Equilibrium Iron Isotope Fractionation at Core-Mantle Boundary Conditions

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What's new

PPV is enriched in heavy iron isotope ($^{57}Fe/^{54}Fe$) relative to metallic iron at ultrahigh pressure

Fe isotope

- ^{54}Fe: stable 5.8% *n*: 28
- ^{56}Fe: stable 91.72% *n*: 30
- ^{57}Fe: stable 2.2% *n*: 31
- ^{58}Fe: stable 0.28% *n*: 32

- ^{60}Fe: radioactive β decay

  Half life: 1.5 X 10^6 years

  DP: ^{60}Co

Unsolved problems for Fe isotope

Why are basalts from Earth and Mars enriched in heavy isotope?

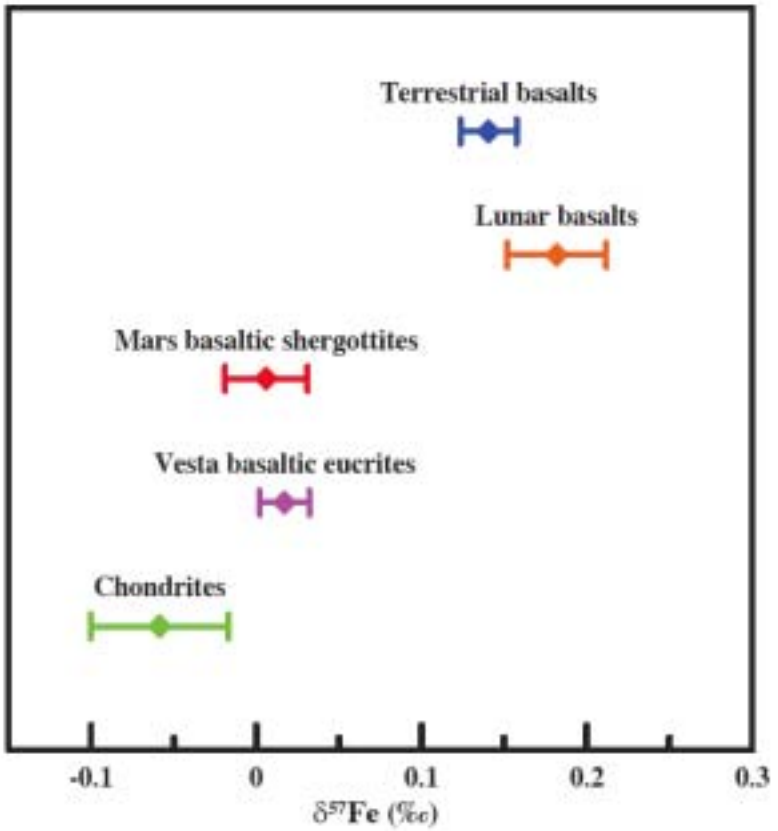
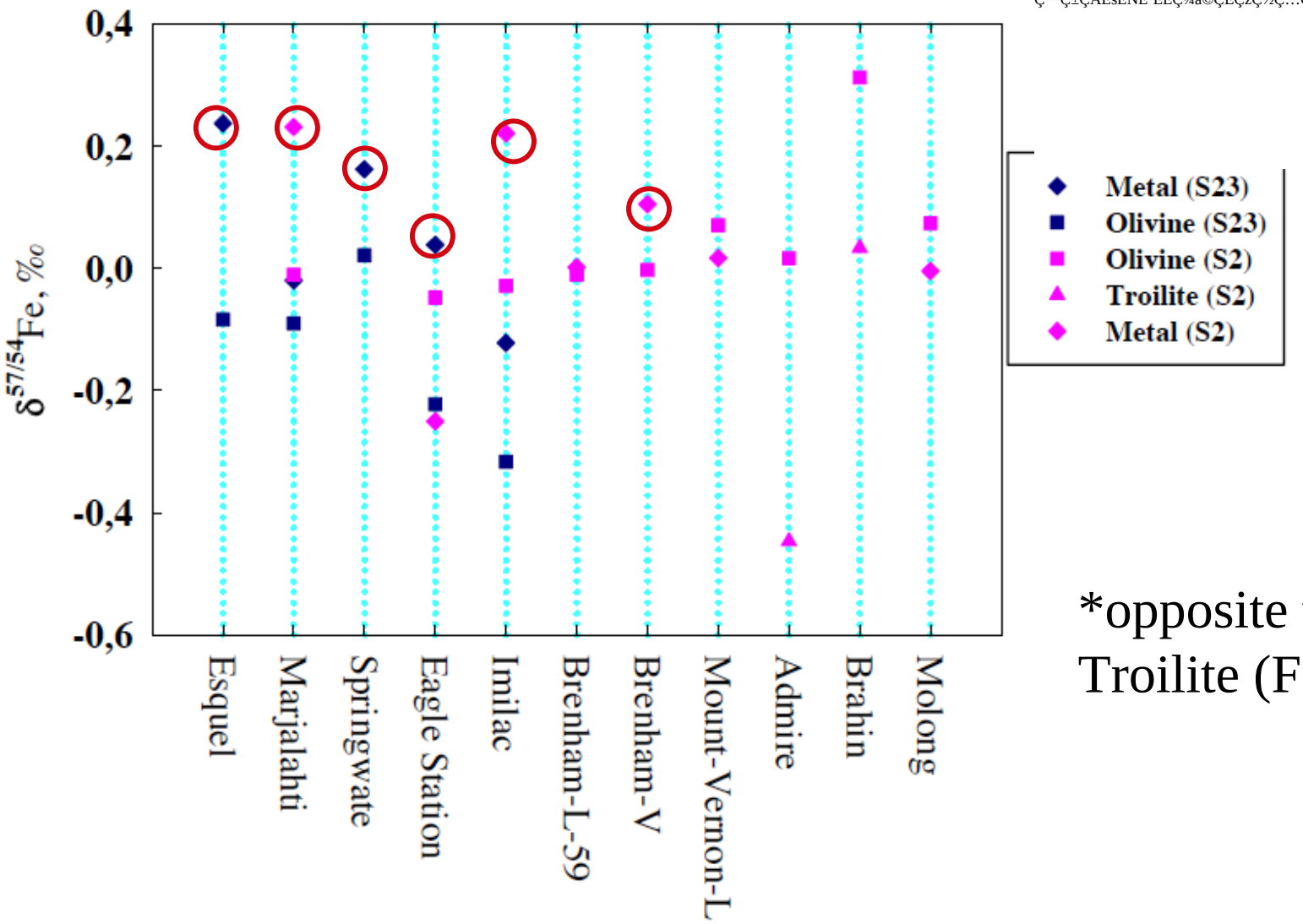


