

IRON ISOTOPE FRACTIONATION DURING PLANETARY DIFFERENTIATION. A. Shahar¹, L. A. Kaufman¹, M. F. Horan², T. D. Mock², L. Deng¹, and C. A. Macris³, ¹Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. N.W. Washington, D.C. 20015, ashahar@ciw.edu, ²Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd. N.W. Washington, D.C. 20015, ³Department of Earth and Space Sciences, UCLA, Box 951567, Los Angeles, CA, 90095.

Introduction: Understanding the behavior of iron is essential to unraveling the chemical and physical processes attending planetary differentiation. One of the few remaining properties of iron where there is still considerable debate is whether iron is isotopically fractionated during core formation. While theoretical calculations predict a small, yet resolvable fractionation between high-pressure silicate phases and metallic iron [1], neither experimental measurements [2] nor natural samples show evidence for high temperatures equilibrium fractionation.

Determining whether there is an equilibrium iron isotope fractionation between metal and silicate is central to understanding the Fe isotope signatures found within different meteorites and planetary bodies. Metal from pallasites has higher $^{57}\text{Fe}/^{54}\text{Fe}$ relative to co-existing olivine [3,4], implying that the core of the Earth also might be enriched in $^{57}\text{Fe}/^{54}\text{Fe}$ relative to the bulk silicate Earth (BSE). However, iron meteorites, the Moon and BSE all have heavier Fe than chondrites [5,6]. If iron meteorites are derived from asteroid cores and the BSE, by definition, excludes the fraction of iron that is in the core, then it is paradoxical that both are higher in $^{57}\text{Fe}/^{54}\text{Fe}$ than chondrites. Despite the isotopic similarity of almost every other element, between the Earth and Moon, the average composition of iron from lunar samples is more enriched in $^{57}\text{Fe}/^{54}\text{Fe}$ than mantle-derived terrestrial samples. Therefore, it is unclear not only if there is an equilibrium iron isotope fractionation between metal and silicate at high temperature, but also in the direction the possible fractionation.

There has been much work done to measure the Fe isotopic compositions of natural samples and to predict theoretically the conditions under which Fe should fractionate. By contrast, only one published experimental study has attempted to constrain Fe fractionation between metal and silicate at high temperature and pressure [2]. Here, we aim to systematically determine whether there is an equilibrium iron isotope fractionation between metal and silicate at high pressure and temperature, with a particular emphasis on attainment of isotopic equilibration during each experiment.

Methods: Starting materials for the experiments were oxides in pyrolitic proportions and iron powder in a 2:1 ratio. Piston cylinder experiments were conducted at 1 GPa using a half-inch talc and Pyrex assembly

at the Geophysical Laboratory. Temperatures ranged from 1600°C-1800°C. The samples were contained in either a graphite or MgO capsule, brought to the desired temperature and pressure and then quenched at several time intervals ranging from 5 to 120 minutes. Run products consisted of Fe metal blobs and olivine crystals surrounded by a silicate glass. The run products were then broken in half. One half of the recovered sample was polished and analyzed on an electron probe. The other half was broken apart and mechanically separated with a magnet into silicate and metal portions. This step was crucial in making sure that there was no contamination of metal in the silicate crystals. Silicate fractions were purified by anion exchange. Finally, the isotope ratios were measured with a Nu Plasma II MC-ICPMS in pseudo high mass resolution mode.

In order to evaluate whether Fe isotopic equilibration was achieved during each experiment, the three-isotope technique was implemented [7,8]. In short, the technique incorporates the use of an isotopic spike (^{54}Fe in this case) to create a secondary fractionation line on which all samples at equilibrium must lie. In order to demonstrate that an experiment was at equilibrium, three criteria were used: 1. Microprobe analyses of several time steps must show uniform chemical compositions, implying minimal incorporation of capsule material. 2. Metal and silicate aliquants must lie on the same fractionation line, as required by the three-isotope technique. 3. Textures of the run products must show that the system had been molten and therefore convecting during the experiment, implying the lack of a temperature gradient.

Results and Discussion: Of the 54 experiments conducted so far, few have passed all the requirements for isotopic and chemical equilibrium. The biggest experimental challenge was interaction with the capsule material. This resulted in either Mg being incorporated into the sample and Fe being lost to the capsule, or in carbon added to the iron metal.

1650°C. A set of experiments at 1650°C showed identical elemental compositions, as measured by microprobe, and plotted on the same Fe isotope fractionation line. In the experiment quenched after 120 minutes, no iron could be detected in the surrounding MgO capsule. The Fe isotopic composition of metal portions of experiments quenched after 5 and 120 minutes were

identical, as expected, because most of the iron is in the metal. As can be seen in Figure 1, the silicate (green circle) from the experiment quenched after 5 minutes had not achieved isotopic equilibrium. However, in the experiment quenched after 120 minutes Fe was isotopically equilibrated. The final fractionation between metal and silicate was $\Delta^{57}\text{Fe}_{\text{metal-silicate}} = 0.12 \pm 0.08 \text{ ‰}$. While this fractionation is small, it is resolvable and shows that the metal is more enriched in $^{57}\text{Fe}/^{54}\text{Fe}$ than silicate.

