THE EFFECTS OF CORE COMPOSITION ON IRON ISOTOPE FRACTIONATION DURING PLANETARY DIFFENENTIATION. S. M. Elardo[1], A. Shahar[1], and R. Caracas[2]. [1]Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. NW, Washington, DC 20015, USA. [2]CNRS, Ecole Normale Supérieure de Lyon, Université Claude Bernard Lyon 1, Laboratorie de Géologie de Lyon, UMR 5276, 69364 Lyon Cedex 07, France. selardo@carnegiescience.edu

Introduction: High-precision analyses of Fe stable isotope ratios in planetary materials have revealed significant variations among the currently sampled planets and asteroids. As Fe is one of the most abundant elements in the bulk Earth and a major element in the cores, mantles, and crusts of the terrestrial planets and large asteroids, these isotopic variations have the potential to record information about the conditions of planetary formation and differentiation. In general, basaltic samples from Mars and Vesta have Fe isotopic compositions similar to the homogeneous chondritic δ^{57}Fe value of ~0‰ [1-5]. Basaltic lavas from the Moon have an average δ^{57}Fe heavier than chondrites, but in detail span a large range in δ^{57}Fe from -0.03 ± 0.05‰ to 0.27‰ ± 0.03‰ [2, 3]. Estimates for the composition of bulk silicate Earth are variable. Peridotites are heterogeneous, but have an average global composition that is chondritic [6, 7], though others have argued that the primitive mantle composition is heavy (roughly 0.10‰) [e.g., 8].

Multiple hypotheses have been proposed to explain the Fe isotopic differences among planetary samples. Some workers have argued that a heavy terrestrial mantle and the heavy average δ^{57}Fe of lunar basalts is representative of light isotope loss during the Giant Impact [e.g., 2]. Other workers have suggested that estimates of the δ^{57}Fe of bulk planets correlate with indicators of volatile depletion and that the δ^{57}Fe differences among planets is a signature of accretion [5]. The disproportionation of Fe^{2+} by bridgmanite in Earth's deep mantle can also cause heavy isotope enrichment in the mantle [9]. We have previously shown that core formation leads to significant Fe isotope fractionation during planetary differentiation, and that this fractionation leads to light Fe isotope enrichment in planetary mantles [10, 11]. The magnitude of this fraction is a function of the amount of S and/or Ni planetary cores, whereas C has essentially no effect. In order to further investigate the effect of planetary core composition on Fe isotope fractionation during differentiation in smaller planetary bodies, we have conducted high-pressure and –temperature experiments to investigate the effects of Si entering cores. Since these experiments do not accurately capture the effects of high pressure relevant to Earth, we have also conducted density functional theory (DFT) calculations to determine Fe isotope beta-factors for phases relevant for terrestrial core formation. These data can be used to constrain the Fe isotope compositions of planetary mantles and address the Fe isotopic differences among planetary basalts.

Experimental and Analytical Methods: High-pressure and -temperature experiments were conducted in an end-loaded piston cylinder at the Geophysical Laboratory (GL). Starting materials consisted of the model peridotite composition used by Elardo and Shahar [11]. The peridotite was mixed Goodfellow $Fe_{91}Si_9$ and Alfa Aesar 99.995% pure Fe metal to create two mixes with nominal metal compositions of $Fe_{91}Si_9$ and $Fe_{95.5}Si_{4.5}$. Starting materials were spiked with ^{54}Fe such that the three-isotope exchange method could be used to assess isotopic equilibrium. Graphite capsules were used despite the fact that C will enter the metal phase. Elardo and Shahar [11] showed that there is no significant Fe isotope fractionation between peridotite and Fe-C alloys at 1850 °C without other metal-bound elements, and C will not react to produce a third Fe-bearing phase. All experiments were conducted at 1 GPa and 1850 °C for between 30 mins to 3 hours. Shahar et al. [10] and Elardo and Shahar [11] showed that isotopic equilibrium is achieved within this timeframe at these P-T conditions, and this was confirmed here with the three-isotope exchange method.

Run products were split for chemical and isotopic analyses. The compositions of Fe-Si alloys and quenched silicate melts were analyzed using the silicon-drift detector energy dispersive spectrometry on the JEOL 6500 field-emission SEM at the Geophysical Laboratory. Samples were coated with Ir and C contents of metal phases were determined using Alfa Aesar 99.999% pure Fe-metal as a C blank. The remaining half was crushed and pure metal and silicate fractions were picked under a microscope with the aid of a magnet. Fractions were dissolved in concentrated acids and Fe was purified from matrix elements using the short-column procedure outlined in [1]. Isotopic compositions were determined using the Nu Plasma II MC-ICP-MS at GL. Analyses were conducted in high-resolution mode and ^{53}Cr was monitored to correct for the Cr isobaric interference ^{54}Fe. Sample-standard bracketing was used to correct for instrumental drift.

Density Functional Theory: Theoretical beta-factors used to calculate the mass dependent iron isotope fractionation were estimated using the standard thermodynamic approach as obtained from phonon integration in crystalline materials. These calculations were made using density functional perturbation theory in the ABINIT implementation. Full details on these calculation methods can be found in Shahar et al. [12].

