

EQUILIBRIUM METAL-SILICATE Fe ISOTOPE FRACTIONATION AND THE IMPLICATIONS FOR DIFFERENTIATION IN PLANETARY BODIES. M. K. Jordan¹ and E. D. Young, ¹Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, USA, mkjordan@ucla.edu, eyoung@ess.ucla.edu.

Introduction: Previous work has shown that there is a measureable Si isotope effect due to core formation [1]. The effect arises because of fractionation between Si in iron metal and Si in silicates [2]. This effect was verified by comparing fractionation in the laboratory and in enstatite achondrites [2, 3]. One might expect to observe a similar effect for Fe isotopes due to fractionation between metal and silicate.

Based on analyses of mantle-derived rocks, Poitrasson [4] suggested that the Earth and Moon have high $^{57}\text{Fe}/^{54}\text{Fe}$ due to evaporation of melt produced during the giant impact that formed the Moon. These arguments are predicated on the assumption that igneous differentiation does not fractionate Fe isotopes, a subject of debate [5, 6]. For example, Craddock et al. [6] found no resolvable difference in $^{57}\text{Fe}/^{54}\text{Fe}$ between abyssal peridotites and chondrites. Mid-ocean ridge basalts were found to be greater than peridotites and chondrites in $^{57}\text{Fe}/^{54}\text{Fe}$. This implies that the bulk silicate Earth is not enriched in $^{57}\text{Fe}/^{54}\text{Fe}$ and is instead chondritic, arguing against both the evaporation effect and core-formation effect. In all cases, evaluation of the potential for a core-formation effect on bulk silicate Earth $^{57}\text{Fe}/^{54}\text{Fe}$ requires an evaluation of the fractionation factor between metal and silicate as a function of temperature.

Magmatic iron meteorites exhibit similar offsets in $^{57}\text{Fe}/^{54}\text{Fe}$ relative to chondrites of $\sim 0.2\%$ [7]. Though not definitive, this is suggestive of heavy Fe partitioning into the cores of differentiated bodies. Understanding equilibrium Fe isotope fractionation between metal and silicate phases is fundamental to assessing the significance of the variation of Fe isotopes in the solar system.

Measurements of Fe isotope fractionations between phases in meteorites, and measurements in the laboratory, have yielded contradictory results for $^{57}\text{Fe}/^{54}\text{Fe}$ equilibrium fractionation between metal and silicate. Using the metal and silicate phases of pallasites, Poitrasson et al. [7] and Zhu et al. [8] found the metal to be high in $^{57}\text{Fe}/^{54}\text{Fe}$ compared to the olivine grains, while Weyer et al. [9] found no systematic difference between the two phases. The equilibration of Fe isotopes between metal and olivine in pallasites is debated [7, 9]. Experimental results have failed to provide a more definitive answer. Shahar et al. [10, 11] used piston cylinder experiments and found the metal to be isotopically heavy relative to silicate, while Hin et al. [12] found no significant fractionation, even at low temperatures.

Here we establish the equilibrium Fe isotope fractionation between the metal and silicate phases using a differentiated aubrite, Norton County. This temperature calibration allows us to assess the degree of equilibration in other differentiated bodies.

Sample Description: Norton County is a brecciated aubrite (enstatite achondrite), consisting primarily of nearly FeO-free enstatite (84.5 vol. %) with forsterite, diopside, and plagioclase comprising the remaining silicate material. The low Fe content in the silicate material is a result of the reducing conditions under which aubrites formed and renders analysis of the silicate phase difficult. The metal occurs mainly as irregular shaped grains and accounts for about 1-1.5 vol% of the meteorite. The metal consists mainly of kamasite, with lesser amounts of perryite and schreibersite [13, 14].

Ziegler et al. [3] determined the $^{29}\text{Si}/^{28}\text{Si}$ fractionation between metal and silicate phases for Norton County. The agreement between the Si isotope temperatures calibrated in the laboratory and previous Si-concentration thermometry establishes that this rock is in isotopic equilibrium at a known temperature of $1130 \text{ K} \pm 80 \text{ K}$ [2, 3, 15].

Analytical Methods: Large grains of enstatite were crushed using a mortar and pestle. Metallic particles were then removed with a hand magnet before dissolution. Silicates were dissolved on a hotplate in a 3:1 mixture of concentrated HF and HNO₃. Samples were then sequentially dissolved in concentrated HNO₃, concentrated HCl, and aqua regia to achieve full dissolution. A diamond-blade saw was used to extract metal pieces. Metals were dissolved in concentrated HCl. The dissolved metal was then centrifuged and decanted to remove any undissolved adhering silicate material.

