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Iron isotope systematics in planetary reservoirs

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ABSTRACT

Iron is the only polyvalent major element, and controls reduction–oxidation (redox) reactions in a host of geologic processes and reservoirs, from the mineral- to planetary-scale, on Earth and in space. Mass transfer of Fe is often accompanied by changes in bonding environment, meaning the resultant variation in bond-strength in crystals, liquids and gases induces stable isotope fractionation, even at high temperatures. In the absence of iron exchange, electron transfer can also affect iron's valence state and calculated oxygen fugacity (fO_2), however its isotope composition remains unchanged. Thus, iron isotopes are a powerful tool to investigate processes that involve mass transfer, redox reactions and changes in bonding environment in planetary systems. Primitive chondritic meteorites show remarkable isotopic homogeneity, $\delta^{57}\text{Fe} = -0.01 \pm 0.01\text{‰}$ (2SE), over a wide range of Fe/Mg vs Ni/Mg, a proxy for fO_2 in the solar nebula. In chondrites, there are iron isotope differences between metal and silicates that become more pronounced at higher metamorphic grades. However, on a planetary scale, Mars and Vesta overlap with chondrites, preserving no trace of core formation or volatile depletion on these bodies. Upon assessment of pristine lherzolites, the Bulk Silicate Earth is heavier than chondrites ($\delta^{57}\text{Fe} = +0.05 \pm 0.01\text{‰}$; 2SE), and similar to or slightly lighter than the Moon. That the mantles of some differentiated inner solar system bodies extend to heavier compositions ($+0.2\text{‰}$) than chondrites may principally result from volatile depletion either at a nebular or late accretion stage. Within terrestrial silicate reservoirs, iron isotopes provide insight into petrogenetic and geodynamic processes. Partial melting of the upper mantle produces basalts that are heavier than their sources, scaling with degree of melting and driving the increasingly refractory peridotite to lighter compositions. Mid-Ocean Ridge Basalts (MORBs) are homogeneous to $\delta^{57}\text{Fe} = 0.10 \pm 0.01\text{‰}$ (2SE) after correction to primary magmas, and can be produced from single stage melt extraction. Conversely, iron isotopes in arc basalts are more varied ($-0.2 < \delta^{57}\text{Fe} (\text{‰}) < +0.2$) than can be produced from partial melting. Their iron isotope compositions are significantly lighter, suggesting they form from mantle re-enriched in light Fe and/or more depleted than Depleted MORB Mantle (DMM). If arc sources are more oxidised, an agent other than iron is required. Magmatic differentiation drives enrichment in heavy isotopes by partial melting of crustal rocks, fluid exsolution and crystallisation. Iron isotope trajectories in evolving magmas depend on their initial fO_2 and whether the system is closed or open to oxygen and/or mass exchange. Granite end-members carry signatures diagnostic of their tectonic setting, where reduced, anorogenic A-type granites ($\delta^{57}\text{Fe} = +0.4\text{‰}$) are heavier than more oxidised I-types ($\delta^{57}\text{Fe} = +0.2\text{‰}$).

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1. Introduction

Iron is the most abundant metal in the Solar System (Lodders, 2003), a product of its high binding energy during nuclear fusion in stars. Its three oxidation states, Fe^0 , Fe^{2+} and Fe^{3+} in terrestrial

bodies make it the most important control on, and indicator of the redox conditions that prevailed during their formation. Further, in planetary crusts and mantles, iron is a major element, and the primary constituent of metallic cores. Therefore, it contributes to determining phase equilibria, meaning that only significant mass transfer processes are able to shift its isotopic composition.

All other factors being equal, equilibrium stable isotope fractionation decreases with $1/T^2$ so that fractionation is smaller at high temperatures. Superimposed on this is the effect of changing iron bonding environment. Equilibrium stable isotope theory

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shows that bond strength is proportional to the isotopic composition of that phase (Urey, 1947), a finding later borne out in experimental work (e.g., Shahar et al., 2008). Therefore, to interpret stable isotope signatures, the parameters that affect bond strength, namely redox, co-ordination, spin state and ligand type (Schauble, 2004) should be deconvolved. These are in turn complex functions of pressure, temperature, composition and oxygen fugacity. Therefore, a sound knowledge of these variables is a pre-requisite in understanding the behaviour of iron isotopes during high temperature processes.

With the introduction of plasma-source multicollector mass spectrometers that *inter alia* efficiently ionise Fe, a growing database of iron isotope compositions revealed readily resolvable high-temperature iron isotope variations (Beard and Johnson, 2004; Williams et al., 2004; Zhu et al., 2001). Interpretation of these variations is not straightforward, pre-empting the more recent push for experimental and theoretical constraints on the direction and magnitude of fractionation (Hin et al., 2012; Poitras et al., 2009; Polyakov et al., 2007).

