., 2013) simulated a peak $R_{\text{eff}}$ of 1.9 $\mu$m which is very close to the cooling limit. This would be consistent with geological evidence which supports a lack of a ‘volcanic winter’ in the aftermath of Toba (Jackson et al., 2015; Lane et al., 2013) and lack of evidence of mass extinctions (Erwin and Vogel, 1992) which would be expected from such significant changes to surface temperatures and vegetation (Robock et al., 2009a). State-of-the-art aerosol simulations and geological evidence argue against the Toba catastrophe theory. However, other environmental effects may be as important or more important than the temperature response. These need to be considered in a holistic way in order to better understand the impacts of large volcanic eruptions on the environment (Schmidt et al., 2014) and on society (Oppenheimer, 2015).

### 3.6.3 Conclusions

The eruption of Mount Samalas led to the largest stratospheric injection of volatile gases in the Common Era. Tree-ring proxy reconstructions and climate model simulations show that the climate cooled in response to the subsequent formation of sulfate aerosols in the stratosphere. While CMIP5 and CESM-LME model simulations overestimate the climate response to Samalas, compared to tree-ring data, previous studies with offline aerosol models are more consistent with the tree-ring data (Stoffel et al., 2015; Timmreck et al., 2009). The first simulations of the climate response to the 1257 eruption of Mount Samalas with a fully coupled AO-GCM with interactive stratospheric chemistry and microphysical
aerosol processes, HadGEM3-ES, suggest that our current understanding of the physical and chemical processes is generally consistent with the tree ring record. As little as a 1% yield of the erupted halogens reaching the stratosphere could lead to substantial ozone depletion which alters the atmospheric radiative imbalance, increases incident ultraviolet light at Earth's surface and alters the evolution of stratospheric sulfate aerosol by increasing the SO$_2$ lifetime and stratospheric circulation. HadGEM3-ES supports a relatively muted climate response, with respect to a climate forcing naively assumed to be linear with aerosol deposition at ice core sites. CESM-LME, which employs such a scheme (Gao et al., 2008) overestimates the climate response compared to all tree-ring reconstructions. This is the first study to comprehensively assess CESM-LME against tree-ring data for Samalas, despite it being widely used to study 13th Century climate change in the context of the Little Ice Age. This suggests extreme caution should be urged when doing so and that future last-millennium studies should include a more physically-based representation of aerosol forcing such as Toohey and Sigl (2017) and extensively document its implementation to facilitate a quantitative comparison of model responses to volcanic forcing over the last millennium.
Chapter 4

Phanerozoic Climate: Impact of Oxygen Variability

The oxygen content of the atmosphere may have varied between 10% and 35% during the Phanerozoic eon (541 Ma–Present). By altering atmospheric mass, this has implications for Earth’s radiative budget and therefore surface temperatures. Previous studies using more simple models have investigated the climate response to atmospheric mass changes but they do not agree on the sign of the temperature response. In this chapter, I have revisited this problem using two fully coupled climate models with a 3D representation of the atmosphere and ocean. I will demonstrate that there is a robust reduction in equator-to-pole temperature gradient, reduction in the seasonal cycle of surface air temperature and reduction in global mean precipitation in response to an increase in oxygen content across the performed simulations. In addition, HadCM3-BL simulates a lower equilibrium climate sensitivity at high oxygen content.

4.1 Background & Literature

The primary driver of climate over the Phanerozoic is atmospheric CO\(_2\) (Royer et al., 2004). However, atmospheric oxygen content may also have varied across the Phanerozoic. Atmospheric dioxygen plays a vital role in the Earth system (Catling et al., 2005), regulating the biosphere through fire ignition (Watson et al., 1978) and metabolism of aerobic biota. Hence variability in \(pO_2\) over time has been invoked as an evolutionary trigger (Berner et al., 2007) of both animals (Falkowski et al., 2005) and plants (He et al., 2012) at many
Fig. 4.1 Oxygen content reconstructions in the Phanerozoic from Algeo and Ingall (2007), Arvidson et al. (2013), Bergman et al. (2004), Berner (2009), Berner and Canfield (1989) and Glasspool and Scott (2010). The mean (black line) and range (grey shading) of the Arvidson et al. (2013), Bergman et al. (2004) and Berner (2009) is indicated as these reconstructions were most consistent with ice core evidence (Stolper et al., 2016). High and low limits on atmospheric oxygen are indicated by grey dashed lines. Present day atmospheric oxygen content is indicated by the grey line.
points in the Phanerozoic (Beerling and Berner, 2000; Edwards et al., 2017; Robinson, 1990; Saltzman et al., 2011; Scott and Glasspool, 2006).

While strong biological and geological feedbacks prevent rapid swings in atmospheric oxygen (Catling and Claire, 2005), reconstructions of past atmospheric oxygen content suggest that there have been substantial excursions from the 21% oxygen content present in today's atmosphere at times in the Phanerozoic eon. These reconstruction methods divide into forward and inversion models. Forward models include nutrient / weathering models (Arvidson et al., 2013; Bergman et al., 2004; Hansen and Wallmann, 2003) and isotope mass balance models (Berner 2009 and Falkowski et al. 2005) while inversion models infer oxygen content from proxies such as charcoal (Glasspool and Scott, 2010), organic carbon to phosphorus ratios (Algeo and Ingall, 2007) and plant resin $\delta^{13}\text{C}$ (Tappert et al., 2013). Figure 4.1 shows the reconstructed oxygen contents for a variety of these methods. There is general agreement between the reconstructions that oxygen content increased from 5-25% in the early Paleozoic to 20-35% in the Permian. Elevated $\text{O}_2$ content is supported by carbon isotope measurements (Beerling et al., 2002). Disagreement is particularly evident in the Mesozoic, with low values simulated by isotope mass balance approaches. Mills et al. (2016) have shown that this could be due to an inappropriate choice of $\delta^{13}\text{C}$ and that adjusting this value with geological constraints leads to a higher reconstructed oxygen content in better agreement with wildfire records. At the time of writing, there are no direct geochemical proxies for $p\text{O}_2$ on the Phanerozoic timescale. However, $p\text{O}_2$ in the last 800,000 years has been reconstructed using $\text{O}_2/\text{N}_2$ ratios in ice cores (Stolper et al., 2016). A secular 7‰ decline in $p\text{O}_2$ is consistent with the ability to change oxygen content by the order of a few percent in ~10 Myr. The reconstructions of Bergman et al. (2004), Arvidson et al. (2013) and Berner (2009) are the most plausible based on ice core data (Stolper et al., 2016). Considering these three models alone would still suggest a large uncertainty for most of the Phanerozoic, except for elevated levels in the late Carboniferous / early Permian and reduced levels in the late Devonian.

‘Phanerozoic’ means ‘visible life’ and the most marked change to carbon cycling between the Proterozoic and Phanerozoic was caused by the emergence of land plants. The radiation of land plants has led to strong regulation of atmosphere $\text{CO}_2$ and $\text{O}_2$ which both play important roles in photosynthesis. Land plants likely led to a substantial sequestration of carbon in the terrestrial biosphere and led to the Ordovician glaciation (Lenton et al., 2012). Increases in organic carbon sequestration in the aftermath of the evolution of lignin production may also have contributed to the cooling (Robinson, 1989). This fundamental change to the Earth system may have constrained $\text{CO}_2$ levels to between
10–200 Pa ever since (Franks et al., 2014) which is consistent with a long-term sensitivity of the Earth system to CO$_2$ changes (Royer, 2016). Watson et al. (1978) have argued that strong fire feedbacks prevent large fluctuations in oxygen levels, due to runaway burning at high oxygen levels. However subsequent experiments using natural fuels support the possibility of the Earth system to support higher oxygen levels (Wildman et al., 2004). Charcoal appears in the fossil record continuously since the late Silurian (~420 Ma, Scott and Glasspool 2006). This suggests a floor on oxygen levels in the region of 12% (Wildman et al., 2004) to 16% (Belcher and McElwain, 2008; Belcher et al., 2010) since then due to limits on ignition.

Variations in pO$_2$ also have important implications for photosynthesis and therefore the operation of the terrestrial carbon cycle. The primary CO$_2$-fixing enzyme Rubisco possesses a dual carboxylase-oxygenase function (Smith, 1976). A photosynthetic carboxylase pathway removes CO$_2$ from the atmosphere while oxygenation leads to photorespiration and CO$_2$ evolution. Therefore, increases in pO$_2$ ought to lead to O$_2$ outcompeting CO$_2$ for active sites on the Rubisco enzyme and leading to a reduction in net primary productivity (less photosynthesis, more respiration). However, photorespiration is likely to be necessary for removal of harmful byproducts in the photosynthetic metabolic pathway (Hagemann et al., 2016) and a recent study suggests that increases in photorespiration may actually promote photosynthesis (Timm et al., 2015). Photosynthesis is itself sensitive to the background CO$_2$ content (Beerling and Berner, 2000). In addition, temperature modifies the relative solubilities of CO$_2$ and O$_2$ (Jordan and Ogren, 1984). Temperature also affects the specificity of Rubisco for CO$_2$ (Long, 1991). Therefore, the coevolution of pO$_2$, pCO$_2$ and temperature across the Phanerozoic has the capacity to significantly impact the terrestrial carbon cycle.

This chapter focuses on investigating the climate impacts of atmospheric mass variation as the result of altering the concentration of O$_2$, a major gas. Lower atmospheric mass leads to less Rayleigh scattering so more shortwave radiation reaches the Earth's surface. This enhances atmospheric convection and the hydrological cycle which leads to more tropospheric water vapour, further enhancing warming. However, lower atmospheric mass leads to a reduction in the pressure broadening of greenhouse gas absorption lines which should lead to a weaker greenhouse effect and lead to cooling. Previous modelling studies have investigated which factor dominates with conflicting results. Goldblatt et al. (2009a) presented radiative-convective model simulations for the Archean (~3 Ga) which suggested that a nitrogen inventory around three times larger than present would help to keep the early Earth warm at a time when solar input was only around 75% of what it is to-
day, potentially solving the ‘Faint Young Sun’ paradox (Feulner, 2012). Charnay et al. (2013) investigated this using a GCM coupled to a slab ocean and found that for their idealised early Earth simulations they achieved a strong warming (+7 °C) in response to a doubling in atmospheric mass. Poulsen et al. (2015) simulated the climate impacts of changes in O₂ content over a range of 5–35% using the GENESIS climate model with a slab ocean and a continental configuration consistent with the Cenomanian (mid Cretaceous, 65 Ma) and found the opposite response – lower atmospheric mass at low pO₂ was associated with a strong warming. Subsequent 1D calculations cast doubt on this result (Goldblatt, 2016; Payne et al., 2016), however it is plausible that other climate feedbacks such as changes to relative humidity and cloud changes may be important as atmospheric mass changes. These would not be accounted for in 1D radiative-convective equilibrium simulations. Cloud feedbacks in particular are a good candidate for explaining the discrepancy as cloud feedbacks under CO₂-driven climate change have strong model dependency (Bony et al., 2015). Another feedback which has not been considered is the possible impact of changes in the mechanical forcing of wind on the ocean circulation. In the absence of this effect, Earth’s surface temperature would be 8.7 K cooler (Saenko, 2009) and the equator-to-pole temperature gradient would be steeper. Wind stress (τ) is parameterized in GCMs as τ = ρ u u where ρ is the atmospheric density and u is the surface wind vector. So as atmospheric density increases, the wind stress on the ocean and therefore ocean heat transport should increase accordingly. While ocean heat transport is a much smaller contributor to the meridional (poleward) heat transport than the atmosphere (Wunsch, 2005), they are not independent (e.g. Koll and Abbot 2013). Increased meridional heat transport in high density atmospheres is also supported by an idealised 2D modelling study of the early Earth (Chemke et al., 2016). As slab ocean models assume a constant or diffusive ocean heat transport, the Charnay et al. (2013) and Poulsen et al. (2015) simulations cannot account for these effects.

The equilibrium climate sensitivity (ECS) is a metric for the sensitivity of a climate model to changes in CO₂. Understanding this value is important for predictions of future climate changes. As the radiative forcing of CO₂ is logarithmic with concentration, theoretically the ECS should be constant with time. However, there is growing evidence that ECS has not been constant over Earth’s history (Caballero and Huber, 2013). Changes to the incoming solar radiation, palaeogeography (Lunt et al., 2016), CO₂ levels themselves (Meraner et al., 2013) and tropical sea-surface temperatures (Caballero and Huber, 2013) may lead to changes in the sensitivity of a particular climate state to changes in CO₂. Given
Table 4.1 Summary of experiments. 21% oxygen simulations were set up by PJV. Experiments marked * were halted in a non-equilibrium state.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Continents</th>
<th>Model</th>
<th>CO₂ / Pa</th>
<th>O₂ / %</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-GEM</td>
<td>PIH</td>
<td>HadGEM3-AO</td>
<td>28</td>
<td>10,21,35</td>
<td></td>
</tr>
<tr>
<td>4x-GEM</td>
<td>PIH</td>
<td>HadGEM3-AO</td>
<td>112</td>
<td>10,35</td>
<td></td>
</tr>
<tr>
<td>PI-CM</td>
<td>PIH</td>
<td>HadCM3-BL</td>
<td>28</td>
<td>10,21,35</td>
<td></td>
</tr>
<tr>
<td>Ma-CM</td>
<td>Maastrichtian</td>
<td>HadCM3-BL</td>
<td>56</td>
<td>10,21,35</td>
<td></td>
</tr>
<tr>
<td>As-CM</td>
<td>Asselian</td>
<td>HadCM3-BL</td>
<td>28</td>
<td>10,21,35</td>
<td></td>
</tr>
<tr>
<td>Wu-CM</td>
<td>Wuchiapingian</td>
<td>HadCM3-BL</td>
<td>112</td>
<td>10,21,35</td>
<td></td>
</tr>
<tr>
<td>τPI-CM*</td>
<td>PIH</td>
<td>HadCM3-BL</td>
<td>28</td>
<td>21</td>
<td>1</td>
</tr>
<tr>
<td>τMa-CM*</td>
<td>Maastrichtian</td>
<td>HadCM3-BL</td>
<td>56</td>
<td>21</td>
<td>1</td>
</tr>
<tr>
<td>τAs-CM*</td>
<td>Asselian</td>
<td>HadCM3-BL</td>
<td>28</td>
<td>21</td>
<td>1</td>
</tr>
<tr>
<td>τWu-CM*</td>
<td>Wuchiapingian</td>
<td>HadCM3-BL</td>
<td>112</td>
<td>21</td>
<td>1</td>
</tr>
<tr>
<td>PI2x-CM*</td>
<td>PIH</td>
<td>HadCM3-BL</td>
<td>56</td>
<td>10,21,35</td>
<td></td>
</tr>
<tr>
<td>Ma2x-CM*</td>
<td>Maastrichtian</td>
<td>HadCM3-BL</td>
<td>112</td>
<td>10,21,35</td>
<td></td>
</tr>
<tr>
<td>As2x-CM*</td>
<td>Asselian</td>
<td>HadCM3-BL</td>
<td>56</td>
<td>10,21,35</td>
<td></td>
</tr>
</tbody>
</table>

Notes: 1) Wind stress to ocean set to zero.

that $pO₂$ changes alter the atmospheric radiative balance, its impacts on the ECS will also be investigated in this chapter.

### 4.2 Methods & Simulations

The impact of oxygen content variability is investigated with two coupled atmosphere-ocean general circulation models (AO-GCMs): HadCM3BL and HadGEM3-AO. Both models simulated the climate response to oxygen variability in a preindustrial Holocene climate. HadCM3-BL was additionally run for three time periods across the Phanerzoic: The Maastrichtian (late Cretaceous, 66.0–72.1 Ma), Wuchiapingian (late Permian, 254.14–259.1 Ma) and the Asselian (early Permian, 295.0–298.9 Ma). Continental reconstructions for these time periods were obtained ©Getech Ltd. All three are periods of time in which models have suggested that atmospheric oxygen may have deviated significantly from the present level of 21% (see Figure 4.1). Modifications were made to alter the oxygen content of the atmosphere as described in detail in Chapter 2. A summary of the experiments performed can be found in Table 4.1. When an experiment with a particular
oxygen content is referred to, it will be indicated in superscript, e.g. EXP\textsuperscript{21} indicates a 21% oxygen simulation. 21% simulations (PI-CM\textsuperscript{21}, As-CM\textsuperscript{21}, Ma-CM\textsuperscript{21} and Wu-CM\textsuperscript{21}) were integrated for 50 model years as these simulations had already been spun up at that CO\textsubscript{2} content by PJV. For HadGEM3-AO, model integrations (PI-GEM\textsuperscript{35}, PI-GEM\textsuperscript{10}, 4x-GEM\textsuperscript{35} and 4x-GEM\textsuperscript{10}) were performed for 300 model years with a 10-times acceleration of the deep ocean to reduce the time for equilibrium then integrated for a further 500 years to spin up the shallow ocean without acceleration. The last 50 years were used for model analysis. The PI2x-CM*, Ma2x-CM* and Wu2x-CM* experiments were spun off from the end of the PI-CM, Ma-CM and Wu-CM experiments and iterated for 100, 1000 and 100 years respectively.

Pre-Quaternary pCO\textsubscript{2} is poorly constrained due to the absence of glacial ice, however there is growing evidence that CO\textsubscript{2} is unlikely to have been significantly higher than ~100 Pa since the radiation of land plants (Breecker et al., 2010; Franks et al., 2014). For the Maastrichtian, 56 Pa is used in agreement with stomatal proxy-based reconstructions (Steinthorsdottir and Pole, 2016). For the Asselian, 28 Pa is used in agreement with carbonate and fossil plant reconstructions (Montañez et al., 2007). For the Wuchiapingian, 112 Pa is used (Brand et al., 2012).

1D atmospheric chemistry simulations have simulated higher O\textsubscript{3} column with increasing pO\textsubscript{2} (Kasting et al., 1979; Payne et al., 2016). More detailed 2D model simulations, which capture critical latitudinal gradients in photolysis and zonal mean transport (Hadjinicolaou and Pyle, 2004; Haigh and Pyle, 1982), support a monotonically increasing ozone column with increasing pO\textsubscript{2} (Harfoot et al., 2007). However, simulated ozone column was more sensitive to N\textsubscript{2}O levels than pO\textsubscript{2} (Harfoot et al., 2007). In addition, while column ozone reduces at low pO\textsubscript{2} in Harfoot et al. (2007) there are increases in ozone concentration in the tropical tropopause region where the radiative effect of O\textsubscript{3} is stronger (Forster and Shine, 1997). Changes in lightning are important for understanding future changes in tropospheric ozone (Banerjee et al., 2014), however are subject to considerable uncertainty (Finney et al., 2018). There may be more lightning at high pO\textsubscript{2} due to a higher pO\textsubscript{2}/pN\textsubscript{2} ratio or less due to reduced convection (Goldblatt et al., 2009a). Low pO\textsubscript{2} may also enhance isoprene emissions (Rasulov et al., 2009), which could enhance tropospheric ozone and alter cloud properties (Kiehl and Shields, 2013). Given ozone sensitivity to changes in CH\textsubscript{4} and N\textsubscript{2}O, the uncertainties in the inventories of these chemically-active species on the Phanerozoic timescale (Beerling et al., 2009, 2011), changes to ozone are not included in these simulations. In HadGEM3-AO the mass of tropospheric and stratospheric ozone is fixed at PIH values simulated by (Nowack et al., 2014) using a tropopause
height matching scheme. This prevents a rising tropopause leading to stratospheric levels of ozone existing in the troposphere, particularly in the 4x-GEM experiments. Not accounting for a rising tropopause has been found to artificially increase climate sensitivity (Heinemann, 2009). In HadCM3-BL, tropospheric ozone is set to 6 ppbv and stratospheric ozone is set to 1.66 ppmv for the 21% simulations. These values are adjusted to conserve total ozone mass in the alternative O\textsubscript{2} scenarios.

