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The role of redox processes in determining the iron isotope compositions of minerals, melts and fluids

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Abstract

Stable isotope fractionation is a response to the minimisation of free energy associated with differences in vibrational frequencies during substitution of isotopic masses between two phases. Site properties are dictated by the bonding environment of iron, and influence its ‘force constant’, a descriptor for bond strength. Because iron readily transitions between its ferrous (Fe^{2+}) and ferric (Fe^{3+}) state over the oxygen fugacities ($f\text{O}_2$) of terrestrial magmas, redox processes are presumed to control iron isotope fractionation. In fact, both co-ordination and redox state are key to interpreting iron isotope variations in high-temperature, high-pressure geological systems. Determinations of iron force constants by experimental, theoretical and spectroscopic means in minerals, melts and fluids are reviewed, emphasising the effect of composition in influencing isotopic fractionation. Within this framework, the application of numerical models of partial melting to iron isotope variations in oceanic basalts and subduction-zone (or arc) magmas has shed light on their genesis. The influence of melt composition, mineral mode and fluid exsolution in producing iron isotope fractionation in evolving magmas is explored. Iron isotopic signatures in magmatic rocks are linked to that of their sources, and are influenced by the iron isotopic evolution of subducting slabs and transfer of fluids to the mantle wedge.

Introduction

The existence of iron in three predominant oxidation states in high temperature processes (Fe^0 , Fe^{2+} , Fe^{3+}) provides considerable scope for the fractionation of its isotopes. This property, together with the fact that iron is the often most abundant polyvalent element in natural systems, has made its isotopic composition the most well-studied of the non-traditional systems (see Dauphas et al. 2017 for a recent comprehensive review).

Owing to the role that iron plays in determining the oxygen fugacity ($f\text{O}_2$) of a geological system, variations in its isotopic composition have often been ascribed to changes in its redox state (*e.g.*, Williams et al. 2004; Dauphas et al. 2009). This approach comes at the expense of consideration of the co-ordination of iron, which can have an equally important role in engendering isotopic fractionation (see Young et al. 2015; Sossi and O'Neill, 2017). Furthermore, the oxygen fugacity of a system may have an indirect effect on the iron isotope composition by modifying the stability of different phases and solid solutions (*e.g.*, the precipitation of pyrite from hydrothermal fluids, Wawryk and Foden 2015; or the composition of spinels in solid solution series, Roskosz et al. 2015). Sossi et al. (2016) and Fujii et al. (2014) emphasised the role of co-ordinating ligand field strength (*e.g.*, $-\text{S}$, $-\text{Cl}$, and $-\text{OH}$) in affecting iron isotopic fractionation in minerals and fluids, respectively, by way of changing bond covalence and hence bond stiffness (Hill et al. 2010). Although this effect is limited in terrestrial mafic magmas in which iron is almost exclusively co-ordinated by oxygen, it becomes an important consideration in intermediate- and silicic magmas that can exsolve hydrothermal fluids (see Heimann et al. 2008) and in fluid-loss during mineral breakdown and subsequent dehydration of subducting slabs (see Debret and Sverjensky, 2017).

Deconvolving these controls is not straightforward because they tend to be intertwined; for example, simply varying temperature will affect the relative stability of minerals that precipitate from a fluid and these differing assemblages would be reflective of a different $f\text{O}_2$. Similarly, because the Fe^{3+} cation has an ionic radius smaller than that of its ferrous counterpart, it prefers to partition into smaller, tetrahedrally-co-ordinated sites, whereas Fe^{2+} has a greater preference for octahedral sites in melts and minerals (*e.g.*, Wilke 2005). As such, these compounding effects on the magnitude of stable isotope fractionation require careful theoretical (*e.g.*, Schauble et al. 2001), experimental (*e.g.*, Shahar et al. 2008) and spectroscopic (*e.g.*, Dauphas et al. 2012) approaches in order to tease out the individual contribution of each.

Rather than tackling iron isotopic variation in natural systems by an inverse approach (*i.e.*, through sample measurement and interpretation), in this review, the role of iron oxidation state and co-ordination number in controlling iron isotope fractionation is critically examined from a first-principles perspective (section 2.0.). In order to do so, the methods by which equilibrium iron isotope fractionation factors can be determined, and a compilation of existing data are briefly reviewed (section 3.0.). A

general introduction to the ways in which iron isotope fractionation between minerals, melts and fluids depend on redox processes is presented in section 4.0. Finally, how these determinations have been applied to interpret variation in natural systems, comprising partial melting, magmatic differentiation and fluid transfer in the crust and mantle is detailed (section 5.0.).

2.0. Principles and nomenclature

Ratios of two isotopes, n and d of an element, E , are generally expressed relative to their ratio in a standard in delta notation, which is given by:

$$\delta^{n/d}E = \left(\frac{(^{n/d}E)_{\text{sample}}}{(^{n/d}E)_{\text{standard}}} - 1 \right) \times 1000. (1)$$

The fractionation factor between two phases A and B is:

$$\Delta^{n/d}E_{A-B} = \delta^{n/d}E_A - \delta^{n/d}E_B, (2)$$

and is related to alpha notation by the equivalence:

$$\Delta^{n/d}E_{A-B} = 10^3 \ln ^{n/d}\alpha_{A-B} (3)$$

The exchange of isotopes between two phases, A and B , can be written:

$$^dE_A + ^nE_B = ^dE_B + ^nE_A. (4)$$

The equilibrium distribution of isotopes between the two phases is described by the fractionation factor, α :

$$\alpha^{n/d}E_{A-B} = \frac{(^{n/d}E)_A}{(^{n/d}E)_B}. (5)$$

When the B phase consists of solely dissociated atoms of element E (as in an ideal, monatomic gas), the fractionation factor is given the name beta factor (or β factor) and represents a convenient way of normalising fractionation factors to a '0' value (as there is no energy associated with isotopic substitution in a dissociated monatomic element, E^0). For cases in which the stoichiometric coefficients are unity, equation (5) is equivalent to an equilibrium constant. Therefore, the free energy of the isotopic substitution at equilibrium can be described:

$$\Delta G_{(5)}^0 = -RT \ln \left(\alpha^{n/d}E_{A-B} \right). (6)$$

At the conditions (temperature, T ; pressure, P) relevant to magmatic processes, classical thermodynamic terms cancel and isotopic fractionation is broadly onset by differences in the energy associated with vibrational frequencies in molecules and in condensed phases among one another. In the harmonic approximation, these vibrational energies ($E_{vib,i}$) are quantised into n equally-spaced

levels, where the finite minimum half quantum of energy that arises from the uncertainty in the positions and momenta that a particle, i , could occupy in its ground state ($n = 0$), corresponds to the 'zero-point' energy:

$$E_{vib,i} = \left(n_i + \frac{1}{2}\right)h\nu_i. \quad (7)$$

Here, h is Planck's constant and ν_i is the vibrational frequency. Because, even at 1000 K, as given by the Boltzmann equation, particles occupy vanishingly small amounts of their excited states ($n > 0$), the differences in vibrational frequencies between two isotopes is solely controlled by differences in zero-point energies. For changes in pressure, the relationship between the mode Gruneisen parameter ($\gamma_{G,i}$), the vibrational frequency and molar volume (V) at constant temperature in the quasi-harmonic approximation (Polyakov and Kharlashina 1994), leads to a predictable increase in frequency with pressure due to contracting molar volumes:

$$\left(\frac{\partial \ln \nu_i}{\partial \ln V}\right) = -\gamma_{G,i}. \quad (8)$$

As volume changes induced by isotopic substitutions are typically small, correspondingly large pressure variations are required to significantly influence isotopic fractionation. Frequencies for a simple diatomic molecule (or, approximately, a mean completely symmetric case) are given by:

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \quad (9)$$

Where K is the force constant of vibration and μ the reduced mass. The derivation of the dependence of isotopic fractionation on the vibrational frequencies of molecules was first expressed by Urey (1947) and Bigeleisen and Mayer (1947) in the harmonic approximation in terms of the vibrational isotopic partition function:

$$Q_{vib,i} = \prod_i \frac{e^{\left(-\frac{h\nu_i}{2kT}\right)}}{1 - e^{\left(-\frac{h\nu_i}{kT}\right)}}. \quad (10)$$

Equation (10) is the product across all vibrational frequencies ν_i for a given isotope in a given phase, where k is Boltzmann's constant and T absolute temperature. Ratios of vibrational partition functions may be equated to fractionation factors in a simplified manner (Urey 1947; Bigeleisen and Mayer 1947):

$$10^3 \ln \alpha_{A-B}^n = \Delta^n E_{A-B} = \frac{10^3 3N}{96} \left(\frac{h}{\pi kT}\right)^2 \left(\frac{1}{m_d} - \frac{1}{m_n}\right) [K_A - K_B]. \quad (11)$$

Here, K_A and K_B refer to the iron force constants in phases A and B, respectively, m_d and m_n the atomic masses of the denominator (d) and numerator (n) isotopes, respectively and the $3N$ term (Avogadro's Number) comes from summation over all vibrations in condensed matter (Bigeleisen and Mayer, 1947).

Equation (11) states that the isotopic fractionation at the high temperature limit ($T \rightarrow \infty$) will approach zero. For a particular element and isotope ratio, most of the equation reduces to a constant term, yielding, for $^{57/54}\text{Fe}$:

$$\Delta^{57}_{54}\text{Fe}_{A-B} = 4284 \frac{[K_A - K_B]}{T^2}. \quad (12)$$

Equally, for $^{56/54}\text{Fe}$;

$$\Delta^{56}_{54}\text{Fe}_{A-B} = 2904 \frac{[K_A - K_B]}{T^2}. \quad (13)$$

In order to minimise the higher free energy of bonds with higher vibrational frequencies (eq. 9), the heavier isotope is favoured over the lighter one.

In general, higher force constants occur in bonding environments with (see Schauble 2004; Young et al. 2015; Sossi et al. 2016):

- i) higher oxidation state
- ii) lower co-ordination number
- iii) covalent bonds
- iv) low spin vs. high spin (for Fe and other transition metals)

To a first order, the first three controls may be estimated empirically to derive values of K (see Young et al. 2015; Sossi and O'Neill, 2017), considering that the interactions between cations and anions in a lattice site can be described quantitatively with ionic interactions. Variations of K then arise due to a change in the charge and co-ordination of the cation, which are described by the bond valence principle (Pauling 1929):

$$\bar{s} = \frac{\bar{Z}}{\bar{C}_N}. \quad (14)$$

In this equation, $\bar{s}$ is the bond valence, $\bar{Z}$ is the average charge on the cation, and $\bar{C}_N$ the mean co-ordination number in the mineral. The force constant is then approximated by solving the Born-Landé equation, after Young et al. (2009), which describes the elastic energy of an ionic lattice:

$$K_{f,Fe,O} = - \frac{\bar{s}_{Fe}\bar{s}_O q^2 (1-B)}{4\pi\epsilon_0 r^3}, \quad (15)$$

where q is the charge on an electron (1.602×10^{-19} C), B is the Born exponent, dependent on lattice compressibility (taken to be 12 for minerals), $1/4\pi\epsilon_0$ is Coulomb's constant ($9 \times 10^9 \text{ Nm}^2/\text{C}^2$) and r is the bond length in metres. More quantitative methods for estimating for K are described in section 3.0.

3.0. Methods for the calibration of iron isotope fractionation factors

The quantity that drives isotope fractionation, the value of the force constant (*cf.* eq. 15), may be calibrated *via* a variety of methods. These include calculating the structure of the phase (theoretical approaches) or by measuring the force constant (spectroscopic methods). Alternatively, methods that involve measurement of the isotopic composition of two or more phases in equilibrium with one another to determine fractionation factors (experimental approaches) are also widely used. All three are described briefly below.

3.1. Theoretical

Ab-initio simulations are the most common way of determining vibrational frequencies, typically with density functional theory (DFT; *e.g.*, Schauble, 2004), one such class of these computations. DFT models the electronic structure and density of electrons in individual atoms to find the most probable equilibrium ground state electronic configuration. Once this state is defined for a system consisting of x number of atoms, the interatomic distances between them define a molecular structure from which the force constants are calculated. The interested reader is referred to Blanchard and Dauphas (this volume) for a fuller description of the method. A simplified calculation based on the bond valence principle can also yield accurate force constants (eq. 15; Young et al., 2015, 2009; Sossi and O'Neill 2017), though it uses the atomic structure of the phase as an input parameter.