Ion-exchange chromatography was used to separate Fe. Samples were loaded on to columns consisting of 0.3 mL AG 1-X8 resin (100-200 mesh, chloride form). Matrix elements are eluted using 8 N HCl and Fe is eluted using 0.5 N HCl. At minimum, we require $\sim 10 \mu\text{g}$ of Fe to make precise measurements. There is a Mg to Fe ratio of 500:1 in the silicate material from Norton County, requiring $\sim 20 \text{ mg}$ of silicate to obtain sufficient Fe from the silicate samples. An additional column is used first to remove the large amounts of Mg, which would overload the column described above. This column consists of 1 mL of AG 50-X8 resin; Mg is eluted with 10 N HCl and Fe is eluted with 4 N HCl.

Data were collected on a ThermoFinnigan NeptuneTM multiple-collector inductively coupled plasma-

source mass spectrometer (MC-ICP-MS). Samples were run in dry plasma mode using the Cetac Aridus IITM desolvating nebulizer system to minimize argon oxide and nitride interferences. Samples were run at a mass resolving power (instrumental $\Delta m/m$) of >9000 to resolve ArO^+ among other isobaric interferences. Corrections for instrumental mass bias were made using sample-standard bracketing and peak height matching between samples and standards. Samples were measured against IRMM-14.

Results: Data are reported as per mil deviations from the standard IRMM-14. The average metal $\delta^{57}\text{Fe}$ value is $0.224\text{‰} \pm 0.017$ (1 SE). The average silicate $\delta^{57}\text{Fe}$ value is 0.014 ± 0.013 (1 SE). The calculated isotopic fractionation is $\Delta^{57}\text{Fe}_{\text{metal-silicate}} = 0.21\text{‰} \pm 0.02$ (1 SE), indicating that, unlike Si, the heavy isotopes partition into the metallic phase.

We can use the equilibration temperature of Norton County in conjunction with the equilibrium Fe isotope fractionation between metal and silicate to establish a temperature calibration since fractionation varies as $1/T^2$ (Figure 1). The experimental result from Shahar et al. [9] for $T = 1923$ K and $P = 1$ GPa, assuming negligible sulfur content, is also plotted for comparison. This result agrees with our calibration within uncertainties. Our results disagree with the findings of Hin et al. [10] that indicate that there is no discernable fractionation, even at low temperatures.

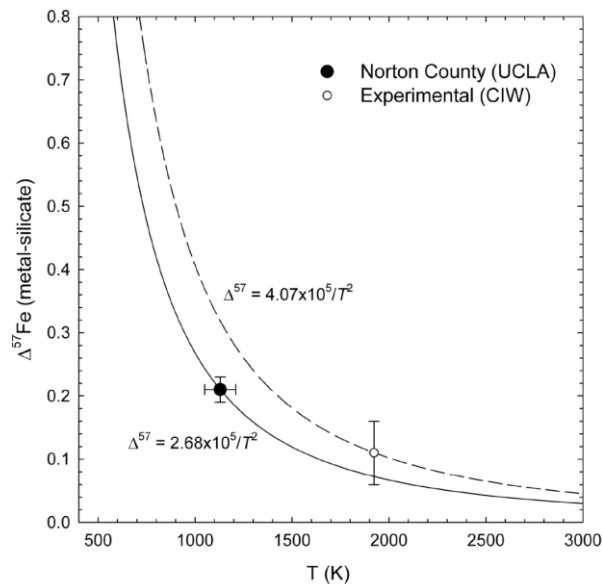


Figure 1. Temperature calibration of equilibrium Fe isotope fractionation based on Norton County Data. Experimental temperature calibration from Shahar et al. (2013) also plotted.

Discussion: This temperature calibration can be used to assess the likelihood and degree of equilibra-

tion in other objects. Unrealistic temperatures from metal-silicate pairs indicate disequilibrium with respect to Fe isotopes. The typical $\Delta^{57}\text{Fe}_{\text{metal-silicate}}$ of $\sim 0.2\text{‰}$ among meteoritical materials implies equilibration temperatures of ~ 1150 K. Applying the temperature calibration to core-mantle differentiation of the Earth gives a Fe metal-silicate isotope fractionation of 0.03‰ , assuming the temperature of equilibration at the base of the magma ocean was 3000 K [16]. Using this information and mass-balance, we would expect the $\delta^{57}\text{Fe}$ of the BSE to be approximately 0.02‰ below chondritic $\delta^{57}\text{Fe}$. This value is at, or just below, our current level of detection. Thus, our results suggest that fractionation at the pressure and temperature conditions relevant to the Earth is, at present, undetectable.

The calibration is better suited for smaller bodies that formed at lower temperatures and pressures, such as Vesta. Using a temperature of less than 2000 K [17] for Vesta, we would expect metal-silicate fractionation of about $0.06\text{--}0.07\text{‰}$, with the bulk silicate material being at least 0.05‰ lighter in $\delta^{57}\text{Fe}$ relative to bulk chondrite.

The Fe isotope fractionation measured here implies that the enrichment in heavy Fe in the Moon and BSE cannot be attributed to core formation. However, there may be a pressure effect for large bodies, like the Earth, complicating the extrapolation of our measured fractionation [18].

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