Proxy data for the Maastrichtian was obtained from Upchurch et al. (2015) and interpolated from their modern locations onto the Getech grid by Dr. Alexander Farnsworth (University of Bristol). Where the proxy locations deviated substantially from those described in Upchurch et al. (2015) (e.g. terrestrial proxy in the ocean) these were adjusted heuristically. The proxy data was obtained by a variety of methods including TEX\textsubscript{86}, δ\textsuperscript{18}O and leaf margin analysis. A full description of the proxy data and methods used can be found in Upchurch et al. (2015) and reference therein.

Data for the Poulsen et al. (2015) 21% O\textsubscript{2} and 10% O\textsubscript{2} simulations were obtained from https://www.ncdc.noaa.gov/paleo/study/18776. At the time of writing the 35% simulation contained missing data so was not used for analysis.

To estimate the climate sensitivity to CO\textsubscript{2} changes, the linear regression methodology of Gregory et al. (2004) is employed. This assumes a linear relationship between the changes in global, annual mean radiative imbalance at the top-of-atmosphere (\(N, \text{W m}^{-2}\)) and surface temperature anomalies (\(T_{\text{surf}}, ^\circ\text{C}\))

\[
N = F + \alpha_g \Delta T_{\text{surf}}
\]  

(4.1)

where \(\alpha_g\) is the effective climate feedback parameter (\(\text{W m}^{-2} \cdot \text{C}^{-1}\)) and \(F\) is the effective forcing (\(\text{W m}^{-2}\)) accounting for fast climate adjustments and effective radiative forcing. The effective ECS is then \(\Delta T_{\text{surf}}\) when \(N = 0\). While there are weaknesses of this approach, particularly due to non-linearities in \(\alpha_g\) as \(\Delta T_{\text{surf}}\) changes (Armour et al., 2013; Li et al., 2013), the climate response when simulations are continued to equilibrium show an accuracy to within 10% (Li and Sharma, 2013). Furthermore, the contributions to \(\alpha_g\) and \(F\) from longwave (\(LW\)) and shortwave (\(SW\)), clear-sky (\(CS\)) and cloudy-sky (\(CRE\)) components can be decomposed by a linear decomposition as

\[
F = F_{CS,SW} + F_{CS,LW} + F_{CRE,SW} + F_{CRE,LW}
\]  

(4.2)
for the effective forcing and

\[ \alpha_g = \alpha_{g,CS,SW} + \alpha_{g,CS,LW} + \alpha_{g,CRE,SW} + \alpha_{g,CRE,LW} \]  

(4.3)

for the effective climate feedback parameter.

### 4.3 Results

Where results are presented from a single simulation, the oxygen content for that run is superscript, e.g. EXP\textsuperscript{21} indicates a 21% oxygen simulation. Where results are presented as an anomaly between simulations with different oxygen contents, EXP\textsuperscript{0} \textsuperscript{21} indicates that the quantity presented is EXP\textsuperscript{21} minus EXP\textsuperscript{0}. A summary of results is shown in Table 4.2. I will show that under PIH conditions, both HadCM3-BL and HadGEM3-AO show an increase in global mean surface temperature with increasing \( pO_2 \) in agreement with 1D model studies (Payne et al., 2016). However, HadCM3-BL simulates a lower climate sensitivity to \( CO_2 \) so this temperature response may be reversed during the warmest of Phanerozoic climates. The HadCM3-BL and HadGEM3-AO simulations suggest that the uncertainty in \( pO_2 \) plays a small role in uncertainty in surface temperature over the Phanerozoic.

### 4.3.1 Surface Climate

Figure 4.2 (left) shows the annual-mean surface air temperature differences between the 35% and 10% runs. For the preindustrial Holocene, PI-GEM\textsuperscript{35} \textsubscript{10} shows a global mean surface temperature response of +1.50 °C while PI-CM\textsuperscript{35} \textsubscript{10} shows a similar global mean surface temperature response of +1.22 °C. This is in reasonable agreement with Payne et al. (2016) who simulated a temperature response between +1.05 and +2.21 °C depending on assumptions about atmospheric ozone. Similarly, the As-CM\textsuperscript{35} \textsubscript{10} case exhibits a global mean surface temperature response of +1.29 °C. For the warmest climates, a response of −0.82 °C is simulated for WU-CM\textsuperscript{35} \textsubscript{10} and +0.17 °C for 4x-GEM\textsuperscript{35} \textsubscript{10}. In the intermediate Ma-CM\textsuperscript{35} \textsubscript{10} case, a global mean surface temperature response of +0.70 °C is simulated. This suggests that oxygen content can modulate the climate response to \( CO_2 \) changes. This will be explored in Section 4.3.3.

There is a strong seasonal dependence in the surface air temperature response. Considering the changes in coolest average monthly temperature in each gridbox (Figure 4.2 centre), the change in cool month dominates the warming response, particularly at high
Table 4.2 Summary of results for EXP<sup>21</sup> then EXP<sup>35</sup><sub>10</sub>. Where applicable, results calculated for the Poulsen et al. (2015) Cenomanian 21%–10% oxygen simulation are also presented.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>PI-GEM</th>
<th>4x-GEM</th>
<th>PI-CM</th>
<th>As-CM</th>
<th>Ma-CM</th>
<th>Wu-CM</th>
<th>Poulsen</th>
</tr>
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<td>+0.22</td>
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Abbreviations: T<sub>eq-pole</sub> (Equator-to-pole surface air temperature gradient), T<sub>eq-pole,cold month</sub> (Equator-to-pole surface air temperature gradient for cold month), EBM (quantities obtained using a Budyko-Sellers 1D energy balance model following Heinemann2015), T<sub>surf</sub> (Surface temperature), T<sub>surf,csky</sub> (Surface temperature change accounting for changes in clear sky radiative fluxes), T<sub>surf,cloud</sub> (Surface temperature change accounting for changes in cloudy sky radiative fluxes), T<sub>surf,mht</sub> (Surface temperature change accounting for changes in meridional heat flux divergence)
4.3 Results

<table>
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<th>Mean Warm Month</th>
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<td>+0.62</td>
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<td>(4) F</td>
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<td>+0.67</td>
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Fig. 4.2 Surface air temperature change for (a) PI-GEM$^{35}_10$, (b) PI-CM$^{35}_10$, (c) As-CM$^{35}_10$, (d) Ma-CM$^{35}_10$, (e) Wu-CM$^{35}_10$ and (f) 4x-GEM$^{35}_10$ in the annual mean (left), cold month mean (centre) and warm month mean (right). The change in global mean values (°C) are offset to the top-right of each plot. Note the strong high latitude warming in the cold month mean and tropical cooling in the warm month mean.
latitudes. By contrast, the warm month mean is smaller/less negative in all cases (Figure 4.2 right). A cooling of continental land masses is evident in the tropics and particularly in the Wu-CM and 4x-GEM cases. These could be in part due to lapse rate changes which should be stronger at high $pO_2$ as for a given topographic height, the change in pressure is higher for high $pO_2$ which should lead to a larger temperature reduction with height. The changes to the seasonal cycle are consistent with the radiative changes associated with changing oxygen content. The reduction in incident surface shortwave radiation should have its strongest effect on extratropical temperatures in the summer, therefore the Rayleigh scattering component will most strongly affect the warm month temperature. Warming from pressure broadening of greenhouse gas absorption lines as atmospheric mass increases will be most evident in extratropical winter, as with anthropogenic climate change, due to sea-ice and surface heat flux changes (Dwyer et al., 2012). The reduction in the amplitude of the seasonal cycle in temperature simulated by both HadGEM3-AO and HadCM3-BL is therefore supported by a consideration of the changes to atmospheric radiation.

The zonal and annual mean surface air temperature changes are shown in Figure 4.3. The Northern-Hemisphere Equator-to-Pole temperature gradient is reduced by 6.6 °C in the PI-GEM$^{35}_{10}$ case (blue line) and 4.0 °C in the PI-CM$^{35}_{10}$ case (not shown). The zonal structure of the surface temperature change is similar in the palaeoclimate case studies. In the Maastrichtian, the equator-to-pole temperature gradient is reduced by 2.0 °C (Ma-CM$^{35}_{10}$) and in the Asselian the equator-to-pole temperature gradient is reduced by 2.3 °C (As-CM$^{35}_{10}$). The equator-to-pole temperature gradient reduces even in the Wu$^{35}_{10}$ case despite the reduction in global mean surface temperatures.

The hydrological cycle is also affected by changing oxygen content. Increases in Rayleigh scattering at high $pO_2$ ought to reduce incident shortwave at Earth’s surface (Poulsen et al., 2015) and inhibit convection (Goldblatt et al., 2009a) which should lead to reductions in precipitation. This is analogous to stratospheric sulfate or solar radiation management geoengineering where precipitation is reduced in geoengineering experiments with respect to an unperturbed climate with the same global mean surface temperature (Irvine et al., 2016). Poulsen et al. (2015) simulated large reductions in precipitation as $pO_2$ increased in the GENESIS climate model, however much of this could be explained by the surface temperature changes. Annually averaged precipitation change between the 10% and 35% oxygen content runs are show in Figure 4.4. In all cases, increasing oxygen content leads to a decline in global mean total precipitation, despite the increase in surface temperatures, however with strong regional differences. For PI-GEM,
Fig. 4.3 Zonally and annually averaged surface air temperature difference (solid lines) for PI-GEM$^{35}_{10}$ (blue), 4x-GEM$^{35}_{10}$ (red), As-CM$^{35}_{10}$ (pink), Ma-CM$^{35}_{10}$ (green) and Wu-CM$^{35}_{10}$ (purple). The difference from the annual-mean to cold month-mean for each run is indicated by the shading. Values are smoothed by a Savitzky-Golay filter (Savitzky and Golay, 1964).
Fig. 4.4 Annually averaged total precipitation change from 10% to 35% oxygen content for (A) PI-GEM$^{35}_{10}$, (B) PI-CM$^{35}_{10}$, (C) As-CM$^{35}_{10}$, (D) Ma-CM$^{35}_{10}$, (E) Wu-CM$^{35}_{10}$ and (F) 4x-GEM$^{35}_{10}$. Global mean values (mm day$^{-1}$) are offset.

PI-CM and 4x-GEM there is a clear northward shift in the tropical rain belts. A northward shift in the ITCZ would be consistent with stronger warming in the Northern hemisphere. Heat transport is more hemispherically symmetric in the Maastrichtian, Asselian and Wuchiapingian cases so latitudinal ITCZ shifts are not evident. While global precipitation is reduced in Wu-CM$^{35}$, the increase in ocean-land temperature contrast leads to a significant increase in tropical land precipitation which suggests that $pO_2$ could mediate monsoon circulations. Despite the increases in global-mean surface temperatures simulated for most cases, precipitation is still reduced in all simulations.

Comparing the surface temperature and precipitation response between HadCM3-BL and HadGEM3-AO suggests that the model responses are broadly consistent. Figure 4.5 shows a gridbox-by-gridbox comparison of annual mean surface air temperature and precipitation anomalies for PI-GEM$^{35}_{10}$ vs PI-CM$^{35}_{10}$. The largest discrepancy in surface air temperature response between the two models occurs for the largest temperature changes simulated by HadGEM, which is strongest in Northern Hemisphere polar regions. This could be linked to differences in the representation of polar climate processes between the two models. There is broad consistency in cold and warm-month means (Figure 4.2A and B) with stronger warming in the cold month mean and terrestrial cooling in the warm month mean.
4.3 Results

Fig. 4.5 Hexbin plots of surface air temperature anomaly (left) and precipitation anomaly (right) comparing PI-GEM$^{35}$ and PI-CM$^{35}$. Note that there is reasonable agreement between HadCM3-BL and HadGEM3-AO, however HadCM3-BL does not simulate the largest temperature anomalies simulated by HadGEM3-AO.

4.3.2 Energy Balance Decomposition

The drivers of the changes in surface temperature can be understood by decomposing the terms which contribute to surface temperature change in a 1D-energy balance model following Heinemann et al. (2009) as described in section 2.6. For PI-CM$^{35}$, these results are shown in Figure 4.6A. These show that the 1D-EBM can reasonably capture the temperature response in the HadCM3-BL simulations, with slight errors evident in the polar regions. This could be due to averaging over the polar rows in the HadCM3-BL model. There are positive contributions to the surface temperature change in the clear sky emissivity and albedo at the poles. This is consistent with the increase in pressure broadening of absorption lines and the simulated reduction in sea-ice extent. By contrast, extrapolar contributions to clear sky albedo provide a negative contribution to the temperature change which is consistent with an increase in Rayleigh scattering which would be expected to be strongest in the tropics where the maximum in incoming solar radiation is located. Combined, the clear sky component of the temperature change is $+1.45 ^\circ C$ and the cloudy sky component is $-0.35 ^\circ C$. This suggests that HadCM3-BL supports a
cloud feedback which acts to cool the climate at high $pO_2$ and partially offset the clear-sky temperature changes.

The same analysis was performed for the HadGEM3-AO PIH simulations. Figure 4.6B shows that a somewhat weaker cloud feedback is simulated by HadGEM3-AO ($-0.21^\circ C$). Clear-sky contributions are slightly stronger ($+1.51^\circ C$). The largest differences between the simulations appear in the all-sky albedo and emissivity changes, where there appear to be competing factors which lead to a similar climate response possibly related to partitioning between the longwave and shortwave contributions to the cloud response. This is perhaps unsurprising, as cloud feedbacks to $CO_2$ changes represent a large uncertainty in future climate change projections and given the relatively small global-mean temperature changes a relatively small change in cloud radiative effects has the power to considerably mediate the climate response. However the qualitative agreement in latitudinal structure of the clear-sky albedo and emissivity changes between these structurally different models gives some confidence that the relevant climate feedbacks are well captured in these simulations.

Analysis of the paleo-case studies (As-CM, Appendix Figure C.3; Ma-CM, Appendix Figure C.4; Wu-CM, Appendix Figure C.5) shows a similar pattern. In all simulations, irrespective of surface temperature response, the clear sky emissivity is a positive contribution to global mean surface temperature change while clear sky albedo is a more negative contribution. The emissivity contribution becomes less positive as $pCO_2$ increases from As-CM to Ma-CM to Wu-CM. By contrast the albedo contribution becomes more negative as $pCO_2$ increases. This is consistent with the reduction in planetary albedo as sea-ice extent is reduced on the ocean and dark vegetated surfaces increase on the land.

### 4.3.3 Climate Sensitivity

The impact of oxygen variability on the climate sensitivity will now be investigated. The HadGEM3-AO and HadCM3-BL results suggest that increasing $CO_2$ content leads to a reduction in the surface temperature change on increasing $pO_2$ (compare 4x-GEM and PI-GEM in Figure 4.2). From the 4x-GEM and PI-GEM experiments, a reduction in climate sensitivity of $0.65^\circ C$ can be inferred, based on the changes in surface temperatures. For HadCM3, $CO_2$-doubling experiments were performed and a regression of the change in top-of-atmosphere radiative imbalance against change in surface temperature following Gregory et al. 2004 (see also section 4.2) is shown in Figure 4.7. The PI-CM$^{35}$ climate state has a smaller ECS than PI-CM$^{10}$ by $0.7^\circ C$. While the changes in total radiative forcing $F$ are
Fig. 4.6 1D-EBM decomposition for A: PI-CM$^{35}$ and B: PI-GEM$^{35}$ simulations. Top left: EBM results (grey) vs GCM results (black). Top right: Decomposition of EBM into the emissivity (purple), albedo (green) and heat transport (orange) components of the temperature change. Bottom left: Clear-sky emissivity (dark purple) and albedo (dark green) components of the EBM. Bottom right: Decomposition of EBM into the total clear-sky (blue), cloudy-sky (red) and all-sky (grey) components.
Fig. 4.7 Gregory analysis: Regression of top-of-atmosphere radiative balance against surface air temperature change (solid lines) for the first 100 years of PI2x-CM$^{10}$ (pink) and PI2x-CM$^{35}$ (blue) cases. Annual averages are indicated by crosses and decadal averages are indicated by filled circles. The regression was performed on the decadal averages.
Fig. 4.8 Dominant surface type for each oxygen level simulation for (A) As-CM and (B) Wu-CM. BLT: Broadleaf trees, NLT: Needleleaf trees.

very similar, \( \alpha_g \) is less negative (-1.08 vs -1.37 W m\(^{-2}\)°C\(^{-1}\)) at low \( pO_2 \). The decomposition of these changes into their longwave and shortwave components, clear-sky and cloudy-sky components is also shown in Figure 4.7. The clear-sky longwave radiative flux changes are higher in PI2x-CM\(^{35}\) (4.0 W m\(^{-2}\)) than PI2x-CM\(^{10}\) (3.8 W m\(^{-2}\)) as would be expected due to the pressure broadening of CO\(_2\). The clear driver for the less negative \( \alpha_g \) value are from the longwave cloud radiative effect changes which is much steeper for PI2x-CM\(^{10}\) (+0.62 W m\(^{-2}\) °C\(^{-1}\)) than PI2x-CM\(^{35}\) (+0.17 W m\(^{-2}\) °C\(^{-1}\)). This is somewhat offset by stronger clearsky shortwave radiative feedbacks in PI2x-CM\(^{35}\) (+1.00 W m\(^{-2}\) °C\(^{-1}\)) than PI2x-CM\(^{10}\) (+0.57 W m\(^{-2}\) °C\(^{-1}\)). This highlights the important role that cloud radiative feedbacks play in determining the climate sensitivity.

An increase in ECS appears to be robust across the HadCM3-BL experiments. For As-CM, ECS is 0.8°C lower at 35% \( O_2 \) than 10% \( O_2 \) (see also Appendix Figure C.6). For Ma-CM, this value is much larger. A 3.3°C reduction in ECS is simulated, which is also driven by the longwave cloud radiative effects in conjunction with a weaker clear sky shortwave radiative effect which tended to cool the low \( pO_2 \) (see also Appendix Figure C.7). It should be noted that attempts were made to simulate 2x-experiments for the Wuchiapingian, however what would have been the Wu2x-CM\(^{10}\) in the nomenclature used in this chapter was numerically unstable.
4.3.4 Earth System Feedbacks

Changes in \( pO_2 \) and surface temperatures have the potential to impact the terrestrial carbon cycle by altering the competition between the oxidative and photosynthetic metabolic pathways for Rubisco. Beerling and Berner (2000) simulated significant changes to vegetation productivity in the Permian due to changes in oxygen content. The modelled changes to vegetation in the final 50 years of the Asselian and Wuchiapingian experiments are investigated. Focusing on changes to vegetation across the Permian, the dominant vegetation fractions for As-CM\(^{35}\), As-CM\(^{10}\), Wu-CM\(^{35}\) and Wu-CM\(^{10}\) are shown in Figure 4.8. For low \( pCO_2 \) in the Asselian, increasing \( pO_2 \) leads to a reduction in the extent of broadleaf trees and greater proliferation of grasses and shrubs. This would be consistent with increases in photorespiration at high \( pO_2 \). The reverse is true in the Wuchiapingian simulations with increases in the extent of tropical broadleaf forests. It should be noted that the simulation of plant functional types is carefully tuned to present day vegetation which was likely considerably different in the past. Therefore, caution should be exercised when extrapolating to past vegetation changes.

Figure 4.9A shows the change in net primary productivity (NPP) for As-CM\(^{35}\)\(_{10}\) and Wu-CM\(^{35}\)\(_{10}\). The Asselian simulations shows a large reduction in net primary productivity (NPP) as \( pO_2 \) is increased (Figure 4.9A, \(-59 \text{ PgC yr}^{-1}\)) while the reverse is true in the Wuchiapingian simulations (\(+33 \text{ PgC yr}^{-1}\)). At low \( pCO_2 \), it is expected that competition for Rubisco will be won out by \( O_2 \) and therefore that rates of photorespiration should lead to a decline in photosynthesis. This is reflected in the gross primary productivity (GPP, \(-34\%\)) and NPP (\(-52\%\)) response for the Asselian. During the Wuchiapingian, there may be sufficient \( CO_2 \) that competition is much less sensitive to the \( pO_2 \) so changes to NPP are much less significant. In fact, NPP is increased by 14\% (GPP +18\%). Tropical water use efficiency is also higher in Wu-CM\(^{35}\) (Figure 4.9C), which suggests that water economy of plants could alter to adapt to a higher \( pO_2 \) (Beerling and Berner, 2000).

