



## Equilibrium Iron Isotope Fractionation at Core-Mantle Boundary Conditions

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11. Using three independent observed parameters (i.e., the surface echo amplitude, the subsurface echo amplitude, and the delay time of the subsurface echo relative to the surface echo), we need to determine four independent parameters (i.e., dielectric constants of two subsurface layers, the loss tangent of the top layer, and the depth of the subsurface reflector). To solve this ill-posed problem, we inversely solve a Fresnel model of three media (i.e., vacuum and two subsurface layers) assuming normal incidence and a moderate value of 4 for the dielectric constant of the top layer.
12. B. A. Campbell, *Radar Remote Sensing of Planetary Surfaces* (Cambridge Univ. Press, Cambridge, 2002).
13. J. W. Head III, *Moon Planets* **21**, 439 (1979).
14. H. Hiesinger *et al.*, *J. Geophys. Res.* **105**, 29239 (2000).
15. W. L. Quaide, V. R. Oberbeck, *Moon* **13**, 27 (1975).
16. C. M. Weitz, J. W. Head, C. M. Pieters, *J. Geophys. Res.* **103**, 22725 (1998).
17. H. J. Moore, C. A. Hodges, D. H. Scott, *Lunar Sci. Conf.* **5**, 71 (1974).
18. R. J. Pike, in *Impact and Explosion Cratering*, D. J. Roddy, R. O. Pepin, R. B. Merrill, Eds. (Pergamon, New York, 1977), pp. 489–509.
19. S. Kodama, Y. Yamaguchi, *Meteorit. Planet. Sci.* **38**, 1461 (2003).
20. J. F. Bell III, B. R. Hawke, *Icarus* **118**, 51 (1995).
21. M. I. Staid, C. M. Pieters, *Icarus* **145**, 122 (2000).
22. S. C. Solomon, J. W. Head III, *J. Geophys. Res.* **84**, 1667 (1979).
23. R. A. De Hon, J. D. Waskom, *Lunar Planet. Sci. Conf.* **7**, 2729 (1976).
24. C. J. Budney, P. G. Lucey, *J. Geophys. Res.* **103**, 16855 (1998).
25. T. A. Maxwell, F. El-Baz, S. H. Ward, *Geol. Soc. Am. Bull.* **86**, 1273 (1975).
26. D. F. Weill, R. A. Grieve, I. S. McCallum, Y. Bottinga, *Lunar Sci. Conf.* **2**, 413 (1971).
27. A. M. Freed, H. J. Melosh, S. C. Solomon, *J. Geophys. Res.* **106**, 20603 (2001).
28. The Kaguya mission was conducted by the Japan Aerospace Exploration Agency (JAXA). We thank Y. Takizawa (project manager), S. Sasaki (project scientist), and M. Kato (science manager) for their efforts in accomplishing the Kaguya mission, and K. Tanaka, Y. Iijima, S. Nakazawa, H. Otake, S. Sobue, H. Hoshino, H. Okumura, Y. Yamamoto, and J. Kimura (team members of the Kaguya mission) for their helpful discussions on achieving a high reliability for the mission instruments.

#### Supporting Online Material

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Figs. S1 to S4

References and Notes

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# Equilibrium Iron Isotope Fractionation at Core-Mantle Boundary Conditions