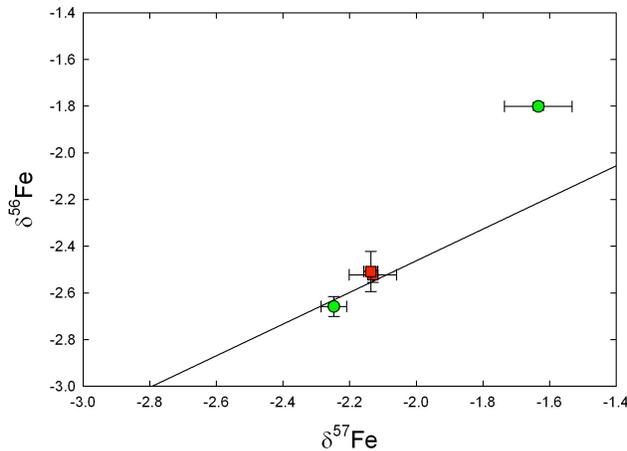


Figure 1. Three-isotope plot showing iron isotope analyses of two experiments (5 and 120 minutes) at 1650°C. Green circles are silicate and red squares are metal.

Temperature. Further experiments at 1700°C also showed an equilibrium fractionation similar to that achieved at 1650°C. A temperature dependent curve drawn through these data, an experimental datum at 1750°C from [2] and the origin can be constructed (Figure 2), resulting in a slope of ~ 0.72 . Although the absolute slope of this line has a large uncertainty, it is resolvably non-zero. Further work will allow for a more accurate temperature dependence.

Planetary Differentiation. Stable isotopes can be a powerful tool for unraveling planetary scale processes. In this work we have determined that there is a resolvable equilibrium iron isotope fractionation between metal and silicate even at high temperature. Heavier Fe is preferentially incorporated into the metal relative to the silicate phase. The result agrees with the direction of the fractionation observed in pallasites, and implies that the iron isotope fractionation seen in pallasites could be a result of equilibrium conditions at high temperature. Extrapolation of these experimental results to $\sim 3000 \text{ K}$, close to the temperature of a magma ocean, suggests that planetary differentiation should result in iron isotopic fractionation of $\sim 0.08 \text{ ‰}$ between core and mantle.

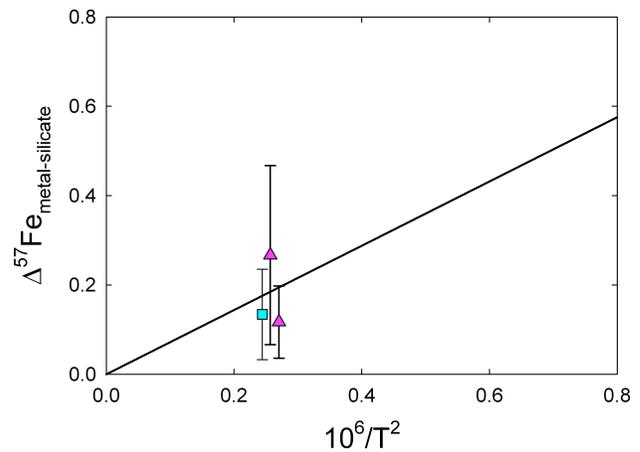


Figure 2. Iron isotope fractionation between metal and silicate as a function of temperature. Pink triangles are from this work, and the blue square is from [2]. Errors are 2 s.e.

The Fe isotope fraction measured in this work suggests that equilibrium fractionation cannot explain the enrichment of heavy Fe in the moon and BSE relative to chondrites, unless a different fractionation mechanism occurs at higher temperature or pressure. Such a mechanism may not be unrealistic as a recent theoretical paper [1] showed that the direction of the fractionation could change as a function of pressure. Experiments at higher pressure are needed to determine if this is indeed the case.

References: [1] Polyakov, V. B. (2009) *Science*, 323, 912-914. [2] Poitrasson F. et al. (2009) *EPSL*, 278, 376-385. [3] Zhu, X. K. et al. (2002) *EPSL* 200, 47-62. [4] Poitrasson F. et al. (2005) *EPSL* 234, 151-164. [5] Schoenberg, R. and von Blanckenburg, F. (2006) *EPSL* 252, 342-359. [6] Poitrasson, F. et al. (2004) *EPSL* 223, 253-266. [7] Matsuhisa Y. et al. (1978) *GCA*, 42, 173-182. [8] Shahar A. et al. (2008) *EPSL*, 268, 330-338.