These net primary productivity changes are reflected in the total carbon storage (Figure 4.9B) which is lower as \( pO_2 \) is increased in As-CM (\(-338 \text{ PgC}\)) and higher as \( pO_2 \) is increased in Wu-CM (\(+379 \text{ PgC}\)). This is dominated by changes in the tropics (in agreement with Beerling and Berner 2000), where broadleaf trees are more expansive in Wu-CM\(^{35}\). Cooler terrestrial tropical temperatures, particularly in the warm month (Figure 4.2E) reduces the \( pO_2 \) inhibition of Rubisco and reduces the rate of respiration by vegetation and soils (Beerling and Berner, 2000; Long, 1991). The changes in terrestrial carbon storage are equivalent to 56\% of the atmospheric \( CO_2 \) content in the Asselian and 16\% in
Fig. 4.9 As-CM\textsuperscript{35} (left) and Wu-CM\textsuperscript{35} (right) anomalies for (A) net primary productivity, (B) total carbon storage and (C) water use efficiency.
Phanerozoic Oxygen Variability

Fig. 4.10 (a) Annual mean surface air temperature in Ma-CM21. Contours for 20 °C (green), 10 °C (purple) and 0 °C (orange) are indicated. Proxy data locations are indicated by black crosses (b) A comparison between proxy reconstructed and Ma-CM21 simulated annual mean surface air temperature interpolated onto the site location. Errors in the proxy values are taken from Upchurch et al. (2015). The standard deviation of the simulated monthly mean surface air temperature is indicated in light grey as an indication of the seasonality simulated at that site.

The Wuchiapingian which suggests that $pO_2$ induced Earth system feedbacks could have significant impacts on atmospheric $pCO_2$. That terrestrial carbon storage increases with $pO_2$ in the Wuchiapingian simulations suggests that the physical climate response to $pO_2$ is important for determining the strength of carbon cycle feedbacks in the Permian.

As these simulations are fully coupled and changes to oxygen content affect temperatures, radiation and precipitation it is challenging to explore all the possible contributions to differences between these results and the more idealised Beerling and Berner (2000) simulations. However, there is general agreement that changes occur in the signs of the response of NPP and total carbon storage. This supports the conclusions of Beerling and Berner (2000) that high $pO_2$ in the early Permian may have played an important role in the evolution of plants. Note that while the simulations are coupled in the physical sense, the carbon cycle is not interactive.

4.3.5 Maastrichtian Model-Proxy Comparison

While the changes to global-mean surface temperature are less substantial than for large changes in $CO_2$, regional changes are comparable to other smaller changes which have been widely investigated such as changes to topography or the differences between $CO_2$ forcing and cloud albedo modification (Carlson and Caballero, 2017). This raises the
### 4.3 Results

Table 4.3 Comparison between the simulated annual mean surface air temperature and the Upchurch et al. (2015) reconstructed surface air temperature. NMB: normalised mean bias. RMSE: root mean square error. NMBF: normalised mean bias factor. NMAEF: normalised mean absolute error factor (Yu et al., 2006). Best performing simulation for a particular metric is indicated in bold.

<table>
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<td>-0.04</td>
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</table>

A question whether oxygen content could reasonably alter the agreement between models and proxy data. For this we employ the Maastrichtian experiments as there is a considerable quantity of widely used proxy data for the Maastrichtian (Upchurch et al., 2015). In addition to the Ma-CM$^{35}$, Ma-CM$^{21}$ and Ma-CM$^{10}$ experiments the Ma2x-CM$^{35*}$ and Ma2x-CM$^{10*}$ experiments were iterated for 1000 model years and the final 50 years were analysed.

Figure 4.10A shows the annual mean surface air temperature simulated for the Ma-CM$^{21}$ case along with the locations of the proxy data employed for comparison with the model in Figure 4.10B. As is commonly observed amongst many climate models, HadCM3-BL struggles to simulate the high latitude warmth indicated by proxy reconstructions. A consideration of the seasonality of the proxies could reconcile some of these differences (Figure 4.10B, grey vertical bars), however it is likely that a number of factors such as model deficiencies or climate feedbacks such as convective clouds or cloud droplet radius changes may play a role in the shallower equator-to-pole temperature gradient. The normalised mean bias, root mean square error, normalised mean bias factor and normalised mean absolute error factor (Yu et al., 2006) of the Ma-CM$^{35}$, Ma-CM$^{21}$, Ma-CM$^{10}$, Ma2x-CM$^{10*}$ and Ma2x-CM$^{35*}$ experiments are shown in Table 4.3. These show that across both CO$_2$ contents that increasing the oxygen content leads to a reduction in all bias metrics against the Upchurch et al. (2015) data, however doubling the CO$_2$ content led to the largest improvement in bias scores.
Saenko (2009) assessed the contribution of wind stress to global climate in the Canadian Centre for Climate Modeling and Analysis model by setting the wind stress experienced by the ocean to zero and simulated a reduction in global mean surface temperature by 8.7 °C. Similar simulations were performed with HadCM3-BL ($\tau_{\text{PI-CM}}$, $\tau_{\text{Ma-CM}}$, $\tau_{\text{Wu-CM}}$ and $\tau_{\text{As-CM}}$) and iterated for 500 model years. This is insufficient to achieve an equilibrium climate response, however as the aim is to investigate the relative magnitude of the changes this was considered adequate to explore this sensitivity study.

The impacts of removing wind stress are shown in Figure 4.11. HadCM3-BL simulated a −7.3 °C surface air temperature change, slightly weaker than Saenko (2009) however it should be noted that HadCM3-BL was iterated for substantially longer (500 years vs 100 years). $\tau_{\text{As-CM}}$ was the most sensitive to the removal of wind stress, with a −15.7 °C SAT change. By contrast, the warmest climates showed more muted cooling in response to the removal of wind stress forcing. $\tau_{\text{Ma-CM}}$ shows an SAT anomaly of −2.7 °C while $\tau_{\text{Wu-CM}}$ shows an SAT anomaly of −3.51 °C. This suggests that the climate response to wind stress changes is likely to depend on the ocean configuration and the background
Fig. 4.12 Simulated annual and zonal mean \( \langle u \rangle \) wind for indicated experiments. The 0 ms\(^{-1} \) isoline is indicated.

climates—warmer climates of the Wuchiapingian and Maastrichtian appear to be much less sensitive to wind stress forcing. This could be due to the lower meridional temperature gradient.

### 4.3.7 Atmospheric Structure

Increases in convection at low \( pO_2 \) (Goldblatt et al., 2009a) could lead to changes in atmospheric circulation (Chemke et al., 2016). The anomalous cooling in Wu-CM\(^{35} \) (see Figure 4.2E), while consistent with the simulated ECS changes, warrants further scrutiny particularly in respect to the increase in surface temperature in the west Panthalassic Ocean at low \( pO_2 \). In the present day atmosphere, strong zonal jets around 200 hPa are centred on 30N/30S with weak Easterly zonal winds at the equator that are associated with a balance between momentum convergence by tropical eddies and divergence by the Hadley circu-
lation (Lee and Lee, 1999). For extremely warm climates the CAM3 climate model exhibits a transition to superrotation (Caballero and Huber, 2010), a phenomenon where the zonal wind is dominated by a Westerly zonal jet centred on the equator. HadCM3-BL simulates this standard ‘teardrop’ jet configuration in the preindustrial baseline (Figure 4.12A), however for Wu-CM\textsuperscript{21} the zonal jet is weaker and positive for much of the equatorial upper troposphere. The onset of westerly equatorial winds is evident from a consideration of the changes from Wu-CM\textsuperscript{35} (Figure 4.12D) to Wu-CM\textsuperscript{10} (Figure 4.12C). This could be caused by the higher tropical sea-surface temperatures at low $pO_2$ (Figure 4.2E), or could suggest that low $pO_2$ enhances the transition to superrotation in hothouse climate states, which would be consistent with more vigorous convection. This could go on to impact a number of aspects of the climate system such as ENSO variability (Tziperman and Farrell, 2009). This highlights the non-linear nature of the climate response to changes in $pO_2$.

### 4.4 Synthesis

Through its impact on atmospheric mass, oxygen content has the capacity to alter the radiative budget of the atmosphere and therefore on Earth’s climate. These simulations suggest that the interactions between radiative and dynamical feedbacks lead to some consistent climatic changes in HadCM3-BL with increasing $pO_2$

- Reduction in the seasonal cycle in surface air temperature.
- Reduction in equator-to-pole temperature gradient.
- Reduction in global precipitation.

HadCM3-BL simulates a reduced equilibrium climate sensitivity due to changes in long-wave cloud feedbacks. HadGEM3-AO results also support a reduced sensitivity to CO\textsubscript{2} content at high $pO_2$. The pre-industrial Holocene results are supported by 1D radiative convective simulations, 2D model simulations and slab ocean 3D model simulations of the Archean. This raises a discrepancy with the Poulsen et al. (2015) study, which simulated a reduction in global mean surface temperature when increasing oxygen content in the GENESIS model. Figure 4.13A shows the surface air temperature change between the 10% and 21% Cenomanian (93.9–100.5 Ma) simulations. These show a $-2.04 \, ^\circ\text{C}$ change in the annual mean. To understand the mechanisms behind this, we performed the 1D-energy balance decomposition on the Poulsen et al. (2015) Cenomanian 21–10% model output. The results are shown in Figure 4.13D. This shows that the cloudy-sky contribution to the
Fig. 4.13 Analysis of the Poulsen et al. (2015) Cenomanian 21% and 10% oxygen simulations. A: Annual mean (left), cold month mean (centre) and warm month mean (right) surface temperature difference (21%–10%). (B) Change to the diurnal cycle (21%–10%). (D) 1D-energy balance decomposition analogous to Figure 4.6 for 21%–10%.
temperature change dominates the climate response, contributing $-1.45^\circ C$. However, the clear sky contribution is also negative ($-0.60^\circ C$) including both clear-sky emissivity ($-0.58^\circ C$) and clear-sky albedo ($-0.11^\circ C$). This appears to support the argument that tropical cloud feedbacks explain the discrepancy between the Poulsen et al. (2015) simulations and results of 1D radiative convective models (Goldblatt, 2016), however this cannot be the only factor. An increase in pressure broadening of absorption lines would be expected to lead to a positive contribution from the clear-sky emissivity. This suggests that cloud feedbacks alone cannot explain the discrepancy and that the implementation of pressure broadening may play a role in the anomalous Poulsen et al. (2015) response. In addition, changes to the seasonal cycle (Figure 4.13A) simulated by Poulsen et al. (2015) are also inconsistent with the HadGEM-AO and HadCM3-BL results, in which all simulations led to a reduced seasonal cycle as $pO_2$ increases. The Poulsen et al. (2015) Cenomanian simulations actually simulate a larger seasonal cycle at high $pO_2$ which is challenging to reconcile with the radiative and physical processes. This change in shortwave-longwave balance could also be evident in the diurnal cycle, which ought to be weaker at high O$_2$ for the same reasons as the seasonal cycle, however this increases between 10% and 21% O$_2$ in the Poulsen et al. (2015) simulation. Sub-daily data was not available from the HadCM3-BL or HadGEM3-AO simulations for comparison. Note that the Poulsen et al. (2015) simulations were for an earlier Cretaceous period than those performed in HadCM3-BL. However, as Poulsen et al. (2015) employed a slab ocean the heat transport is fixed so ocean heat transport changes caused by changes in continental configuration will not have been simulated.

The simulations presented in this chapter suggest that perturbations to the wind-driven ocean circulation by increasing atmospheric mass leads to warmer temperatures, particularly at high latitudes. The magnitude of the results varies depending on the precise continental configuration and background climate state. Gyre circulations vary between the preindustrial and the Maastrichtian and Asselian case studies. Given the importance of the wind-driven ocean circulation response this suggests that a 3D representation of ocean circulation is necessary in order to capture the temperature response to atmospheric mass changes. It should be noted however that Charnay et al. (2013) simulated higher surface temperatures for the early Earth at high atmospheric mass with a slab ocean model. The use of 3D ocean is now widespread in the palaeoclimate community, however are not widely used in the exoplanet community (e.g. Kilic et al. 2017) and for early Earth studies such as the Archean (e.g. Charnay et al. 2013). While boundary conditions for these studies are sparse or in some cases non-existent the additional uncertainty associated with using
a slab ocean should be considered. AO-GCM studies remain the best way to assess the complex coupling between potentially competing radiative and dynamical effects.

Increased oxygen content may also contribute to explaining the very low temperature gradients for hothouse climates in the Phanerozoic – the “shallow gradients paradox” (Huber and Caballero, 2011). However, there are other mechanisms which could lead to similar changes. Increases in the effective radii of liquid clouds leads to considerable warming, particularly at high latitudes. While the tropics also warm the equator-to-pole temperature gradient is reduced. Abbot and Tziperman (2008) describe a convective cloud feedback which warms the high latitudes, particularly in winter. Upchurch et al. (2015) found that CCSM3 is able to reasonably simulate the shallow Maastrichtian temperature gradient when the effective radii of cloud droplets was set to 17 µm globally (compared to typical values today around 8 µm over land surfaces and 14 µm over ocean surfaces and 17 µm only observed for the most pristine of clouds in the current atmosphere), however this is hard to reconcile with the high primary productivity likely in hothouse climates and the large contributions of biogenic sources of volatile organic compounds and ammonia in the pre-industrial atmosphere (Gordon et al., 2017). In addition, the seasonality of cloud droplet changes is likely to lead to the strongest temperature changes in the warm months which may increase lead to unreasonably high temperature changes in the tropics.

One criticism of high oxygen variability in the Phanerozoic is the possibility of runaway fire at high oxygen contents (Watson et al., 1978). While subsequent experiments have put this in doubt, fire is undoubtedly a negative feedback on oxygen content. However, the cooling of warmest month temperatures over tropical and midlatitude continents in Wu-CM may provide somewhat of a protective mechanism against runaway fire regimes taking hold. Lightning is a major cause of paleofire (Scott and Jones, 1994) so the reduction in convection at high $pO_2$ would also lead to fewer lightning strikes which would reduce fire initiation. In addition, higher fire risk could have favoured the evolution and spread of more fire-resistant species (Robinson, 1990).

The simulations of Permian climate (As-CM and Wu-CM) also suggest a strong role for $pO_2$ variability in the terrestrial carbon cycle. However, there are many limitations to the modelling approach employed here. The plant functional types employed here are the same as present day. In particular, C$_4$ photosynthesis likely evolved in the Oligocene (Sage, 2004) although there is evidence of vegetation which causes C$_4$-like fractionation, suggesting different vegetation adaptations operating in the past (Jones, 1994). In addition, angiosperms did not evolve until the Cretaceous so gymnosperms such as cycads were more widespread in the Permian (Taylor et al., 2009). TRIFFID and other dynamic plant
models were not developed with these changes in plant types in mind so simulating past vegetation changes is still a considerable challenge. However, scientific understanding of the role of plants in the climate in the Paleozoic is still immature. While early evidence suggested that late Paleozoic vegetation was unproductive based on analysis of the closest modern relatives, this perspective is increasingly being challenged (Wilson et al., 2017). Other approaches such as trait based methods (Van Bodegom et al., 2012) may be able to achieve more insights into the role of \( pO_2 \) in the Earth system. We also have not accounted for changes to the ocean carbon cycle. A biogeochemical model study suggests that pervasive oceanic anoxia and euxinia only occur below an oxygen level of around 10% (Ozaki and Tajika, 2013) which may be below the fire threshold (Belcher et al., 2010) and therefore not of relevance to many periods in the Phanerozoic. However, the extent of oceanic anoxic events may be sensitive to atmospheric \( pO_2 \) (Clarkson et al., 2018).

Given the relatively small contribution of \( O_2 \) to improving the proxy-model agreement for the Maastrichtian at the largest oxygen changes and the small changes in global mean surface temperature (GMST, 1.5°C maximum) compared to ECS (-3°C), this raises the question of how much \( pO_2 \) variability contributes to uncertainty in Phanerozoic surface temperature even with such large uncertainties in \( pO_2 \) reconstructions. Figure 4.14 shows reconstructed Phanerozoic surface temperatures based on \( CO_2 \) content and climate sensitivity from the Geocarb model (purple, Royer et al. 2014) The uncertainty associated with the 95% confidence interval in simulated \( pCO_2 \) is also indicated (purple shading). Analysis of the Poulsen et al. (2015) simulations suggests a global mean surface temperature reduction of 0.21°C per percentage increase in \( O_2 \). Accounting for the \( pO_2 \) simulated by Royer et al. (2014) leads to a mean absolute difference in global mean surface temperature of 0.80°C and maximum absolute difference of 2.59°C (Figure 4.14 orange line). The largest deviations from the Geocarb values occur during the largest deviations from PAL \( O_2 \) during the Permian. However, \( pO_2 \) contributes little to the uncertainty in reconstruction of global mean surface temperature compared to \( pCO_2 \) (Figure 4.14 orange dashed lines), even if the temperature changes simulated by Poulsen et al. (2015) are reasonable. The HadGEM3-AO and HadCM3-BL simulations show even less sensitivity of global mean surface temperature to \( pO_2 \) changes which suggests this is likely an overestimate.

\( pO_2 \) therefore remains a secondary contribution to climatic variability in the Phanerozoic but most likely to be important during the Permian. The Artinskian (early Permian, 283.5–290.1 Ma) is associated with a rapid increase in \( CO_2 \) content from ~500 to ~3500 ppmv of atmospheric \( CO_2 \) which is associated with considerable restructuring of tropical vegetation (Montañez et al., 2007). The results in this chapter suggest that \( pO_2 \) variability
Fig. 4.14 A: Reconstructed CO$_2$ (doublings from Pleistocene values, blue) and O$_2$ content (red) and 95% confidence intervals (shading) from Royer et al. (2014) Geocarb simulations. B: GMST reconstructed using Geocarb $p$CO$_2$ and climate sensitivity values (dark blue) and the uncertainty in GMST from $p$CO$_2$ uncertainty (dark blue shading). GMST reconstructed, accounting for $p$O$_2$ according to Poulsen et al. (2015) global mean temperature sensitivities (solid orange) and the uncertainty due to Geocarb $p$O$_2$ (orange dashed).
could have modulated the climate and terrestrial vegetation response to this increase in CO$_2$ content. Feulner (2017) suggested that Earth was close to entering a Snowball Earth in the late Carboniferous, when $pO_2$ were higher than today. I hypothesise that the carbon cycle and physical climate feedbacks described in this chapter would strongly mitigate against this. If $pCO_2$ and $pO_2$ are intimately linked such that cooler climates tends to increase $pO_2$ this would suggest that $pO_2$ responses have helped to prevent Snowball Earth initiation in the Phanerozoic. Simulations of the impacts of oxygen variability on Snowball Earth initiation will be presented in Chapter 5.
Chapter 5

Snowball Earth: Impacts of Oxygen Variability & Volcanic Aerosol from the Franklin Large Igneous Province

The Cryogenian Snowball Earth glaciations in the Neoproterozoic represent one of the most extreme climates in Earth’s history, which makes the Snowball Earth an ideal case study for understanding the climate response to changes in forcing. I will investigate these glaciations using the HadCM3-BL climate model. Previous climate model experiments have investigated the roles of external forcing such as palaeogeography, greenhouse gas inventory and solar input. Model settings including sea-ice albedo parametrisation, cloud radiative forcing and sea-ice dynamics representation have also been widely studied. However, the role of oxygen variability and volcanic forcing have yet to be assessed using a climate model. The HadCM3-BL climate model was adapted to use Cryogenian boundary conditions and different oxygen levels by adjusting the atmospheric mass. I will show that the CO$_2$ level required to enter a Snowball Earth is higher under $pO_2$ levels in the Proterozoic than present-day. This suggests that low oxygen levels primed the Cryogenian for Snowball Earth. HadCM3-BL was employed to simulate the climate effects of volcanic forcing using sulfate aerosols with a wide variety of size distributions using aerosol loadings consistent with the emplacement of the Franklin Large Igneous Province 717 Ma. I will show that the climate response depends very strongly on the aerosol size distribution. For the size distributions most consistent with the size of the eruption, a Snowball Earth is not simulated. These simulations suggest that $pO_2$ and volcanic forcing could be factors which significantly modify the radiative forcing required to enter a Snowball Earth.
5.1 Background & Literature

The Neoproterozoic eon was characterised by the presence of two substantial glaciation episodes – so-called Snowball Earth events – the Sturtian (720 Ma) and Marinoan (635 Ma). Harland (1964) first postulated this “Great Infra-Cambrian Glaciation” on the basis of tillite in the geological record, suggesting evidence of glacial activity. J.L. Kirschvink (1992) proposed that a Snowball Earth, driven by a runaway ice albedo feedback would explain low-palaeolatitude glacial deposits. This hypothesis is supported by $\delta^{13}C$ isotopic excursions (Hoffman et al., 1998). Evidence of glaciation in the Sturtian is the first since the Makganyene glaciation in the Paleoproterozoic over a billion years earlier (Proterozoic glacial gap, see Figure 5.1C). This would suggest that there was a stronger greenhouse effect during the so-called ‘boring billion’ year period between glaciations. Fossilised soil records weakly (Roberson et al., 2011) constrain $pCO_2$ to below 10-times present atmospheric levels 1.2 Ga (Sheldon, 2006). Methane and nitrous oxide could also contribute to the extra greenhouse effect that would have been required to maintain continents free of glaciation (Roberson et al., 2011). Elevated methane was required to keep continents free of glaciation in climate model simulations of the Mesoproterozoic (Fiorella and Sheldon, 2017). However, a recent modelling study suggests that methane must have played a limited role in the Proterozoic greenhouse climate state as likely oxygen levels are sufficient for a resilient ozone layer and oxidation of methane, limiting methane levels to similar values as present-day (Olson et al., 2016). The geological record during the Proterozoic is sparse, so absence of evidence of any glaciated continents in the ‘boring billion’ may not be conclusive proof of lack of any continental glaciation.

