

EXPERIMENTAL EVIDENCE FOR ISOTOPE FRACTIONATION DURING PLANETARY DIFFERENTIATION. A. Shahar¹, K. Ziegler², E. D. Young^{2,3}, A. Ricolleau¹, C. A. Macris³, E. A. Schauble³ and Y. Fei¹, ¹Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. NW, Washington D.C. 20015, ashahar@ciw.edu, ²Institute of Geophysics and Space Physics, UCLA, 603 Charles Young Drive East, Los Angeles, CA, 90095, ³Department of Earth and Space Sciences, UCLA, 595 Charles Young Drive East, Los Angeles, CA, 90095-1567.

Introduction: One of the broader goals in planetary science is to determine the chemical consequences of planet formation. Since the 1950's it has become apparent that chondrites provide the best estimates for the mean abundances of condensable elements in the solar system as they were not (for the most part) affected by physiochemical processes. Since then, many studies have compared the chemical and isotopic compositions of meteorites with that of the Earth in order to better understand processes such as solar system formation and planetary differentiation.

In this study, we introduce a new method to aid in the understanding of planetary formation processes. Through the use of high-pressure experiments and isotope geochemistry we are able to learn a great deal about processes that occurred in the early stages of the solar system. The combination of these two fields is a particularly valuable tool as the information learned is not based on prior assumptions or constraints. The goal of this work is to determine fractionation factors between two phases at high pressure and temperature and then use those values to explain the difference in isotopic ratios found in natural materials. In this presentation, we focus on isotope fractionations in the iron, silicon and sulfur systems between metal and silicate at high pressure and temperature.

Methods: We have developed a method for tracing the evolution towards isotopic equilibrium in high pressure experiments based on the so-called three-isotope exchange method pioneered years ago at the University of Chicago [1] and recently adapted to mineral-mineral fractionation factors [2]. Our implementation of the three-isotope method utilizes mono-isotopic spikes for the elements of interest (²⁸Si, ⁵⁴Fe, ³²S) in one of the participating reactant phases. Experiments are then conducted at several time steps and the isotope ratios are monitored for both minerals until equilibrium is reached on a fractionation line.

Experiments were conducted in both a piston cylinder apparatus and a multi-anvil apparatus, depending on the pressure attained in the experiment. Samples were contained in graphite capsules, brought to the temperature and pressure desired and then quenched at several time intervals. The run products were then polished so as to keep as much material as possible but still image on an electron probe. In the case of Fe and Si the samples were then separated, dissolved and puri-

fied. Isotope ratios were then measured on a ThermoFinnigan Neptune MC-ICPMS instrument at high mass resolution.

Planetary Differentiation: Several recent studies [e.g. 3] have shown that comparisons between meteorites and terrestrial stable isotope ratios can be used to elucidate the composition of the Earth's core. This is only the case however, if fractionation factors between the minerals of choice are known and at the conditions of core formation. While there are some theoretical calculations for these fractionation factors, experiments are the most effective way of determining them.

Silicon. It has been known for some time that seismic velocities are inconsistent with an outer core made of pure iron and nickel and it is hypothesized that there is at least one light element in the core that accounts for the seismic deficit. Silicon is one of the elements that has been considered to be incorporated in the core, based on mineral physics experiments showing that silicon alloys with iron easily at reduced conditions and cosmochemical arguments based on the sub-chondritic Mg/Si ratio on Earth.

A recent study [3] tested the idea that there is substantial Si in the core by comparing the Si isotopic composition of Earth's mantle to chondrites. They found that the Earth has 0.2‰ higher ³⁰Si/²⁸Si than chondrites and concluded that the difference is a consequence of Si fractionation between core and mantle. In order to test this idea we conducted the first silicon isotope experiments at high P/T. Our results (Fig. 1) show that there is a 2‰ ³⁰Si/²⁸Si fractionation between iron metal (core analog) and silicate (mantle).

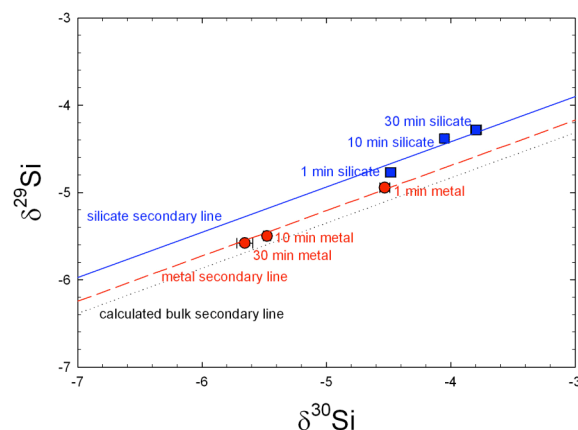


Fig. 1 Silicon three-isotope plot showing the experimental determination of Si isotopic fractionation between silicate (blue) and metal (red) at 1800°C and 1 GPa. Errors are 1se.

Using this experimentally-determined fractionation factor between silicate and metal, we can estimate the amount of silicon in the core based on mass balance:

$$\delta^{30}\text{Si}_{\text{BSE}} X_{\text{Si}} + \delta^{30}\text{Si}_{\text{Core}} (1-X_{\text{Si}}) = \delta^{30}\text{Si}_{\text{chondrite}}$$

where $\delta^{30}\text{Si}_{\text{BSE}}$ is the $^{30}\text{Si}/^{28}\text{Si}$ value of the bulk silicate Earth in delta notation, X_{Si} is the fraction of Earth's silicon that is in the silicate portion of the planet, $\delta^{30}\text{Si}_{\text{Core}}$ is the $^{30}\text{Si}/^{28}\text{Si}$ of the core and $\delta^{30}\text{Si}_{\text{chondrite}}$ is the $^{30}\text{Si}/^{28}\text{Si}$ of chondrites. Based on this expression we find that there is ~ 4.4 wt % Si in the core.