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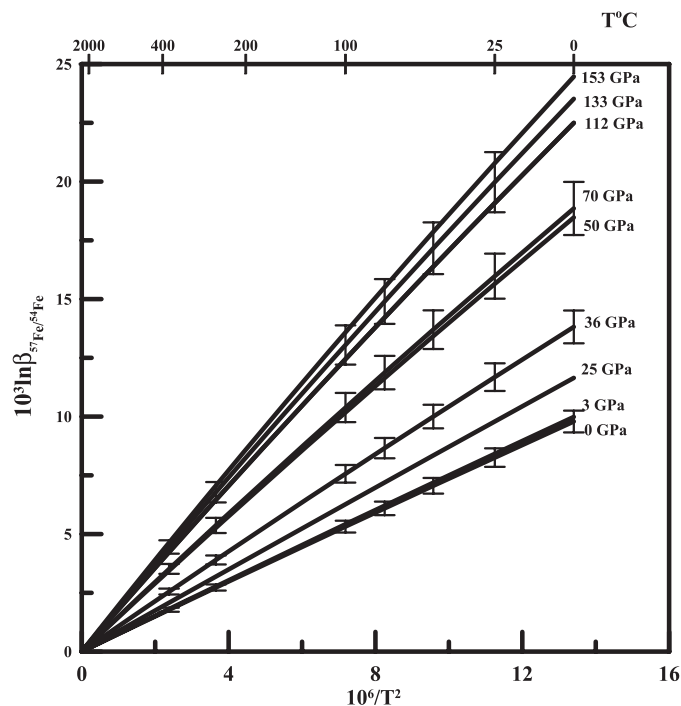
The equilibrium iron isotope fractionation between lower mantle minerals and metallic iron at core-mantle boundary conditions can be evaluated from the high-pressure  $^{57}\text{Fe}$  partial vibrational density of states determined by synchrotron inelastic nuclear resonant x-ray scattering spectroscopy using a diamond anvil. Ferroperricite  $[(\text{Mg},\text{Fe})\text{O}]$  and  $(\text{Fe},\text{Mg})\text{SiO}_3$ -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 compo-

sition of terrestrial and lunar basalts. The pallasite 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  $\beta$  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



**Fig. 1.** Temperature and pressure dependence of the  $^{57}\text{Fe}/^{54}\text{Fe}$   $\beta$  factor for metallic Fe. The  $^{57}\text{Fe}/^{54}\text{Fe}$   $\beta$  factor of Fe metal is computed from the  $^{57}\text{Fe}$  PVDOS obtained by Mao *et al.* (14) using the high-pressure synchrotron INRXS. The mathematical algorithm is described in the text and justified in (11, 17). Error bars for  $\ln\beta$  are calculated from the experimental uncertainties in the  $^{57}\text{Fe}$  PVDOS (14) for ambient pressures and at 36, 70, and 133 GPa using the Monte-Carlo technique (17) (SOM text). The significant increase of the Fe  $\beta$  factor with increasing pressure to ultrahigh pressures is not a unique feature of Fe metal (see text and Figs. 2 and 3)

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$^{57}\text{Fe}$  partial vibrational densities of states (PVDOSs) derived from high-pressure synchrotron inelastic nuclear resonance x-ray scattering (INRXS) spectroscopy (14–16) and a calculation method allowing computation of the  $\beta$  factor from the PVDOS (11, 17).

The synchrotron INRXS spectroscopy, in conjunction with a diamond anvil, allows an estimate of the  $^{57}\text{Fe}$  PVDOS at different pressures (14–16), which are input data for computing Fe  $\beta$  factors. The kinetic energy of the thermal vibrations of the  $^{57}\text{Fe}$  isotope can be calculated from the  $^{57}\text{Fe}$  PVDOS with the following equation

$$K_{^{57}\text{Fe}}(T) = \int g(e)E(e,T)de \quad (1)$$

where  $K_{^{57}\text{Fe}}$  is the kinetic energy of the  $^{57}\text{Fe}$  isotope per nucleus,  $g(e)$  is the  $^{57}\text{Fe}$  PVDOS at given pressure, and  $E(e,T)$  is the Einstein function for energy of the single harmonic oscillator at temperature  $T$