What factors contributed to the Cryogenian glaciations? Three factors that are typically invoked are

- **Lower solar constant**: The TSI in the Neoproterozoic was approximately 94% of its present day value (Gough, 1981). CO$_2$ would need to be around 12 times preindustrial concentrations to achieve a global mean surface temperature similar to the preindustrial Holocene (Pierrehumbert et al., 2011).

- **Tropical continents**: The Neoproterozoic continental configuration was dominated by large tropical continents and the Snowball Earth events took place in the aftermath of the breakup of the Rhodenia supercontinent (Hoffman and Li 2009, see also Figure 5.1A). The domination by tropical continents increases Earth's albedo in the tropics and reduces it at the poles, which reduces global temperatures.
Fig. 5.1 (A) Continental configurations reconstructed for the Marinoan (top) and Sturtian (bottom). (B) Illustration of bifurcation: ice-line latitude as a function of solar flux/greenhouse gas content. The red line indicates an ice-free climate, green indicates ice caps and blue indicates a Snowball Earth. The x-axis represents an idealised climate forcing, which could be solar or greenhouse gas forcing, for instance. The filled yellow circles indicate the equilibrium climate states possible at current greenhouse gas and solar forcing. Time spans indicate the approximate timescale for the transition between climate states. (a to b) The initiation of a Snowball Earth. (b to c) The build up of CO$_2$ during the Snowball Earth event. (c to d) The rapid deglaciation of the Snowball Earth. (d to e) The draw down of CO$_2$. (e to f to a) The build up of ice sheets at intermediate forcing scenarios. (C) Evidence of glaciation in the last 3 By. The 740–620 Ma region has been expanded. Figures adapted from Hoffman et al. (2017)
• **Lower CO$_2$ content**: Tropical continents (Figure 5.1A) would lead to enhanced continental weathering so a more vigorous drawdown of CO$_2$ (Donnadieu et al., 2004). Degassing of CO$_2$ was also lower during this time (Mills et al., 2017), so sources of CO$_2$ were lower and sinks were higher which lead to a reduced CO$_2$ content. However, CO$_2$ content is very poorly constrained for this time period.

These factors are thought to have primed the Cryogenian for glaciations.

Alternative theories to a Snowball Earth have been put forward to explain tropical glaciers. Williams (1975) postulated that higher obliquity would be consistent with glaciation at tropical latitudes, due to enhancements in seasonality and increases in the incident solar radiation at the poles compared to the tropics. An obliquity–oblateness feedback was put forward to explain how Earth’s obliquity could transition from high values in the Proterozoic to much lower values in the Phanerozoic (Williams et al., 1998). This interpretation is partially supported by climate model results (Donnadieu et al., 2002), however fails to explain the presence of cap carbonates at the glacial termination which are consistent with the build up of high levels of CO$_2$ over the course of the Snowball Earth event (Hoffman et al., 1998). There is also palaeomagnetic evidence for low obliquity at this time (Evans, 2006). There is ongoing debate on some aspects of the geological record, such as evidence of strong seasonality (Williams et al., 2016). However, as the Snowball Earth hypothesis best fits the geological record at the time of writing (Hoffman et al., 2017) this interpretation will be assumed throughout the rest of this chapter.

As well as changes to climate forcing, due to changes in solar constant and greenhouse gas inventory, climate feedbacks are important as these cause an extreme case of bifurcation – current solar input and CO$_2$ content would be consistent with both the temperate climate Earth experiences today as well as a frozen Snowball Earth state. If solar input were reduced today the planet would cool. Ice would extend further, increasing Earth’s albedo – a positive climate feedback. If the solar input were reduced sufficiently, the ice albedo feedback would dominate and the Earth would enter a globally-glaciated state. Were solar radiation then increased again, the Earth would not necessarily return to its original state as the water vapour feedback is substantially weaker in a cold climate state (Pierrehumbert, 2005). Therefore, a much larger increase in radiative forcing would be required in order to return to the original climate state and large areas in radiative forcing–ice line space which are not stable (Figure 5.1B). The entry to a Snowball Earth therefore represents reaching a tipping point in the Earth system from which recovery on a short timescale is not possible. The Earth may have come close to entering a Snowball Earth on other occasions, such as during the end Carboniferous due to low CO$_2$ content (Feulner,
2017) or due to climate shocks such as the end Cretaceous bolide event (Sigurdsson et al., 1992).

Snowball Earth therefore represents one of the most extreme climates in Earth’s history. Understanding how the Earth entered such an extreme climate regime is important for our understanding of the operation of the Earth system including climate forcing and feedbacks. Snowball Earth also represents a considerable challenge for climate models, as the Snowball Earth climate is substantially different from present-day.

5.1.1 Past Modelling Studies

Many climate models have investigated Snowball Earth initiation. Hyde et al. (2000) simulated the initiation of a Snowball Earth using a coupled energy balance/ice sheet model and were able to simulate a Snowball Earth at reasonable CO$_2$ and solar constants with a GCM. An area of open water was also simulated for some GCM configurations, which could act as an oasis for life during this time. Poulsen et al. (2001) performed the first coupled GCM study of the Neoproterozoic Snowball Earth and determined that ocean dynamics plays an important role in halting the advance of ice in the mid latitudes, which called into question previous studies which employed slab ocean models which are unable to capture this effect (Baum and Crowley, 2001; Chandler and Sohl, 2000; Jenkins and Frakes, 1998; Jenkins and Smith, 1999). Poulsen et al. (2002) extended this to an investigation of paleogeographic controls and found that increasing the fraction of land nearer the equator led to cooler temperatures, however insufficiently to initiate a Snowball Earth in the FOAM model. Since these early ground-breaking studies, idealised studies investigating a transition to a Snowball Earth for a present day continental configuration have also been performed (Voigt and Marotzke, 2010; Yang et al., 2012) as well as with Neoproterozoic boundary conditions (e.g. Liu et al. 2013; Voigt et al. 2011) using a combination of solar forcing or CO$_2$ forcing. While a lack of consistent boundary conditions has prevented a proper intercomparison of models, a number of factors have been identified which are important for Snowball Earth initiation, in addition to CO$_2$ and solar constant:

1. Sea-ice albedo parametrisation: Employing a lower ice albedo leads to larger forcing (reduction in CO$_2$ or solar flux) to enter a Snowball Earth. Yang et al. (2012) argue for a low ice albedo as implemented by the CCSM3 climate model (0.43–0.50) due to tropical melt ponds. Voigt et al. (2011) employ a higher sea-ice albedo in the ECHAM climate model (0.55–0.75), which is more consistent with recent experimentally
determined albedos of sea ice and salt crusts likely to be present in tropical locations (Carns et al., 2016; Light et al., 2016).

2. Ocean heat transport: The transport of heat by the ocean prevents ice margins progressing towards the equator (Poulsen et al., 2001).


These factors are model dependent and impact the strength of the sea-ice albedo feedback, so there is likely to be considerable disagreement in radiative forcing required to enter a Snowball Earth between different climate models.

A range of possible climate states have been put forward as consistent with the geological evidence from the Neoproterozoic which have been simulated with climate models of a range of complexity:

- Hard Snowball – complete sea-ice cover (e.g. Pierrehumbert 2005). Cloud feedbacks have been identified as an important factor in model discrepancies when simulating the climate state of a ‘hard snowball’ (Abbot et al., 2012), as they are in present day climate (Bony et al., 2015).

- Waterbelt – large regions of tropical ocean free of ice cover (e.g. Rose 2015, often incorrectly termed a ‘slushball’) but consistent with glaciated continents. This is likely to be most consistent with the ability for complex life to survive the Snowball Earth glaciations.

- Jormungand – a seasonal cycle of narrow tropical sea-ice free ocean (Abbot et al., 2011) which relies on very low tropical ice albedo.

The ability to simulate a particular climate state is model dependent and depends on the strength of ice albedo feedbacks in a particular climate model. While the role of model configurations (Yang et al., 2012) and changes in boundary conditions such as continental configuration (Feulner and Kienert, 2014) have been investigated before, changes in oxygen content and the role of volcanic forcing have not to date been explored in a fully coupled climate model.
5.1.2 Oxygen Variability

The rise of oxygen on Earth is discussed in detail in Chapter 1. There is considerable uncertainty in the rise in atmospheric oxygen levels between typical Proterozoic levels (~1%) and typical Phanerozoic levels (~10–35%). The Palaeoproterozoic glaciations (~2.4 Ga) are associated with the GOE, and the subsequent collapse of high methane levels in the Archean may have played a role in the glaciation. A collapse in methane has been invoked for the Proterozoic, however this seems unlikely. Oxygen levels were high enough for a substantial ozone layer and therefore significant atmospheric oxidising capacity which prevents the build up of methane in the atmosphere (Olson et al., 2016). Snowball Earth episodes may themselves provide the capacity for oxygen levels change by providing a significant perturbation to the Earth’s redox balance (Laakso and Schrag, 2017).

Changes in oxygen content from 1 to 10–35% have the capacity to significantly alter the atmospheric mass, which has been considered at length in Chapter 4. To briefly recap, a lower atmospheric mass in the Proterozoic would reduce Rayleigh scattering leading to an increase in flux of shortwave radiation at the surface but reduce the pressure broadening of absorption lines. Pressure broadening dominates in the present day climate (Payne et al., 2016) – a higher greenhouse gas inventory and lower solar constant would enhance this further in the Proterozoic. Pierrehumbert et al. (2011) suggest that lower oxygen levels in the Proterozoic may have been a factor in Snowball Earth initiation, however the magnitude of this effect has yet to be quantified in a climate model.

5.1.3 Franklin Large Igneous Province

Volcanic eruptions have a significant influence on climate (see Chapters 1 and 3). Volcanological evidence points to the emplacement of the Franklin Large Ingeous Province (LIP) around 720 Ma (Ernst et al., 2008). Large igneous provinces are associated with climatic changes on a variety of timescales depending on the type, length and magnitude of eruption (Kidder and Worsley, 2010). In the short term (order of months to years), formation of stratospheric aerosols causes climatic cooling. This has been invoked for climatic changes in the Sturtian (Macdonald and Wordsworth, 2017; Stern et al., 2008). In the medium term (order of centuries to millennia), increase in CO$_2$ outgassing from the volcano leads to warming (e.g. Petersen et al. 2016). LIPs in the Phanerozoic have been linked to large CO$_2$ injections and subsequent climatic changes. In the long term (order of hundreds of hundreds of thousands of years), the availability of highly weatherable surfaces left behind after the emplacement of the igneous province leads to cooling. This
has also been invoked as a driver for the Sturtian Snowball Earth (Cox et al., 2016). While the radiative forcing of stratospheric aerosols from the Franklin LIP have been assessed (Macdonald and Wordsworth, 2017), the role of climate feedbacks have not been assessed.

5.1.4 Summary

In summary, there is strong geological evidence of tropical glaciation on at least two occasions in the Neoproterozoic. This is likely due to the break-up of the tropical Rodinia supercontinent and emplacement of the Franklin Large Igneous province, which would enhance silicate weathering and lead to removal of large quantities of CO$_2$ from the atmosphere. Previous modelling results support the existence of different climate states which could be consistent with this geological evidence.

5.2 Methods & Simulations

5.2.1 Atmosphere-Only

Abbot et al. (2012) performed an atmosphere GCM study of an idealised Snowball Earth atmosphere in order to compare different model responses in this extreme climate state. In order to determine whether HadCM3-BL performed similarly to other models which have explored the Snowball Earth climate, this experiment was performed with HadAM3-B (HadCM3-BL with ocean and sea-ice deactivated, Valdes et al. 2017). In this experiment, CO$_2$ is set to 10 Pa. All other greenhouse gases and all aerosols are set to zero. Orbital obliquity is set to 23.5° and eccentricity to zero. Glacial ice surfaces with albedo of 0.6 and zero orography are prescribed globally. This experiment was performed with the Valdes et al. (2017) configuration (CM3-Abb) and a version with ice nuclei radius fixed to 5 µm.

5.2.2 Coupled Atmosphere-Ocean

For all other experiments the AO-GCM used is HadCM3-BL (Valdes et al., 2017). For more details see Chapter 2. Summaries of all experiments are shown in Tables 5.1 and 5.2. The model is initialised with a continental configuration consistent with the Marinoan (635 Ma, Voigt et al. 2011), a solar constant 94% of that used in the pre-industrial base run (1283.1 W m$^{-2}$) and 224 Pa of CO$_2$ (8-times preindustrial) in order to obtain sea-surface temperatures which are comparable to the Pre-Industrial Holocene and consistent with a climate state free of permanent continental glaciers. As there is considerable uncertainty
associated with Precambrian continental configuration, and model studies disagree on
the climate response for the continental evolution between the Sturtian and Marinoan
(Feulner and Kienert, 2014; Liu et al., 2013), we argue that our model setup is generally
consistent with a late Neoproterozoic climate state. Other trace and major gases were
set to pre-industrial levels. Land surfaces were initialised with bare soil, the dynamic
vegetation scheme was switched off and snow-free (snow-covered) soil albedo set to 0.272
(0.800). The ocean was initialised at rest with a zonally-averaged PIH temperature profile,
before being allowed to evolve for 3050 model years (Base-21). Figure 5.2 shows that
between years 2750-2999 the trend in ocean temperatures is below 0.008 °C per Century
at all depths and between years 2950-2999 the top-of-atmosphere radiative imbalance is
0.14 Wm⁻². These are well within the tolerances specified for a ‘spun-up’ model for the
experimental design for the DeepMIP contribution to PMIP4 (Lunt et al. 2017, 0.100 °C
per Century and 0.30 Wm⁻² respectively) which suggests that the model is sufficiently
spun-up after 3000 model years.

Oxygen Variability

For the 1% oxygen run (Base-01), the model was initialised from Base-21 at year 1000 and
its oxygen content reduced to 1% in an analogous way to the experiments performed in
Chapter 4. The model was then iterated from 1000-3050. Figure 5.2 shows that between
years 2750-2999 the trend in ocean temperatures is below 0.014 °C per Century at all depths
and between years 2950-2999 the top-of-atmosphere radiative imbalance is 0.18 Wm⁻²,
Table 5.1 Summary of oxygen variability HadCM3-BL Experiments.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>O₂ / %</th>
<th>CO₂ / Pa</th>
<th>Initialised</th>
<th>Years run</th>
<th>Notes</th>
</tr>
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<td>224.0</td>
<td>Rest</td>
<td>0–3050</td>
<td></td>
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<td>224.0</td>
<td>Base-21</td>
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<td>112.0</td>
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<td>3000–3470</td>
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<td></td>
</tr>
<tr>
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<td>56.0</td>
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<td>78.4</td>
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<td></td>
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<tr>
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<td>4x-21</td>
<td>3609–4116</td>
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<td>3609–4040</td>
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<tr>
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<td>Base-01</td>
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<td>Base-01</td>
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<tr>
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<td>190.4</td>
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<td>112.0</td>
<td>Base-21</td>
<td>3000–3100</td>
<td>1</td>
</tr>
<tr>
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<td>21</td>
<td>112.0</td>
<td>Base-21</td>
<td>3000–3100</td>
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<td>Base-21</td>
<td>3000–3400</td>
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<td>1</td>
<td>112.0</td>
<td>Base-01</td>
<td>3000–3400</td>
<td>3</td>
</tr>
</tbody>
</table>

Notes: (1) CH₄ doubled, (2) N₂O doubled, (3) Free-drift ice dynamics activated and ocean timestep halved.

also within the required limits. To investigate the impact of oxygen variability on the CO₂ limit for Snowball Earth initiation, simulations were spun off from Base-21 and Base-01 at year 3000 and the CO₂ contents were reduced to 112.0 Pa, 56.0 Pa and 28.0 Pa. Simulations at intermediate CO₂ values were also integrated – 78.4 Pa, 84.0 Pa and 89.6 Pa at 21% O₂ and 145.6 Pa, 168.0 Pa and 190.4 Pa at 1% O₂. Sensitivity experiments exploring the role of sea-ice dynamics representation were performed where the CO₂ content was halved from the Base-21 and Base-01 simulations and simultaneously free-drift ice dynamics was enabled (4x-21_ALT and 4x-01_ALT). Sensitivity experiments exploring the role of non-CO₂ greenhouse gas inventory were also performed where CO₂ content was halved from the Base-21 experiment and simultaneously methane was doubled (4x-21+CH₄) or nitrous oxide was doubled (4x-21+N₂O). A summary of these experiments is presented in Table 5.1.
Volcanic Forcing

To investigate the potential role of volcanic forcing, simulations were spun off from Base-21 at year 3000. For a $25 \times$-Pinatubo sized injection (Macdonald and Wordsworth, 2017) using an aerosol size distribution consistent with the Mount Pinatubo eruption (0.5 \( \mu \)m) will likely overestimate the radiative response due to an incorrect treatment of aerosol coagulation effects (Timmreck et al., 2010). The size distributions of 1.0 and 1.3 \( \mu \)m were selected as these best simulate the temperature response to the 1257 Samalas volcanic eruption (Timmreck et al., 2009), which was 5-7 times as strong in the magnitude of sulfur dioxide injection as Mount Pinatubo (Oppenheimer, 2003; Vidal et al., 2016). The Sato et al. (1993) aerosol climatology was scaled by 25 times in accordance with the methods described in Chapter 2. The sulphate mass loading imposed is shown in Figure 5.3. A summary of these experiments is presented in Table 5.2. As a number of previous studies have investigated the role of sea ice/snow albedo parametrisations, sea-ice dynamics etc. in great detail, the simulations presented in this chapter will not repeat this analysis but investigate oxygen variability and volcanic forcing which are yet to be investigated in the context of the Snowball Earth glaciation in an AO-GCM.

