

Iron Isotope Fractionation in an Fe-S alloy: Implications for Core Formation. A. Shahar¹, V. J. Hillgren¹, J. Mesa-Garcia¹, M.F. Horan², T. D. Mock² and L. Deng^{1,3}, ¹Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. NW, Washington D.C. 20015; ashahar@ciw.edu, ²Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd. NW, Washington D.C. 20015, ³Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China.

Introduction: Using iron isotope fractionations measured in planetary and meteorite samples to trace planetary differentiation or formation has yielded contradictory results [1,2]. Iron from lunar samples is more enriched in $^{57}\text{Fe}/^{54}\text{Fe}$ than mantle-derived terrestrial samples, in contrast to the isotopic similarity for almost every other element between the Earth and Moon. SNC (Shergottite, Nakhilite, Chassigny) and HED (Howardite, Eucrite, Diogenite) meteorites, which are thought to be derived from the mantles of Mars and Vesta, respectively, show no isotopic fractionation relative to chondrites [3]. While the Bulk Silicate Earth (BSE) value is debated, recent work has shown effectively that basalts (mid-ocean ridge basalts, terrestrial basalts, and ocean island basalts) are enriched in $^{57}\text{Fe}/^{54}\text{Fe}$ relative to chondrites, but the causes of that fractionation are unclear [4]. Angrites, basaltic achondrite meteorites, also show enrichment in $\delta^{57}\text{Fe}$ [5]. Possible mechanisms include high-pressure core formation [1], oxidation during perovskite disproportionation [6], evaporation during the giant impact [3], and mantle melting [4]. It is important to reconcile why the Earth's basalts are enriched in $^{57}\text{Fe}/^{54}\text{Fe}$ but the meteorites from Mars and Vesta are not. A possible explanation is that Mars and Vesta are smaller and the lower pressure attenuated the potential Fe fractionation during core formation [1], or that the intrinsic oxidation states of the planets are causing the differences [4]. Another option is that the light elements (e.g. S, C, O, H, Si) in the cores of differentiated bodies control the iron isotope fractionation during differentiation, and that Mars and/or Vesta are enriched in $^{57}\text{Fe}/^{54}\text{Fe}$ relative to their respective cores. For Mars, in particular, sulfur is thought to play a major role in its differentiation history resulting in ~14 wt. % S in the core.

Methods: We conducted experiments at 1 GPa and 1650°C in a piston cylinder apparatus using a mixture of synthetic Martian composition mantle and an Fe-Ni-S alloy with varying sulfur contents (5, 10, 17 wt. %). By varying the sulfur content, but nothing else, we aimed to determine the effect of bond partner on the isotopic fractionation of iron between metal and silicate. All experiments were conducted in boron nitride capsules to minimize interactions between the experimental run products and the capsule. The experiments were conducted for durations of 5 to 150 minutes and the three-isotope technique [7] was used

to prove isotopic equilibrium. After each experiment, the capsule was broken in half. One side of the experiment was polished and analyzed with an electron microprobe or SEM for chemical analysis. The rest of each sample was crushed, separated, and purified for iron isotope analyses. Iron isotope ratios were measured with a Nu Plasma II multiple collector inductively coupled plasma mass spectrometer.

Results: Figure 1 shows the iron isotopic fractionation between metal and silicate ($\Delta^{57}\text{Fe}_{\text{metal-silicate}}$) as a function of the atomic percent sulfur in the experimental run products. There is a strikingly strong dependence of the fractionation factor between metal and silicate with sulfur content in the iron alloy. Calculating the oxygen fugacity of the experiments is problematic due to the presence of S in the metal. However, the similarity in Fe content of the glasses and metals suggests that all experiments have nearly the same $f\text{O}_2$ as demonstrated by a simple calculation comparing the mole fraction of FeO in the silicate to the mole fraction of Fe in the metal. While $f\text{O}_2$ has been argued to be the leading mechanism for iron isotopic fractionation at high temperature, in this case, the addition of a light element into the metal is causing the fractionation [8].

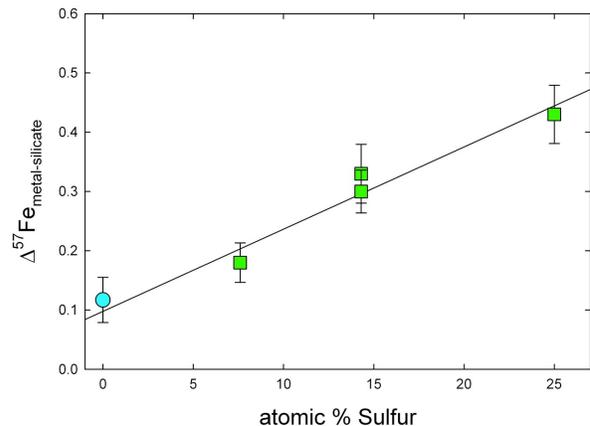


Fig. 1 $\Delta^{57}\text{Fe}_{\text{metal-silicate}}$ versus atomic % sulfur in the experiments. Green squares show results obtained from Mars-like starting compositions, while the blue circle has an Earth-like starting composition and contains no sulfur in the metal.