3.2. Experimental

Here, the phases of interest are synthesised by subjecting a known composition to a specific pressure and temperature. The isotopic composition of one of the resultant phases is measured with respect to that of a second phase, yielding the fractionation factor, α^n_{A-B} . That the two phases grown experimentally are in equilibrium with one another may be determined by two different means: (i) chemical and isotopic equilibrium is demonstrated to have been obtained between the phases of interest (*e.g.*, by time-series and reversal experiments) and (ii) by the three isotope method (Shahar et al. 2008). Here, a series of experiments that approach equilibrium are performed, and the true equilibrium composition is calculated by extrapolation of the experiments to the known bulk composition. Considerations in designing and interpreting the results of experimentally-determined isotopic fractionation are summarised in Shahar et al. (2017) and in Bourdon et al. (2018).

3.3. Spectroscopic

Measurement of force constants relies upon the excitation of the vibrational modes of motion of the mineral lattice by incoming X-rays which collide with a ^{57}Fe nucleus (the only iron isotope sensitive to this effect). Such information can be determined by Mössbauer spectroscopy (Polyakov and Mineev 2000) or by Nuclear-Inelastic Resonant X-Ray Scattering, NRIXS (Polyakov et al. 2007; Dauphas et al. 2012). The latter method is preferred because the characteristics of the impacting photons can be

tuned and scanned for purpose at a synchrotron. Both of these methods are dealt with in more detail in Blanchard and Dauphas (this volume).

4.0. Fundamental controls on isotopic fractionation between minerals, melts and fluids

4.1. Minerals

The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in minerals is controlled by the stoichiometry of the phase. Some series display complete solid solution between compositional end-members, and common igneous examples include:

- i) Magnetite-Ulvöspinel: $\text{IVFe}^{3+}\text{VI}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4 - \text{IVFe}^{2+}\text{VI}(\text{Fe}^{2+}\text{Ti}^{4+})\text{O}_4$

Magnetite has a complete solid solution with ulvöspinel, an exchange that forms the basis for the Fe-Ti exchange oxybarometer of Buddington and Lindsley (1964) (see also Arató and Audétat, this volume). Both are spinel group minerals *sensu lato*, with the general formula AB_2O_4 , where, if the B cations occupy both the tetrahedral and octahedral sites, the structure is said to be ‘inverse’. Magnetite is a 2-3 spinel (one 2+ cation with two 3+) and has an inverse cation distribution at room temperatures, though it tends to the random distribution at magmatic temperatures around 1000°C (Wu and Mason 1981). Ulvöspinel, a 4-2 spinel, also has an inverse structure with Ti exclusively occupying the octahedral site while ferrous iron is both VI- and IV-fold co-ordinated. Intermediate compositions have site distributions that are temperature-dependent and are controlled by electron exchange between the two valence states of Fe, with the random distribution being favoured at higher temperature (O’Neill and Navrotsky 1984; Wechsler et al. 1984; Bosi et al. 2009).

Shahar et al. (2008) determined the fractionation factor between magnetite and fayalite experimentally in a piston cylinder to be $\Delta^{57}\text{Fe}_{\text{mag-fay}} = +0.30 \times 10^6/\text{T}^2$, reflecting the preference of heavier iron for the stronger, Fe^{3+} -bearing IV- and VI-fold sites of magnetite relative to the exclusively octahedral ferrous iron in fayalite. Sossi and O’Neill (2017) measured the fractionation factor between magnetite and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ fluid in piston cylinder experiments in Ag capsules at 800°C. They estimated the magnetite-ulvöspinel fractionation factor from fits to their experimental data using bond valence theory, giving $\Delta^{57}\text{Fe}_{\text{mag-usp}} = +0.32 \times 10^6/\text{T}^2$ (Fig. 1), very similar to that measured between magnetite and fayalite. There is considerable disagreement as to the force constant of Fe bonds in magnetite; Polyakov et al. (2007) report a value of 228 N/m calculated from NRIXS spectra, similar to that given thereafter by Dauphas et al. (2012), 230 N/m, using the same technique. Roskosz et al. (2015) report a higher value of 264 N/m using NRIXS via extrapolation of trends based on solid solutions of Mg-Fe-Al-Cr spinels, and they note that discrepancies may be due to the quality of the spectra at high energies and the energy range over which spectra are collected. Importantly, though the absolute force constants may vary, the magnitude of mineral-mineral fractionation factors in these studies are in good agreement.

- ii) Ilmenite-Hematite: $\text{VIFe}^{2+}\text{TiO}_3 - \text{VIFe}^{3+}_2\text{O}_3$

Iron passes from entirely ferrous to entirely ferric along the solid solution series, whilst remaining in octahedral co-ordination (*e.g.*, Wechsler and Prewitt 1984). Ilmenite shows limited solid solution with hematite at the fO_2 s typical of igneous systems, where X_{Ilm} varies from 0.98 at 2 log units below the Fayalite-Magnetite-Quartz (FMQ) buffer to 0.90 at $\Delta\text{FMQ}+1$ during crystallisation of a dry tholeiitic ferrobasalt (see Toplis and Carroll 1995).

Determinations of force constants in hematite via Mössbauer spectroscopy (Polyakov and Mineev 2000) *ab-initio* calculations (Blanchard et al. 2009) and NRIXS (Polyakov et al. 2007; Dauphas et al. 2012) are all in good agreement, and yield mean Fe-O force constants of between 235 and 252 N/m. Note that the spinel trend measured in Roskosz et al. (2015) yields higher values for the purely ferric iron-bearing endmembers, 303 ± 6 N/m ($n = 3$). Polyakov and Mineev (2000) report a force constant for ilmenite of 90 N/m, and hence a fractionation factor of $\Delta^{57/54}\text{Fe}_{\text{hem-ilmenite}} = 4284(235 - 90)/T^2 = 0.61 \times 10^6/T^2$. Sossi and O'Neill (2017) measured the isotopic fractionation between ilmenite and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ fluid at 800 °C, and estimated the ilmenite-hematite fractionation factor from fits to their experimental data using bond valence theory to give $0.58 \times 10^6/T^2$ (Fig. 1). Both fractionation factors are in very good agreement and highlight the importance of mineral composition within a solid solution in determining the isotopic fractionation factor.

Ferrous iron is dodecahedrally-co-ordinated by oxygen in almandine garnet, a rarity among Fe-bearing minerals, in which it typically occupies VI-fold sites. Ferric iron in andradite garnet is in octahedral co-ordination.

Sossi and O'Neill (2017) reported fractionation factors between almandine and other Fe-bearing minerals and showed that its iron isotope composition was invariably lighter than all other phases investigated (including FeCl_2 fluid) by virtue of its longer Fe-O bonds (average of 2.37 Å). They calculated a force constant of 147 N/m for almandine (Fig. 1). No measurements of force constants or fractionation factors involving andradite garnet are presently available. However, natural andradite-bearing garnets show heavier iron isotope compositions relative to their ferrous iron-bearing counterparts (Urosevic et al. 2018) while garnet is almost always the isotopically lightest phase in eclogitic rocks (Williams et al. 2009; Huang et al. 2019), reflecting their generally low $\text{Fe}^{3+}/\Sigma\text{Fe}$ in mafic and ultramafic rocks (<0.1 ; Williams et al. 2009; Berry et al. 2010).

The coupled substitution $\text{NaFe}^{3+}(\text{CaFe}^{2+})^{-1}$ across the aegirine (acmite)-hedenbergite series involves a change in ferric to ferrous iron in the same octahedral crystallographic site (the M1 site). This transition

is associated with an increase in mean Fe-O bond length from 2.05 Å in aegirine to 2.15 Å in hedenbergite at igneous temperatures of $\approx 1000^\circ\text{C}$ (see Cameron et al. 1973).

Both end-members of the series were analysed by Mössbauer spectroscopy and force constants calculated according to the second-order Doppler shift by Polyakov and Mineev (2000), yielding N/m for aegirine and 112 N/m for hedenbergite, the latter being similar to other $^{57}\text{Fe}^{2+}$ -bearing silicates determined in the same study (olivine, diopside and enstatite; Polyakov and Mineev 2000). More importantly, the fractionation factor between the two is then $\Delta^{57/54}\text{Fe}_{\text{aeg-hed}} = 0.68 \times 10^6/T^2$, similar in magnitude to that for the exchange of octahedral Fe^{2+} and Fe^{3+} in the ilmenite-hematite series (Fig. 1).

Riebeckite-group amphiboles are typically found in alkaline magmatic rocks (*cf.* Schoenberg et al. 2009). They can contain between 100% and 40% of their Fe as Fe^{3+} , in which ferric iron is ordered on the M2 site and small amounts on the M1 (Hawthorne 1978) whereas glaucophane hosts ferrous iron exclusively, and is distributed across its M1 and M3 sites.

From Mössbauer spectroscopy data, Schoenberg et al. (2009) calculated the beta factors for two riebeckitic amphiboles with $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.46 and 0.44, and found $10^3\ln\beta^{57/54}\text{Fe}_{\text{rbk}} = 0.90$ and $0.74 \times 10^6/T^2$ respectively, which correspond to force constants of 214 and 175 N/m.

Spinel-group minerals are ubiquitous in terrestrial mafic and ultramafic lithologies (*e.g.*, Barnes and Roeder 2001) and show extensive solid solutions with first-row transition metals representing the A and B cations (O'Neill and Navrotsky 1984). Natural spinels tend to exhibit Cr-Al or Fe^{3+} -Cr exchange, with a paucity of Fe^{3+} -Al spinels caused by positive deviations from ideality and hence a solvus in the binary system (*e.g.*, Petric et al. 1981; Nell et al. 1989). Chromium, owing to its high octahedral site preference energy ($6/5\Delta_{\text{oct}}$)¹, is strongly ordered onto the octahedral site, conferring a normal cation distribution on the spinel structure, meaning Fe^{2+} is found exclusively on the tetrahedral site. Similarly, Fe^{3+} is displaced from the octahedral site in magnetite to the tetrahedral site with increasing ferrochromite component (O'Neill and Navrotsky 1984).

Spinel group minerals are generally found in association with olivine, for example in mantle peridotites and in komatiitic magmas, and are used together with orthopyroxene to determine oxygen fugacities (*e.g.*, Woodland et al. 1992). In reciprocal solid solution with Fe-Mg olivine, Fe^{2+} substitution is favoured

¹ In crystal field theory, Δ_{oct} relates to the energy difference between the *d*-shell electrons that are split into the e_g and t_{2g} orbitals. For an octahedral field, t_{2g} orbitals are stabilised with respect to the barycentre by $2/5\Delta_{\text{oct}}$ and e_g by $-3/5\Delta_{\text{oct}}$. Thus, the minimum Δ_{oct} is 0 (*e.g.*, Zn^{2+} , Cu^+) and the maximum is $6/5\Delta_{\text{oct}}$ (*e.g.*, V^{2+} , Cr^{3+}).

such that $\text{Cr}/(\text{Cr}+\text{Al})$ increases with increasing $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg})$ (e.g., Poustovetov and Roeder 2000). At high Fe^{3+} contents, the spinel structure inverts and extensive exchange with Ti occurs as discussed above.