5.3 Atmosphere Model Comparison

There is considerable uncertainty in model simulations of a ‘hard snowball’ due to cloud radiative feedbacks (Abbot et al., 2012). To investigate how HadAM3-B (HadCM3-BL without the ocean or sea-ice components) compared to other atmosphere models which
Table 5.2 Summary of volcanic forcing HadCM3-BL Experiments.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Initialised</th>
<th>Years run</th>
<th>Volc. Forc. (R&lt;sub&gt;eff&lt;/sub&gt;)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base-21</td>
<td>Rest</td>
<td>0–3050</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.2v</td>
<td>Base-21</td>
<td>3000-3056</td>
<td>25×PIN (0.2)</td>
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</tr>
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<td>Base-21</td>
<td>3000-3066</td>
<td>25×PIN (0.5)</td>
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<tr>
<td>0.7v</td>
<td>Base-21</td>
<td>3000-3107</td>
<td>25×PIN (0.7)</td>
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</tr>
<tr>
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<td>Base-21</td>
<td>3000-3500</td>
<td>25×PIN (1.0)</td>
<td></td>
</tr>
<tr>
<td>1.3v</td>
<td>Base-21</td>
<td>3000-3500</td>
<td>25×PIN (1.3)</td>
<td></td>
</tr>
<tr>
<td>RE1</td>
<td>0.5v</td>
<td>3042-3092</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>RE2</td>
<td>0.5v</td>
<td>3043-3093</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.7v-α10</td>
<td>Base-21</td>
<td>3000-3104</td>
<td>25×PIN (0.7) 1</td>
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<tr>
<td>0.7v-α20</td>
<td>Base-21</td>
<td>3000-3150</td>
<td>25×PIN (0.7) 1</td>
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<tr>
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<td>Base-21</td>
<td>3000-3500</td>
<td>25×PIN (1.3) 2</td>
<td></td>
</tr>
</tbody>
</table>

Notes: (1) 10N-10S/20N-20S sea-ice albedo set to 0.45, (2) Stratospheric H<sub>2</sub>O in radiation limited to 20 ppmv.

Fig. 5.4 Tropical surface temperatures simulated for Abb (HadAM3, green-blue) and Abb* (HadAM3 with altered cloud properties, light purple) against cloud radiative forcing compared to models which contributed to Abbot et al. (2012).
have investigated the Snowball Earth the 10 Pa CO$_2$ experiment from Abbot et al. (2012) was performed in the standard configuration (HadAM3) and a configuration where cloud radiative forcing (CRF) was artificially increased by setting the ice crystal effective radius to 5 µm (HadAM3*). A comparison between the tropical (20N-20S) surface temperatures and the cloud radiative forcing achieved for these model runs and from other studies is shown in Figure 5.4. Simulated CRF varies between 1.1 Wm$^{-2}$ for FOAM and 35.1 Wm$^{-2}$ for GENESIS so HadAM3 is well within the model range but is lower (7.7 Wm$^{-2}$) than the mean (16.8±10.0 Wm$^{-2}$). The lower surface temperatures simulated are consistent with a smaller CRF than the mean. HadAM3* exhibits a larger cloud radiative forcing as smaller ice crystal radii lead to increases in longwave absorption, which is more important for CRF when the Earth is ice covered (c.f. increases in cloud droplet radii leading to warming, Kiehl and Shields 2013). Based on this alone, it would be expected that HadCM3 would exhibit a larger critical CO$_2$ content for Snowball Earth initiation than LMDz, CAM3 (component of CCSM4) and ECHAM (component of MPI-OM). This would make it easier to initiate a Snowball Earth in HadCM3.
5.4 Impacts of Oxygen Variability

5.4.1 Impacts on the baseline Neoproterozoic climate

Reducing oxygen content from 21% to 1% leads to a global mean surface air temperature change of $-2.7^\circ C$ from 12.7 $^\circ C$ to 10.0 $^\circ C$ (Figure 5.5) which is consistent with the results of experiments performed in Chapter 4. However, despite considerably lower surface temperatures precipitation over land surfaces only reduces by 0.9% which suggests that continental weathering would be similar between the 1% and 21% scenarios. Therefore we can compare the evolution of the climate after abrupt reductions in $pCO_2$ to investigate whether $pO_2$ content impacts the $pCO_2$ required to initiate a Snowball Earth in HadCM3-BL. The output of daily minimum and maximum temperatures permits the change to the diurnal cycle to be assessed. Poulsen et al. (2015) simulated an increase in the diurnal cycle in the tropics and reduction at high latitudes as $pO_2$ decreases in the Cenomanian (100.5–93.9 Ma, see Figure 4.13). For HadCM3-BL an increase in the diurnal cycle is simulated. This is consistent with the increases in downwelling solar radiation at the surface warming the daily maximum and increases in atmospheric emissivity cooling the night. This would act to enhance the strength of the diurnal cycle as simulated.

Figure 5.6 shows the 1D energy balance decomposition for the surface temperature anomaly Base01–Base21. Consistent with the results of Chapter 4, reducing atmospheric mass leads to a reduction in surface temperature due to clear-sky emissivity changes. However, there is also a negative temperature contribution from clear-sky albedo. This is likely related to the strong sea-ice changes which will be in part driven by changes to the wind-driven ocean circulation (see Figure 5.5c). There is also a strong positive contribution from cloud radiative effects. The 1D-EBM results suggest that the drivers of climatic change due to $pO_2$ variability described in Chapter 4 also apply to the simulations of the late Neoproterozoic presented here.

5.4.2 Impacts on the critical CO$_2$ content for glaciation

The CO$_2$ content was then reduced from the Base-21 and Base-01 simulations in order to assess whether the CO$_2$ content required to initiate global sea-ice cover is different under different background oxygen levels. Figure 5.7 shows the evolution of sea-ice extent, planetary albedo and effective surface emissivity for instantaneous reductions of CO$_2$ content to 112.0 Pa (21-4x solid red, 01-4x dashed red), 56.0 Pa (21-2x solid blue, 01-2x dashed blue) and 28.0 Pa (21-1x solid yellow, 01-1x dashed yellow). All simulations achieve
Fig. 5.6 1D-EBM decomposition for Base01–Base21 annual and zonal mean surface temperature anomalies. Top left: EBM results (grey) vs GCM results (black). Top right: Decomposition of EBM into the emissivity (purple), albedo (green) and heat transport (orange) components of the temperature change. Bottom left: Clear-sky emissivity (dark purple) and albedo (dark green) components of the EBM. Bottom right: Decomposition of EBM into the total clear-sky (blue), cloudy-sky (red) and all-sky (grey) components.
Fig. 5.7 Simulated (A) global percentage sea-ice extent, (B) tropical (20N-20S) area-weighted mean surface temperature, (C) planetary albedo and (D) effective surface emissivity for 21-4x (red solid), 01-4x (red dash), 21-2x (blue solid), 01-2x (blue dash), 21-1x (yellow solid) and 01-1x (yellow dash). Note the strong increase in planetary albedo and effective surface emissivity on the approach to a Snowball Earth.
a Snowball Earth state, except for 21-4x which has ice-free tropical regions after 1000 model years. As the simulations progress, the planetary albedo increases from a value of ~0.30 to values greater than 0.55. This reflects the operation of the sea-ice albedo feedback – as global mean temperatures drop, sea ice extent increases which further increases global albedo. The effective emissivity of Earth's surface also increases as it enters a Snowball Earth state. Effective emissivity should increase due to the imposed reduction in CO$_2$ content. This would be enhanced by a significant reduction in atmospheric water vapour as the planet cools (Pierrehumbert, 2005). A combination of the increase in both Earth's effective emissivity and planetary albedo leads to global sea-ice cover. Considering these experiments alone, there is a qualitative difference in critical CO$_2$ required for glaciation. The required CO$_2$ level is higher at Proterozoic oxygen levels, which supports the hypothesis that the lower Proterozoic oxygen content primed the Snowball Earth glaciations.

To attempt to narrow down the ranges for critical CO$_2$ content, additional simulations were performed as detailed in Table 5.1. Simulations were spun off from Base-01 and 4x-21 and $p$CO$_2$ reduced by intermediate values from the CO$_2$ doubling. The evolution of sea-ice in these simulations is shown in Figure 5.8. 78.4-21 simulated a Snowball Earth by year 4148 while neither 100.8-21 nor 89.6-21 entered a Snowball Earth. A Gregory et al. (2004) analysis is performed to assess whether the resulting climate states were stable to glaciation. If the gradient in the regression between the top-of-atmosphere radiative imbalance and the change in surface temperature becomes flat or positive it suggests that the climate state is not stable to glaciation. A positive slope suggests a negative climate feedback parameter. Figure 5.8C (pink line) suggests that the climate feedback parameter for 89.6-21 has become negative considering the final 50 years of the simulation so is unstable to glaciation. The critical CO$_2$ content for Snowball Earth initiation for the 21% O$_2$ scenario is likely between 89.6 and 100.8 Pa. None of 145.6-01, 168.0-01 or 190.4-01 simulated entry to a Snowball Earth, however a Gregory et al. (2004) analysis suggests that 145.6-01 and 168.0-01 are entering an unstable region of forcing-climate space (Figure 5.8D, green and red lines). This suggests that the critical CO$_2$ content for Snowball Earth initiation in the 1% O$_2$ scenario is likely between 168.0 and 190.4 Pa. This is approximately a doubling of CO$_2$ which is consistent with the temperature difference between the Base-21 and Base-01 scenarios, approximately equal to the sensitivity to a CO$_2$ doubling. However, it should be noted that even the 4x-21 experiment is still cooling at the end of the simulation. This suggests that the model may not be sufficiently spun up to conclude that a Snowball Earth has or has not taken place. Unfortunately, constraints on
Fig. 5.8 Simulated global percentage sea-ice extent for intermediate CO₂ contents. (A) 21% O₂, (B) 1% O₂. Gregory et al. (2004) analysis of each experiment for (C) 21% O₂ and 1% O₂. Regression performed on the final 50 years of simulation. Note the positive gradients indicate climate instability and that the simulation is likely to enter a Snowball Earth.
computational resource prevented further integration of the model simulations. Therefore, some caution should be exercised when interpreting the precise CO₂ values.

### 5.4.3 Sensitivity to sea-ice dynamics treatment

The treatment of sea-ice dynamics in HadCM3-BL is less detailed than some models which have recently investigated the Snowball Earth initiation problem. While the focus of this chapter has not been the role of sea-ice dynamics, given its comprehensive study to date, it may affect the results presented. This is due to the role that wind-stress plays in sea-ice dynamics which is not accounted for in the HadCM3-BL parametrisation. To explore the role that wind stress changes may have played, two additional simulations were performed where the simple ice advection scheme was deactivated and a free-drift dynamics model which accounts for surface wind stress was activated. These simulations also required halving the ocean timestep due to numerical instability with the free-drift dynamics model as the ice-line progressed towards the equator. This was performed concurrently with the halving of pCO₂ from 224.0 Pa to 112.0 Pa in both the 21% O₂ (4x-21_ALT) and 1% O₂ (4x-01_ALT) cases. After 400 model years 4x-01_ALT had entered a globally ice covered state while 4x-21_ALT was still in a temperate state. This suggests that while a more detailed treatment of sea ice dynamics might alter the critical CO₂ content, it would not sufficiently affect the main conclusion that the critical CO₂ content is influenced significantly by pO₂.

### 5.4.4 Sensitivity to N₂O and CH₄

CO₂ was selected as the main tuning of greenhouse gas content, however N₂O or CH₄ may have played more significant roles in maintaining a sea-ice free tropics (Roberson et al., 2011). Given the cold climate and oxic atmosphere, it is unlikely that CH₄ or N₂O values were significantly elevated from typical Phanerozoic levels. To assess the sensitivity to a small increase in CH₄ or N₂O, the 4x-21 simulation was repeated with a doubling of pCH₄ (4x-21+CH₄) and a doubling of pN₂O (4x-21+N₂O) and iterated for 100 model years. Employing an analysis of top-of-atmosphere radiative budget following Gregory et al. (2004) suggests that for the first 100 years of the 4x-21, 4x-21+CH₄ and 4x-21+N₂O experiments, doubling CH₄ offsets approximately 10% of a CO₂ halving (Equilibrium ΔTₜₙₛₕ −2.77 °C vs −3.09 °C) while doubling N₂O offsets approximately 29% (Equilibrium ΔTₜₙₛₕ −2.19 °C. This suggests that any increase in non-CO₂ greenhouse gases, particularly N₂O could contribute significantly to preventing a Snowball Earth. 1D photochemical
simulations suggest that low $p_{O_2}$ would also significantly reduce the $N_2O$ concentration, given the same emission of $N_2O$ due to the photolysis of $N_2O$ (Roberson et al., 2011). Accounting for this would exacerbate the cooler climate at 1% $O_2$, compared to the 21% simulation. The lack of higher dimensional model studies prevents a conclusive link between $N_2O$ and $O_2$ given the lack of latitudinal variation in insolation and the use of a clear-sky approximation in Roberson et al. (2011). Additional $N_2O$ or $CH_4$ could substantially lower the critical $CO_2$ level required for glaciation, however the enhancement of pressure broadening of these greenhouse gases also applies to $CH_4$ and $N_2O$ (Byrne and Goldblatt, 2014) so this should not affect the main conclusion that $p_{O_2}$ affects the critical $p_{CO_2}$ for Snowball Earth initiation.

5.4.5 Discussion

In the simulations hitherto presented, there appears to be a very strong bifurcation between temperate and hard snowball climate states: HadCM3-BL does not support a ‘waterbelt’ or ‘Jormungand’ climate state. This may be due to the ice albedo parametrisation employed. HadCM3-BL employs an ice albedo of 0.50 at a sea-ice temperature of 0 °C linearly increasing to 0.80 at −10 °C. MPI-OM employs an ice albedo of 0.55 at 0 °C and 0.75 below −1 °C, similar to HadCM3-BL (Voigt and Marotzke, 2010) By contrast, CCSM4 employs an ice albedo of 0.425 at 0 °C, linearly increasing to 0.5 at −1 °C (Yang et al., 2012). Yang et al. (2012) argue that the substantially lower ice albedo employed by CCSM4 is more consistent with observations, however the large range of ice albedos employed by different models highlights the uncertainty associated with this important parametrisation – for HadCM3-BL the ‘warm’ ice albedo is closer to the CCSM4 values while the ‘cold’ ice albedo is closer to the MPI-OM values. Recent laboratory studies on salt crusts on sea-ice support a high ice albedo particularly at low temperatures (Carns et al., 2016; Light et al., 2016). There therefore remains considerable uncertainty as to the most suitable ice albedo values to select for application to the Neoproterozoic Snowball Earth. Unfortunately, limits to computational time prevented a full study of all possible contributions to the uncertainty in critical $p_{CO_2}$.

HadCM3-BL therefore simulates a higher critical $CO_2$ content for Snowball Earth initiation at Proterozoic $p_{O_2}$ values (−1%) than present-day $p_{O_2}$ (21%). Voigt et al. (2011) simulated a stable climate for their equivalent of the 2x-21 experiment (TSI94-2CO2) with the same background conditions. The TSI94-2CO2 and TSI96 experiments evolved similar global mean surface temperature and a subsequent reduction in TSI from 96% of present
5.5 Impacts of Volcanic Forcing

In this section, the possible role of volcanic aerosols from the Franklin Large Igneous Province in the Snowball Earth initiation is investigated. Please refer to Table 5.2 for the list of experiments, the results of which will be presented in this section.

5.5.1 Role of Volcanic Forcing

To assess the role of sustained volcanic forcing in the Snowball Earth initiation, the 0.2v, 0.5v, 0.7v, 1.0v and 1.3v experiments are assessed. Figure 5.9a (solid blue line) shows that for an annually-repeating volcanic forcing 25-times as powerful as the Mount Pinatubo eruption, assuming a similar aerosol size distribution (0.5 μm, 0.5v), the global mean surface temperature cools. There is an instantaneous reduction in the net shortwave radiation reaching the surface (−53.9 W m⁻²), which is somewhat counteracted by longwave (+8.1 W m⁻²), sensible heat (+3.9 W m⁻²) and latent heat (+15.8 W m⁻²) feedbacks (all net downward), which is consistent with the changes to the radiative budget of the atmosphere that would be expected on addition of sulfate aerosols to the stratosphere. The
Fig. 5.9 (A) Global mean surface air temperature (GMSAT) after addition of volcanic forcing for 0.2 µm background aerosol (0.2v, orange), 0.5 µm Pinatubo-sized aerosol (0.5v, blue), 0.7 µm aerosol (0.7v, green), 1.0 µm aerosol (1.0v, purple) and 1.3 µm (1.3v, pink). The Base-21 temperature is indicated (dashed black line). In an additional simulation, the volcanic forcing was removed from 0.5v after 42 years (RE1, dashed blue) and 43 years (RE2, dotted blue). Black stars indicate the model year (80) in which SAT is plotted for (B) RE1 and (C) RE2. The climate forcing in both simulations is identical, demonstrating the hysteresis caused by the volcanic eruption. (D) Tropical (20N-20S) mean SAT (solid lines) and 50% sea ice line (dashed lines) after addition of volcanic forcing for 0.7v for the standard ice albedo (green), an albedo of 0.45 in the 10N-10S band (0.7v-α10, dark green) and an albedo of 0.45 in the 20N-20S band (0.7v-α20, black) for simulation years 50 to 140. Tropical albedo reduction can considerably delay the transition to the Snowball state.
model achieves a globally sea-ice covered state after 41 model years, which is defined here as global sea ice cover exceeding 377 million square km. As the climate cools, the short-wave feedback becomes stronger due to the ice-albedo feedback: the globally-averaged surface albedo increases from 0.2 initially to 0.7 in the globally-glaciated state. Under such a strong volcanic forcing, glaciation is inevitable. Further experiments assess the impact of assumptions about the size distribution of aerosol particles, maintaining the total aerosol mass. Globally glaciated states were also achieved for aerosol size distributions with $R_{\text{eff}} = 0.2 \mu m$ ($0.2v$) and $0.7 \mu m$ ($0.7v$). $0.2v$ led to glaciation after 34 years and $0.7v$ glaciated in 74 years. For the largest of the aerosol size distributions, $1.0 \mu m$ ($1.0v$) and $1.3 \mu m$ ($1.3v$), a Snowball state is not achieved (Figure 5.9a, purple and pink lines), even after 500 model years.

5.5.2 Resilience to Snowball Earth initiation

To test the resilience to this global glaciation, the volcanic forcing was removed from $0.5v$ after 42 model years, at a global mean surface temperature of $-30^\circ C$ and the climate state evolved under the background climate forcing (RE1). The climate rapidly recovers to above freezing (Figure 5.9A, dashed blue line). This shows that globally averaged temperatures substantially below $0^\circ C$ can be achieved without entering a Snowball Earth state. If instead the volcanic forcing is removed from $0.5v$ after 43 model years (RE2), the climate evolves towards a Snowball Earth. The global distribution of surface air temperature in year 80 is shown for RE1 in Figure 5.9B and RE2 in Figure 5.9C. This demonstrates the hysteresis between the two climate states, as both are consistent with the baseline climate forcing. In addition, there is a timescale for cooling the shallow ocean – Voigt and Marotzke (2010) found a 14 year transition to a Snowball Earth state under present-day boundary conditions by reducing the solar constant to 0.01% of its present value. This shows that any perturbation needs to be on the order of decades to initiate a Snowball Earth.

5.5.3 Sensitivity to tropical albedo

Snowball Earth initiation is sensitive to tropical albedo (e.g. Voigt and Abbot 2012). Ash from tropical eruptions is rapidly removed from the atmosphere so its radiative effects are usually ignored. However, its deposition on tropical ice could substantially reduce its albedo. The broadband albedo of dusty snow can be as low as 0.45 (Warren and Wiscombe, 1980). In order to assess the potential impact of albedo reduction by ash deposition on
Fig. 5.10 Annually-averaged top-of-atmosphere radiative imbalance as a function of global mean surface air temperature for (a) 1.0v (purple crosses) and (b) 0.7v (green crosses). Decadal averages are indicated with filled circles. Note that 1.0v achieves a ‘cool’ equilibrium climate state while 0.7v enters a Snowball Earth.

the snowball initiation, 0.7v was repeated with albedo of sea ice in different latitude bands reduced. For a 10N-10S tropical band (0.7v-α10), reducing the albedo to 0.45 increases the timescale for snowball initiation by 5 years (Figure 5.9c). A 20N-20S band (0.7v-α20) was more effective still, increasing the time to glaciate from 74 years to 140 years but still not sufficient to prevent glaciation. This suggests that a ‘Jormungand’ climate state is unlikely in the model configuration used here. If such an equilibrium climate state is consistent with the late Neoproterozoic, volcanic forcing could provide a method for transition to one of these ‘waterbelt’ solutions. However, the stability of these solutions to volcanic forcing and the magnitude of forcing required to enter one of these solutions is uncertain and ought to be assessed in a model which simulates these ‘waterbelt’ or ‘Jormungand’ solutions.

