

CONTROLS ON IRON ISOTOPE VARIATIONS IN PLANETARY MAGMAS. N. Dauphas¹, M. Roskosz², E.E. Alp³, C.K. Sio¹, F.L.H. Tissot¹, D. Neuville⁴, M. Hu³, J. Zhao³, L. Tissandier⁴, and E. Médard⁵, ¹Origins Laboratory, The University of Chicago, Department of the Geophysical Sciences and Enrico Fermi Institute (dauphas@uchicago.edu), ²Unité Matériaux et Transformations, Université de Lille, ³Advanced Photon Source, Argonne National Laboratory, ⁴Institut de Physique du Globe de Paris, ⁴Centre de Recherches Pétrographiques et Géochimiques-CNRS, Nancy, ⁵Laboratoire Magmas et Volcans, Université de Clermont-Ferrand.

Introduction: Of all documented planetary bodies such as Mars, Vesta, and the angrite parent-body (APB), Earth is the most oxidized [1]. Understanding how and when Earth's mantle acquired its present redox conditions is a major standing question in planetary sciences. Previous studies have suggested that iron isotopes could be good tracers of redox conditions during melting [2]. Terrestrial basalts, as well as more felsic rocks, tend to have heavy iron isotopic composition relative to chondrites and Earth's mantle [2, 3 and references therein]. For example, the average MORB $\delta^{56}\text{Fe}$ value is $\sim +0.1$ ‰ while chondrites have $\delta^{56}\text{Fe} \sim 0$ ‰ (Fig. 1). In contrast, basalts from Mars and Vesta have Fe isotopic compositions identical to chondrites within uncertainty. Three interpretations have been proposed to explain this feature: (1) during the Moon-forming giant impact, some isotopically light Fe was evaporated, leaving a residue enriched in heavy Fe isotopes [4]; (2) equilibration between metal and high-pressure phases such as ferropiclasite and post-perovskite created iron isotopic fractionation in Earth's mantle [5]; or (3) the isotopic composition measured in crustal rocks from Earth was produced by equilibrium or kinetic isotope fractionation between mantle peridotite and melt [2,6,7]. This poses several critical questions. What aspect of the melting process produces Fe isotopic fractionation? Why does melting on Earth or the APB fractionate Fe isotopes while on Mars and Vesta such fractionation is absent?

A difficulty addressing these interrogations is that we lack a database of equilibrium fractionation factors between melts and minerals to interpret the rock record. Iron equilibrium fractionation factors (or more specifically reduced partition function ratios, β) can be derived from Nuclear Resonant Inelastic X-ray Scattering (NRIXS) experiments at a synchrotron facility [5,8]. We have used this technique to determine the β -factors of olivine and geologically relevant silicate glasses. This study provides a solid reference for interpreting Fe isotopic variations in igneous rocks. Specifically, it reveals the potential of using Fe isotopes to trace redox variations and magmatic differentiation processes in planets.

Samples and Methods: NRIXS is a relatively new spectroscopic technique that allows one to probe the vibrational properties of certain elements in

solids [9,10]. Polyakov and coworkers have promoted the use of NRIXS for isotope geochemistry. In their approach, the PDOS is used to calculate the vibrational kinetic energy of ^{57}Fe , which is then employed to derive the β -factor. We have developed a new method (*i.e.*, the *general moment* approach), based on a Bernoulli expansion of the reduced partition function ratio, to calculate β -factors from the moments of the raw NRIXS spectrum. The first term in this expansion corresponds to the mean force constant of the iron bonds [11], a quantity that is readily measured and often reported in NRIXS studies,

$$1,000 \times \ln \beta(^{56}\text{Fe}/^{54}\text{Fe}) = 2,904 \frac{\langle F \rangle}{T^2}, \quad (1)$$

with $\langle F \rangle$ in N/m and T in K. Note that this equation is only valid at high temperature, as higher order moment terms should be included at lower temperature [8]. The cube of the energy is a factor in the integrand that give the force constant [12]. This means that even small bumps in the high-energy tails of the excitation function can have sufficient weight to affect the force constant and hence the equilibrium isotopic fractionation factors. Because these tails are characterized by low counting statistics, determining mean force

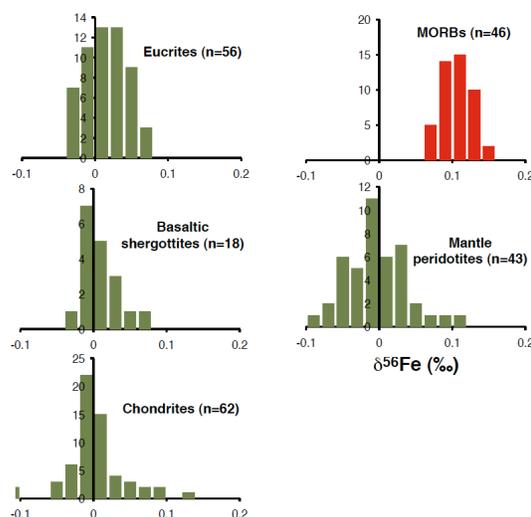


Fig. 1. Histograms of $\delta^{56}\text{Fe}$ values of planetary reservoirs [2, 3 and references therein]. The reason why Earth's crust has heavy $\delta^{56}\text{Fe}$ value compared to the mantle, chondrites, and basalts from other planetary bodies (Mars and Vesta) is not well understood.

constants is particularly challenging, as it requires broad energy scans and long acquisition times.

