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SUPPLEMENTARY MATERIALS

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GEOCHEMISTRY

Pressure-dependent isotopic composition of iron alloys

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Our current understanding of Earth's core formation is limited by the fact that this profound event is far removed from us physically and temporally. The composition of the iron metal in the core was a result of the conditions of its formation, which has important implications for our planet's geochemical evolution and physical history. We present experimental and theoretical evidence for the effect of pressure on iron isotopic composition, which we found to vary according to the alloy tested (FeO, FeH_x, or Fe₃C versus pure Fe). These results suggest that hydrogen or carbon is not the major light-element component in the core. The pressure dependence of iron isotopic composition provides an independent constraint on Earth's core composition.

The separation of iron metal from silicate to form Earth's core represents a fundamental physical and chemical differentiation process in our planet's history. Differentiation of planets and asteroids in general is based on temperature, pressure (or size of body), oxygen fugacity, and impact history. On Earth, core formation left behind many clues in the form of siderophile element patterns, seismic observations, and radiogenic isotope ratios that enable studies on how and when differentiation occurred. Seismic data show a density difference between pure iron and the inferred density from the velocities of the seismic waves within Earth's interior. This discrepancy implies that there are “light” elements other than iron within the core of Earth. However, because direct sampling of the core is impossible, its composition remains a hotly debated topic [e.g., (1)]. During the differentiation process, the molten iron metal will alloy with other elements on its route to the center of the planetary body. The elements it bonds with will be a function of the conditions attending core formation. To understand the history of our planet (or of any planetary body that experienced core formation), we must constrain this light element in the core.

The principle of using stable isotopes to probe the bulk chemical composition of planets is rooted in understanding isotope fractionation during the sequestration of elements in unseen reservoirs such as the core. Isotope fractionation will exist between phases with distinct bonding environments (e.g., Earth's core and mantle), and separation of elements between reservoirs man-

ifests this fractionation. Many variables influence the fractionation, including temperature, oxygen fugacity, and composition. For example, isotopic partitioning between metal and silicate was shown to increase when increasing amounts of sulfur were added to iron metal (2). However, those experiments were performed at low-pressure conditions (1 GPa) relative to the putative conditions of core formation (~60 GPa), and pressure was not considered a critical variable in affecting isotope fractionation. Joy and Libby (3) calculated the effect of pressure on isotope fractionation and suggested that oxygen isotope fractionation might be pressure-dependent at low temperatures. However, the following year, a study (4) examined the effect of pressure experimentally and observed no pressure effect on oxygen isotope partitioning between water and bicarbonate. Later, Clayton and co-workers (5–7) found no pressure effect on mineral-water fractionation over a range of pressures (up to 2 GPa) and temperatures (up to 1000 K). As a result of these initial studies, the effect of pressure on isotope fractionation has been assumed to be negligible for all elements. A pressure effect on isotope fractionation was suggested in other theoretical work (8) and confirmed experimentally for hydrogen (9) but not for heavier elements and higher pressures (10). However, better instrumentation may eventually be able to resolve very small fractionation effects, and higher pressures may illuminate the predicted fractionation (11, 12).

To test whether the light element bonded with iron alters iron isotope fractionation between metal and silicate, we conducted nuclear resonant inelastic x-ray scattering (NRIXS) experiments on FeO, FeH_x, Fe₃C, and Fe from 2 to 40 GPa. Polyakov and co-workers (11, 13, 14) pioneered the use of synchrotron NRIXS data to obtain vibrational properties of minerals for calculating isotopic fractionation factors. We can use NRIXS data to derive reduced partition function ratios (β factors), from which we can determine equilibrium isotopic fractionation factors: δ_A – δ_B = 1000 × (ln β_A – ln β_B), where A and B are two