In a comprehensive study of the effect of solid solution on the mean strength of the Fe-O bonds, Roskosz et al. (2015) determined the force constants for eight spinel-group minerals. They focused largely on Mg-Al-Fe spinels with variable $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, from 0 to 1, and one magnesiochromite composition. Their results show that the Fe-O force constant is linearly correlated with $\text{Fe}^{3+}/\Sigma\text{Fe}$ with only subsidiary influence from other structural parameters, ranging from 207 ± 14 in Fe^{2+} -bearing spinels to 303 ± 6 N/m ($n = 3$) for solely ferric iron-bearing spinels (Fig. 2). These values compare with Fe-O force constants of $197 - 165$ N/m for $^{\text{VI}}\text{Fe}^{2+}$ -bearing silicates (average = 181 ± 15 N/m, $n = 4$), namely olivine and orthopyroxene (Roskosz et al. 2015), and hence $\Delta^{57/54}\text{Fe}_{\text{sp(FeII)}-\text{sil(FeII)}} = 0.11 \pm 0.08 \times 10^6/T^2$. In attempting to characterise the influence of co-ordination environment on iron isotopic fractionation, Sossi and O'Neill (2017) determined the fractionation factor between two spinels; hercynite (FeAl_2O_4) and chromite (FeCr_2O_4) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ fluid at 800°C . They calculated force constants of 238 N/m and 225 N/m, respectively, higher than that of fayalite (178 N/m), yielding $\Delta^{57/54}\text{Fe}_{\text{sp(FeII)}-\text{sil(FeII)}} = 0.21 \times 10^6/T^2$, reflecting the influence of IV-fold vs. VI-fold co-ordination of Fe in spinel and olivine, respectively (Fig. 1). Compilation of spinel-olivine fractionation factors measured in peridotitic rocks show generally positive $\Delta^{57/54}\text{Fe}_{\text{sp-ol}}$ at low Cr# (molar $\text{Cr}/(\text{Cr}+\text{Al}+\text{Fe}^{3+})$) compared with negligible or slightly negative $\Delta^{57/54}\text{Fe}_{\text{sp-ol}}$ at high Cr# (Zhang et al. 2019), in qualitative agreement with lowering of the force constant in chromite with respect to hercynite (Sossi and O'Neill, 2017) though a change in sign is not predicted.

vii) Bridgmanite – Ferropericlasite $^{\text{VIII}}(\text{Fe}^{2+}, \text{Mg}^{2+}, \text{Fe}^{3+})^{\text{VI}}(\text{Fe}^{3+}, \text{Al}^{3+}, \text{Si}^{4+})\text{O}_3 - ^{\text{VI}}\text{Fe}_x(\text{Mg}_{1-x})\text{O}$

Though not a solid solution, it is instructive to assess the body of work for these two minerals given their importance for controlling iron isotopic fractionation in the Earth's lower mantle. Iron is present primarily as ferrous iron in the octahedral site of ferropericlasite (cubic) and as Fe^{2+} and Fe^{3+} in the dodecahedral A and octahedral B sites of bridgmanite (orthorhombic). The substitution of ferric iron into bridgmanite is strongly facilitated through its coupled substitution with Al^{3+} (McCammon 1997), which forces Fe^{3+} onto the dodecahedral site by the mechanism $^{\text{VIII}}(\text{Fe}^{2+}, \text{Mg}^{2+})^{\text{VI}}\text{Si}^{4+} \leftrightarrow ^{\text{VIII}}\text{Fe}^{3+}\text{VI}\text{Al}^{3+}$ (Vanpeteghem et al. 2006).

Further, the variety of iron spin transitions in lower mantle minerals leads to additional electronic configurations that modify $\langle\text{Fe-O}\rangle$ bond lengths and therefore influence isotopic fractionation. At low pressures, the crystal field splitting energy (see footnote 1) is lower than that required to pair electrons, meaning iron exists in its high spin (HS) configuration. However, compression at lower mantle pressures reduces the interatomic distance between Fe and O, destabilising the e_g orbitals and making electron spin pairing energetically more favourable, resulting in a low spin (LS) configuration. This

effect is most prevalent in the octahedral sites of ferropericlasite and bridgmanite for Fe^{2+} and Fe^{3+} respectively (see Lin et al. 2013 for a review). Along a mantle adiabat, $^{\text{VI}}\text{Fe}^{2+}$ in ferropericlasite begins the transition from HS to LS near 60 GPa (Badro et al. 2003; Wentzcovitch et al. 2009) and is complete by 120 GPa. The transformation is displaced to lower pressures for $^{\text{VI}}\text{Fe}^{3+}$ in bridgmanite, occurring over a range from 30 – 70 GPa (Jackson et al. 2005a; Fujino et al. 2012), while $^{\text{VIII}}\text{Fe}^{2+}$ experiences a spin transition only under very high pressures (> 120 GPa; Badro et al. 2004; McCammon et al. 2010). Rustad and Yin (2009), using DFT simulations, recorded a systematic increase in force constant for ferropericlasite ($10^3 \ln \beta^{57/54}\text{Fe}_{\text{fp}} = 0.145$ at 4000 K for low spin at 120 GPa and 0.098 for high spin), corresponding to force constants of ≈ 540 N/m and ≈ 365 N/m, respectively. By contrast, no such shift was observed for purely Fe^{2+} -bearing bridgmanite due to the asymmetric distortion of the iron-oxygen bonds, and has $10^3 \ln \beta^{57/54}\text{Fe}_{\text{bg}}$ identical to that of ferropericlasite in its LS state. Force constants derived from Polyakov (2009) for $\text{Fe}_{0.25}\text{Mg}_{0.75}\text{O}$ ($P = 0 - 109$ GPa) and from (Shahar et al. 2016) for FeO ($P = 5 - 39$ GPa) using NRIXS yield very similar pressure-dependencies; $K_{\text{Fe-O}} = (2.39 \pm 0.17)P$ (GPa) + 164 ± 10 N/m and $(2.56 \pm 0.16)P$ (GPa) + 169 ± 4 N/m, respectively. If extrapolated linearly to 120 GPa, these calibrations yield $K_{\text{Fe-O}}$ between 450 and 475 N/m, lower than that calculated by Rustad and Yin (2009) for LS ferropericlasite. Williams et al. (2012) reported the first direct measurement of the iron isotope composition of experimentally-synthesised Al-bearing (≈ 0.23 per formula unit, pfu) bridgmanite, with $\text{Fe}^{3+}/\Sigma\text{Fe} \sim 0.37$ in equilibrium with iron metal at 24 GPa and 1850 °C. Their preferred $\Delta^{57/54}\text{Fe}_{\text{bg-met}}$ is +1.35 ‰, whose sense is in accord with recent NRIXS determinations of Yang et al. (2019), though the magnitude is much larger ($\Delta^{57/54}\text{Fe}_{\text{bg-met}}$ by NRIXS is +0.2 ‰ at 2000 K and 30 GPa). These authors collected an extensive set of *in-situ* high-pressure data for ferropericlasite ($\text{Fe}_{0.25}\text{Mg}_{0.75}\text{O}$) and bridgmanites (both Al-free and Al-bearing at 0.11 pfu). Bridgmanite reaches a maximum $K_{\text{Fe-O}}$ of 449 ± 46 N/m (46 GPa), and is isotopically heavier than ferropericlasite below 60 GPa, after which the latter transitions to its LS state that produces a drastic increase in force constant with a slope of $dK_{\text{Fe-O}}/dP$ of ~ 3 N/m/GPa, reaching 626 ± 31 N/m at 94 GPa. Above 60 GPa, the force constant of bridgmanite is unchanging around 335 ± 15 N/m up to 104 GPa, independent of $\text{Fe}^{3+}/\Sigma\text{Fe}$ and Al content.

4.2. Melts

Because of the lack of long-range order in silicate melts (or fluids), the variation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ is unbound by stoichiometry and can vary freely. The ratio of ferrous to ferric iron in silicate liquids can be understood quantitatively by considering the homogeneous equilibrium:

The equilibrium constant of this reaction is:

$$K^* = \frac{a(Fe^{2+}O)f(O_2)^{1/4}}{a(Fe^{3+}O_{1.5})}. \quad (17)$$

Where a refers to the activity of the iron oxide component dissolved in the liquid and K^* accounts for their possible deviations from the ideal case (K). Written in terms of $Fe^{3+}/\Sigma Fe$:

$$\frac{XFe^{3+}O_{1.5}}{\Sigma Fe} = \frac{1}{1 + 10^{\left(-\frac{1}{4}\log f(O_2) + \log K - \log \frac{\gamma FeO}{\gamma FeO_{1.5}}\right)}}. \quad (18)$$

The γFeO and $\gamma FeO_{1.5}$ refer to the activity coefficients of these species in the silicate melt referenced to the standard states of the pure liquid oxides at the conditions of interest. Using thermodynamic data for reaction (16), Jayasuriya et al. (2004) calculated values of $\gamma FeO = 1.37$ and $\gamma FeO_{1.5} = 1.08 \pm 0.33$ based on Fe^{3+}/Fe^{2+} ratios determined by Mössbauer spectroscopy. These determinations are valid at infinite dilution (which they inferred at 1 wt. % FeO^T) in an Anorthite-Diopside eutectic composition at 1400 °C and 1 bar, meaning that iron dissolution in silicate melts is close to ideal. Furthermore, their data showed that $\log(Fe^{3+}/Fe^{2+})$ is proportional to $(fO_2)^{0.245}$, within uncertainty of the theoretical dependence expected from eq. (16), suggestive of no interactions between Fe^{2+} - Fe^{3+} in silicate liquids as a function of fO_2 . This hypothesis, that $\frac{\gamma FeO}{\gamma FeO_{1.5}}$ is independent of fO_2 for a fixed composition, was later confirmed by Berry et al. (2018) for a natural MORB composition with higher quantities of iron (10 wt. % FeO^T).

By contrast, $\frac{\gamma FeO}{\gamma FeO_{1.5}}$ is readily affected by silicate composition. Dickenson and Hess (1986) show that potassium stabilises tetrahedrally-co-ordinated ferric iron by charge balance. Recent work by Borisov et al. (2017) illustrates that this stabilisation occurs inversely proportional to their bond valence in silicate melts (e.g. Farges et al. 2004) whereas Al competes with Fe^{3+} for tetrahedral sites. This effect is manifest in the higher $Fe^{3+}/\Sigma Fe$ in $(Na,K)_2Si_3O_7$ silicate melts (Knipping et al. 2015) relative to alkali-poor MORB compositions (Berry et al. 2018) at the same fO_2 .

The effect of composition on $Fe^{3+}/\Sigma Fe$ is evident in the study of Dauphas et al. (2014), the first to combine quantification of X-Ray Absorption Near-Edge Structure (XANES) spectra to determine the redox ratio of glasses with NRIXS spectra to calculate Fe-O force constants. They analysed glass of four different compositions corresponding to basaltic, andesitic, dacitic and rhyolitic liquids melted at 1550°C and 1 bar. Notably, the rhyolitic glass has relatively higher $Fe^{3+}/\Sigma Fe$ than the more mafic compositions at the same fO_2 . While tempting to correlate this shift with silica content, Borisov and McCammon (2010) show that increasing silica results in decreases in $Fe^{3+}/\Sigma Fe$ up to 60% SiO_2 , all else being equal, suggestive instead of the role of alkali metals in stabilising tetrahedrally-co-ordinated Fe^{3+} .

Dauphas et al. (2014) report an increase in the Fe-O force constant from 199 ± 15 N/m in Fe^{2+} -bearing mafic-intermediate composition, which they extrapolate to 351 ± 29 N/m for $Fe^{3+}/\Sigma Fe = 1$ (Fig. 3).

Independently of fO_2 , the rhyolitic composition is displaced to higher Fe-O force constants for a given $Fe^{3+}/\sum Fe$, 240 ± 13 N/m ($Fe^{3+}/\sum Fe = 0$) and 385 ± 24 ($Fe^{3+}/\sum Fe = 1$). This distinction therefore likely reflects the greater proportion of IV-fold co-ordinated Fe^{3+} in rhyolitic compositions relative to more basic melts. Although ferrous and ferric iron in basaltic glasses have co-ordination numbers close to V (though this may be through a combination of IV- and VI-fold rather than V-fold itself), ferric iron tends to be in slightly lower co-ordination environments than does ferrous iron (Wilke et al. 2007; Knipping et al. 2015). In both cases, the addition of alkalis stabilises tetrahedrally co-ordinated iron, the effect being more pronounced for Fe^{3+} (Jackson et al. 2005b; Knipping et al. 2015; Borisov et al. 2017), again inversely proportional to their bond valence ($Rb^+ > K^+ > Na^+ > Li^+$).

The relative compressibility of oxide components in silicate melts leads to structural changes as a function of pressure (*e.g.*, Kress and Carmichael 1991) that can affect isotopic fractionation (section 2.0). At equilibrium, differences in molar volumes ($\bar{V}$) of the FeO and $FeO_{1.5}$ components with pressure (P) impact upon their stability, with the resultant change in Gibbs Free Energy of formation (ΔG°) described by:

$$\Delta G_{(15), T, P}^\circ = \Delta G_{(15), T, 1 \text{ bar}}^\circ + \int_{1 \text{ bar}}^P \Delta \bar{V}_{T, P} dP, (19)$$

and, with the relation $\Delta G = -RT \ln K$, the ferric-ferrous ratio is given by:

$$\ln \left(\frac{X_{FeO_{1.5}}}{X_{FeO}} \right) = - \left(\frac{\Delta G_{(15), T, 1 \text{ bar}}^\circ + \int_{1 \text{ bar}}^P \Delta \bar{V}_{T, P} dP}{RT} \right) - \ln \left(\frac{\gamma_{FeO_{1.5}}}{\gamma_{FeO}} \right) + \frac{1}{4} \ln fO_2. (20)$$

The volume change for eq. (16) at 1 bar is negative, such that FeO would be expected to be stabilised with respect to $FeO_{1.5}$ with increasing pressure at constant relative fO_2 , assuming no change in their molar volumes. Calculations of iron redox state by Mössbauer and XANES spectra for iron in andesitic melts at the Ru-RuO₂ oxygen buffer as a function of pressure bear out this prediction, and show increasing Fe^{2+}/Fe^{3+} ratios up to 7 GPa (O'Neill et al. 2006; Zhang et al. 2017). This tendency was modelled using a Murnaghan equation of state with molar volumes from Lange and Carmichael (1987) and bulk moduli of 30.3 GPa and 16.6 GPa for FeO and $FeO_{1.5}$, respectively (Kress and Carmichael, 1991). Zhang et al. (2017) recognised a densification of the FeO component by a progressive shift in average iron co-ordination number from 5.5 to 6 over this pressure range, whereas that of $FeO_{1.5}$ remained constant at ≈ 5.3 . However, higher pressure experiments show that the trend of increasing Fe^{2+}/Fe^{3+} is reversed between 7 and 15 GPa (Armstrong et al. 2017) with Fe^{2+}/Fe^{3+} decreasing thereafter up to 23 GPa, suggesting ferric iron also transitions to higher co-ordination numbers above 15 GPa.