$$E(e) \equiv \frac{e}{\exp(e/kT) - 1} + 0.5e \quad (2)$$

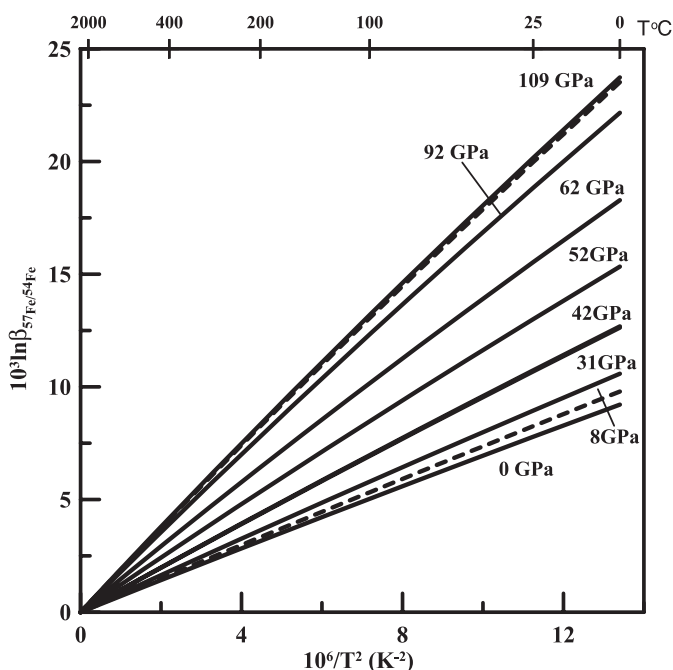
where  $k$  is the Boltzmann constant.

Starting from the  $^{57}\text{Fe}$  kinetic energy, one can calculate the Fe  $\beta$  factor with the following equation (18)

$$\ln\beta = -\left(\frac{K_{^{57}\text{Fe}}}{kT} - \frac{3}{2}\right) \frac{\Delta m}{m} \quad (3)$$

where  $m$  is the mass of an iron isotope (the mass of the  $^{54}\text{Fe}$  for  $^{57}\text{Fe}/^{54}\text{Fe}$  isotope substitution);  $\Delta m = m - m_{^{57}\text{Fe}}$  (19). This technique does not require any additional assumptions except the harmonic approximation used in Eq. 1 for calculating the kinetic energy of the  $^{57}\text{Fe}$  isotope (10, 11).

**Fig. 2.** Temperature and pressure dependence of the  $^{57}\text{Fe}/^{54}\text{Fe}$   $\beta$  factor for  $(\text{Fe}_{0.25}\text{Mg}_{0.75})\text{O}$ -ferropericlase. The  $^{57}\text{Fe}/^{54}\text{Fe}$   $\beta$  factors for  $(\text{Fe}_{0.25}\text{Mg}_{0.75})\text{O}$ -ferropericlase are computed using the  $^{57}\text{Fe}$  PVDOS at different pressures from Lin *et al.* (16). The  $^{57}\text{Fe}/^{54}\text{Fe}$   $\beta$  factors for metallic Fe (dashed lines) are also presented at CMB and ambient pressures for comparisons. The Fe  $\beta$  factor for ferropericlase increases significantly with increasing pressure, similar to that found for the  $^{57}\text{Fe}/^{54}\text{Fe}$   $\beta$  factors for metallic Fe.



Anharmonic effects may be substantial at high temperatures, which decrease the  $\ln\beta$  (20). One can show that high pressure reduces the effect of anharmonicity: for instance, the anharmonic correction to iron  $\ln\beta$  at 130 GPa is about 2.5 times smaller than that at ambient pressure (SOM text). The method for determination of the Fe  $\beta$  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  $[(\text{Mg},\text{Fe})\text{O}]$  and  $(\text{Fe},\text{Mg})\text{SiO}_3$ -post-perovskite. Because the equation relating the equilibrium isotopic shift ( $\Delta$ ) between phases A and B and appropriate isotope fractionation factors ( $\alpha$ ) and  $\beta$  factors (SOM text) is

$$\begin{aligned} \Delta_{\text{A-B}}(\text{‰}) &\approx 10^3 \ln \alpha_{\text{A-B}} \\ &= 10^3 \ln \beta_{\text{A}} - 10^3 \ln \beta_{\text{B}} \quad (4) \end{aligned}$$