5.5.4 Visualising the ice-albedo instability

The initiation of the ice-albedo instability can be visualised by regressing the top-of-atmosphere radiative imbalance against the surface air temperature (Gregory et al., 2004). For 1.0v, a tight correlation between these quantities (Figure 5.10a) suggests that the climate is evolving towards a global mean surface air temperature of 6.6 °C, whereas for 0.7v,
5.5 Impacts of Volcanic Forcing

Fig. 5.11 Annually-averaged differences between Base-21 and 1.0v for (A) surface air temperature, (B) net downward shortwave radiation incident at the surface, (C) evaporation from the sea and (D) total precipitation. Global mean values inset top-right.

this correlation begins to break down below global mean surface air temperatures below -3 °C (Figure 5.10b), when the relationship becomes flat. As surface temperatures drop the Earth emits less longwave radiation which normally reduces the net radiative imbalance (Planck feedback). This begins to falter when the ice albedo effect becomes too strong and the decrease in net shortwave radiation at the surface overwhelms the latent heat and longwave radiation feedbacks. Once global glaciation has occurred, the relationship between surface temperature and radiative imbalance becomes much stronger (Figure 5.10b, green line), confirming that the so called hard snowball is the equilibrium climate state under this forcing scenario.

5.5.5 Impacts on the hydrological cycle

Volcanic forcing leads to substantial impacts on the hydrological cycle. Global mean surface precipitation drops by 36% in 1.0v (0.84 mm day$^{-1}$) compared to the baseline simulation (Figure 5.11D). The injection of stratospheric aerosols is associated with a
significant reduction in net downward shortwave radiation at the surface, reducing by 39.8 W m$^{-2}$ globally (Figure 5.11B). Evaporation (Figure 5.11C) and precipitation drop accordingly with temperature (Figure 5.11A). Precipitation over land, which could contribute to continental weathering, drops by 33%. Global cooling and drying would both slow continental weathering, making the drawdown of CO$_2$ by LIP basalts slower. Reductions in precipitation also occur for 1.3v (0.36 mm day$^{-1}$, not shown), which suggests this is a robust change with respect to differing aerosol size distributions.

### 5.5.6 Analysis of 1.0v and 1.3v

For 1.0v global mean surface temperature averaged over the final 50 years of model simulation was 5.2 °C lower than Base-21. For 1.3v, global mean SAT actually increases – 3.5 °C higher than Base-21 averaged over years 3450-3500. The contributions to heating or cooling can be assessed using a Budyko-Sellers type 1D energy balance decomposition following Heinemann et al. (2009) and described in Chapter 2. Figure 5.12 (left) shows that the surface temperature changes simulated by HadCM3-BL can be reasonably approximated by this EBM approach for 1.0v–Base-21 (solid) and 1.3v–Base-21 (dashed).
The relative contributions from surface emissivity, albedo and heat transport changes are shown in Figure 5.12 (right) and show that imposing stratospheric sulfate leads to a sharp reduction in temperature due to planetary albedo changes. For 1.0v, planetary albedo increases by 0.14 compared to Base-21. This effect is dampened by emissivity feedbacks, which are a positive contribution to the surface temperature change. This is unsurprising due to longwave absorption and re-emission by aerosol particles which becomes important at large $R_{\text{eff}}$. For 1.3v, the albedo change is less negative which is due to larger particles which are less able to scatter shortwave radiation. There is also a more positive emissivity contribution for the same aerosol mass which suggests that the enhanced surface temperatures in 1.3v are due to climate feedbacks.

Figure 5.13A shows the change to zonal mean temperature between Base-21 and 1.0v. Stratospheric warming is evident with a correspondingly cooler troposphere. A reduction in the tropospheric lapse rate ought to lead to tropical cooling and polar warming (Pithan and Mauritsen, 2014) and to some extent this is reflected in the greater increase in the contribution of emissivity to surface temperature changes between 1.0v and 1.3v at high latitudes (Figure 5.12). Substantial increases in water vapour probably play the greatest role in contributing to the temperature changes, particularly in the stratosphere where water vapour concentrations increase over ten-fold. This can be quantified by fixing stratospheric water vapour concentrations in 1.3v-$H_2O$. Now global mean surface temperatures drop by $-5.30$ °C (Figure 5.14C) and there is a stronger precipitation response. Therefore, the stratospheric water vapour feedbacks in 1.3v contribute 8.7 °C to the temperature response. How realistic is such a large increase in stratospheric water vapour? Jones et al. (2005) simulated a warmer stratosphere and lower tropopause in the HadCM3 model for simulations of the 75 ka Toba eruption. Other models also simulate a substantial increase in stratospheric water vapour in response to large volcanic forcing (Robock et al., 2009a). However the Jones et al. (2005) and Robock et al. (2009a) study employ small size distributions which are not consistent with such large eruptions so the stratospheric water vapour feedbacks are not sufficient to offset much warming in their simulations. While stratospheric water vapour feedbacks are clearly important for the climate response in the 1.3v simulations, the surface temperature response in 1.3v-$H_2O$ is similar to the 1.0v case which suggests that removing this water vapour response is not sufficient to prevent glaciation altogether.
Fig. 5.13 Anomalies between Base-21 and 1.0v (left) and 1.3v (right). A: Change in atmospheric temperature (purple: Base-21 tropopause, black: experiment tropopause). B: Change in specific humidity (contours indicate percentage differences).
Fig. 5.14 Anomalies between Base-21 and 1.3v (left) and 1.3v-H\textsubscript{2}O (right). (A) surface air temperature changes (global mean values inset top-right), (B) atmospheric temperature change (purple: Base-21 tropopause, black: experiment tropopause). (C) Specific humidity change (contours indicate percentage differences).
5.6 Discussion

The results of these simulations highlight the crucial role of aerosol size in the radiative forcing by volcanic eruptions (Lacis et al., 1992; Pinto et al., 1989; Timmreck et al., 2010): In this case the choice of aerosol size distribution determines the equilibrium climate state achieved. In addition, climate feedbacks such as latent heat and stratospheric water vapour are also important. We have neglected some other possible aerosol impacts. Tropospheric aerosol could be important if the eruptions are effusive and not explosive (Schmidt et al., 2012b) and lead to smaller cloud droplets which could enhance the cooling, though it should be noted that the magnitude of this effect is not as large as once thought (Malavelle et al., 2017). An assessment of these factors would require a detailed model study of gas phase chemistry and aerosol and cloud microphysics and given the uncertainties in simulating these in past climates (Carslaw et al., 2013; Kiehl and Shields, 2013), quantifying this contribution would be scientifically and computationally challenging and may change substantially as the fundamental understanding of cloud nucleation processes becomes more developed.

Climate dependence of aerosol processing has also not been accounted for in this study. The main oxidation pathway for SO$_2$ is

$$\text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HOSO}_2 + \text{M}$$ (R1.1)
$$\text{HOSO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2$$ (R1.2)
$$\text{SO}_3 + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_2\text{SO}_4 + \text{M}$$ (R1.3)

to produce H$_2$SO$_4$ which can condense into the aerosol phase (Seinfeld and Pandis, 2006). As the climate approaches the snowball state, a reduction in water vapor would lead to less OH, so slower SO$_2$ oxidation. A reduction in the SO$_2$ lifetime could alter the total aerosol burden (Bekki, 1995) and the importance of SO$_2$ in the radiative budget (Lary et al., 1994) would increase as its lifetime becomes significant compared to the frequency of eruption and aerosol lifetime. Indeed, OH concentration was the most sensitive parameter in the model developed by Macdonald and Wordsworth (2017) - a tenfold reduction in OH led to a 60% reduction in aerosol burden. Dynamical feedbacks could also be important in determining the aerosol evolution. Isotopic evidence (Geng et al., 2017) and modelling studies (Rind et al., 2009) point towards an enhanced Brewer-Dobson circulation at the Last Glacial Maximum due to a stronger equator-to-pole temperature gradient. This effect would lead to a shorter aerosol lifetime and therefore a reduced radiative forcing as the
climate approaches a Snowball Earth. Simulations with a well-resolved stratosphere and interactive stratospheric chemistry and microphysical aerosol would be required to test this mechanism. Unfortunately such simulations are currently prohibitively expensive for centennial-scale studies (LeGrande et al., 2016), however the chemical and dynamical effects described here could counteract some of the increase in SO$_2$ injections expected from a lower tropopause height (Glaze et al., 2017).

While neither a Jormungand nor any other ‘soft’ snowball climate states were simulated in this study, even with a reduced tropical albedo, its existence is not implausible. There is considerable model disagreement about possible equilibrium climate states, and the presence of a particular state can depend on model parameters such as sea-ice albedo (Voigt and Abbot, 2012). However, the impact of albedo reductions is more limited than might otherwise be expected as the aerosol reduces the shortwave radiation reaches the surface. We have not considered the potential insulating effect of thicker ash layers, though these could be important in the context of deglaciation (cf. Abbot and Pierrehumbert 2010). As discussed earlier, HadCM3-BL has a higher sea-ice albedo parametrisation than some models which likely raises its critical CO$_2$ for achieving a Snowball Earth. The use of a lower ice albedo would then make achieving a Snowball Earth even more challenging.

The results described here suggest that entering a new equilibrium climate state is asymmetrical and there is a strong pullback effect. This could be due to the relatively short timescale of the applied climate forcing, however this effect should be considered when considering very large, short, perturbations to climate such as super-eruptions and asteroid strikes. This does not discount the possible role of volcanism in inducing climatic shifts. However, the climate-dependence of the aerosol cloud evolution must be accounted for, including the critical factors of oxidising capacity and dynamical changes. This could have important effects on the resulting radiative forcing.

If stratospheric aerosol from volcanic eruptions alone is insufficient to initiate the Snowball Earth from a late Neoproterozoic baseline climate state, drawdown of CO$_2$ would be needed before volcanic eruptions could perturb the climate sufficiently to enter a Snowball Earth. In this case, volcanic forcing is the proximal cause but the CO$_2$ reduction is a crucial priming mechanism. However, transiently applied climate forcings could provide a key to understanding the plausibility of some of the ‘soft’ snowball solutions that have been simulated with GCMs. Future studies should assess the stability of such equilibrium climate states to transiently applied forcings.
5.7 Synthesis

GCMs have been developed in the context of present-day climate state and are focused on simulating those climates, and those likely to face us in the future. Hence, applying GCMs to such an extreme climate state as the Snowball Earth, during a time when solar input was substantially lower, continental position were vastly different, greenhouse gas concentrations were substantially altered and even the bulk composition of the atmosphere was different, is challenging. “The results of GCMs should not be taken uncritically as truth, any more than should the results of [energy balance models]. GCMs have the advantage that they rest on physics that is closer to first principles, and therefore provide a better basis for understanding mechanisms.” (Pierrehumbert, 2005) The goal of this chapter has not been to ascribe the ‘cause’ of the Neoproterozoic Snowball Earth nor to put a definitive ‘radiative forcing’ in terms of CO$_2$ or stratospheric aerosol but to investigate the plausibility of mechanisms for promoting or inhibiting its occurrence. There are considerable uncertainties in continental configuration, orography, bathymetry, surface albedo and roughness, greenhouse gas inventory, oxygen content and stratospheric circulation that make simulating this time period a challenge. However treating important mechanisms such as radiative transfer in a physically consistent way permits an investigation of the mechanisms for changes – the feedback of water vapour on volcanic aerosol for instance would not be possible to simulate in a 1D radiative transfer approach. These feedbacks may vary in magnitude between models – this is a poor reason to neglect them entirely.

Simulations of 10 000 Pa $p_{CO_2}$ were not performed for HadAM3, as also simulated by Abbot et al. (2012). This is due to an underestimation of the radiative forcing due to CO$_2$ at extremely high CO$_2$ levels, which would make HadCM3 an inappropriate model to use to investigate the Snowball Earth deglaciation (Goldblatt et al., 2009b). We therefore focused on glaciation, which occurs at CO$_2$ contents where it performed similarly to RRTM, a state-of-the-art radiation scheme. This is supported by a similar performance to other GCMs in the Snowball Earth scenario. It should be noted however that other factors which are affected by such large CO$_2$ levels were neglected in Abbot et al. (2012), such as the resulting increase in atmospheric pressure, assuming a constant Nitrogen/Oxygen inventory. Increase in atmospheric pressure would be expected to lead to an increase in global mean surface temperature, however this would likely affect the lowest temperatures. Increase in heat transport may actually make achieving the warm temperature required for deglaciation less straightforward. In addition, CO$_2$ is a linear triatomic molecule which leads to a weaker dry adiabatic lapse rate that reduces the strength of its own greenhouse
effect. Finally, CO$_2$ sublimes at $-78^\circ$C at 1 bar which means it could sublime to a solid under some conditions of Snowball Earth at high CO$_2$ content.

The main results in this chapter explore the role of $p$O$_2$ variability and volcanic forcing in the Neoproterozoic Snowball Earth initiation for the first time with a fully coupled AO-GCM. $p$O$_2$ impacts the initiation of Snowball Earth in the Neoproterozoic. It may also have played a role at other times. O$_2$ underwent a considerable ‘overshoot’ towards near-Phanerozoic values after the four Paleoproterozoic glaciations – this could have increased atmospheric mass and prevented further such glaciation episodes. In the Phanerozoic, high $p$O$_2$ in the early Permian could have helped to prevent a Snowball Earth in the late Carboniferous / early Permian, contrary to claims about the possible role of $p$O$_2$ by Feulner (2017). This would be consistent with the occurrence of Snowball Earth events in the Proterozoic and absence of them in the Phanerozoic, however a plethora of possible mechanisms can be invoked to explain this including changes in CO$_2$ sources (Mills et al., 2017). The impact of low $p$O$_2$ on biological productivity in the Proterozoic, which was primarily in the ocean, has not been considered. Changes in atmospheric oxygenation has been invoked as an important mechanism for biodiversification in the Ordovician (Edwards et al., 2017), so the low $p$O$_2$ in the Proterozoic may have been important for determining the role of biology in initiating the Snowball Earth (Tziperman et al., 2011). Tziperman et al. (2011) argue that enhanced export of organic matter from the upper ocean into anoxic subsurface waters and sediments can explain the light carbon isotopic excursions in preglacial deposits in the late Neoproterozoic. This mechanism would be prevented by the increase in oxygenation into the Phanerozoic, suggesting that both biological and physical mechanisms would act to prevent a Phanerozoic Snowball Earth. While a Snowball Earth may have been necessary to cause the increase in oxygenation (Laakso and Schrag, 2017), the resulting oxygenation may have played an important role in stabilising the climate since.

Exploring the role of volcanic forcing provides a climate feedbacks context for a volcanically induced Snowball Earth (Macdonald and Wordsworth, 2017; Stern et al., 2008). The climate response to large volcanic aerosol loadings depends critically on aerosol size distribution. Climate feedbacks such as latent heat and stratospheric water vapour play an important role in limiting surface temperature change. In addition, global mean surface temperatures of less than $-30^\circ$C can be achieved by a transient climate forcing without entering a Snowball Earth state. Removal of the transient climate forcing leads to a rapid recovery of the surface climate. This resistance suggests a much longer or larger climate forcing is required in order to achieve global glaciation than would be suggested
using a 1D modelling approach. In HadCM3-BL, a ‘cool’ climate state with warm, moist tropical regions and widespread polar sea ice is still the equilibrium climate state until ice reaches the equator, after which a Snowball Earth is inevitable. While volcanic forcing can be turned up sufficiently to initiate a Snowball Earth, for the most plausible aerosol size distribution the climate did not transition to a globally-glaciated state. This suggests that volcanic forcing by stratospheric aerosols may have been insufficient to have caused global glaciation. A concurrent increase in weathering and subsequent drawdown in CO$_2$ by the LIP may have been necessary in order to cause glaciation, however this would be made more challenging due to the slowdown in the hydrological cycle.
Chapter 6

Conclusions & Future Work

In this chapter the key results from Chapters 3, 4 and 5 will be reiterated. Possible future directions will then be briefly discussed.

6.1 Conclusions

6.1.1 Climate Response to 1257 Samalas Eruption

In Chapter 3 it was demonstrated that:

- The CMIP5 Past1000 ensemble generally overestimates the climate cooling in the aftermath of the 1257 eruption of Mount Samalas compared to tree-ring records.

- The CESM-LME also overestimates the climate cooling in the aftermath of the eruption of Mount Samalas compared to tree-ring records, particularly for 1259.

- A new configuration of the MetUM climate model, HadGEM3-ES was developed which allows the climate impacts of a volcanic eruption to be quantified directly from stratospheric SO$_2$ emissions. HadGEM3-ES agrees well with the CMIP5 Historical ensemble and observations of global mean surface temperature, when ENSO variability is accounted for, in the aftermath of the 1991 eruption of Mount Pinatubo.

- The forced climate response was relatively insensitive to uncertainty in the total SO$_2$ injection. However, internal variability leads to a large range of climate responses despite using the same SO$_2$ injection.

- HadGEM3-ES agrees reasonably well with the tree-ring records for 1258 but underestimates the cooling for 1259 compared to the SG17 MXD-based reconstruction.
Stoffel et al. (2015) also were not able to simulate cooler conditions in 1259 than 1258, which is consistent with the reduced climate forcing. This suggests that internal variability may play a role as some HadGEM3-ES simulations were cooler in 1259 than 1258. HadGEM3-ES better agrees with the SCH15 and N-TREND2015 reconstructions.

- This suggests that our understanding of microphysical aerosol processes are consistent with the ‘muted’ climate response to the eruption of Samalas, and invoking mechanisms like missing-tree rings (Mann et al., 2012) or seasonality of eruptions (Stevenson et al., 2017) is not required.

- Large halogen emissions from Mount Samalas may have led to substantial catastrophic ozone depletion. For a yield of 20% of halogens released from the eruption reaching the stratosphere, almost total stratospheric ozone depletion is simulated. This would extend the duration of climate cooling.

6.1.2 Climate Impacts of Phanerozoic Oxygen Variability

In Chapter 4 it was demonstrated that:

- Under pre-industrial Holocene conditions, increasing atmospheric $pO_2$ leads to an increase in global-mean surface temperature in agreement with 1D radiative-convective model simulations. This increase is greater in the cold-month mean than the warm month-mean. The equator-to-pole temperature gradient is reduced, particularly in the cold-month mean, consistent with a stronger greenhouse effect at high atmospheric pressure.

- Lower incident surface shortwave radiation leads to a slow down of the hydrological cycle. Precipitation decreases globally under high $pO_2$, with regional variations.

- The climate sensitivity is lower at high $pO_2$, particularly in the Maastrichtian. This appears to reconcile the results of the 1D and 3D modelling approaches.

- For the Maastrichtian, model-proxy agreement is stronger at high $pO_2$ irrespective of $pCO_2$. Both simulations at 112.0 Pa CO$_2$ agree better with the Upchurch et al. (2015) proxy reconstruction than those at 56.0 Pa CO$_2$.

- The climate response simulated by Poulsen et al. (2015) is inconsistent with the radiative changes when considering a 1D-energy balance model decomposition of
the surface temperature changes. Tropical cloud feedbacks alone were not sufficient to explain the discrepancy.

- The climate response to oxygen content variability is state-dependent so should be considered on a case-by-case basis. However, the changes are relatively small compared to the role of CO$_2$ in the Phanerozoic (Royer et al., 2014).

### 6.1.3 Impacts of Oxygen Variability and Volcanic Forcing in the Neo-proterozoic Snowball Earth Initiation

In Chapter 5 it was demonstrated that:

- For a Neoproterozoic climate state with a similar global-mean surface temperature to present-day, consistent with ice-free continents, a lower oxygen content would have cooled the climate relative to a atmosphere with 21% O$_2$.

- The critical $p$CO$_2$ level for global glaciation is higher at low $p$O$_2$ and the increase of atmospheric $p$O$_2$ into the Phanerozoic may have helped to protect against Snowball Earth events since.