Although co-ordination number increases with pressure, the associated bond stiffening (recalling the inverse proportionality of volume and vibrational frequency, eq. (8)) results in considerable increases in $\langle Fe-O \rangle$ force constants in silicate glasses (Liu et al. 2017). At ambient pressure, K_{Fe-O} in Fe^{3+} -free basaltic glass is ≈ 190 N/m (Fig. 3; Dauphas et al. 2014) whereas it reaches 355 N/m at 65.4 GPa (Fig.

4; Liu et al. 2017); equivalent to the effect of quantitative substitution of ferrous for ferric iron at 1 bar. The determined gradient, dK_{Fe-O}/dP , shows two regimes, 0 – 25.8 GPa; $dK_{Fe-O}/dP = 1.22 \pm 0.25$ N/m/GPa and 35.1 – 65.4 GPa; $dK_{Fe-O}/dP = 1.81 \pm 0.10$ N/m/GPa, with a discontinuous jump between them (Fig. 4). Therefore, despite evidence for a gradual increase in FeO co-ordination number in silicate glasses under conditions that are relevant to partial melting in the upper mantle (< 7 GPa, Zhang et al. 2017), this structural change induces little- or no increase in K_{Fe-O} . By contrast, the step-wise increase in K_{Fe-O} from ≈ 220 N/m to ≈ 300 N/m between 25 – 35 GPa coincides with pronounced densification in basaltic melts, inferred to be caused by the passage of Si from tetrahedral to octahedral co-ordination (Sanloup et al. 2013). Therefore, bulk structural changes in the melt may be more effective in modifying Fe-O force constants than are changes in local bonding environment.

4.3. Fluids

The compositional parameter space for fluids is larger than that for silicate melts, in which most components are dissolved as oxide species. By contrast, metals can be complexed by Cl-, C-, S- and OH ligands in geologically-relevant fluids (see Burnham 1979; Candela 1989; Manning 2004; Richards 2011 for summaries of fluid compositions in arc magmatic and hydrothermal systems). Magmatic fluids are predominantly aqueous, with dissolved components ranging from 17 – 83% (Manning 2004), which are broadly correlative with the P - T conditions at which the fluid equilibrated. Low temperature fluids have metal-bearing species dominated by alkali-chloride complexes (NaCl, KCl), in addition to HCl and SO₂ as other major volatiles (*e.g.*, Richards 2011). The dissolution of Si becomes important at higher temperatures as the composition of the fluid-rock system approaches supercritical behaviour, which occurs at 1.5 GPa and 700°C in the system albite-H₂O (Manning, 2004).

Iron, like the alkali metals, likely dissolves as Cl-bearing species in hydrothermal fluids, as evidenced by its strong solubility in Cl-rich fluids (*e.g.*, Kwak et al. 1986). It is expected to be predominantly ferrous; the stability of ferric chloride species are much lower (Testemale et al. 2009; Saunier et al. 2011) except during dissolution under very oxidising conditions (*e.g.*, with hematite; Brugger et al. 2016). Spectroscopic techniques that have been employed to probe speciation in acidic chloride solutions for a range of Cl molalities from 0.5 to 12 up to 450 °C suggest the presence of higher-order complexes, with the predominance of FeCl₄²⁻ as the dominant Fe-bearing species (Testemale et al. 2009). By contrast, speciation of Fe in fluids at relevant P - T conditions (up to 650 °C, 2 kbar; Chou and Eugster 1977; Boctor et al. 1980; Fein et al. 1992) is largely informed by the stoichiometry of mineral dissolution reactions. Iron solubility in fluids is expected to be influenced by temperature, pressure, pH and by the presence of chlorine. The data of Chou and Eugster (1977) on magnetite solubility in HCl solutions conform to a stoichiometry with FeCl₂ as the stable fluid species, whose solubility is given as $\log m(\text{FeCl}_2) = 6887/T(\text{K}) - 8.44^2$. Ding & Seyfried (1992) experiments showed that (FeCl)⁺ and

² m refers to the molality, in mol/kg; whereas mmolal refers to mmol/kg

particularly FeCl_2 are the dominant Fe species in aqueous fluids at the hematite-magnetite buffer and up to 450 °C and 0.3 to 0.5 kbar. The solubility of Fe increases drastically with increasing NaCl concentrations, passing from 0.369 mmolal of Fe at 350°C and 29.1 mmolal of Na to 1.285 mmolal of Fe at 500°C and 1233 mmolal of Na (see also Fig. 12 in Testemale et al., 2009). These authors also observed FeCl_2 as the dominant species with increasing temperatures. Indeed, thermodynamic calculations at high pressure and temperature (630-660 °C and 2 GPa) show that Fe is mobile in slab-derived fluids as FeCl_2 during antigorite breakdown (Debret & Sverjensky, 2017). It should be noted that the complexation of Fe^{2+} with sulfate, carbonate or silica was not considered in these thermodynamic models due to the absence of thermodynamic data; although this is not proof that these species do not exist. Furthermore, even though Fe^{3+} -complexes were included, they were found to be unimportant at the investigated conditions.

These studies all point to the predominance of FeCl_2 , particularly at high temperatures. Nevertheless, there is a dearth of experimental studies at conditions relevant to that of subduction zone magmatism or high-temperature ore-forming hydrothermal fluids (> 800 °C). One of the few are the magnetite solubility experiments of Simon et al. (2004) who also presumed FeCl_2 as the stable species and measured up to 7.3 wt. % iron in the fluid phase at high NaCl molalities. Sanchez-Valle et al. (2017) recorded XANES spectra of chlorinated-aqueous fluids equilibrated with Fe-bearing minerals in a diamond anvil cell at 2.5 GPa and 800°C. Their results imply the transport of Fe with $(\text{Fe}^{2+}\text{Cl}_x)^{2-x}$ stoichiometries, with the stability of Fe^{3+} -bearing chloride species decreasing with increasing temperature.

In a series of studies, Hill and co-workers calculated and measured experimentally the isotopic fractionation between a variety of iron chlor-aquo species at ambient temperatures (Hill and Schauble 2008; Hill et al. 2009, 2010). These studies show several trends at 298 K:

- 1) The iron isotope fractionation factor and calculated force constants decrease with increasing chlorinity. Specifically, $10^3 \ln \beta^{56/54}\text{Fe}(\text{FeCl}_x(\text{H}_2\text{O})_{6-x})^{3-x}$ is 9.41, 8.54, 8.10, 7.13 and 7.14 for $x = 0, 1, 2, 3$ and 4, respectively.
- 2) In the equivalent ferrous-iron bearing system, the species have $10^3 \ln \beta^{56/54}\text{Fe}(\text{FeCl}_x(\text{H}_2\text{O})_{6-x})^{2-x}$ of 6.39, 5.98, and 5.91 for $x = 0, 1$, and 2, respectively.
- 3) Regardless of the basis set used for the *ab-initio* calculations, the fractionation factor $10^3 \ln \alpha_{3+, 2+} \approx 3\text{‰}$.

Fujii et al. (2014) calculated β factors for a host of aqueous, ferric- and ferrous iron-bearing species (Fig. 5). Though there are minor differences in $10^3 \ln \beta^{56/54}\text{Fe}$ among species of a given Fe oxidation state, these differences become small (<0.3 ‰) by 573 K. Invariably, species with chloride ligands are the lightest among other species studied, particularly compared to PO_4^{3-} , OH^- and SO_4^{2-} which are stronger-field ligands and therefore concentrate the heavier isotopes (Fig. 5). A similar order can be

observed among Fe^{3+} -bearing compounds (Fig. 5). As per the study of Hill et al. (2010), the isotopic fractionation between Fe^{2+} and Fe^{3+} -bearing species is most marked. At 573 K, the value of $10^3 \ln \beta^{56/54} \text{Fe}_{3+-2+} \approx 0.90$ ‰, suggesting iron isotopes should be a powerful discriminant of the oxidation state of iron in fluids, even at high temperatures, but not between different ligands for the same oxidation state of iron.

Iron isotope compositions of chlorine-bearing fluids relevant to hydrothermal systems (300 – 350 °C) were explored for the systems fluid-pyrite (Syverson et al. 2013) and fluid-chalcopryrite (Syverson et al. 2017). Solutions equilibrated with pyrite contained ≈ 10 mmol/kg Fe^{2+} and ≈ 1000 mmol/kg Na, and, at low pH (≈ 3 at 350°C) and 500 bar, $\text{Fe}(\text{H}_2\text{O})^{2+}$ was calculated to have been stable, and defined a fractionation factor $10^3 \ln \alpha^{(57/54) \text{Fe}_{\text{pyr-fluid}}} = +1.49 \pm 0.44$ ‰. This gives a force constant for $\text{Fe}(\text{H}_2\text{O})^{2+}$ of ≈ 150 N/m (given that of pyrite is ≈ 280 N/m; Blanchard et al. 2009). Under the same conditions, the fractionation between chalcopryrite and fluid, $10^3 \ln \alpha^{(57/54) \text{Fe}_{\text{ccp-fluid}}} = +0.09 \pm 0.17$ ‰ is negligible within uncertainty (Syverson et al. 2017). At 300 °C and $\text{NaCl-HCl}\pm\text{FeCl}_2$ fluids, dissolution/precipitation of hematite yielded $10^3 \ln \alpha^{(57/54) \text{Fe}_{\text{hem-fluid}}} = +0.54 \pm 0.15$ ‰ in which the fluid species was likely $\text{FeCl}_2^0(\text{aq})$ or FeCl^+ , however no fractionation was observed at 450 °C and 600 bar, nor at 200 °C, where the fluid phase was inferred to be dominated by Fe^{3+} -bearing aqueous species (Saunier et al. 2011). Nevertheless, this sequence of isotopic fractionation ($\delta^{57}\text{Fe}_{\text{pyr}} > \delta^{57}\text{Fe}_{\text{hem}} > \delta^{57}\text{Fe}_{\text{mag}} > \delta^{57}\text{Fe}_{\text{ccp}} \geq \delta^{57}\text{Fe}_{\text{fluid}}$) is borne out in measurements of hydrothermally-precipitated ore phases (Wawryk and Foden 2015, 2017; Li et al. 2018). Higher temperature experiments carried out at 800°C and 10 kbar by Sossi and O'Neill (2017) found strong isotopic fractionation between $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ fluid and Fe^{3+} -rich minerals (namely magnetite), where $10^3 \ln \alpha^{(57/54) \text{Fe}_{\text{mag-fluid}}} = +0.44 \pm 0.01$ ‰. By contrast, $^{56}\text{Fe}^{2+}$ -bearing minerals (fayalite, ilmenite) had similar iron isotope compositions to the fluid, and almandine garnet was lighter still, at $10^3 \ln \alpha^{(57/54) \text{Fe}_{\text{alm-fluid}}} = -0.14 \pm 0.03$ ‰, which gives the iron force constant for FeCl_2^0 in the fluid of 175 N/m. This compares well with force constants of 153 – 186 N/m for $\text{FeCl}_2(\text{H}_2\text{O})_4$ calculated in Hill et al. (2010) depending on the DFT basis set used, their Table A1.

5.0. Effect of redox processes in influencing iron isotope fractionation in natural systems

5.1. Magmatic processes

5.1.1. Partial Melting

Partial melting is the process that describes the incomplete transformation of a solid(s) to a liquid phase. In terrestrial magmatic settings, this process can occur in both the crust and mantle. Should liquid-solid segregation occur, this process has the capacity to impart isotopic fractionation on its constituent phases.