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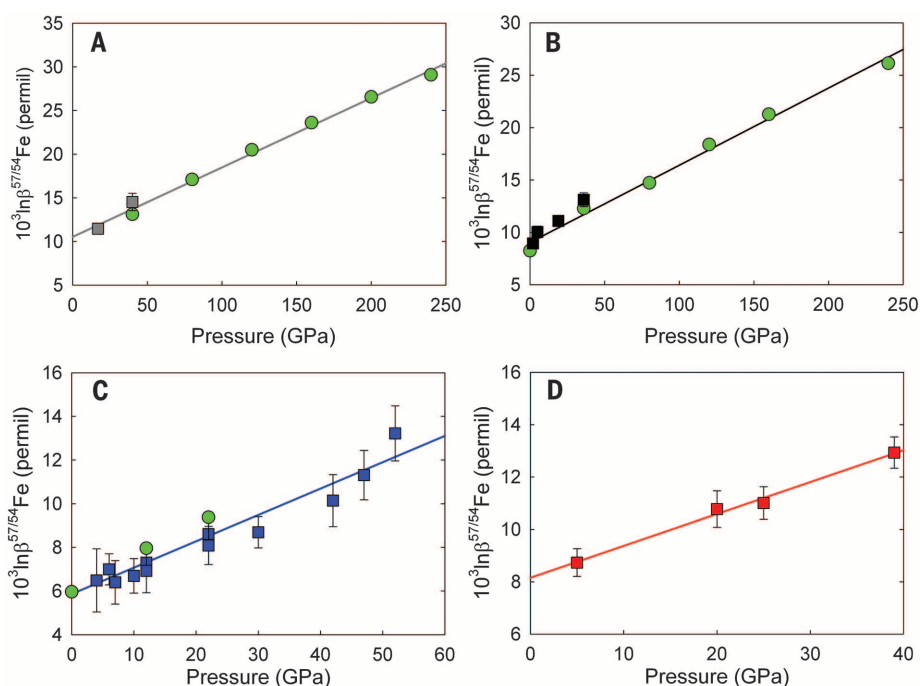


Fig. 1. Pressure dependence of the $^{57/54}\text{Fe}$ β factor for the different iron phases investigated. A clear pressure dependence on the β factor can be seen for all the phases analyzed. (A) The β factor as a function of pressure for pure Fe. Gray squares are experimental data; green circles are theoretical calculations. (B) The β factor as a function of pressure for Fe_3C . Black squares are experimental data; green circles are theoretical calculations. (C) The β factor as a function of pressure for FeH_x . Blue squares are experimental data; green circles are theoretical calculations. (D) The β factor as a function of pressure for FeO . Red squares are experimental data. Each pressure point was measured at least 19 times and as many as 40 times. The errors on the experimental data are ± 2 SD.

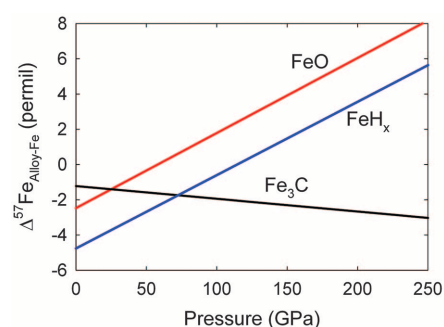


Fig. 2. Difference in the iron isotope ratios of the alloy with respect to pure Fe as a function of pressure. The red line is the isotope ratio difference of $\text{FeO} - \text{Fe}$, the blue line is $\text{FeH}_x - \text{Fe}$, and the black line is $\text{Fe}_3\text{C} - \text{Fe}$. Where the lines cross 0 on the y axis represents the pressure where there is no isotope fractionation between the phases and pure Fe. The iron isotope fractionation can be seen to change with pressure. $\Delta^{57}\text{Fe}_{\text{alloy} - \text{Fe}} = \delta^{57}\text{Fe}_{\text{alloy}} - \delta^{57}\text{Fe}_{\text{Fe}} = 10^3 \times (\ln \beta_{\text{alloy}}^{57/54}\text{Fe} - \ln \beta_{\text{Fe}}^{57/54}\text{Fe})$.

different phases of interest. Dauphas *et al.* (15) provided an excellent introduction to this technique and its applicability to isotope geochemistry. A major benefit of NRIXS experiments is that

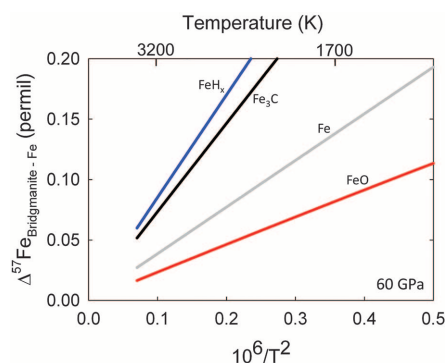


Fig. 3. Iron isotope fractionation between bridgmanite and iron phases as a function of temperature. The red line is the isotope ratio difference of bridgmanite - FeO , the gray line is bridgmanite - Fe, the black line is bridgmanite - Fe_3C , and the blue line is bridgmanite - FeH_x . At the conditions of core formation, a small but resolvable fractionation can be seen in all alloys, with that for Fe_3C and FeH_x much greater than for Fe and FeO . $\Delta^{57}\text{Fe}_{\text{bridgmanite} - \text{Fe}} = \delta^{57}\text{Fe}_{\text{bridgmanite}} - \delta^{57}\text{Fe}_{\text{Fe}}$.

we can probe the vibrational properties of one phase at a time. More traditional methods used for measuring isotope fractionation require having two phases at equilibrium that then need

to be separated and analyzed for their isotope ratios.