three Fe  $\beta$  factors for metallic Fe, ferropericlase, and  $(\text{Fe},\text{Mg})\text{SiO}_3$ -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,  $^{57}\text{Fe}/^{54}\text{Fe}$   $\ln\beta$  determined from the  $^{57}\text{Fe}$  PVDOS (14) at pressures corresponding to CMB conditions (>100 GPa) exceed those at ambient pressures by a factor of 3 (Fig. 1).  $^{57}\text{Fe}/^{54}\text{Fe}$   $\beta$  factors for ferropericlase  $(\text{Fe}_{0.25}\text{Mg}_{0.75}\text{O})$  calculated from the  $^{57}\text{Fe}$  PVDOS obtained from synchrotron INRXS experiments at different pressures (16) reveal an analogous pressure dependence (Fig. 2).  $^{57}\text{Fe}$  PVDOS data are also available for  $(\text{Fe}_{0.4}\text{Mg}_{0.6})\text{SiO}_3$ -post-perovskite at 130 GPa (15), and the calculated  $^{57}\text{Fe}/^{54}\text{Fe}$   $\ln\beta$  is higher than those of many other minerals at high pressures (Fig. 3).

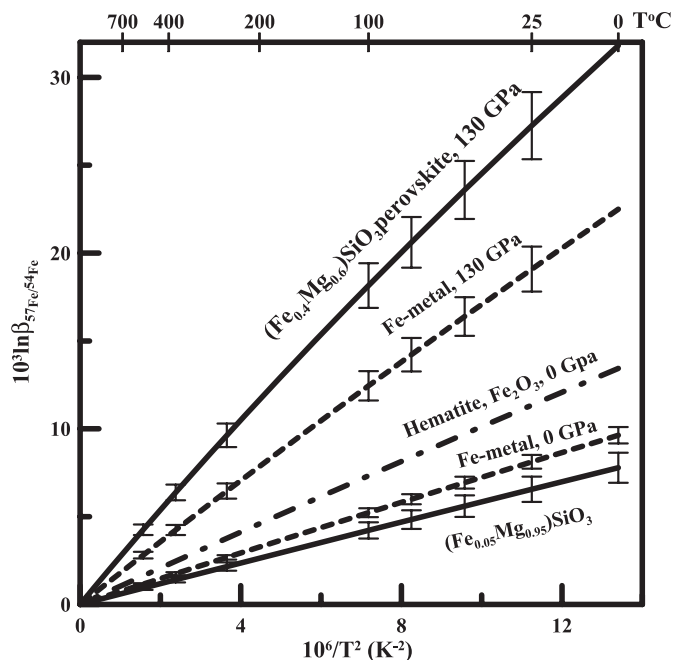
Equilibrium  $^{57}\text{Fe}/^{54}\text{Fe}$  isotope fractionation factors between the lower mantle Fe-bearing minerals and metallic Fe have opposite signs at ambient and CMB pressures (Fig. 4). The equilibrium Fe isotope fractionation at CMB pressures between ferropericlase and Fe varies from  $0.012 \pm 0.029\text{‰}$  at 2000 K to  $0.0010 \pm 0.0053\text{‰}$  at 4000 K (which is very small), whereas that between  $(\text{Fe}_{0.4}\text{Mg}_{0.6})\text{SiO}_3$ -post-perovskite and Fe is significant and varies from  $0.24 \pm 0.043\text{‰}$  at 2000 K to  $0.062 \pm 0.012\text{‰}$  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  $^{57}\text{Fe}/^{54}\text{Fe}$  isotopic shift between the silicate mantle and the core of Earth is  $0.13 \pm 0.053\text{‰}$  at 2000 K and  $0.04 \pm 0.014\text{‰}$  at 4000 K. This estimate of the equilibrium  $^{57}\text{Fe}/^{54}\text{Fe}$  isotope fractionation at the CMB, which significantly exceeds the previous estimate of  $\sim 0.02\text{‰}$  at 2000 K (13), is in good agreement with the enrichment of terrestrial basalts in heavy Fe isotopes of  $\sim 0.1\text{‰}$  for  $^{57}\text{Fe}/^{54}\text{Fe}$  (1, 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  $\sim 100$  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.