Though early studies considered that the compositions of mantle peridotites and basaltic rocks were indistinguishable (e.g. Zhu et al. 2001; Beard et al. 2003a) leading to the development of the concept of 'mean mafic Earth' with $\delta^{57}\text{Fe} = +0.10 \pm 0.03$ ‰, later, higher-precision studies soon overturned this

perception. In particular, two studies, Williams et al. (2005) and Weyer and Ionov (2007) presented an extensive number of analyses of whole rock peridotites and, in the case of the former, their constituent minerals. The conclusion from both of these works was that peridotitic rocks were isotopically lighter ($\delta^{57}\text{Fe} = +0.03 \pm 0.05 \text{ ‰}$ at $\text{Mg\#} = 0.894$, that of fertile mantle) than their basaltic counterparts and secondly, that partial melting of the mantle could induce resolvable isotopic fractionation in which the residual peridotite composition would tend to lighter isotopic values with progressive extraction of heavier basaltic melt. Weyer and Ionov (2007) assigned bulk peridotite-liquid fractionation factors that fit arrays of $\delta^{57}\text{Fe}$ vs. $\text{Mg\#}$ (molar $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$) to quantify this effect, finding $10^3 \ln \alpha(^{57/54}\text{Fe}_{\text{mantle-melt}}) = -0.1$ to -0.3 ‰ . These fractionation factors were also used to fit the observation of the isotopically heavy ($\delta^{57}\text{Fe} = +0.15 \text{ ‰}$) compositions of basaltic rocks measured to that stage.

As recognised by Williams et al. (2005) and Weyer and Ionov (2007), iron isotope fractionation arises mechanistically from the incompatibility of Fe^{3+} relative to Fe^{2+} , reflected in the higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ of MORB glasses (0.10 ± 0.02 ; Berry et al. 2018) relative to peridotites (0.037 , Canil et al. 1994). Clinopyroxene is the major contributor to partial melting at low pressures ($<3 \text{ GPa}$) (e.g., Hirschmann et al. 1999), and $D(\text{Fe}^{2+})/D(\text{Fe}^{3+})^3 \approx 10$, where $D(\text{Fe}^{2+}) \approx 1$ (e.g., Mallmann and O'Neill 2009; Davis et al. 2013). Therefore, during melt extraction, the modal olivine content increases and, as it contains less ferric iron than ortho- and particularly clinopyroxene or spinel (Canil and O'Neill 1996), tends to concentrate the lighter isotopes. Dauphas et al. (2009) developed a melting model predicated on the difference of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios of the mantle source and the partial melt. As ferric iron behaves as an incompatible element, the extent of isotopic fractionation is highest in the melt at low degrees of melting, a feature also attributable to the mass balance considerations (i.e., the 'lever rule'). However, this treatment implicitly neglected the effect of co-ordination environment, whose isotopic effect was unconstrained until the study of Dauphas et al. (2014), whose measurement of Fe-O force constants in magmatic glasses revealed a preference for the heavier isotopes in lower co-ordination environments (section 4.2.). With this knowledge, combined with $K_{\text{Fe-O}}$ of mantle minerals, Sossi and O'Neill (2017) were able to build self-consistent modal and non-modal melting equations based on the mass balance equations of Shaw (1970), re-cast in terms of isotopic fractionation between phases 1 and 2:

$$\frac{C_l^i}{C_o^i} = \frac{1}{\left(\left(D_{1-2}^i \alpha_{E1-2}^i \right) + F \left(1 - P \left(D_{1-2}^i \alpha_{E1-2}^i \right) \right) \right)} \quad (21)$$

where C_l^i and C_o^i denote the concentration of isotope i of element E in the liquid and bulk, respectively, F is the melt fraction and P the product of a phase's melting reaction coefficient and elemental D

³ The elemental partition coefficient, denoted 'D', is given by the ratio of the concentration of the element in a solid phase with respect to that in the liquid phase.

summed over each phase. Solutions are found for the concentration of each isotope, and hence the resulting isotopic composition of the liquid is:

$$10^3 \ln \left(\frac{C_l^i}{C_l^j} \right) = \delta^i E. \quad (22)$$

The above equations can be applied to any isotope system. For iron, the crucial free variable, D_{1-2}^i , is controlled by the temperature and difference in iron force constants between phases 1 and 2 (mineral and melt):

$$D_{Min-Melt}^{54+nFe} = (D_{Min-Melt}^{54Fe}) e^{\left(\frac{1435n(K_{Fe-O}^{Min} - K_{Fe-O}^{Melt})}{T^2} \right)}. \quad (23)$$

Here, $n = 2$ ($^{56/54}Fe$) or 3 ($^{57/54}Fe$). The force constant for each phase is given in the form:

$$K_{Fe-O} = a \times \frac{Fe^{3+}}{\Sigma Fe} + b \quad (24)$$

where a describes the slope of the dependence of the force constant with the $Fe^{3+}/\Sigma Fe$, and b the y-intercept, which depends on co-ordination ($VIII < VI < IV$). Values of constant a and b can be calculated from Figs. (1 - 3), and yield $a = 125$ and $b_{VIII} = 145$ N/m, $b_{VI} = 185$ N/m and $b_{IV} = 225$ N/m.

Systematics of iron isotope fractionation applying this partial melting model are summarised in Figs. 6a and b. As in the models presented in Dauphas et al. (2009), iron isotope fractionation between the melt and its source is inversely proportion to the melt fraction (Fig. 6a), as the $Fe^{3+}/\Sigma Fe$ of the melt is maximised at low F due to the relative incompatibility of ferric iron. Independent of this effect is the modal mineralogy of the source; as the modal abundance of garnet increases at the expense of olivine (e.g., via increasing pressure or in a bimineraleclogite), the fractionation factor increases due to the retention of the light isotopes in its VIII-fold sites.

This mineralogical control on the extent of iron isotope fractionation can account for the isotopic differences between mantle peridotites, MORBs and OIBs. The iron isotope variations observed in mantle peridotites are more scattered than those in basaltic rocks. Studies reporting analyses of peridotitic or ultramafic lithologies include (Poitrasson et al. 2004, 2013; Williams et al. 2004, 2005, 2009; Weyer et al. 2005; Weyer and Ionov 2007; Zhao et al. 2010, 2012, 2017; Huang et al. 2011; Craddock et al. 2013; Sossi et al. 2016) and were summarised by Sossi et al. (2016), who filtered the data for unmetasomatised, unaltered, and fertile peridotites. This procedure greatly reduced data variability enabling a 2SE uncertainty to be taken of 60 peridotite analyses that yielded $\delta^{57}Fe = +0.05 \pm 0.01$ ‰ for the value of fertile mantle. These authors noted that significant iron isotope fractionation in fresh, unmetasomatised peridotites was not evident until reaching $Mg\#s > 0.91$, reflecting the retention of the bulk of the iron budget in the peridotite.

Relative to ultramafic rocks, oceanic basalts almost exclusively preserve heavier iron isotope compositions (Weyer and Ionov 2007). Nevertheless, data for oceanic basalts remained sporadic until the study of Teng et al. (2013), in which 93 iron isotope analyses of basaltic rocks were presented, comprising 43 MORBs, whereas the remainder were OIBs from the Society Islands, the Cook-Austral chain and Hawai'i. The isotopic composition of MORB gave a mean value of $\delta^{57}\text{Fe} = 0.15 \pm 0.01 \text{ ‰}$ (2SE, $n = 43$), some 0.1 ‰ heavier than fertile mantle. Considering that the maximum iron isotope fractionation permitted during melting of peridotite in the spinel facies is 0.05 ‰ at FMQ (Fig. 6a), this poses a conundrum for the derivation of MORB from peridotitic upper mantle (see discussion in Dauphas et al. 2014). However, as noted by Sossi et al. (2016), MORBs have Mg#s that are too low ($0.54 < \text{Mg\#} < 0.68$) to have been in equilibrium with Fo₉₀ mantle olivine, which, since $K_D^{\text{Fe-Mg}}$ ($[\text{Fe}^{2+}/\text{Mg}]_{\text{Ol}}/[\text{Fe}^{2+}/\text{Mg}]_{\text{Melt}}$) is equal to ≈ 0.3 (Toplis 2005), should produce melts with $\text{Mg\#} \approx 0.74$ (compositional effects on $K_D^{\text{Fe-Mg}}$ broadly cancel such that the use of a single value introduces minimal uncertainty). In this scenario, the low-pressure evolution of MORB magmas during decompression expands the olivine phase volume (Kinzler and Grove 1992) and light iron isotopes preferentially sequestered into olivine, resulting in heavier values than could be accounted for by single-stage melt extraction. Correction of the iron isotope composition of MORB to a fictive primary melt composition with $\text{Mg\#} \approx 0.74$ yields $\delta^{57}\text{Fe} = 0.10 \text{ ‰}$ (Sossi et al. 2016) that can be reconciled with partial melting. Additional possibilities, including diffusive effects during partial melting (*e.g.*, Weyer and Ionov 2007; Poitrasson et al. 2013; Su et al. 2015), may also become important in fractional melting regimes where melt parcels and residual mantle equilibrate only at infinitesimally small increments (see Asimow et al. 1997). Here, preferential transport of the lighter iron isotopes into peridotite minerals during ascent, due to its faster diffusivity, would lead to heavier isotopic compositions than predicted by equilibrium fractionation factors.

With respect to MORBs, OIBs are frequently (though not always; Peters et al. 2019) higher in $\delta^{57}\text{Fe}$ (Teng et al. 2013), a tendency that was highlighted in the data of Williams and Bizimis (2014) and Konter et al. (2016) on MgO-rich pyroxenites and OIBs from Hawai'i and Samoa, respectively. In these samples, whose Mg# reaches 0.69, $\delta^{57}\text{Fe}$ can extend to +0.45 ‰, up to 0.4 ‰ heavier than recent estimates for fertile mantle peridotite. All things being equal, OIBs should be heavier than MORBs by virtue of the lower degrees of partial melting involved in their genesis (section 5.1.1., Fig. 6). Nevertheless, this offset is greater than can be produced by degree of melting alone, and the combination of isotopically heavy iron and high Mg# requires additional source-related melting controls. Both studies argue for the presence of pyroxenite in the source, which has the dual effect of i) increasing the $\delta^{57}\text{Fe}$ of the source (pyroxenites from Oahu, Hawai'i have $\delta^{57}\text{Fe}$ between +0.10 and +0.27 ‰, Williams and Bizimis, 2014) and ii) enhancing iron isotope fractionation during partial melting. This second point was quantified in Sossi and O'Neill (2017) who demonstrated that such heavy values were difficult to create during melting of mantle peridotite, and instead required a high fraction of garnet in the source

that simultaneously acted as a sink for light iron isotopes (see Fig. 6a) and increased the Gd/Yb ratio of the basalts (Fig. 7).

The expected effect of source oxidation is to increase the iron isotope fractionation observed in products of partial melting (Dauphas et al. 2009; Fig. 6b). Although the consensus is that arc magmas are more oxidised than those from oceanic settings (MORBs and OIBs; see Carmichael 1991; Kelley and Cottrell 2009), conjecture still abounds as to whether the sources of arc magmas are more oxidised than their equivalents under mid-ocean ridges or ocean islands (Lee et al. 2005; Mallmann and O'Neill 2009). In this scenario, the higher oxygen fugacity of arc magmas could be acquired after segregation from their mantle sources, by fractional crystallisation or degassing of reduced species, such as H₂ or CH₄ (Mathez 1984). The sensitivity of iron isotopes to the redox state of iron may in turn be able to distinguish between these two hypotheses.