We conducted high-pressure NRIXS experiments at sector 16-ID-D (HPCAT) of the Advanced Photon Source at Argonne National Laboratory. We obtained energy spectra from -120 meV to $+150$ meV in steps of 0.5 meV with an energy resolution of 2 meV. The counting time varied between 6 and 7 s per point, with each NRIXS scan lasting about 1 hour and with 19 to 50 scans per pressure point. One hundred percent isotopically enriched ^{57}FeO , $^{57}\text{Fe}_3\text{C}$, or ^{57}Fe powder was loaded into a sample chamber drilled into a beryllium gasket in a panoramic diamond anvil cell. For the hydride, the chamber was loaded with pure ^{57}Fe and fluid H_2 , which reacted to form FeH_x . Pressure was calibrated using the ruby scale at HPCAT (16). We also calculated the theoretical β factors from the vibrational levels of different isotope-bearing structures. We computed these using density functional perturbation theory (17) in the ABINIT and Quantum Espresso implementation (18, 19) with plane waves and pseudopotentials, from which we obtained the theoretical phonon density of states (20).

We found linear relationships with pressure for Fe, Fe_3C , FeH_x , and FeO that showed excellent agreement with our theoretical calculations of β factors (Fig. 1). Each phase shows an increase in the β factor with pressure; moreover, the slopes of each line are different. The isotopic fractionation between each phase and pure Fe metal shows different slopes and intercepts indicative of varying pressure dependences (Fig. 2). We can explain this by the expected differences in bonding between iron and its different alloying elements.

At equilibrium, isotope fractionation is a quantum mechanical effect caused by differences in the free energy of structures populated by different isotopes. Isotopic pressure dependences can be the result of isotopic effects on molar volume or can be caused by force constant stiffening as structures contract. The molar volume isotope effect has been discussed extensively [e.g., (8, 11, 21, 22)] and occurs when heavy isotopes make slightly shorter bonds and therefore pack more tightly than light ones. Theoretical and experimental studies of isotope effects on the molar volumes of elements with atomic numbers spanning iron (e.g., carbon and germanium) indicate that isotope effects on volume are very small at standard temperature and pressure (less than one part in 10^{-3} for ^{13}C versus ^{12}C in diamond, $\sim 10^{-5}$ for ^{74}Ge versus natural germanium). Furthermore, molar volume effects fade as temperature increases beyond the Debye temperature (21, 22) and also as pressure increases (22). We therefore expect this effect to be negligible for iron isotope fractionation at pressures and temperatures relevant to core segregation. The same conclusion was reached in a previous theoretical study of high-pressure iron isotope fractionation (11). Our theoretical calculations target the increase in force constants and corresponding vibrational frequencies due to bond stiffening under compression.

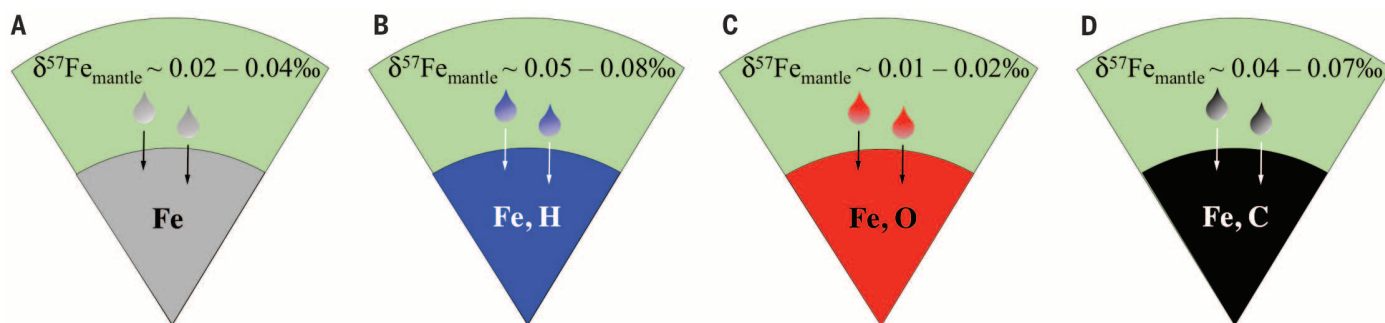


Fig. 4. A schematic of the implications of this study with regard to the iron isotope ratios of the current mantle. (A) Cross section of Earth showing the iron isotope ratio of the mantle after core formation if Fe were the only element in the core. **(B to D)** Same as (A) if hydrogen (B), oxygen (C), or carbon (D) were present. The $^{57}\text{Fe}_{\text{mantle}}$ values in (A) and (C) are not resolvable with current technological capabilities, but the values in (B) and (D) are very resolvable.