- Volcanic aerosol resulting from the eruption of the Franklin Large Igneous Province in the Sturtian may have led to a Snowball Earth state. However, achieving a Snowball Earth state is challenging when using larger aerosol size distributions consistent with such large volcanic eruptions. Volcanic aerosols can also lead to global-mean warming for the largest size distributions, due to stratospheric H$_2$O feedbacks which would not be accounted for in a 1D model.

- It is also possible to reverse a Snowball Earth at near-total glaciation due to the transient nature of a volcanic forcing and residual heat in the upper ocean.

- Deposition of volcanic ash could lower the tropical ice albedo sufficiently to substantially increase the timescale to initiate glaciation, however fails to simulate a soft-snowball or Jormungand climate state in HadCM3-BL

### 6.2 Future Directions

There are a wide range of possible future directions, some of which are detailed below.
6.2.1 Microphysical Simulations of Sulfate Geoengineering

Concerns that actions to decarbonise the energy system are progressing too slowly to prevent significant climatic changes has led to suggestions that direct human intervention to alter Earth's climate may be desirable Keith (2000). This could be achieved by reducing incoming solar radiation with reflective mirrors in space (e.g. Govindasamy and Caldeira 2000), by increasing the reflectivity of Earth's surface (e.g. Irvine et al. 2011), dumping iron into the oceans to enhance ocean productivity (Williamson et al., 2012) or by injecting stratospheric aerosol precursors into the stratosphere (e.g. Rasch et al. 2008). Note that injection of aerosol precursors is physically distinct from solar radiation management as reducing solar input would not alter the clear-sky longwave forcing while stratospheric aerosols are active in the longwave region of the spectrum.

There has been considerable work to investigate the climate response to different geoengineering scenarios (Kravitz et al., 2013b) including with stratospheric aerosols (Kravitz et al., 2013a). However, most simulations either prescribe atmospheric chemistry or physical aerosol properties, or decouple the aerosol and climate processes (e.g. Laakso et al. 2017). Simulating the climate response in a holistic way to stratospheric SO$_2$ injections would help to understand the plausibility of such a scenario for mitigating climate change.

Using HadGEM3-ES a feasibility study was performed to investigate whether it could be used to study geoengineering. From the Base PIH HadGEM3-ES experiment (see Chapter 2), the CO$_2$ content is instantaneously quadrupled to 1120 Pa, values which are likely to be seen under RCP8.5 by 2100. At the same time, SO$_2$ is continuously injected into the tropical (30N-30S) stratosphere. The evolution of the global mean surface temperature for injections of 40 and 100 TgSO$_2$yr$^{-1}$ is given in Figure 6.1. These simulations suggest that as little as 40 TgSO$_2$yr$^{-1}$ is sufficient to offset a quadrupling of CO$_2$ emissions. However, geoengineering the climate in this way has a large number of legal and regulatory issues (Armeni and Redgwell, 2015), ethical and technological issues (Robock et al., 2009b). It would be challenging to inject uniformly in space and time so it is likely that fewer, larger and less reflective particles would be formed in reality which would inhibit their ability to reflect sunlight. It is reassuring however that such strong cooling can be achieved should such a mitigation strategy become required, for example to prevent the melting of the West Antarctic Ice Sheet.
6.2.2 Climate state dependence of volcanic forcing

There has been renewed interest in how the ability of volcanoes to cool the climate are mediated by the background climate state. Macdonald and Wordsworth (2017) suggested that a lower tropopause height during the Sturtian would have significantly increased the flux of SO$_2$ to the stratosphere and contributed significantly to the initiation of Snowball Earth. This would also explain why other LIP emplacements did not lead to glaciation, as they occurred during much warmer climates in the Phanerozoic. This is somewhat supported by state-of-the-art plume modelling (Glaze et al., 2017), however changes for the most explosive of eruptions, which were invoked by Macdonald and Wordsworth 2017 (annually-paced $25 \times$-Pinatubo sized injections) are relatively insensitive to tropopause height changes (Hopcroft et al., 2017). The climate state dependence of volcanic forcing has been investigated by Hopcroft et al. (2017), simulating a reduced climate impact to a Tambora-sized eruption due to less sea-ice in a warmer world. This does not take into account changes in aerosol production or transport. Rind et al. (2001) simulate a warmer stratosphere, cooler tropopause and increased strength of the Brewer-Dobson circulation during glacial periods. This would increase the transport of aerosols out of the stratosphere, reduce nucleation rates and reduce stratospheric OH in colder climates.
These factors would counteract the impact of tropopause height changes. Simulating changes to stratospheric circulation in palaeoclimates remains an open question. Future work could investigate fundamental controls on the Brewer Dobson circulation on the past Earth, as has recently been done for tidally-locked planets (Proedrou and Hocke, 2016). How the magnitude of the climate impact of volcanic eruptions may change in the future could be investigated using the next generation of CMIP6 models which include interactive stratospheric composition.

6.2.3 Cloud properties as a function of changing climate

Climate models struggle to simulate the shallow equator-to-pole temperature gradients that have been reconstructed for the warmest periods of the Phanerozoic (Huber and Caballero, 2011). This so-called ‘shallow gradients’ paradox has led to a plethora of hypotheses which aim to reconcile these differences. One which has gained considerable traction is possible changes to liquid cloud properties in a changing climate. Kump and Pollard (2008) suggested that a collapse in biological productivity in the Cretaceous could have led to significant reductions in cloud condensation nuclei (CCN). This would lead to an increase in cloud droplet radii which would make clouds more transparent to shortwave radiation. Rosing et al. (2010) applied this to the early Earth, suggesting that very low CCN and less extensive land surface could solve the ‘Faint Young Sun’ paradox. Kiehl and Shields (2013) suggested that cloud droplet radii of 17 µm globally would be more consistent with pre-anthropogenic CCN concentrations and that this could lead to considerable warming for the Eocene. On the face of it, changes in cloud properties are a plausible method to achieve warming – cloud radiative effects are very large so small changes can achieve a large warming. However, anthropogenic aerosol emissions were significantly lower before the industrial revolution. If this was such a large control on surface temperatures, it would be expected that Earth would have cooled substantially since, particularly over the continents, when emissions began. In addition, as can be observed from Kump and Pollard (2008) Figure 1, changes to the shortwave cloud budget cause large increases in tropical temperatures. Polar temperatures increase primarily due to albedo feedbacks. This raises the possibility that the tropics may heat too strongly for a reduction in cloud albedo to be a plausible mechanism for high latitude warmth. While aerosols have undoubtedly influenced climate particularly over Europe and North America, recent evidence has cast doubt on the strength of the indirect aerosol effects (Malavelle et al., 2017). Anthropogenic sources of CCN precursors are undoubtedly
high, however there are a multitude of sources of CCN in the pre-industrial atmosphere including sea salt and dust which will be have been present since the Archean. In particular, recent work at the CERN cloud chamber (Dunne et al., 2016) has shown that anthropogenic \( \text{SO}_2 \) is not required for new particle formation – biogenics particularly from monoterpenes can undergo new particle formation which suggests that pre-industrial aerosol may be higher than previously thought (Gordon et al., 2017). Fires are also a source of aerosol. Commonly considered an anthropogenic source of pollution, a continuous charcoal record belies the fact that biomass burning is a likely new source of continental CCN. Future work should provide fundamental constraints on possible cloud droplet radii for use in climate model simulations.

### 6.2.4 Impact of oxygen levels on physiology and evolution

The rise of oxygen to typical Phanerozoic levels is commonly associated with the rise of life (Saltzman et al., 2011). Within the Phanerozoic, the coincidence between higher Paleozoic oxygen levels and the presence of giant insects has led to suggestions that \( pO_2 \) could be a limit on animal size (Graham et al., 1995). Elevated \( pO_2 \) could increase oxygen supply to tissues, allowing larger body sizes (Kaiser et al., 2007). Metabolism required for flight has been shown to be sensitive to \( pO_2 \) in dragonflies (Harrison and Lighton, 1998).

"I, for one, welcome our new insect overlords"

— Popularised by Kent Brockman, *The Simpsons*

This argument has been extended to placental animals (Falkowski et al., 2005), however this application in particular has attracted criticism (Butterfield, 2009). The physical impacts of oxygen variability have not been widely explored, despite acknowledgements that these would be significant (Graham et al., 1995). Increases in atmospheric mass in high \( pO_2 \) episodes ought to increase lift, which should support flight in more massive birds. In addition, higher oxygen levels in the Cretaceous (up to >30%) may be important for interpreting the mechanisms of flight mechanics in early birds (Voeten et al., 2018) or Pterosaurs (Witton and Habib, 2010). Air pressure at lift-off has been identified as being important for modelling bird flight (Pennycuick, 2008). This could be extended to these fossilised bird examples.
### 6.2.5 Oases for Life in a Snowball Earth

The evolution of photosynthesis is the key to life on Earth – the ability to harness the sun’s energy originated in the ancestors of cyanobacteria (Blankenship and Hartman, 1998) and the complex dual photosystem mechanism appears to be conserved in all photosynthetic life today which suggests it evolved only once (Blankenship, 2010). Therefore, life must have survived in some form continuously since around 2.4 Ga. This is seemingly at odds with the occurrence of harsh glaciation episodes at the start and end of the Proterozoic, particularly for a ‘hard’ Snowball Earth with global sea-ice cover.

Figure 6.2A, with results from the Had-AM3 (Abbot et al., 2012) experiment, shows that at all latitudes daily mean surface temperatures remain well below freezing for an idealised snowball Earth climate at 10 Pa CO$_2$, which would make it inhabitable for multicellular organisms. However, bacteria are able to survive on present-day ice sheets. The bacterial life cycle slows and enters suspended animation below freezing, however can survive and continue when temperatures rise again. This suggests that the daily maximum temperature could be a more appropriate metric for determining a minimum capacity for supporting life. This is shown in Figure 6.2B – for a narrow band around 30S/30N daily maximum temperatures go above freezing three months of the year. Given that bacteria can survive for hundreds of thousands of years in glacial ice (Christner et al., 2003), this suggests that bacteria are likely to be able to survive under these conditions. However, this may not be sufficient for the survival of more complex forms of life, which may require some ice-free ocean or localised geothermal sources of heat.
Many bacteria undergo vitrification (Clarke et al., 2013), a form of 'suspended animation' from which the cell can survive but not grow or reproduce. This suggests that if daytime surface temperatures go above freezing it could be sufficient to allow life to continue during a Snowball Earth. This could also be exacerbated by geothermal sources of power such as volcanoes, which could cause periodic regions of warmer surface temperatures. This suggests life may have been more resilient to a hard snowball climate than is first evident from considering the mean climate state. Life may have also played a role in the deglaciation. Many algae for instance are coloured, such as *Chlamydomonas nivalis* which has been linked to algal blooms in the Arctic (Lutz et al., 2016). This would not be consistent with widespread proliferation of life in the 10 Pa CO$_2$ scenario however raises the prospect that as tropical temperatures rise as CO$_2$ builds its abundance could increase and the albedo would increase, trapping more heat in a region of net ablation. This raises the prospect of the role of a biologically induced escape from Snowball Earth, as a larger fraction of days in tropical regions remain above zero. Abbot et al. (2012) suggested that volcanic dust/ash could accumulate and lower ice albedo at the equator. This could also provide nutrients which would increase biological productivity in the vicinity, enhancing albedo reductions. Numerical studies could determine the likelihood of such a mechanism.
Appendix A

Steady-State Ozone

For steady-state ozone calculations, the reduced set of Chapman reactions are employed

\[ \text{O}_2 \xrightarrow{J(\text{O}_2)} \text{O} + \text{O} \quad \text{(R1.4)} \]
\[ \text{O} + \text{O}_2 + \text{M} \xrightarrow{k_2} \text{O}_3 + \text{M} \quad \text{(R1.8)} \]
\[ \text{O}_3 \xrightarrow{J(\text{O}_3)} \text{O} + \text{O}_2 \quad \text{(R1.7)} \]
\[ \text{O} + \text{O}_3 \xrightarrow{k_3} \text{O}_2 + \text{O}_2 \quad \text{(R1.9)} \]

where the rate constants are given by

\[ k_2(T) = 6 \times 10^{-34} (300/T)^2 \text{ cm}^6 \text{ s}^{-1} \]
\[ k_3(T) = 1 \times 10^{-11} \exp(-2100/T) \text{ cm}^3 \text{ s}^{-1} \]

and photolysis rates vary by altitude according to

\[ J_X(z) = \int q_X(\lambda) \sigma_X(\lambda) I(z, \lambda) \text{ d}\lambda \]

where \( q_X \) is the quantum yield for the photolysis of \( X \), \( \sigma_X \) is the absorption cross section of \( X \) and \( I \) is intensity of radiation at wavelength \( \lambda \). \( I \) is given by

\[ I(z, \lambda) = I(\infty, \lambda) e^{-\delta(z, \lambda)} \]

where \( I(\infty, \lambda) \) is the wavelength-dependent intensity of incoming solar radiation at the top of the atmosphere and \( \delta \) is the optical depth

\[ \delta(z, \lambda) = \int_z^\infty (\sigma_{\text{O}_2}(\lambda) |\text{O}_2|(z') + \sigma_{\text{O}_3}(\lambda) |\text{O}_3|(z')) \text{ d}z' \]

which assumes that the majority of the absorption of radiation is due to \( \text{O}_2 \) and \( \text{O}_3 \). Oxygen is assumed to be fully mixed in the atmosphere \( |\text{O}_2| \) to its concentration can be approximated as

\[ |\text{O}_2|(z) = |\text{M}|_0 \exp(-z/H) \]
where $H$ is some scale height, often taken to be 7 km, and $[M]_0$ is the surface gas concentration. As ozone is variable throughout the atmosphere the integral has to be determined numerically. When calculating the ozone column from first principles it is necessary to start at the top layer of the atmosphere as $\delta$ varies according to the ozone column. Photolysis cross sections are taken from Sander et al. (2011). In the steady state, the concentration of ozone is given by

$$[O_3] = \sqrt{\frac{J(O_2) k_3 [M]}{J(O_3) k_4} [O_2]}.$$  \hspace{1cm} (A.1)
Appendix B

Code Modifications

This Appendix contains a non-exhaustive description of the necessary code changes required for the simulations detailed in this thesis.

B.1 HadGEM3-AO

For HadGEM3-AO, alterations to the code required for the 35% oxygen simulations are detailed here. Similar alterations were made for 10% oxygen simulations.

Index: UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/atmosphere/convection/conv_diag_4a.F90

--- UM/trunk/src/atmosphere/convection/conv_diag_4a.F90 (revision 1678)

+++ UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/atmosphere/convection/conv_diag_4a.F90 (revision 21878)

@@ -745,8 +745,8 @@
- & * ( TSTAR(I,j)*((100000.0/PSTAR(I,j))**kappa) - theta1 )
+ & * ( TSTAR(I,j)*((121640.0/PSTAR(I,j))**kappa) - theta1 )
- & * ( TSTAR(I,j)*((100000.0/PSTAR(I,j))**kappa) - theta1
- &
+ & * ( TSTAR(I,j)*((121640.0/PSTAR(I,j))**kappa) - theta1
+ &
@@ -806,5 +806,5 @@
- & * ((100000.0/PSTAR(I,j))**kappa)
+ & * ((121640.0/PSTAR(I,j))**kappa)
@@ -816,5 +816,5 @@
- & / ( (100000.0/PSTAR(I,j))**kappa +
- &
+ & / ( (121640.0/PSTAR(I,j))**kappa +
+ &
@@ -850,5 +850,5 @@
- & * ((100000.0/PSTAR(I,j))**kappa)
+ & * ((121640.0/PSTAR(I,j))**kappa)
 @@ -867,5 +867,5 @@
- & ( (100000.0/PSTAR(I,j))**kappa +
- & (121640.0/PSTAR(I,j))**kappa +
+ & ( (100000.0/PSTAR(I,j))**kappa )
+ & (121640.0/PSTAR(I,j))**kappa )
@@ -1394,8 +1394,8 @@
- & ( (100000.0/P_theta_lev_c(ii,K))**kappa ) )
+ & ( (121640.0/P_theta_lev_c(ii,K))**kappa ) )
- & ( (100000.0/P_theta_lev_c(ii,K))**kappa ) *
- & (121640.0/P_theta_lev_c(ii,K))**kappa ) *
+ & (121640.0/P_theta_lev_c(ii,K))**kappa ) *

Index: UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/atmosphere/
     convection/evp-evp3a.F90
===================================================================
--- UM/trunk/src/atmosphere/convection/evp-evp3a.F90 (revision 1678)
+++ UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/atmosphere/
     convection/evp-evp3a.F90 (revision 21878)
 @@ -136,5 +136,5 @@
- & (100000.0/PKM1(I))
+ & (121640.0/PKM1(I))
@@ -155,8 +155,8 @@
- ECON = 1.7405E-5*(100000.0/PKM1(I))
+ ECON = 1.7405E-5*(121640.0/PKM1(I))
- & (100000.0/PKM1(I))
- & (121640.0/PKM1(I))
+ & (121640.0/PKM1(I))

Index: UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/include/
     constant/c_epslon.h
===================================================================
--- UM/trunk/src/include/constant/c_epslon.h (revision 1678)
+++ UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/include/
     constant/c_epslon.h (revision 21878)
 @@ -10,8 +10,8 @@
- Real, Parameter :: Epsilon = 0.62198
- Real, Parameter :: Epsilon = 0.61056
+ Real, Parameter :: Epsilon = 0.61056

Index: UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/include/
     constant/c_r_cp.h
===================================================================
--- UM/trunk/src/include/constant/c_r_cp.h (revision 1678)
+++ UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/include/
     constant/c_r_cp.h (revision 21878)
 @@ -2,5 +2,5 @@
- Real, Parameter :: R = 287.05
- Real, Parameter :: CP = 1005.
+ Real, Parameter :: R = 281.79
+    Real, Parameter :: CP = 988.
-    Real, Parameter :: Pref = 100000.
+    Real, Parameter :: Pref = 121640.

Index: UM/branches/dev/dc32/vn7.3_pressure_35_nochem/src/include/
constant/c_sulchm.h
===================================================================
--- UM/trunk/src/include/constant/c_sulchm.h (revision 1678)
+++ UM/branches/dev/dc32/vn7.3_pressure_35_nochem/src/include/
constant/c_sulchm.h (revision 21878)
@@ -80,5 +80,5 @@
    & RMM_AIR = 2.896E-2,
    &
+    & RMM_AIR = 2.9506E-2,
    &

Index: UM/branches/dev/dc32/vn7.3_pressure_35_nochem/src/include/
constant/c_v_m.h
===================================================================
--- UM/trunk/src/include/constant/c_v_m.h (revision 1678)
+++ UM/branches/dev/dc32/vn7.3_pressure_35_nochem/src/include/
constant/c_v_m.h (revision 21878)
@@ -8,95 +8,134 @@
    REAL, PARAMETER :: C_O3P = 0.5523
+    REAL, PARAMETER :: C_O3P = 0.5523 *0.9817

Index: UM/branches/dev/dc32/vn7.3_pressure_35_nochem/src/include/
constant/o3crits.h
===================================================================
--- UM/trunk/src/include/constant/o3crits.h (revision 1678)
+++ UM/branches/dev/dc32/vn7.3_pressure_35_nochem/src/include/
constant/o3crits.h (revision 21878)
@@ -23,10 +23,14 @@
    Real, Parameter :: O3_grad_crit = 99.423E-12
+    !DIVIDE BY 1.2164
+    Real, Parameter :: O3_grad_crit = 99.423E-12
+    Real, Parameter :: O3_grad_crit = 81.735E-12
-    Real, Parameter :: O3_conc_crit = 132.56E-09
-    Real, Parameter :: O3_conc_crit = 108.98E-09
+    Real, Parameter :: O3_conc_crit = 128.56E-09
+    Real, Parameter :: O3_conc_crit = 108.98E-09
-    Real, Parameter :: O3_strat_crit = 182.27E-09
-    Real, Parameter :: O3_strat_crit = 149.84E-09
+    Real, Parameter :: O3_strat_crit = 182.27E-09
+    Real, Parameter :: O3_strat_crit = 149.84E-09

#endif

Index: UM/branches/dev/dc32/vn7.3_pressure_35_nochem/src/include/
constant/phycn03a.h
===================================================================
--- UM/trunk/src/include/constant/phycn03a.h (revision 1678)
+++ UM/branches/dev/dc32/vn7.3_pressure_35_nochem/src/include/
constant/phycn03a.h (revision 21878)
@@ -1,7 +1,7 @@
+    !DIVIDE BY 1.2164
- REAL, PARAMETER :: MOL_WEIGHT_AIR=28.966E-3
+ REAL, PARAMETER :: MOL_WEIGHT_AIR=29.506E-3
- REAL, PARAMETER :: N2_MASS_FRAC=0.781E+00
+ REAL, PARAMETER :: N2_MASS_FRAC=0.609E+00

Index: UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/include/
other/physical_constants_0_ccf3z.h
===================================================================
--- UM/trunk/src/include/other/physical_constants_0_ccf3z.h (revision 1678)
+++ UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/include/other/
physical_constants_0_ccf3z.h (revision 21878)
@@ -13,9 +13,9 @@
- & MOL_WEIGHT_AIR=28.966E-03_real64
 &
- & , N2_MASS_FRAC=0.781E+00_real64
 &
+ & , N2_MASS_FRAC=0.609E+00_real64
 &

Index: UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/include/
other/physical_constants_1_ccf3z.h
===================================================================
--- UM/trunk/src/include/other/physical_constants_1_ccf3z.h (revision 1678)
+++ UM/branches/dev/dcw32/vn7.3_pressure_35_nochem/src/include/other/
physical_constants_1_ccf3z.h (revision 21878)
@@ -16,7 +16,7 @@
- & , R_GAS_DRY=287.026E+00_real64
 &
- & , CP_AIR_DRY=1.005E+03_real64
 &
- & , RATIO_MOLAR_WEIGHT=28.966E+00_real64/18.0153E+00_real64
 &
+ & , R_GAS_DRY=282.184E+00_real64
 &
+ & , CP_AIR_DRY=0.989E+03_real64
 &
+ & , RATIO_MOLAR_WEIGHT=29.506E+00_real64/18.0153E+00_real64
 &

B.2 HadCM3

For HadCM3, the following modsets were used, in addition to the baseline model described
in Valdes et al. (2017). The base code can be accessed at http://cms.ncas.ac.uk/code_browsers/UM4.5/UMbrowser/. As of 1\textsuperscript{st} March 2018, registration is required to access the source code. Unified Model code is Crown Copyright.
Oxygen Content

The modsets in this section were developed jointly at the University of Bristol by the author and Prof. Paul Valdes (University of Bristol).

