Equilibrium Iron Isotope Fractionation at Core-Mantle Boundary Conditions

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The equilibrium iron isotope fractionation between lower mantle minerals and metallic iron at core-mantle boundary conditions can be evaluated from the high-pressure $^{57}$Fe partial vibrational density of states determined by synchrotron inelastic nuclear resonant x-ray scattering spectroscopy using a diamond anvil. Ferropericlase [(Mg,Fe)O] and (Fe,Mg)SiO$_3$—post-perovskite are enriched in heavy iron isotopes relative to metallic iron at ultrahigh pressures, as opposed to the equilibrium iron isotope fractionation between these compounds at low pressure. The enrichment of Earth and Moon basalts in heavy iron isotopes relative to those from Mars and asteroid Vesta can be explained by the equilibrium iron isotope fractionation during the segregation of Earth’s core and the assumption that Earth was already differentiated before the Moon-forming “giant impact.”

Iron isotopes may provide important information for understanding the mechanisms of planetary differentiation and core formation. Basalts from Earth and the Moon are enriched in heavy Fe isotopes relative to those from Mars and asteroid Vesta and from chondrites, which are primitive undifferentiated meteorites (1–3) [supporting online material (SOM) text and fig. S1]. In addition, possible differences in the Fe isotope compositions between lunar and terrestrial basalts (1, 2, 4–6) (SOM text and fig. S2) are currently under debate. The mechanism for the heavy Fe isotope compositions of Earth and Moon basalts is unclear (4–6). The heavier Fe in Earth and Moon basalts has been suggested to result from evaporation and condensation during the “giant impact” that is thought to have created the Moon (1, 4, 7) or from Fe isotope fractionation caused by partial melting and magmatic differentiation (5, 8). Core-mantle differentiation has not been considered to explain the enrichment of the bulk silicate Earth (BSE) in heavy Fe isotopes, because the Fe isotope composition of Fe metal in pallasites (differentiated stony-Fe meteorites) is heavy relative to that of the silicate fraction (olivine) (2, 7, 9) (fig. S3). This implies that the silicate-metallic Fe differentiation depleted the silicate fraction in heavy Fe isotopes and cannot be responsible for the heavier Fe isotope composition of terrestrial and lunar basalts. The Palasite data agree with equilibrium Fe isotope fractionation factors (SOM text) between Fe-metal and ferrous silicates at low pressures (10–12). Georg et al. (13) calculated small equilibrium Fe isotope fractionation between Earth’s core and mantle [0.02 per mil (‰) at 2000 K] from low-pressure β factors (SOM text) derived from Mössbauer spectroscopy data (10). Here I present a method for determining the equilibrium Fe isotope fractionation at higher pressures (up to ~150 GPa) and use this method to estimate equilibrium Fe isotope fractionation between lower mantle minerals and Fe-metal at core-mantle boundary (CMB) conditions and show that core separation on Earth can explain the observed differences in the Fe isotope data from the Earth, Moon, and meteorites.

I determined the equilibrium Fe isotope fractionation between Fe-bearing minerals using their
Anharmonic effects may be substantial at high temperatures, which decrease the lnβ (20). One can show that high pressure reduces the effect of anharmonicity: for instance, the anharmonic correction to iron lnβ at 130 GPa is about 2.5 times smaller than that at ambient pressure (SOM text). The method for determination of the Feβ factor at high pressure can be directly applied to the problem of equilibrium Fe isotope fractionation at CMB conditions.

Two main Fe-bearing minerals are thought to be present in the lower mantle at CMB pressure: ferropericlase [(Mg,Fe)O] and (Fe,Mg)SiO3–post-perovskite. Because the equation relating the equilibrium isostropic shift (Δ) between phases A and B and appropriate isotope fractionation factors (α and β factors (SOM text)) is
\[ \Delta_{\alpha,\beta}(%) = 10^3 \ln \alpha_{\alpha,\beta} \]

three Feβ factors for metallic Fe, ferropericlase, and (Fe,Mg)SiO3–post-perovskite at CMB conditions—are needed for evaluating the equilibrium Fe isotope fractionation factors between the lower mantle minerals and the core.

For metallic Fe, 57Fe/54Fe lnβ determined from the 57Fe PVDOS (14) at pressures corresponding to CMB conditions (>100 GPa) exceed those at ambient pressures by a factor of 3 (Fig. 1). 5Fe/54Fe β factors for ferropericlase (Fe0.25Mg0.75) calculated from the 57Fe PVDOS obtained from synchrotron INRXS experiments at different pressures (16) reveal an analogous pressure dependence (Fig. 2). 5Fe PVDOS data are also available for (Fe0.25Mg0.75)SiO3–post-perovskite at 130 GPa (15), and the calculated 57Fe/54Fe lnβ is higher than those of many other minerals at high pressures (Fig. 3).