Glasses were synthesized from reagent grade oxides and pure ^{57}Fe ferric oxide. For each composition (basalt, andesite, dacite, rhyolite), three different samples, with different redox ratios were prepared in a CO/CO_2 gas mixing furnace. Redox ratios were then determined either by XANES or Mossbauer spectroscopy. Olivine crystals were prepared from a mixture of MgO , ^{57}FeO and SiO_2 . After annealing at ambient pressure under reducing conditions, the synthesis was performed at a few kilobars in a piston-cylinder apparatus (LMV, Clermont-Ferrand, France). Several olivine grains were then handpicked and characterized both by Raman spectroscopy and electron microprobe.

Results and Discussion: Examples of partial phonon density of states (PDOS) of olivine and basaltic glasses are shown in Fig. 2. Jackson et al. [13] measured the force constants of orthoenstatite pyroxene and obtained values of 195 ± 5 N/m (En93), 170 ± 3 N/m (En87), and 165 ± 5 N/m (En80). For olivine, we have obtained a value of 185 ± 5 N/m, similar to pyroxene. The force constant of magnetite is 230 ± 5 N/m [8]. We calculate from Eq. 1 an equilibrium $\delta^{56}\text{Fe}$ isotopic fractionation between magnetite and olivine of $+0.17 \pm 0.03$ ‰ at 600°C . Shahar et al. [14] determined experimentally the equilibrium isotopic fractionation between these two minerals at the same temperature and obtained a value of $+0.25 \pm 0.04$ ‰, very close to the value that we obtain. The small departure could be due to the fact that Shahar et al. studied fayalite (Fo0) while we analyzed Fo80.

At a given $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, the force constants of basaltic, andesitic, and dacitic glasses are identical. However, the force constant of rhyolitic glass is higher. For all samples, the force constant increases with the Fe^{3+} content. Thus, for mafic melts, there is little structural control on iron isotopic fractionation; redox effects seem to dominate. The relationship between force constant and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ for basalt, andesite, and dacite is approximately linear. We can estimate the force constants of Fe^{2+} and Fe^{3+} in basalt by interpolating the data to $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}=0$ and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}=1$. We thus estimate that $\langle F \rangle$ for Fe^{2+} in basaltic melt is close to olivine (~ 200 N/m) while $\langle F \rangle$ for Fe^{3+} is much higher (~ 350 N/m). At $1,200^\circ\text{C}$, this corresponds to an equilibrium $\delta^{56}\text{Fe}$ fractionation between the two oxidation states of iron in magmas of $+0.2$ ‰. This represents a very large equilibrium Fe isotopic fractionation for igneous rocks.

The average $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of MORBs is approximately 0.16 [15]. Using a force constant of ~ 180 N/m for olivine and pyroxene, ~ 200 N/m for Fe^{2+} in basaltic melts, and ~ 350 N/m for Fe^{3+} , we calculate an equilibrium fractionation between the melt and the residue of $\sim +0.05$ ‰ ($+0.03$ ‰ due to $\delta\text{Fe}^{2+}\text{melt}-\delta\text{Fe}^{2+}\text{solid}$ and

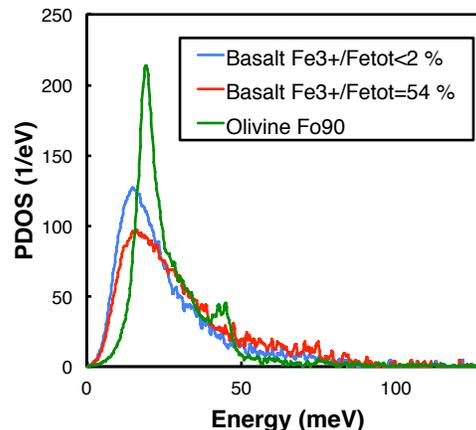


Fig. 2. Measured partial phonon density of states of two basaltic glasses and olivine. The force constant that gives the equilibrium iron isotope fractionation between phases can be calculated by taking the second moment of the PDOS or the third moment of the excitation function (not shown) [8,12].

$+0.02$ ‰ due to $\delta\text{Fe}^{3+}\text{melt}-\delta\text{Fe}^{2+}\text{solid}$). MORBs have a $\delta^{56}\text{Fe}$ value of $\sim +0.1$ ‰. Earth's mantle $\delta^{56}\text{Fe}$ value is still uncertain but may be around $+0.04$ ‰ [6,16], corresponding to a melt-solid $\delta^{56}\text{Fe}$ fractionation of $\sim +0.06$ ‰. The inferred fractionation from NRIXS data is thus very close to that measured in terrestrial basalts. This demonstrates that partial melting and magmatic differentiation processes can explain iron isotope variations in planetary basalts.

This study also provides a basis for developing other redox-sensitive isotope tracers such as V for Earth or Cr for the Moon.

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