Discussion: The dependence of iron isotope fractionation between metal and silicate on sulfur content can be understood by considering the work of Alfe and Gillan [9]. The authors conducted first-principles electronic structure calculations on a liquid Fe-S alloy

with 12 wt. % S. They concluded that the covalent Fe-S bond is stronger than the metallic Fe-Fe bond, that sulfur atoms repel, and that the distribution of Fe and S in the alloy is essentially random. These results suggest that, when more S is added to an Fe alloy, it forms a greater number of covalent Fe-S bonds. Because these bonds are stiffer, they are more enriched in ^{57}Fe and consequently enrich the alloy in ^{57}Fe . Increasing sulfur content in the alloy, therefore, should result in larger $\Delta^{57}\text{Fe}_{\text{metal-silicate}}$. There are no theoretical calculations of the iron isotopic fractionation expected in the Fe-Ni-S alloy system. The presence of iron sulfide minerals, by contrast, appears to drive fractionation in the opposite direction [10], which suggests that sulfur in alloys and in sulfide minerals has very different bonding structures.

This study shows that high-temperature iron isotopic fractionation between metal and silicate increases when S is incorporated into the metal portion of the system. It therefore has wide implications for tracing differentiation processes and the sulfur content of differentiated bodies. The nature of the light element in an Fe-Ni core is directly related to the mode of formation, for example, the pressure of differentiation and the redox conditions present. Of all the light elements that alloy with Fe at high pressure and temperature, the Fe-FeS system has the lowest eutectic temperature. That is, as a planetary body heats up and starts to melt, a small amount of Fe-S melt will be generated and core formation will begin. We find that the amount of sulfur in a Fe-Ni core should influence the extent of equilibrium iron isotopic fractionation measured in samples of the mantle, relative to the core and to the planetary building blocks. Our study suggests that adding S to the metallic portion of a differentiated body enriches the core in the heavy Fe isotopes and should leave the mantle more depleted in the heavy isotopes.

Figure 2 shows the $\delta^{57}\text{Fe}$ of a Martian mantle calculated as a function of the weight % S in the core, at several temperatures. If the content of sulfur in the core were the only parameter controlling the $\delta^{57}\text{Fe}$ of the mantle and the SNC meteorites, then the meteorites should show a slightly negative $\delta^{57}\text{Fe}$, dependent on the temperature of core-mantle differentiation. It could therefore be argued that the Martian core segregated with no sulfur. There is ample evidence, however, that sulfur is one of the light elements present in the Martian core as it is thought that the core is liquid [11], [12]. If there is sulfur in the core of Mars, then our study suggests that another process fractionated iron isotopes in the SNC meteorites post differentiation. A possibility is partial melting to form basalts on Mars, as on Earth and on the angrite parent body, could cause

$\sim 0.1\%$ enrichment in $\delta^{57}\text{Fe}$ in the melts, relative to their mantle source. More experiments are necessary to determine if melting the martian mantle can produce iron isotope compositions measured in the SNC meteorites.

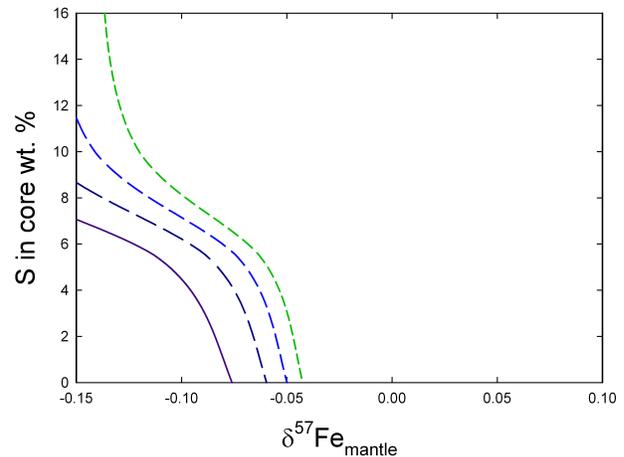


Fig. 2 This plots compare the Fe isotope compositions measured in SNC meteorites with models for the Fe isotope compositions of the martian mantle as predicted by the results of this study. The curves show the $\delta^{57}\text{Fe}$ expected for a Martian mantle that differentiated at different sulfur contents and temperatures. The solid curve shows the temperature (1923 K) at which the experiments in this study were conducted. The dotted curves represent the range of temperatures (2100K \pm 200 K) of Martian differentiation inferred from siderophile element partitioning [13]. In all cases the modeled mantle compositions have lighter Fe than measured in SNC meteorites (with $\delta^{57}\text{Fe} \sim 0$).

References: [1] Polyakov V. B. (2009) *Science*, 323, 912-914. [2] Weyer S. et al. (2005) *Earth and Planet. Sci. Lett.* 240, 251-264. [3] Poitrasson F. et al. (2004) *Earth and Planet. Sci. Lett.* 223, 253-266. [4] Craddock P. R. et al. (2012) *LPSC XLIII* Abstract # 1672. [5] Wang K. et al. (2012) *Geochim. Cosmochim. Acta* 89, 31-45. [6] Williams H. M. et al. (2012) *Earth and Planet. Sci. Lett.* 321, 54-63. [7] Shahar et al. (2008) *Earth and Planet. Sci. Lett.* 268, 330-338. [8] Daphaus N. and Craddock P. R. (2009) *Earth and Planet. Sci. Lett.* 288, 255-267. [9] Alfe D. and Gillan M. J. (1998) *Physical Rev. B.* 58, 8248-8256. [10] Polyakov V. B. and Sultantov D. M. (2011) *Earth and Planet. Sci. Lett.* 252, 342-359. [11] Williams J. P. and Nimmo F. (2004) *Earth and Planet. Sci. Lett.* 321, 54-63. [12] Yoder C. F. et al. (2003) *Science* 300, 299-303. [13] Righter K. and Chabot N. L. (2011) *Meteoritics & Planet. Sci.*, 46, 151-176.