We find that pressure has a clear effect on isotope fractionation between solid phases, and that this effect is different for the different alloys (Figs. 1 and 2). In particular, we find that the iron alloys we studied do not concentrate the iron isotopes to the same degree. As carbon, hydrogen, and oxygen are all cosmochemically abundant and have been proposed as possible candidates for the main light element in planetary cores, iron isotope fractionation may be a tracer of light-element compositions in planetary cores. The iron-hydrogen alloy and the iron-carbon alloy have the largest fractionation relative to pure iron in a typical magma ocean setting at ~ 60 GPa (23). The hydrogen content in the core is poorly constrained, with estimates ranging from negligible up to the equivalent of 100 hydrospheres (24). Estimates for the carbon content of the core are less than ~ 1 weight percent (25, 26). Because our data were collected at room temperature, we calculated the temperature effect on the fractionation of bridgmanite (27) relative to the iron phases (Fig. 3) (18). At 3500 K, the fractionation for pure Fe is ~ 0.03 per mil (‰) and that for FeH_x is $\sim 0.07\%$.

Initial iron isotope work on natural samples determined that “Earth” (i.e., mantle-derived rocks) was $\sim 0.1\%$ heavier in $\delta^{57/54}$ than rocks from Mars and Vesta (28). Predictions (11) concluded that core-mantle differentiation would leave an imprint on the iron isotope signature of Earth because of the valence state difference of Fe between lower-mantle Fe^{2+} -bearing minerals and Fe^0 metal at the core-mantle boundary. That study suggested that the enrichment of terrestrial and lunar basalts in heavy iron isotopes relative to those from Mars or Vesta is due to equilibrium iron isotope fractionation during Earth’s core formation. Subsequent explanations, however, argued that the bulk silicate Earth is chondritic and that it is the terrestrial basalts that are anomalous (29). The model suggests that the iron isotopic composition of the basalts was different from that of the source rock from which they came; that is, fractionation of iron isotopes occurs during partial melting. Therefore, if the bulk silicate Earth is chondritic in its iron isotope ratios, it should have a $\delta^{57/54}$ of 0‰. If that

is the case, then any light element that causes a large enough fractionation at high pressure and temperature to deviate from that value cannot be a major constituent of the core. A caveat is that if the bulk silicate Earth were found to be nonchondritic, then the light element that causes a fractionation large enough to be seen—such as hydrogen—would be the most likely candidate for the light element in the core.

Our results suggest that core formation could leave an isotopic imprint on the silicate portion of Earth even at the highest pressures and temperatures. Moreover, the addition of different light element(s) will modulate this imprint. In particular, our results indicate that if hydrogen or carbon were used to explain the density deficit in Earth’s core, we would expect an isotopic signature imprinted in mantle rocks, which is not seen in the rock record. The lack of evidence for this signature suggests that hydrogen and carbon should be excluded as the main light element in Earth’s core (Fig. 4). There has been substantial disagreement in the literature concerning whether carbon and/or hydrogen are likely major constituents of the core, on the basis of other evidence [e.g., (30–32)], so this study provides an independent constraint. In contrast, we found that oxygen does not leave an imprint on the silicate mantle, implying that at least for the phases we have analyzed, oxygen is a possible light element in the core (1). It is intriguing that the light element changes the isotope ratios with these end-member compositions. The effects of other light elements (such as silicon and sulfur) on the iron isotope ratios need to be investigated, as well as the effects of nickel and pressure-induced structure, electronic, and magnetic transitions. However, it is now clear that pressure cannot be ignored when discussing equilibrium stable isotope fractionation in the deep Earth.

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Pressure-dependent isotopic composition of iron alloys

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Iron isotopes constrain core chemistry

The overall composition of Earth's core is an important constraint on the chemistry and evolution of our planet's interior. A longstanding problem has been determining the minor element contribution to its predominately iron-nickel alloy. Based on the iron isotope fractionation of various iron alloys with pressure, Shahar *et al.* find that carbon and hydrogen are probably not primary components of the core. The fractionation occurs at the high pressures of core formation, suggesting that the stable iron isotope ratios of Earth are a new and independent constraint on core composition.

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