Should the sources of arc magmas be more oxidised, then the mechanics of iron isotope fractionation would predict an iron isotope composition heavier than oceanic basalts. Analyses of arc magmas were, until recently, surprisingly sparse, restricted to studies of back-arc basalts (Nebel et al. 2013; 2018) and two arcs; New Britain (Dauphas et al. 2009) and the sediment-rich Banda (Nebel et al. 2015) prior to the extensive dataset comprising 130 arc magmas of Foden et al. (2018). These authors discovered, contrary to expectations, that arc magmas have systematically lighter iron isotope composition relative to MORBs, extending to values even lighter than fertile mantle peridotites, around -0.15 ‰ in Avachinsky, Klyuchevskoy and Ploskiy volcanoes of the Kamchatka arc (Foden et al. 2018). This result has two important implications. Firstly, if the sources of arc magmas are indeed more oxidised than ambient mantle, then iron itself cannot be the cause of this oxidation. Rather, the role of S⁶⁺ as the oxidising agent for arc magmas is supported by quantitative calculations of the redox budget of subduction zones (Evans and Tomkins 2011), largely due to its efficiency in oxidising iron via an 8-electron transition from sulfate to sulfide:

This means 8 moles of Fe are oxidised for every mole of S, which equates to 1.8 wt. % FeO per 1000 ppm S; the S content of MORB, though those of arc magmas are even higher (Wallace and Edmonds 2011). This comes about due to the higher solubility of sulfur in silicate melts at anhydrite saturation with respect to sulfide saturation (O'Neill and Mavrogenes 2002; Li and Ripley 2009; Smythe et al. 2017). Alternatively, the idea that the oxygen fugacities of arc magma sources are similar to ambient mantle stands. In either case, iron isotopes show no evidence for the oxidation of arc magmas sources.

Secondly, the observation that arc magmas are *lighter* than oceanic basalts begs explanation. Nebel et al. (2015) argued that the isotopically light sources could be generated by the prior extraction of melt from peridotite sources, which are known to be more refractory than ambient mantle on the basis of

lower abundances of incompatible high field strength elements (Nb, Ti) in arc magmas. These elements behave conservatively during slab fluid transfer to the mantle wedge and represent the composition of mantle wedge peridotite (Woodhead et al. 1993). Degrees of partial melting needed to explain the degree of isotopic fractionation is close to 30%, which are observed in xenoliths from the Bismarck arc (Bénard et al. 2018). However, Foden et al. (2018) asserted that values as low as -0.15 ‰ cannot be produced by melt depletion alone, and considered additional scenarios. In particular, diffusive stripping of lighter isotopes in preference to their heavier counterparts was cited as a mechanism to promote light isotope compositions in partial melts. As discussed in section 4.3., the iron isotope composition of aqueous fluids are light provided the speciation of iron is dominated by Fe²⁺-bearing species, particularly FeCl₂, as inferred from the measurements of Sanchez-Valle et al. (2017). However, it remains uncertain as to whether the Fe content of these fluids is high enough to shift the iron isotope composition of the mantle wedge (Ayers et al. 1997; see also section 5.2.3). Indeed, supra-subduction zone ophiolitic peridotites, despite their high degree of depletion (≈ 25 – 35 %) and re-enrichment with subduction zone fluids, resulting in a distinctive ‘U-shape’ REE pattern, are not systematically lighter than abyssal peridotites (Su et al. 2015; Zhang et al. 2019). Although certain samples extend to the requisite light values (δ⁵⁷Fe ≈ -0.15 ‰), this variation is, at best, weakly-dependent on proxies for degree of melt extraction (Mg#, Cr# in spinel or clinopyroxene) or fluid addition (Ba/Th, Ba/La). By contrast, Turner et al. (2018) observe a positive correlation between δ⁵⁷Fe and δ⁷Li to very low values (-0.46 ‰ and -1.78 ‰, respectively), pointing to fluid addition and/or diffusive processes, though the primary mechanism for inducing these variations remains uncertain. Further studies of sub-arc mantle peridotites are required to evaluate the degree to which these process are liable to affect their iron isotopes compositions locally.

On a global scale, Foden et al. (2018) recognised a negative correlation between the iron isotope composition of global arc magmas and the thermal parameter (ϕ):

$$\phi = age \times \sin \theta u, \quad (26)$$

the product of slab age and vertical descent velocity, u , where θ is the dip angle (Kirby et al. 1996) (Fig. 8). Subducting slabs that are old and cold tend to descend at faster rates, such that they do not thermally equilibrate as much with surrounding mantle, and slab geotherms are too cold to permit slab melting. By contrast, hotter slabs descend more slowly due to their thermal buoyancy, and hence heat up to greater extents during their protracted residence time in the mantle, allowing partial melting of the slab. Foden et al. (2018) also suggested that the mantle wedge peridotite in longer-lived and therefore colder subduction zones remained trapped in the sub-arc mantle by convective ‘Richter rolls’ (Davies et al. 2016), subjecting the same mantle to continual melt-extraction and fluid ingress, which may have been partially kinetic in nature (see also Zhao et al. 2012), resulting in isotopically light arc magma sources. Alternatively, on the basis of the similarity in iron isotope compositions of sub-arc and

convecting mantle, Zhang et al. (2019) propose that redox-unbuffered melting of arc sources may account for their lighter composition than MORB, yet this does not address the very light isotope signatures observed in magmas from high ϕ arcs such as Kamchatka and Samoa.

5.1.2. Differentiation

Magmatic differentiation comprises the range of processes involving, but not limited to, fractional crystallisation, crustal assimilation, fluid exsolution, Soret diffusion and vapour-phase degassing, all of which have the potential to fractionate iron isotopes by mass transfer.

The earliest concerted effort to study the effect of magmatic differentiation on iron isotope fractionation was that of Poitrasson and Freydier (2005), who analysed a collection of granites including peralkaline, metaluminous and peraluminous varieties, broadly corresponding to A-, I- and S-type magmas, respectively (Chappell and White 1974; Frost and Frost 2010). These granitic rocks recorded a near-exponential increase in $\delta^{57}\text{Fe}$ with falling MgO (below 1 wt. %) or rising SiO_2 (above 70 wt. %) contents (their Figs. 5 and 6) relative to the 'mean mafic earth' value of $\delta^{57}\text{Fe} = +0.10 \pm 0.03 \text{ ‰}$ reaching $+0.59 \pm 0.03 \text{ ‰}$ (Poitrasson and Freydier 2005). In order to explain this monotonic increase, Poitrasson and Freydier (2005) appealed to the exsolution of Fe^{2+} -rich fluids that transported isotopically light iron. A similar trend was observed by Schoenberg and von Blanckenburg (2006), who cited that additional constraints were required to explain the isotopic relationship with SiO_2 content. A fluid-exsolution hypothesis was extended further by (Heimann et al. 2008), who, compiling much of the data available to date (Fig. 9), confirmed the trend of Poitrasson and Freydier (2005) in which silicic igneous rocks exhibited strong positive deviations from mafic igneous rocks above 70 wt. % SiO_2 . These authors considered that the lack of correlation of iron isotope composition with incompatible element concentrations (which can be inverted to yield the fraction of melt remaining) argued against the role of fractional crystallisation in determining iron isotope compositions. The observed inverse correlation between Zr/Hf and $\delta^{57}\text{Fe}$ was taken as evidence for the effect of fluid exsolution, as Heimann et al. (2008) asserted that these trace elements remain little-affected by crystal fractionation (but see Linnen and Keppler 2002). In these highly differentiated rocks, most of the iron is contained in Fe-Ti oxides (specifically magnetite in oxidised granites and rhyolites), and therefore should retain the heavy isotopes, where Heimann et al. (2008) modelled $\Delta^{57}\text{Fe}_{\text{mag-fluid}}$ between $\approx +0.45 \text{ ‰}$ at 700°C and $\approx +0.75 \text{ ‰}$ at 500°C . Because the solubility of FeCl_2 decreases with temperature and isotopic fractionation is proportional to $1/T^2$, the more fractionated granites should preserve the heaviest iron isotope compositions.

Contemporaneously, Teng et al. (2008) and Schuessler et al. (2009) published two studies showing unequivocal evidence for the role of crystal-liquid fractionation in controlling iron isotope variations in differentiating magmatic systems. Whole rocks from the Kilauea Iki lava lake, Hawai'i, record progressive enrichment of the heavy isotopes of iron with decreasing MgO, from values close to 0 ‰

in olivine cumulates to + 0.3 ‰ in evolved basaltic samples (Teng et al. 2008). Importantly, isotopic fractionation is observed below 70 wt. % SiO₂, in contrast to other differentiating magmatic systems. This variation broadly correlates with the Fe³⁺/ΣFe content of the whole rock, and, more precisely, reflects the incorporation of isotopically light iron into the ^{VI}Fe²⁺ sites of olivine relative to the residual melt, fit with a fractionation factor $10^3 \ln^{57/54}\text{Fe}_{\text{ol-melt}} = -0.20 \pm 0.10$ ‰. Unlike at Kilauea Iki, isotopic fractionation at the Hekla volcano, Iceland, occurs only around 70 wt. % SiO₂, in line with earlier studies (Schuessler et al. 2009). These authors rejected the hypothesis of fluid exsolution as the cause for this variation, based on the constancy of the isotopes of Li, an element even more fluid-mobile than iron, in the same rocks. Instead, they argued for crystallisation of Ti-rich titanomagnetite, which crystallises as Mag₃₅ at Hekla (Baldrige et al. 1973), in elevating the iron isotope composition in evolved rocks.

The absence of iron isotope fractionation below 70 wt. % SiO₂, except for the differentiating sequence of basalts at Kilauea Iki behaved an explanation. The Red Hill intrusion, southern Tasmania, exhibits a vertical continuum of compositions created by in situ fractional crystallisation of a single injection of magma in a closed system (Sossi et al. 2012). Much like the Kilauea Iki lava lake, the iron isotope composition of dolerites from Red Hill increased in δ⁵⁷Fe at high MgO contents, before reaching a maximum near +0.30 ‰ and declining following the crystallisation of magnetite (Mag₉₅), an effect that had been expected, but never observed, on the basis of experimental constraints (Shahar et al. 2008). Thus, iron isotopic evolution for the tholeiitic series mirrored that followed by the liquid line of descent on an AFM (Alkalis-FeO-MgO) diagram, and Sossi et al. (2012) were able to derive fractionation factors; $\Delta^{57}\text{Fe}_{\text{cpx-melt}} = -0.25 \times 10^6/T^2$ and $\Delta^{57}\text{Fe}_{\text{mag-melt}} = +0.20 \times 10^6/T^2$. These authors also pointed out that the differing behaviour of Kilauea Iki and Red Hill on one hand and Hekla on the other could be attributed to the extent to which the differentiating system remained open to oxygen exchange (Fig. 10). Systems that are closed to oxygen exchange, which may be imposed by the formation of chilled margins, have only a finite oxygen budget. Therefore, the early crystallisation Fe²⁺-rich phases increases the Fe³⁺/ΣFe and δ⁵⁷Fe of the melt, prior to the crystallisation of magnetite-rich titanomagnetite, whose high Fe³⁺/ΣFe ratio and hence δ⁵⁷Fe is higher than that of the melt. By contrast, systems open to O₂ exchange are buffered at values near FMQ, potentially by chemical and mass exchange with surrounding wall rocks (Carmichael 1967). Here, the Fe³⁺/ΣFe of the melt and minerals remains similar, and they precipitate Ti-rich titanomagnetite, with potentially lower Fe³⁺/ΣFe than the melt, causing an increase in the iron isotope composition of the residual melt.

Studies of layered intrusions reveal more complex histories that involve the introduction of several pulses of magma and crystal accumulation that blurs the isotopic signal of the evolving melt(s). However, the conclusion from these studies is that magmatic differentiation does not induce significant isotopic fractionation in the bulk rocks (Chen et al. 2014; Liu et al. 2014; Bilenker et al. 2017), notwithstanding the fact that the individual minerals comprising these rocks can be strongly fractionated. Isotopic fractionation generally occurs in the sequence magnetite > clinopyroxene >

olivine > ilmenite, in broad agreement with the hierarchy depicted in section 4.1. Equilibration temperatures of ilmenite-magnetite pairs suggest slow cooling as anticipated for intrusive magmas, and point to sub-solidus re-equilibration as the cause for these disparate isotopic signatures, thereby leaving the composition of the whole rock unaffected.

The uniformly heavy iron isotope composition of silicic melts also has its origin in the increased bond strength of iron in these highly polymerised, alkali-rich compositions (section 4.2.), as suggested by Schuessler et al. (2009) and Sossi et al. (2012). This behaviour was conclusively illustrated in the combined NRIXS-XANES study of Dauphas et al. (2014), which showed an increase in Fe–O force constants of felsic melts relative to mafic and intermediate compositions at a given $\text{Fe}^{3+}/\Sigma\text{Fe}$ (see section 4.2.). Foden et al. (2015), upon analysing 42 A-, I- and S-type granites, and compiling literature data, found that only the A-type granites, especially the peralkaline ones, that form from protracted crystallisation of basaltic magma (Turner et al. 1992) exhibited heavy iron isotope compositions. As these granites are typically reduced and H_2O - and volatile-poor, their heavy compositions likely reflect extensive crystal-liquid segregation rather than fluid exsolution. More reduced, ilmenite-bearing S-type granites also display a similar isotopic evolution, whereas more oxidised, magnetite-series I-type granites never reach heavy iron isotope compositions, likely due to the combined effect of isotopically light olivine and heavy magnetite in cancelling each other out. This behaviour is evident in evolving magmatic rocks from the Anatahan volcano of the Marianas arc (Williams et al. 2018), in which the effect of magnetite crystallisation is less pronounced than at Red Hill (a change in $\delta^{57}\text{Fe}$ of $\approx 0.15\text{‰}$) after displaying mildly rising iron isotopic values prior to this point. The iron isotopic evolution then increases towards heavier values at very low MgO contents below 2 wt. %, as per other siliceous igneous rocks.