Results: Our piston cylinder experiments resulted in Fe-Si-C alloys containing between 1.3 and 8.1 at. % Si. The $\Delta^{57}Fe_{Core\text{-}Mantle}$ (i.e., $\delta^{57}Fe_{Metal}$ - $\delta^{57}Fe_{Silicate}$) values for these experiments are generally consistent with the results for S- and Ni-bearing Fe alloys from Shahar et al. [10] and Elardo and Shahar [11] (Fig. 1). The results of DFT calculations show that at pressures of 40 and 80 GPa, the $\Delta^{57}Fe_{Metal\text{-}Bridgmanite}$ is negative. The $\Delta^{57}Fe_{Metal\text{-}Bridgmanite}$ for FeSi at 80 GPa is positive and roughly a factor of two greater in magnitude than the Fe metal.

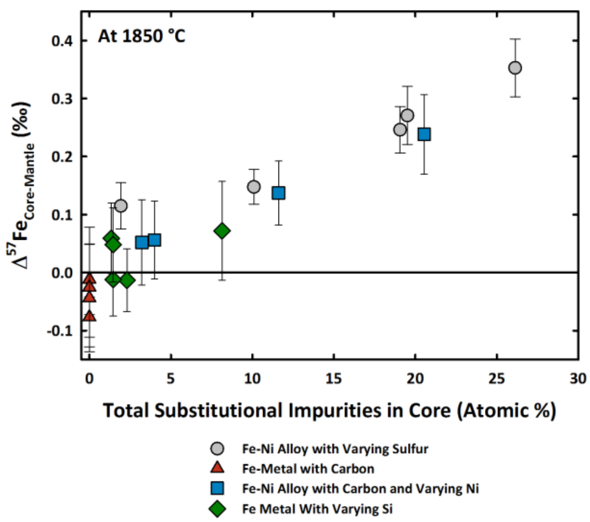

Fig. 1: Experimentally determined Fe isotopic differences between metal and silicate in per mil units.

Interpretations: The results of our experiments suggest that Si entering planetary cores may have a similar effect to Ni and S. The $\Delta^{57}Fe_{Core\text{-}Mantle}$ at 1850 °C of the experiment containing the most Si-rich metal is the highest among our Si-bearing experiments and falls close to the trend in the Ni- and S-bearing experiments (Fig. 1). This would be consistent with the model suggested by Elardo and Shahar [11] wherein elements that substitute for Fe in the alloy structure result in a metal-silicate isotope fractionation due to their effects on the average bonding environment of Fe, whereas elements such as C that partitioning into interstitial regions of the alloy do not have a resolvable effect at 1850 °C. However it is difficult to draw any definitive conclusions from this dataset because all of the Si-bearing experiments have $\Delta^{57}Fe_{Core\text{-}Mantle}$ values at 1850 °C within analytical error of 0‰. Experiments with greater amounts of Si in the metal phase are needed, but are extremely challenging due to the low FeO

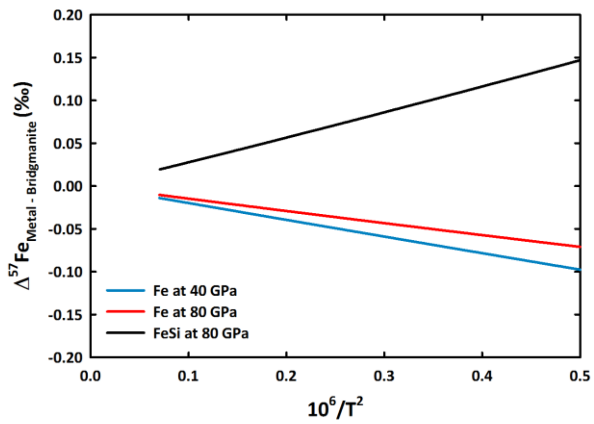

Fig. 2: Metal – bridgmanite Fe isotope fractionation factors for Fe-metal and FeSi determined from DFT calculations as a function of temperature.

abundances in the silicate melt caused by reduction of FeO to Fe metal by Si metal.

Shahar et al. [12] presented similar DFT calculations to those in Fig. 2 and showed that Fe isotope fractionation between bridgmanite and Fe metal, Fe_3C, FeH_X and FeO all result in the silicate becoming heavier than the Fe alloy. Our results show that FeSi has the opposite effect, indicating that Si entering the core at terrestrial magma ocean conditions would result in the light Fe enrichment in the mantle. FeSi is an end-member phase that is used for ease of calculation; however it indicates the sign of the metal-silicate fractionation factor for Si-bearing Fe alloys would be positive, which is broadly consistent with our experiments. Although the identity of the light element(s) in Earth's core is still uncertain, Si (and potentially O) is favored by many recent models [e.g., 13]. Our calculations indicate that the presence of Si in the core would be inconsistent with the supposition that the $\delta^{57}Fe$ of the bulk Earth is heavy with respect to chondrites and would instead favor a chondritic or slightly light bulk Earth.

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