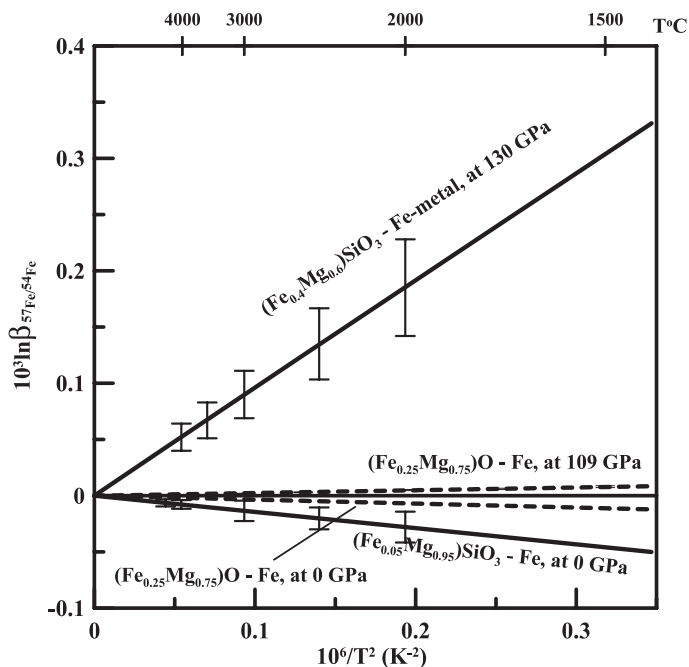
The estimated Fe isotope fractionation at CMB conditions implies that the enrichment of terrestrial basalts in heavy Fe isotopes relative to those from Mars, Vesta, and chondrites was caused by core-mantle differentiation in Earth occurring mainly at high pressure. Core formation in Mars and Vesta at 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) that 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.

**Fig. 3.** The Fe  $\beta$  factor for the post-perovskite and perovskite phases at CMB and ambient pressures, respectively. The Fe  $\beta$  factor for  $(\text{Fe}_{0.4}\text{Mg}_{0.6})\text{SiO}_3$ -post-perovskite at 130 GPa was calculated from the  $^{57}\text{Fe}$  PVDOS obtained by the synchrotron INRXS (15). Error bars are calculated from experimental uncertainties using the Monte-Carlo technique (17) (SOM text). The  $\beta$  factor for  $(\text{Fe}_{0.05}\text{Mg}_{0.95})\text{SiO}_3$ -perovskite was calculated from the Mössbauer second-order Doppler shift (27) by a method described elsewhere (10, 18). The  $\beta$  factors for metallic Fe (Fig. 1) and hematite (10, 11) are also shown for comparisons. The  $\beta$  factor for hematite at ambient pressure from (10) was used as an analog for the perovskite phase by Georg *et al.* (13).



**Fig. 4.** Equilibrium Fe isotope fractionations between lower mantle minerals and metallic Fe at CMB and ambient pressures. The equilibrium Fe isotope fractionations are calculated from  $\beta$  factors presented in Figs. 1 to 3 using Eq. 4. One can see the different directions of the equilibrium Fe isotope fractionation between ferrous ( $\text{Fe}^{2+}$ ) lower mantle minerals and metallic Fe ( $\text{Fe}^0$ ) at ambient and CMB pressures.



The Fe isotope fractionation between core and mantle estimated in this study reflects equilibrium Fe isotope fractionation between lower-mantle  $\text{Fe}^{2+}$ -bearing minerals and  $\text{Fe}^0$ -metal at the CMB, not an isotope fractionation between  $\text{Fe}^{3+}$  and  $\text{Fe}^0$  (23). If only 2 to 3% of the lower mantle Fe is ferric (24), one can conclude, from isotope mass balance, that  $^{57}\text{Fe}/^{54}\text{Fe}$  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  $^{57}\text{Fe}/^{54}\text{Fe}$  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 magmatic 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  $\beta$  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**