Within this framework, recent years have seen a flurry of studies focusing on better understanding the nature of inter-mineral and mineral-melt fractionation in evolved magmatic systems (Du et al. 2017; He et al. 2017; Wu et al. 2017; Xia et al. 2017; Li et al. 2019). These studies argue for the predominant role of fractional crystallisation in producing the heavy $\delta^{57}\text{Fe}$ values of high silica igneous rocks, by a combination of the crystallisation of Ti-rich titanomagnetite and increasing Fe–O bond strength in highly silicic melts with high total alkali/alkaline earth cation ratios (Du et al. 2017; Wu et al. 2017), with residual garnet contributing in peraluminous compositions (He et al. 2017). Noteworthy is the very heavy isotopic composition of plagioclase (Fig. 11), which attests to the preferential incorporation of ferric iron into its structure, as expected on thermodynamic grounds (Lundgaard and Tegner 2004). However, the proportion of total iron hosted in plagioclase is so low so as to be unimportant.

5.2. Fluid transfer from mantle to crust

High-pressure (HP) metamorphic ophiolites (meta-ophiolites) returned from former subduction zones provide information on deep geochemical processes occurring in subduction zones (Poli and Schmidt

2002). They constitute an alternative and complementary way to arc magmas to study the isotopic composition and redox state of the fluids released during slab dehydration and devolatilisation at depth. This is of particular importance for establishing the mass balance of key redox-sensitive elements, such as iron, in subduction zones. However, direct constraints on the redox state and the isotopic evolution of Fe in oceanic lithosphere during subduction remain challenging and the constraints sparse.

5.2.1. Altered oceanic lithosphere

The subducting slab consists of ultramafic oceanic mantle, the mafic oceanic crust and their sedimentary cover, all of which undergo seafloor hydrothermal alteration prior to subduction. In the ultramafic parts, this alteration is manifest in the oxidation of primary Fe^{2+} -bearing phases, such as olivine, pyroxenes, to form Fe^{3+} -bearing phases, namely magnetite at high temperature or Fe^{3+} -bearing serpentine at low temperatures (Andreani et al. 2013; Klein et al. 2014; Bonnemains et al. 2016). All abyssal peridotites are variably- to highly serpentinised (Mével 2003) and therefore display high $\text{Fe}^{3+}/\Sigma\text{Fe}$ (0.58 ± 0.03 ‰, 2SE, $n = 111$; Andreani et al., 2013, 2014; Paulick et al., 2006). However, their iron contents and isotopic compositions are relatively constant, with the exception of peridotites affected by hydrothermal activity (*e.g.*, the Rainbow hydrothermal site) where Fe mobility and therefore isotopic fractionation can be enhanced by the circulation of sulfur-bearing fluids (*e.g.*, Severmann et al., 2004; Debret et al., 2018a). They range from -0.18 ± 0.03 ‰ to 0.10 ± 0.06 ‰ (Craddock et al., 2013 – unweathered samples; Debret et al., 2016; Debret et al., 2018a – non-mineralised samples) with a mean value, -0.03 ± 0.03 ‰ (2SE, $n = 32$), indistinguishable from that of orogenic lherzolites (section 5.1.). Although some variations have been observed among different sites; for example the South West Indian (0.00 ± 0.03 ‰) and Gakkel ridge (0.01 ± 0.02 ‰) samples display higher $\delta^{57}\text{Fe}$ values relative to Mid-Atlantic Ridge Kane (-0.13 ± 0.02 ‰) and Rainbow (-0.05 ± 0.05 ‰) samples. This difference has been attributed to melting processes occurring prior to oceanic lithosphere alteration (Debret et al., 2018a). Despite large equilibrium isotope fractionation between Fe^{3+} and Fe^{2+} aqueous species and minerals (see section 4.3), these observations suggest that the conversion of peridotites to serpentinites occurs without significant loss or gain of Fe, producing little net change in their Fe isotope compositions.

Relative to fresh oceanic basalts, seafloor-altered basalts record larger variations of $\delta^{57}\text{Fe}$ (-2.49 ‰ $\leq \delta^{57}\text{Fe} \leq +2.05$ ‰; Rouxel et al., 2003), attributed to crystallisation of secondary Fe-bearing minerals at low temperature (Rouxel et al., 2003). Indeed, the interaction of mafic rocks with seawater results in oxidation from Fe^{2+} to Fe^{3+} through seawater sulfate reduction at high temperature (200–350°C; Shanks et al., 1981) and hydrolysis at low temperature ($< 150^\circ\text{C}$; Bach and Edwards, 2003). The limiting factor for the progress of these reactions is the amount of available reacting seawater (water–rock ratio). Their $\text{Fe}^{3+}/\Sigma\text{Fe}$ is therefore expected to be highest in the uppermost mafic crust (from seafloor to depth of about 200m) where permeability is highest. However, the relatively low mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ (0.22 ± 0.08) of hydrothermally-altered mafic rocks suggests they largely escape oxidation (Lécuyer and Ricard

1999). Similarly, highly fractionated $\delta^{57}\text{Fe}$ values in mafic rocks may therefore be restricted to the uppermost crust. Indeed, oceanic mafic rocks show a limited range of Fe isotope compositions; in ophiolite sections ($+0.18 \pm 0.08 \leq \delta^{57}\text{Fe} (\text{‰}) \leq +0.43 \pm 0.11$; Inglis et al., 2017) or at mid-oceanic ridges ($-0.07 \leq \delta^{57}\text{Fe} (\text{‰}) \leq 0.33$; Beard et al., 2003, Nebel et al., 2013, Teng et al., 2013, Weyer and Ionov, 2007, Williams et al., 2009). Thus, there is no clear evidence of any significant or consistent leaching or addition of iron in metabasites during hydrothermal alteration at depth.

5.2.2. Subducted oceanic lithosphere

The subduction of oceanic lithosphere and overlying sediments initiates a continuum of metamorphic reactions and dehydration/rehydration events between the downgoing slab (Schmidt and Poli, 1998), the slab-mantle wedge interface and/or the mantle wedge, which are strongly controlled by intensive variables, such as temperature, pressure and oxygen fugacity ($f\text{O}_2$), and the initial composition and mineralogy of the rocks (e.g., Debret & Sverjensky, 2017; Evans et al., 2017). For a given lithology, the metamorphic evolution is therefore not unique and may vary according to the considered setting. We report here some of the main observations on Fe mobility and redox state in metamorphic lithologies composing meta-ophiolites.

Metamorphic ultramafic rocks outcropping in mountain ranges are often highly deformed and recrystallised into antigorite (high P-T variety of serpentine) and metamorphic olivine during prograde metamorphism (e.g., Trommsdorff et al. 1998; Hermann et al. 2000; Padron-Navarta et al. 2011; Scambelluri et al. 2014; Kempf and Hermann 2018). The recrystallisation of slab serpentinites during subduction results in a net decrease of magnetite mode and $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Debret et al., 2014, 2015; Merkulova et al., 2017). In addition, observations of hematite-magnetite assemblages in dehydrated serpentinites (Debret et al., 2015) suggest high $f\text{O}_2$ ($\Delta\text{FMQ}+1$ to $+5$), during antigorite breakdown in subduction zones, compatible with the release of oxidised S and C in slab-derived fluids (Debret & Sverjensky, 2017). Fluid loss is manifest as an increase in subducted serpentinite $\delta^{57}\text{Fe}$ values, which range from $0.00 \pm 0.10 \text{ ‰}$ to $0.21 \pm 0.10 \text{ ‰}$ (Debret et al., 2016). The negative correlation between $\delta^{57}\text{Fe}$ and $\text{Fe}^{3+}/\Sigma\text{Fe}$ of bulk serpentinites provides direct evidence for the release of Fe-bearing fluids during serpentinite devolatilisation in subduction zones (Fig. 12; Debret et al., 2016). Such a correlation is consistent with the release of sulfate-rich and/or hypersaline fluids, which preferentially complex isotopically light Fe in the form of $\text{Fe}^{2+}\text{-SO}_x$ or $\text{Fe}^{2+}\text{-Cl}_2$ species, during ultramafic rock devolatilisation. No such correlation is observed in eclogitic rocks from meta-ophiolites, suggesting limited Fe mobility during their dehydration, and their compositions likely reflect protolith variations instead (El Korh et al. 2017; Inglis et al. 2017). In accord with these observations, Huang et al. (2019) report typical basaltic values for eclogites from the Dabie Sulu orogeny, with $-0.01 \pm 0.10 \text{ ‰}$ to $+0.15 \pm 0.04 \text{ ‰}$ ($n = 9$), however, they are associated with oxidised, omphacite-epidote veins inferred to have been formed from the breakdown of lawsonite ($\pm$ phengite). These veins have elevated $\text{Fe}^{3+}/\Sigma\text{Fe}$ ($\approx 0.6 - 0.9$) with respect

to the adjacent eclogite ($\approx 0.3 - 0.5$) and, consequently higher $\delta^{57}\text{Fe}$, from 0.09 ± 0.06 ‰ to 0.32 ± 0.05 ‰ (Huang et al. 2019). Though these veins are concluded to have been locally-derived from the proximal eclogites on the strength of their similar Sr- and Nd-isotope compositions, they could only have constituted a volumetrically minor fraction of the eclogite source rocks in order to leave their iron isotope compositions unperturbed.

Analyses of metasedimentary rocks in meta-ophiolites are rather sporadic in the literature and show a limited range of $\delta^{57}\text{Fe}$, from 0.08 ± 0.03 ‰ to 0.17 ± 0.02 ‰ (Inglis et al., 2017). Nebel et al. (2015) analysed a series of currently subducting sediments sampled from the Banda arc whose $\delta^{57}\text{Fe}$ is between $+0.10 \pm 0.07$ to $+0.25 \pm 0.02$ ‰ with a mean of 0.17 ± 0.03 ‰ (2SE, $n = 9$), without any co-variation between $\delta^{57}\text{Fe}$ and detrital element proxies or radiogenic isotope compositions or total organic carbon contents. Siderite (FeCO_3) and ankerite ($\text{Ca}(\text{Fe},\text{Mg},\text{Mn})(\text{CO}_3)_2$) are the most common Fe-bearing carbonates occurring in seafloor sediments. Both phases are expected to preferentially incorporate light iron relative to olivine (Polyakov & Mineev, 2000) and can display highly fractionated $\delta^{57}\text{Fe}$ values down to -2.94 ± 0.03 ‰ in sediments (*e.g.*, Johnson et al. 2008). These minerals are also particularly soluble in fluids emanating at temperatures ranging from 200 to 300 °C during shallow subduction (Milesi et al. 2015) and their dissolution would contribute to the formation of carbonate-bearing fluids with a light Fe isotope signature. Consequently, investigations of carbonated serpentinites from blueschist terrains show that the transfer of carbon-bearing fluids from metasediments to serpentinite can contribute to a strong decrease of $\delta^{57}\text{Fe}$ of serpentinite, down to -0.40 ‰ (Debret et al., 2018b). Although the exact nature of Fe complexation in sediment-derived fluids is poorly constrained, this observation further corroborates the release of isotopically light fluids during sediment decarbonation and dehydration in subduction zones.

5.2.3. Iron bearing fluids transferred to the mantle wedge

Most studies of meta-ophiolites suggest release of isotopically light Fe in slab-derived fluids during subduction, consistent with the transport of iron with chlorine, sulfate and/or carbonate, as these ligands preferentially complex light Fe with respect to Fe^{3+} -rich antigorite and magnetite (*e.g.*, see section 4.3., Fujii et al., 2014; Hill et al., 2010). Although the vector of fractionation is correct, it remains unknown whether or not enough Fe can be mobilised in slab-derived fluids to significantly modify the $\delta^{57}\text{Fe}$ of mantle wedge peridotites to produce the light iron isotope composition of arc magmas (Foden et al. 2018).