Here, we highlight some key advances at the forefront of iron isotope research at high temperatures and pressures; from the solar system to mineral scale. To facilitate quantitative analysis of stable isotope fractionation in nature, a compilation of experimentally-determined fractionation and β -factors for common igneous phases and planetary reservoirs is presented in Appendix A. Using these systematics, we show iron isotopes reflect processes in the nascent Solar System through investigation of chondrites, with implications for isotope variations in planetary bodies, including the Earth–Moon system. On Earth, we explore how iron isotopes can be exploited to detect igneous processes. A comparison amongst mafic igneous rocks from divergent and convergent tectonic settings reveals systematic isotopic differences between them, a feature also observed in their granitic equivalents. Here we demonstrate that iron isotopes, particularly when coupled with petrology and geochemistry, offer unique insight into high temperature and pressure geological processes.

2. Controls on iron isotope fractionation

2.1. A theoretical basis for isotope fractionation

The isotopic fractionation factor, $\Delta^{57}\text{Fe}_{A-B} = \delta^{57}\text{Fe}_A - \delta^{57}\text{Fe}_B$, that defines the isotopic partitioning between coexisting phases is related to the free energy of the isotopic exchange reaction, and is proportional to $1/T^2$ (Urey, 1947). The free energy change depends on the differences in force constant, K , between the two phases, a function of bond character. Condensed phase site properties can be estimated with the Pauling, 1929 bond valence principle, where the sum of bond valence of cations must equal anionic charge. All other factors being equal, heavier isotopes are preferentially incorporated into sites with higher charge (Z), lower coordination (C) and shorter bond length (r).

2.2. Oxidation and co-ordination environment of iron in high temperature and pressure systems

In phases whose composition is unconstrained by stoichiometry (i.e., fluids and melts), the relative proportions of Fe^{2+} and Fe^{3+} can change continuously, depending on the oxygen fugacity ($f\text{O}_2$):



Equilibrium (1) dictates that $\text{Fe}^{3+}/\Sigma\text{Fe}$ increases in a sigmoidal fashion, proportional to $\log f\text{O}_2^{1/4}$, where the transition from Fe^{2+} to Fe^{3+} occurs over ca. 16 log units (Berry and O'Neill, 2004). The

equilibrium constant describes the displacement of the sigmoid along the $\log f\text{O}_2$ axis, and is a complex function of temperature, pressure and composition (Jayasuriya et al., 2004; Kress and Carmichael, 1991).

This behaviour contrasts with $\text{Fe}^{3+}/\text{Fe}^{2+}$ in minerals, which is controlled by stoichiometry. Therefore, mineral composition must be known because iron may exist in different oxidation states and crystallographic sites depending on the extent of solid solution, affecting the force constant. For example, in titanomagnetite, iron varies from 2/3 Fe^{3+} in both IV- and VI-fold co-ordination in magnetite to wholly octahedrally co-ordinated ferrous iron in ulvöspinel.

The effect of melt or fluid composition on the co-ordination and oxidation state of iron can be understood in terms of the bond valence model:

$$\sum_i s_i = \sum_T s_T + s_{\text{Fe}} = |Z_{\text{O}}| = 2, \quad (2)$$

where s is the bond valence ($= Z/C$) between element i and O, and T is the total number of cations except Fe. If the oxidation state of Fe is constant, its co-ordination number, C , is given by:

$$C_{\text{Fe}} = \frac{Z_{\text{Fe}}}{(2 - \sum_T s_T)}. \quad (3)$$

It follows that $0 < s_T < 2$, meaning increasing the proportion of ions with lower bond valence causes C_{Fe} to increase. This is consistent with observations, where melts with higher alkali contents (low s) tend to stabilise iron in IV-fold co-ordination, whereas addition of alkaline earth metals (Ca, Mg, higher s) increases the mean co-ordination number (Jackson et al., 2005).

Similarly, equation (3) can be re-arranged to solve for the valence state of the element of interest:

$$Z_{\text{Fe}} = -C_{\text{Fe}} \left(-2 + \sum_T s_T \right) \quad (4)$$

Here, the oxidation state of Fe is inversely proportional to the bond valences of the other elements that co-ordinate oxygen. Again, these systematics are verified because alkalis, inversely proportional to their ionisation potential, are known to stabilise Fe^{3+} (Bingham et al., 2007; Mysen and Richet, 2005).

2.2.1. Pressure

The shortening and re-arrangement of atomic bonds as a response to increasing pressure means that this variable also influences the bonding environment of iron. Although changes in volume have only a small contribution to the free energy of the isotope substitution (Polyakov et al., 1994), pressure changes of the order of GPa induce significant bond strengthening, even within the same phase, thus concentrating heavier isotopes (Polyakov, 2009). Independent of this effect, iron also transitions to higher co-ordination in melts and minerals (polymorphism) with increasing pressure (Sanloup et al., 2013). Pressure-induced spin crossovers, from high- to low-spin as in ferroperricite in Earth's lower mantle (Badro et al., 2003), also causes significant bond shortening (Rustad and Yin, 2009). Further, the differential compressibility of Fe^{3+} and Fe^{2+} in silicate melts and minerals means that pressure can induce oxidation (O'Neill et al., 2006) and structural (Kress and Carmichael, 1991) changes. A manifestation of this is the co-existence of Fe^{3+} -rich perovskite with iron metal (Frost et al., 2004; Rohrbach et al., 2007) at lower mantle pressures.

2.2.2. Mass transfer

Iron isotope composition and oxygen fugacity are seldom directly related, because the oxidation and co-ordination of iron, and therefore its isotope composition, are influenced by other variables

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