1. F. Poirasson, A. N. Halliday, D. C. Lee, S. Levasseur, N. Teutsch, *Earth Planet. Sci. Lett.* **223**, 253 (2004).
2. S. Weyer *et al.*, *Earth Planet. Sci. Lett.* **240**, 251 (2005).
3. R. Schoenberg, F. von Blanckenburg, *Earth Planet. Sci. Lett.* **252**, 342 (2006).
4. F. Poirasson, *Earth Planet. Sci. Lett.* **256**, 484 (2007).
5. S. Weyer *et al.*, *Earth Planet. Sci. Lett.* **256**, 638 (2007).
6. B. L. Beard, C. M. Johnson, *Earth Planet. Sci. Lett.* **256**, 633 (2007).
7. F. Poirasson, S. Levasseur, N. Teutsch, *Earth Planet. Sci. Lett.* **234**, 151 (2005).
8. S. Weyer, D. A. Ionov, *Earth Planet. Sci. Lett.* **259**, 119 (2007).
9. X. K. Zhu *et al.*, *Earth Planet. Sci. Lett.* **200**, 47 (2002).
10. V. B. Polyakov, S. D. Mineev, *Geochim. Cosmochim. Acta* **64**, 849 (2000).
11. V. B. Polyakov, R. N. Clayton, J. Horita, S. D. Mineev, *Geochim. Cosmochim. Acta* **71**, 3833 (2007).
12. M. Roskosz, B. Luais, H. C. Watson, M. J. Toplis, C. M. O'D. Alexander, B. O. Mysen, *Earth Planet. Sci. Lett.* **248**, 851 (2006).
13. R. B. Georg, A. N. Halliday, E. A. Schauble, B. C. Reynolds, *Nature* **447**, 1102 (2007).
14. H. K. Mao *et al.*, *Science* **292**, 914 (2001).
15. W. L. Mao *et al.*, *Science* **312**, 564 (2006).
16. J.-F. Lin *et al.*, *Geophys. Res. Lett.* **33**, L22304 (2006).
17. V. B. Polyakov, S. D. Mineev, R. N. Clayton, G. Hu, K. S. Mineev, *Geochim. Cosmochim. Acta* **69**, 5531 (2005).
18. V. B. Polyakov, *Geochim. Cosmochim. Acta* **61**, 4213 (1997).
19. Equation 3 allows calculation of the  $\beta$  factor for Fe isotope fractionation between a given Fe isotope and the  $^{57}\text{Fe}$  isotope. For example,  $m = m_{^{54}\text{Fe}} \approx 54$  atomic units (au) and  $\Delta m = m_{^{54}\text{Fe}} - m_{^{57}\text{Fe}} \approx -3$  au in the case of  $^{57}\text{Fe} \rightarrow ^{54}\text{Fe}$  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:  $\ln^{m_1/m_2}\beta = \ln^{m_1/57}\beta - \ln^{m_2/57}\beta$ . Here, the  $m_1/m_2$  notation is used for the  $\beta$  factor relating to  $^{m_1}\text{Fe} \rightarrow ^{m_2}\text{Fe}$  isotope substitution. In particular,  $\ln^{57/54}\beta = -\ln^{54/57}\beta$ ;  $\ln^{56/54}\beta = \ln^{57/54}\beta - \ln^{57/56}\beta$ . See (18) for details.
20. V. B. Polyakov, *Geochim. Cosmochim. Acta* **62**, 3077 (1998).
21. U. Wiechert, A. N. Halliday, *Earth Planet. Sci. Lett.* **256**, 360 (2007).
22. T. Magna, U. Wiechert, A. N. Halliday, *Earth Planet. Sci. Lett.* **243**, 336 (2006).
23. H. Williams *et al.*, *Earth Planet. Sci. Lett.* **250**, 486 (2006).
24. D. J. Frost, C. A. McCammon, *Annu. Rev. Earth Planet. Sci.* **36**, 389 (2008).
25. F.-Z. Teng, N. Dauphas, R. T. Helz, *Science* **320**, 1620 (2008).
26. S. Weyer, *Science* **320**, 1600 (2008).
27. C. A. McCammon, *Phys. Chem. Miner.* **25**, 292 (1998).
28. Discussions with J. Horita, E. D. Young, R. N. Clayton, A. A. Ariskin, and S. D. Mineev are appreciated. I thank three anonymous reviewers for constructive comments.

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