Polyphase inclusions trapped in high pressure minerals represent the fluid released at high pressure and temperature during the devolatilisation of the subducting lithosphere in subduction zones. Scambelluri et al. (2015) showed that these olivine-hosted HP-fluids have variable FeO contents from 0.17 to 2.13 wt% (assuming ΣFe as FeO), in which Cl is often associated with Fe, as inferred from solubility measurements and thermodynamic calculations (see section 4.3.). In addition, the presence of sulfide

phases that are not stable in pristine or altered mantle rocks indicates the mobilisation of sulfur concomitant with chlorine and iron. These authors also report the existence of magnesite in inclusions from chlorite harzburgite, providing compelling evidence of carbon mobilisation in the meta-peridotite dehydration fluid.

The interaction of slab-derived fluids during their migration through the slab/mantle interface and the mantle wedge may modify their isotopic signature. In order to test how faithfully this fluid signature is transferred to the mantle wedge (*i.e.*, during subduction), Debret et al. (2018b) analysed metamorphic gem olivines in veins from the Sapat complex, part of the sub-arc mantle of the Kohistan-Ladakh Arc. The vein-forming minerals crystallised from a fluid that migrated through the fore-arc mantle, and display light $\delta^{57}\text{Fe}$ values ($-0.13 \pm 0.13 \text{ ‰}$ to $-0.54 \pm 0.14 \text{ ‰}$) relative to that of mantle olivine (*e.g.*, San Carlos olivine $\delta^{57}\text{Fe}$ has $\approx +0.02 \pm 0.05 \text{ ‰}$; Sossi et al., 2015) supporting the hypothesis that they crystallised through reaction with an isotopically fractionated fluid. Similarly, Turner et al. (2018) reported sub-arc mantle xenoliths with light $\delta^{57}\text{Fe}$ (from $+0.03$ to -0.46 ‰) relative to mantle peridotites. Such values are too fractionated to result solely from partial melting and require slab fluid addition and/or diffusive effects that produce light values. This is confirmed by the correlation between $\delta^{57}\text{Fe}$ and U/Th ratios in these sub-arc xenoliths. Although not all sub-arc peridotites show such isotopically light values (section 5.1.1.), these observations provide empirical evidence for the transfer of isotopically light Fe across subduction zones, in which Fe can be complexed by chlorine or sulfate or carbonate anions. Existing models (Huang et al. 2019) suggest, given the composition of polyphase inclusions (Scambelluri et al. 2015) and inferred iron isotope fractionation factors between olivine and fluids (Debret et al. 2018), that 30 – 40 % fluid addition to the mantle wedge would be required to shift their iron isotope compositions to sufficiently light values observed in some arc basalts (-0.15 ‰ ; Foden et al. 2018), but this increases to unrealistically high values for sub-arc mantle xenoliths with compositions as low as -0.46 ‰ (Turner et al. 2018). The predominant uncertainties with such models remain (*i*) the fraction of fluid permitted to metasomatise the mantle wedge, (*ii*) its iron content and iron isotope composition (*iii*) the degree of disequilibrium during fluid-rock interaction and (*iv*) the nature and identity of the Fe-bearing fluid species. Determining the dominant Fe-bearing species will require experimental work that can produce thermodynamic data for these species at the pressures, temperatures and compositions of interest.

6.0. Conclusion

At the high temperature conditions relevant to the formation of igneous and metamorphic rocks, the differences in the ground-state vibrational frequencies of isotopic substitutions, a quantum mechanical phenomenon, control isotope partitioning between two phases. These frequencies are in turn determined by the bonding environment of iron; where higher redox state and lower co-ordination number tends to favour the heavier isotopes. Similarly, a reduction in partial molar volume of the iron-bearing site in a condensed phase due to either increasing pressure and/or a transition to a low spin electronic

configuration engenders bond contraction and strengthening, also concentrating the heavier isotopes. The role of changing redox state and co-ordination environment in modifying iron force constants is highlighted, particularly along mineral solid solutions, magmatic liquid compositional series (basalt to rhyolite) and for different ligand identities and complexation stoichiometries in aqueous fluids.

Partial melting in the Earth's upper mantle results in small ($\approx +0.05\%$) iron isotopic enrichment in the liquid relative to its source because isotopically-heavy, ferric iron is preferentially concentrated in the melt with respect to lighter ferrous iron, in addition to its slightly lower mean co-ordination number in silicate liquids relative to minerals. The difference between the melt and its residue decreases with higher degrees of melting and in more reduced sources. Contrastingly, the degree of iron isotopic enrichment in the melt is enhanced in some ocean island basalts due to the presence of heavy isotope-enriched mafic, garnet-bearing components with respect to mid-ocean ridge basalts. Arc magmas are, on average, lighter still, and have iron isotope compositions that are inversely correlative with the *i*) age of the subducting slab and *ii*) its downgoing velocity. The mechanisms that contribute to this isotopic signature may include continued episodes of light, fluid-fluxed melting in stationary sub-arc mantle that are continuously depleted with time in mature subduction zones. However, understanding the relative contribution of each process requires concerted experimental, natural and spectroscopic work to determine the budget, speciation and transport of iron in subduction zones.

Magmatic rocks show a tendency towards heavy isotope-enriched compositions with increasing differentiation; however, the conditions under which these liquids cool and crystallise controls their subsequent evolution. Isotopic equilibria between minerals and melt play a predominant role in determining their liquid line of descent; conditions closed to O_2 exchange result in heavy isotope enrichment in mafic tholeiitic systems, whereas systems open O_2 exchange (typically calc-alkaline magmas in arc environments) exhibit little change in their iron isotope composition prior to $\approx 65\text{--}70\%$ SiO_2 . The uniformly heavy iron isotope composition of granites above this value stems from a strengthening of Fe-O bonds in alkali-rich siliceous melts in tandem with crystallisation of Fe^{2+} -bearing phases. Because A-type granites undergo more extensive crystal fractionation than do S- and particularly I-types, they tend to have the heaviest isotopic compositions, while the Fe^{3+} -rich mineral assemblage of I-type granites limits heavy isotopic enrichment.

Metamorphism accompanying cooling of the oceanic lithosphere and its hydration at mid-oceanic ridges imparts surprisingly little- to no iron isotopic fractionation at the lithospheric scale, whereas local reactions in the uppermost mafic crust or nearby hydrothermal areas (*e.g.*, Rainbow hydrothermal site) show evidence for iron mobility relative to fresh basalts or peridotites. The analyses of mafic rocks in high pressure meta-ophiolites appear to record primary magmatic signatures and have imprints inherited from prior partial melting episodes. In contrast, sedimentary and ultramafic rocks show progressively heavier iron isotope compositions with increasing metamorphic grade, consistent with the loss of Fe^{2+} -bearing species with an isotopically light signature, in which iron is likely complexed by chlorides or oxidised ligands (*i.e.*, sulfate or carbonate). Whether iron is sufficiently concentrated in these fluids to influence the iron isotope composition of the sub-arc mantle remains an area of research.

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Figure Captions

Fig. 1. After Sossi and O'Neill (2017). Dependence of the calculated force constants on the co-ordination number and oxidation state of iron. Lines of constant $\text{Fe}^{3+}/\Sigma\text{Fe}$ are drawn on in black. Effects of two common solid solutions on the force constant (magnetite–ulvöspinel and hematite–ilmenite) are shown in grey. Minerals are shown in white squares; Her = Hercynite, Chr = Chromite, Usp = Ulvöspinel, Mag = Magnetite, Hem = Hematite, Ilm = Ilmenite, Fay = Fayalite, Alm = Almandine.

Fig. 2. Iron-oxygen force constant in spinel group minerals (after Roskosz et al. 2015). The regression and associated uncertainty refers to Al-bearing spinels only, and the rhyolite and basalt trend are from the data of Dauphas et al. (2014). P&M = Polyakov and Mineev 2000; P = Polyakov et al., 2007; M = Mineev et al. 2007; D = Dauphas et al. 2012.

Fig. 3. After Dauphas et al. (2014). Mean force constants of Fe-O bonds in silicate glasses for basalt (circle), andesite (square), dacite (triangle) and rhyolite (diamond) compositions as a function of their $\text{Fe}^{3+}/\Sigma\text{Fe}$ content measured by XANES. The linear trends defined by the data permit extrapolation of Fe-O force constants to $\text{Fe}^{3+}/\Sigma\text{Fe} = 1$. Uncertainties on the error envelopes are 95% confidence intervals.

Fig. 4. After Liu et al. (2017). Force constants (N/m) of iron bonds in Fe^{3+} -free basaltic glass (black squares) with their associated 95% confidence intervals as a function of pressure (GPa) at room temperature (300 K). Black lines are linear fits to the data. Also shown are iron force constants in bridgmanite (Rustad and Yin, 2009, dashed line and Shahar et al., 2016, purple square).

Fig. 5. After Fujii et al. 2014. Temperature dependence of the $10^3 \ln \beta^{56/54}\text{Fe}$ for aqueous a) Fe^{2+} and b) Fe^{3+} species. The vertical scale factor of b) is $1.5\times$ that of a).

Fig. 6. Melting models from Sossi & O'Neill (2017) (see eqs. 21–24). a) Variation of the fractionation factor between liquid and solid as a function of source lithology and degree of melting. Peridotites in the spinel (sp) and garnet (gt) fields show similar fractionation, whereas partial melts of eclogites (ecl) have a more pronounced enrichment in heavy isotopes. b) Variation of the fractionation factor between solid and liquid as a function of $\text{Fe}^{3+}/\Sigma\text{Fe}_{\text{Melt}}$ for three different source compositions; 'Ox' = oxidised ($\text{Fe}^{3+}/\Sigma\text{Fe}_{\text{Source}} = 0.051$), 'Int' = intermediate ($\text{Fe}^{3+}/\Sigma\text{Fe}_{\text{Source}} = 0.036$), 'Red' = reduced ($\text{Fe}^{3+}/\Sigma\text{Fe}_{\text{Source}} = 0.021$). Dashed lines are fraction of melting (F) contours, listed to their right. Melting of more oxidised sources is associated with greater isotopic fractionation.

Fig. 7. After Sossi and O'Neill (2017). Iron isotope composition of mafic rocks (black triangle, MORB; white square, Hawai'i; grey circle, Tahiti) from the ocean basins (Teng et al., 2013), corrected to their primary magma compositions, plotted against Gd/Yb_N . Black lines show the iron isotope compositions of melts modelled by batch melting (Eq. (21)), at melt fractions given in grey, in both the garnet (gt) and spinel (sp) fields from a primitive mantle source (grey star), and of eclogite partial melts (ec), from an N-MORB source ($\delta^{57}\text{Fe} = +0.1\text{‰}$).

Fig. 8. After Foden et al. (2018). $\delta^{57}\text{Fe}_{(\text{IRMM-14})}$ vs. Slab Thermal Parameter (ϕ)/100km for population means for each arc or arc segment. The error bars are 2SE and the 95% uncertainty envelope of the linear regression is indicated as the black curves. Value for MORB is from Teng et al. (2013).

Fig. 9. After Heimann et al. 2008. An early compilation of iron isotope analyses in igneous rocks.

Fig. 10. $\delta^{57}\text{Fe}$ of whole rocks against their Mg#, characterising the change in iron isotope composition with differentiation. a) Analyses of co-genetic whole-rock samples from tholeiitic suites: green squares = Kilauea Iki (Teng et al. 2008), blue diamonds = Hekla (Schuessler et al. 2009), orange circles = Red Hill (Sossi et al. 2012) display disparate behaviour depending on whether the system evolved open (Hekla) or closed (Red Hill, Kilauea Iki) to oxygen exchange (see Systems open and closed to oxygen exchange). b) Simplified versions of Figs 4 and 7 from Toplis and Carroll (1996), highlighting the contrasting

1513 change in fO_2 relative to the FMQ buffer and Fe_2O_3 (wt. %) for conditions open and closed to oxygen exchange, respectively.
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1516 Fig. 12: After Debret et al. (2016). Increase in $\delta^{56}Fe$ and decrease of $Fe^{3+}/\Sigma Fe$ ratio in serpentinites during subduction. Bulk
1517 sample iron isotope composition versus $Fe^{3+}/\Sigma Fe$ in subducted Alpine lizardite (Liz-) and antigorite (Atg/Liz- and Atg-)
1518 bearing serpentinites are compared to the one of abyssal serpentinites.

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112x102mm (300 x 300 DPI)

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