Iron. On a planetary scale, the iron isotopic ratios of bulk chondrites, iron meteorites and Earth have been measured [4]. These previous studies found that bulk chondrites tend to be slightly lower in $^{57}\text{Fe}/^{54}\text{Fe}$ than iron meteorites and bulk silicate Earth (BSE). As iron meteorites are classically thought to represent remnants of asteroid cores and the BSE does not include the fraction of iron that is in the core, there seems to be a contradiction as to why both were higher in $^{57}\text{Fe}/^{54}\text{Fe}$ than chondrites.

To gain a better understanding of the fractionation factor between iron metal and iron in silicate, and hence to better understand the disparities in $^{57}\text{Fe}/^{54}\text{Fe}$ among meteorites and planetary materials, we included a ^{54}Fe spike in the experiments described above. Results (Fig. 2) show that there is a small but resolvable fractionation of $0.22\text{‰} \pm 0.12\text{‰}$ between silicate and metal. Using this value and the relative amounts of Fe in the core and mantle,

$$\delta^{57}\text{Fe}_{\text{BSE}} X_{\text{Fe-BSE}} + \delta^{57}\text{Fe}_{\text{Core}} X_{\text{Fe-Core}} = \delta^{57}\text{Fe}_{\text{Earth}}$$

where $\delta^{57}\text{Fe}_{\text{BSE}}$ is the $^{57}\text{Fe}/^{54}\text{Fe}$ value of the bulk silicate Earth, $X_{\text{Fe-BSE}}$ is the mass of Earth's iron that is in the silicate portion of the planet, $\delta^{57}\text{Fe}_{\text{Core}}$ is the $^{57}\text{Fe}/^{54}\text{Fe}$ value of the core, $X_{\text{Fe-Core}}$ is the mass of Earth's iron that is in the core and $\delta^{57}\text{Fe}_{\text{Earth}}$ is the $^{57}\text{Fe}/^{54}\text{Fe}$ value of the whole Earth, one arrives at a bulk Earth $^{57}\text{Fe}/^{54}\text{Fe}$ value of -0.028‰ . The value measured in [4] for bulk chondrite, -0.04‰ , is a fairly close match to the calculated bulk Earth value. We can therefore explain the difference in $^{57}\text{Fe}/^{54}\text{Fe}$ between Earth and chondrite as an isotopic remnant of core formation where ^{54}Fe iron was preferentially sequestered in the core.

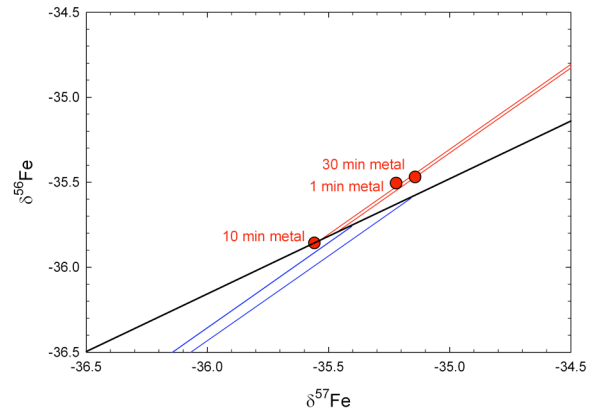


Fig. 2 Iron three-isotope plot showing the experimental determination of Fe isotopic fractionation between silicate and metal. Silicate data points are off the plot. Error envelopes are 95% confidence.

Sulfur. Geochemical models suggest that the core of Mars is composed of ~ 14 wt % sulfur. It is unknown whether this partitioning of sulfur into the core of Mars left an isotopic signature on the planet and therefore on the SNC meteorites. While sulfur isotopic data for Martian meteorites exist, the idea that there was a stable isotope fractionation during core formation on Mars has not been discussed or tested. Since it was found that equilibrium between core forming metal and silicates on Mars occurred at relatively low pressures (e.g., at ~ 1 GPa and 2200°C [5]), high P/T experiments could be done at these conditions to test for an isotopic fractionation. We have begun to perform experiments using a Martian mantle composition [6] with added FeS incorporating a ^{32}S spike. Isotopic analyses will be measured with a Cameca 6F instrument. Preliminary results on this topic will be discussed as well.

Conclusions: Our results suggest that isotope fractionation of major elements at high pressure and temperature can be significant, and further suggest that calibrations of stable isotope fractionation between metal and silicate/oxide are essential for interpreting stable isotope data on the planetary scale.

References: [1] Matsuhisa Y. et al. (1978) *GCA*, 42, 173–182. [2] Shahar A. et al. (2008) *EPSL*, 268, 330–338. [3] Georg R. B. et al. (2007) *Nature*, 447, 1102–1106. [4] Poitrasson F. et al. (2005) *EPSL* 234, 151–164. [5] Kong P. et al. (1999) *GCA* 63, 1865–1875. [6] Bertka C. M. and Fei Y. (1997) *JGR*, 102, 5251–5264.