Equilibrium 57Fe/54Fe isotope fractionation factors between the lower mantle Fe-bearing minerals and metallic Fe have opposite signs at ambient and CMB pressures (Fig. 4). The equilibrium Fe isotope fractionation at CMB pressures between ferropericlase and Fe varies from 0.012 ± 0.029‰ at 2000 K to 0.0010 ± 0.0053‰ at 4000 K (which is very small), whereas that between (Fe0.1Mg0.9)SiO3–post-perovskite and Fe is significant and varies from 0.24 ± 0.043‰ at 2000 K to 0.062 ± 0.012‰ at 4000 K. Following (13) and assuming that the total amount of Fe is equally distributed between post-perovskite and periclase phases at the CMB, the calculated equilibrium 57Fe/54Fe isotope shift between the silicate mantle and the core of Earth is 0.13 ± 0.053‰ at 2000 K and 0.04 ± 0.014‰ at 4000 K. This estimate of the equilibrium 57Fe/54Fe Fe isotope fractionation at the CMB, which significantly exceeds the previous estimate of ~0.02‰ at 2000 K (13), is in good agreement with the enrichment of terrestrial basalts in heavy Fe isotopes of ~0.1‰ for 57Fe/54Fe (7, 2).

The equilibrium Fe isotope fractionation factor between silicate and Fe metal is negative at low pressures (Fig. 4) (10–12) but changes its sign and becomes positive at ultrahigh pressures of ~100 GPa (Fig. 4). The sign of the equilibrium Fe isotope fractionation factor between metallic Fe and ferrous silicates may thus be considered as the indicator of ultrahigh pressure in silicate-metal differentiation processes.

The estimated Fe isotope fractionation at CMB conditions implies that the enrichment of terrestrial basalts in heavy Fe isotopes relative to those from Mars, Vesta, and chondrites was caused by core-mantle differentiation in Earth occurring mainly at high pressure. Core formation in Mars and Vesta at low-pressure conditions would have resulted in small isotope enrichments of silicates in light Fe isotopes. The BSE is also enriched in the heavy isotopes of Si. These data can be explained by the preferable accumulation of the light Si isotopes in Earth's core (13). Thus, analogous isotope fractionation of Fe and Si might have occurred during the core segregation. In contrast, no measurable differences among planets and meteorites in isotope compositions were detected for light elements such as Mg and Li (21, 22), which are not likely to be present in Earth's core. The absence of such differences for Mg and Li isotopes, which have volatilities higher than (Li) or comparable to (Mg) of Fe, also renders evaporation unlikely as an explanation of the interplanetary differences in Fe isotope composition (13).

One can explain the enrichment of lunar basalts in heavy Fe isotopes, similar in magnitude to those of terrestrial basalts, in terms of the equilibrium Fe isotope fractionation during Earth's core-mantle differentiation, if Earth was already differentiated before the Moon-forming giant impact. However, the putative enrichment of lunar basalts in heavy Fe isotopes relative to those from the Earth (1, 4) (SOM text and fig. S2) requires other mechanisms.
The Fe isotope fractionation between core and mantle estimated in this study reflects equilibrium Fe isotope fractionation between lower mantle Fe\(^{2+}\)-bearing minerals and Fe\(^0\)-metal at the CMB, not an isotope fractionation between Fe\(^3+\) and Fe\(^0\) (23). If only 2 to 3% of the lower mantle Fe is ferric (24), one can conclude, from isotope mass balance, that 57Fe/54Fe isotope fractionation between ferric and ferrous Fe would have to range from 3 to 5‰ to provide the isotope shift of as much as 0.1‰ in the total Fe. Such a large 57Fe/54Fe isotope fractionation seems to be unrealistic at temperatures in the lower mantle.

Teng et al. (25) provided evidence that Fe isotopes fractionate during low-pressure magmatic differentiation, accompanied by a change of the Fe oxidation state. This process is considered as a possible explanation of the differences in Fe isotope composition of basalts from different planetary bodies (26). However, it would require that the high-temperature magmatically differentiation processes leading to basalt formation on Earth and the Moon be different from those on Mars and Vesta. It is more likely that the magmatic differentiation is responsible for the range of variations of Fe isotope compositions within a single planetary body and that the primary interplanetary differences reflect the influence of pressure on core formation.

The method developed in the present study for determining Fe β factors at ultrahigh pressures can be directly applied to any chemical elements that have at least one Mössbauer-sensitive isotope, if the synchrotron INRxs technique is available for them.

References and Notes
18. Equation 3 allows calculation of the β factor for Fe isotope fractionation between a given Fe isotope and the 57Fe isotope. For example, m = m\(_{\text{Fe}^{2+}}\) = 54 atomic units (au) and \(\Delta m = 0\) to \(-3\) au in the case of 55Fe–56Fe isotope substitution. However, in fact this does not impose a limitation on the application of Eq. 2 to Fe isotope fractionation, because the following equation holds: \(\ln m_{\text{Fe}^{2+}}/m_{\text{Fe}^{0}} = \ln m_{\text{Fe}^{2+}}/m_{\text{Fe}^{0}}\). Here, the \(m_{\text{Fe}^{2+}}/m_{\text{Fe}^{0}}\) notation is used for the β factor relating to 55Fe–56Fe isotope substitution. In particular, \(\ln m_{\text{Fe}^{2+}}/m_{\text{Fe}^{0}}\) is \(\leq 10\) (18) for details.
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Supporting Online Material
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SOM Text
Figs. S1 to S3
References
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