**oxy_35**

This modset applies changes necessary for setting the oxygen content to approximately 35%. Similar files were developed for other oxygen contents.

```plaintext
*ID OXYGEN
*/
*/ MODSET FOR OXYGEN
*DECLARE C_R_CP
*D C_R_CP.8,9
   PARAMETER(R=281.79,
   & CP=987.9,
*D C_R_CP.11
   & PREF=121640.)
*DECLARE C_EPSLON
*D C_EPSLON.6
   PARAMETER(EPSILON=0.61056,
*DECLARE PHYCN03A
*D PHYCN03A.14,15
   & MOL_WEIGHT_AIR=29.506E-3
   & , N2_MASS_FRAC=0.609E+00
*DECLARE PHYDIA1A
*D PHYDIA1A.354
   PP= AK(K) + BK(K) * 121640 ! Pstar assumed to be 1000MB
*/not don't think I need LSPEVA2E as the 1000hPa is a reference pressure
*/not a strict surface pressure
*/DECLARE LSPEVA2E
*DECLARE GWVERT3B
*D GWVERT3B.331
   PU=121640.*BKH(K+1) + AKH(K+1)
*DECLARE GWVERT3A
*D GWVERT3A.319
   PU=121640.*BKH(K+1) + AKH(K+1)
*DECLARE GWSURF3A
*D GWSURF3A.160
   PU=121640.*BKH(K+1) + AKH(K+1)
*DECLARE GWSCOR3A
*D GWSCOR3A.136
   PU=121640.*BKH(K+1) + AKH(K+1)
*D GWSCOR3A.150,152
   P(K)=121640.*BKH(K+1) + AKH(K+1)
   IF ( K .LE. K_LEE_MAX ) THEN
   P_LIM(K) = 2*P(K) - 121640.
*DECLARE COFUV1C
```
*D COFUV1C.177
  PRESSURE_LEVEL=AK(LEVEL)+121640.0*BK(LEVEL)
*DECLARE COFUV1A
*D COFUV1A.127
  PRESSURE_LEVEL=AK(LEVEL)+121640.0*BK(LEVEL)
*DECLARE COFTHQ1C
*D COFTHQ1C.164
  PRESSURE_LEVEL=AK(LEVEL)+121640.0*BK(LEVEL)
*DECLARE COFTHQ1A
*D COFTHQ1A.121
  PRESSURE_LEVEL=AK(LEVEL)+121640.0*BK(LEVEL)
*DECLARE THETAW1A
*D THETAW1A.221
  P_TARGET=121640.0  ! 1000 mb
*DECLARE SFSTOM7A
*D SFSTOM7A.118
  PARAMETER (O2 = 0.38)
*D SFSTOM7A.113
  PARAMETER (RAIR = 281.79)

**ozone_35**

This adjusts the ozone mass mixing ratio for the 35% oxygen content scenario. Similar files were produced for other oxygen contents.

*/
/*/Ozone_mod from FAMOUS, ozone_mod from FAMOUS differs from HadCM3 in that differentiates between low/mid stratosphere and high stratosphere. The original ozone_mod from HadCM3 has an ozone concentration in the stratosphere 5.5 times greater than the original modification
*/
*ID CONSTANT O3
*DECLARE TROPIN1A
*D TROPIN1A.132
  DTI=MAX_TROP_LEVEL
*DECLARE RAD_CTL1
*I ADB2F404.937
  DO ROW=1,P.Rows
    DO I=1,ROW_LENGTH
      POINT=I+(ROW-1)*ROW_LENGTH
      DO LEVEL=1,OZONE_LEVELS
        IF(LEVEL.LT.TRINDX(POINT)) OZONE_1(POINT,LEVEL)=1.6442E-8
        IF(LEVEL.EQ.TRINDX(POINT)) OZONE_1(POINT,LEVEL)=1.6442E-7
        IF(LEVEL.GT.TRINDX(POINT)) OZONE_1(POINT,LEVEL)=4.5215E-6
        IF(LEVEL.EQ.OZONE_LEVELS) OZONE_1(POINT,LEVEL)=4.5215E-6
      ENDDO
    ENDDO
  ENDDO
ENDDO
Volcanism

These modsets were adapted from those originally developed in Jones et al. (2005) by the author.

volvar_25_eq_ar

This modset applies the volcanic aerosol.

*DECLARE RAD_CTL1 
*I RAD_CTL1.118 
& VOLCMASS(P_FIELDDA), ! VOLCTS expanded to full fields, 
! converted to mass loading & possibly multiplied by a fudge factor 
*I RAD_CTL1.140 
& I30N, IEQR, I30S, ! Indices for rows at 30' & 0'. 
*I RAD_CTL1.159 
& MASCON, ! Conversion factor from optical depth to mass 
! - can also incorporate fudge factor ! 
*B ADB2F404.929 
PARAMETER ( MASCON = 
& .0025 * 2.33464E-04 ) 
!DCW COMMENTS 
! .0025 converts the numbers in the DATA statement to 25*optical depth 
! 2.33464E-04 converts the optical depth to a column aerosol (kg m-2) by 
! dividing the OD by the sum of the absorption and scattering in the SW 
! by Pinatubo sized aerosols (0.5 um). This is different from the value 
! of 1.917E-04 in the standard modset and accounts for the suggested 
! 'fudge factor'. No such fudge factor is necessary here as the 
! larger aerosol size is accounted for. 
*I RAD_CTL1.330 
CL Expand aerosol optical depth time series to global field, ignoring 
CL haloes, which aren’t passed down: 
C datastart(2) (in comdeck PARVARS) gives the index in the global field 
C of the first non-halo row of this processor. 

  I30N = glsize(2)/3 + 1 - datastart(2) + offy 
  IEQR = glsize(2)/2 + 1 - datastart(2) + offy 
  I30S = 2*glsize(2)/3 + 1 - datastart(2) + offy 
C The +1 in combination with the rounding of the INTEGER division 
C gives the right place, given there being one more row of data 
C on the first row of processors. 
C 
C "hopefully" this has been changed from 45 zones to 90-30,30-0 etc 
DO ROW=1+offy, MIN(I30N,P_ROWS-offy) 
  DO I=1, ROW_LENGTH 
    VOLCMASS(I+(ROW-1)*ROW_LENGTH) = 
    & MASCON * VOLCTS(I,I_MONTH,I_YEAR)
ENDDO
ENDDO
IF ( I3ON .GE. offy .AND. I3ON .LT. P_ROWS-offy ) THEN
  DO I=1, ROW_LENGTH
    VOLCMASS(I+I3ON*ROW_LENGTH) = .5 * MASCON * 
    ( VOLCTS(1,I_MONTH,I_YEAR) + VOLCTS(2,I_MONTH,I_YEAR) )
  ENDDO
ENDIF
ENDDO
DO ROW=MAX(1+offy,I3ON+2), MIN(IEQR,P_ROWS-offy)
  DO I=1, ROW_LENGTH
    VOLCMASS(I+(ROW-1)*ROW_LENGTH) = 
    MASCON * VOLCTS(2,I_MONTH,I_YEAR)
  ENDDO
ENDDO
ENDIF
DO ROW=MAX(1+offy,IEQR+2), MIN(IEQR,P_ROWS-offy)
  DO I=1, ROW_LENGTH
    VOLCMASS(I+(ROW-1)*ROW_LENGTH) = 
    MASCON * VOLCTS(3,I_MONTH,I_YEAR)
  ENDDO
ENDDO
ENDIF
DO ROW=MAX(1+offy,I30S+2), P_ROWS-offy
  DO I=1, ROW_LENGTH
    VOLCMASS(I+(ROW-1)*ROW_LENGTH) = 
    MASCON * VOLCTS(4,I_MONTH,I_YEAR)
  ENDDO
ENDIF
ENDDO
ENDDO
IF ( I30N .GE. offy .AND. I30N .LT. P_ROWS-offy ) THEN
  DO I=1, ROW_LENGTH
    VOLCMASS(I+I30N*ROW_LENGTH) = .5 * MASCON * 
    ( VOLCTS(1,I_MONTH,I_YEAR) + VOLCTS(2,I_MONTH,I_YEAR) )
  ENDDO
ENDIF
ENDDO
DO ROW=MAX(1+offy,I30N+2), MIN(IEQR,P_ROWS-offy)
  DO I=1, ROW_LENGTH
    VOLCMASS(I+(ROW-1)*ROW_LENGTH) = 
    MASCON * VOLCTS(2,I_MONTH,I_YEAR)
  ENDDO
ENDDO
ENDIF
DO ROW=MAX(1+offy,IEQR+2), MIN(I30S,P_ROWS-offy)
  DO I=1, ROW_LENGTH
    VOLCMASS(I+(ROW-1)*ROW_LENGTH) = 
    MASCON * VOLCTS(3,I_MONTH,I_YEAR)
  ENDDO
ENDDO
ENDIF
DO ROW=MAX(1+offy,I30S+2), P_ROWS-offy
  DO I=1, ROW_LENGTH
    VOLCMASS(I+(ROW-1)*ROW_LENGTH) = 
    MASCON * VOLCTS(4,I_MONTH,I_YEAR)
  ENDDO
ENDIF
ENDDO

*/ The added argument has to share a line with an existing one, as the
*/ code on the library has reached the limit of 99 continuation lines.
*D ADB2F404.994
   & DISS_SULPHATE(FIRST_POINT_SULPC, 1), VOLCMASS(FIRST_POINT),
*I ADB2F404.1024
   & VOLCMASS(FP_LOCAL(I)),
*/
*DECLARE LWRAD3A
*/
*I ADB2F404.635
   & , VOLCMASS
*I ADB1F401.516
   & , VOLCMASS(NPD_FIELD)
! Mass of stratospheric volcanic aerosol at each point
*I ADB1F402.516
   & , VOLCMASS
*/
*DECLARE SWRAD3A
*/
* 
*I ADB2F404.1507
   & , VOLCMASS
*I ADB1F401.1044
   & , VOLCMASS(NPD_FIELD)
! Mass of stratospheric volcanic aerosol at each point
*I ADB1F402.724
   & , VOLCMASS
*/
*DECLARE FILL3A
*/
*I ADB1F402.161
   & , VOLCMASS
*I ADB1F402.200
   & , VOLCMASS(NPD_FIELD)
! Mass of stratospheric volcanic aerosol at each point
!JME Pass the imposed volcanic aerosol down into the climatology
*I ADB2F404.261
   & , VOLCMASS
*I ADB2F404.366
   & , VOLCMASS
*I ADB2F404.414
   & , VOLCMASS(NPD_FIELD)
! Mass of stratospheric volcanic aerosol at each point
*D ADB2F404.461,462
!JME Replace N_AEROSOL with the hard-wired 5 of this climatology
!JME IF ( I .LT. N_AEROSOL ) THEN
      IF ( I .LT. 5 ) THEN
!JME Add suffix _CLIM to aerosols.
      AEROSOL_MIX_RATIO_CLIM(L,NLEVS+1-TRINDX(LG),I) = 0.
      ELSE
      AEROSOL_MIX_RATIO_CLIM(L,NLEVS+1-TRINDX(LG),I) =
      & VOLCMASS(LG) * G /
*I ADB2F404.464
ENDIF
vol_marin

This modset holds the annual climatology from Sato et al. (1993).

*/
*DECLARE RAD_CTL1
*/
*I ADB2F404.913
   & , VOLCTS(4,12,3151:3670)
C ! 10000 * stratospheric volcanic aerosol optical depth at .55
C ! microns for the 4 quarters of the world from 1850 to 1999.
*B ADB2F404.929
*/ VOLCTS(4,12,1850:1999) holds 10000 * stratospheric volcanic aerosol
*/ optical depth at .55 microns for the 4 quarters of the world from
*/ 1850 to 1999 - 7200 integers in all.
   DATA (((VOLCTS (I,J,JS), I=1, 4), J=1, 12), JS=3151,3160)
& / 569,
   & 1756, 1609, 771, 774, 1748, 1814, 1116, 1370, 1556, 1507, 1078,
   & 1596, 1654, 1537, 1122, 1701, 1680, 1453, 1128, 1581, 1587, 1395,
   & 1133, 1425, 1482, 1407, 1216, 1367, 1475, 1367, 1294, 1177, 1217,
   & 1263, 1404, 1069, 1233, 1186, 1420, 1054, 1078, 1076, 1361, 1018,
   & 1023, 941, 1202, 569,
   & 1756, 1609, 771, 774, 1748, 1814, 1116, 1370, 1556, 1507, 1078,
   & 1596, 1654, 1537, 1122, 1701, 1680, 1453, 1128, 1581, 1587, 1395,
   & 1133, 1425, 1482, 1407, 1216, 1367, 1475, 1367, 1294, 1177, 1217,
   & 1263, 1404, 1069, 1233, 1186, 1420, 1054, 1078, 1076, 1361, 1018,
   & 1023, 941, 1202, 569,
   & 1756, 1609, 771, 774, 1748, 1814, 1116, 1370, 1556, 1507, 1078,
   & 1596, 1654, 1537, 1122, 1701, 1680, 1453, 1128, 1581, 1587, 1395,
   & 1133, 1425, 1482, 1407, 1216, 1367, 1475, 1367, 1294, 1177, 1217,
   & 1263, 1404, 1069, 1233, 1186, 1420, 1054, 1078, 1076, 1361, 1018,
   & 1023, 941, 1202, 569,
   & 1756, 1609, 771, 774, 1748, 1814, 1116, 1370, 1556, 1507, 1078,
   & 1596, 1654, 1537, 1122, 1701, 1680, 1453, 1128, 1581, 1587, 1395,
   & 1133, 1425, 1482, 1407, 1216, 1367, 1475, 1367, 1294, 1177, 1217,
   & 1263, 1404, 1069, 1233, 1186, 1420, 1054, 1078, 1076, 1361, 1018,
   & 1023, 941, 1202, 569,
   & 1756, 1609, 771, 774, 1748, 1814, 1116, 1370, 1556, 1507, 1078,
   & 1596, 1654, 1537, 1122, 1701, 1680, 1453, 1128, 1581, 1587, 1395,
   & 1133, 1425, 1482, 1407, 1216, 1367, 1475, 1367, 1294, 1177, 1217,
   & 1263, 1404, 1069, 1233, 1186, 1420, 1054, 1078, 1076, 1361, 1018,
   & 1023, 941, 1202, 569,
   & 1756, 1609, 771, 774, 1748, 1814, 1116, 1370, 1556, 1507, 1078,
   & 1596, 1654, 1537, 1122, 1701, 1680, 1453, 1128, 1581, 1587, 1395,
   & 1133, 1425, 1482, 1407, 1216, 1367, 1475, 1367, 1294, 1177, 1217,
B.2 HadCM3

etc.
Appendix C

Figure Overflow

This Appendix contains overflow figures.
Fig. C.1 Annually averaged surface temperature for (A) PI-CM, (B) Ma-CM, (C) Wu-CM and (D) As-CM. Global mean values (°C) are offset. Pink line indicates the 0 °C isoline.
Fig. C.2 Annually averaged total precipitation for (A) PI-CM, (B) Ma-CM, (C) Wu-CM and (D) As-CM. Global mean values (mm day$^{-1}$) are offset.
Fig. C.3 1D-EBM decomposition for As-CM$^{35}$. Top left: EBM results (grey) vs GCM results (black). Top right: Decomposition of EBM into the emissivity (purple), albedo (green) and heat transport (orange) components of the temperature change. Bottom left: Clear-sky emissivity (dark purple) and albedo (dark green) components of the EBM. Bottom right: Decomposition of EBM into the total clear-sky (blue), cloudy-sky (red) and all-sky (grey) components.
Fig. C.4 1D-EBM decomposition for Ma-CM$^{35}$. Top left: EBM results (grey) vs GCM results (black). Top right: Decomposition of EBM into the emissivity (purple), albedo (green) and heat transport (orange) components of the temperature change. Bottom left: Clear-sky emissivity (dark purple) and albedo (dark green) components of the EBM. Bottom right: Decomposition of EBM into the total clear-sky (blue), cloudy-sky (red) and all-sky (grey) components.
Fig. C.5 1D-EBM decomposition for Wu-CM. Top left: EBM results (grey) vs GCM results (black). Top right: Decomposition of EBM into the emissivity (purple), albedo (green) and heat transport (orange) components of the temperature change. Bottom left: Clear-sky emissivity (dark purple) and albedo (dark green) components of the EBM. Bottom right: Decomposition of EBM into the total clear-sky (blue), cloudy-sky (red) and all-sky (grey) components.
Fig. C.6 Gregory analysis: Regression of top-of-atmosphere radiative balance against surface air temperature change (solid lines) for a transient doubling of CO$_2$ from the As-CM$_{10}^{10}$ (pink) and As-CM$_{35}^{35}$ (blue) cases. Annual averages are indicated by ticks and decadal averages are indicated by filled circles. The regression was performed on the decadal averages.
Fig. C.7 Gregory analysis: Regression of top-of-atmosphere radiative balance against surface air temperature change (solid lines) for a transient doubling of CO$_2$ from the Ma-CM$^{10}$ (pink) and Ma-CM$^{35}$ (blue) cases. Annual averages are indicated by ticks and decadal averages are indicated by filled circles. The regression was performed on the decadal averages.
Fig. C.8 1453 JJA surface air temperature anomaly against a 30 year running-mean for the CESM-LME simulations (1-13), the ensemble mean (M) and the Guillet et al. (2017) MXD reconstruction. 40-90N land surface averaged temperature anomalies are inset right. For each ensemble member (1-13), green (red) anomalies indicates the ensemble response is (not) within the range reported by Guillet et al. (2017).
Fig. C.9 As C.8 for 1454.
Fig. C.10 As C.8 for 1601.
Fig. C.11 As C.8 for 1602.
Fig. C.12 As C.8 for 1816.
Fig. C.13 As C.8 for 1817.
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