Fig. S1. Interplanetary differences in iron isotope compositions of basalts. Horizontal bars correspond to two-standard-error ranges. One can observe the enrichment of terrestrial and lunar basalts relative to those from the Mars, Vesta and chondrites samples at two-standard-error level. Parameters of datasets are following:

Some hypotheses

- Evaporation and condensation during the “giant impact”
- Fe isotopic fractionation caused by partial melting and magmatic differentiation
- Core-mantle differentiation

Heavy iron partitions into metal



*opposite trend
Troilite (FeS)

Fig. S3

Inelastic Nuclear Resonance X-ray Scattering (INRXS)

- Mössbauer effect (nuclear resonanace)

Gamma ray: Nuclear transition from an unstable high-energy state, to a stable low-energy state

Energy of the emitted gamma ray = Energy of the nuclear transition, minus an amount of energy that is lost as recoil to the emitting atom. The gamma ray can be absorbed by a second atom of the same type.

Emission and subsequent absorption **Resonanace**

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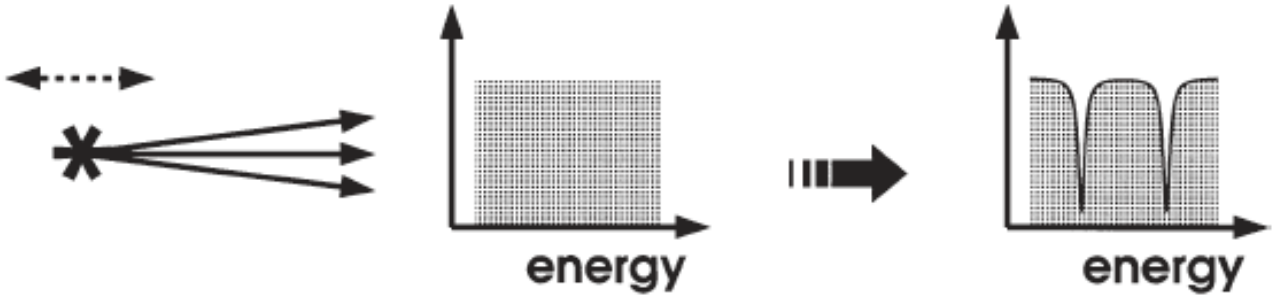
In a solid, the nuclei are bound to the lattice and do not recoil in the same way as in a gas. The lattice as a whole recoils but the recoil energy is negligible because the *M* in the above equation is the mass of the whole lattice. However, the energy in a decay can be taken up (or supplied by) lattice vibrations. The energy of these vibrations is quantised in units known as *phonons*.

Wikipedia

A difference between Mössbauer spectra and INRXS

Energy-resolved spectroscopy (Radioactive source)



Time-resolved spectroscopy (Synchrotron)

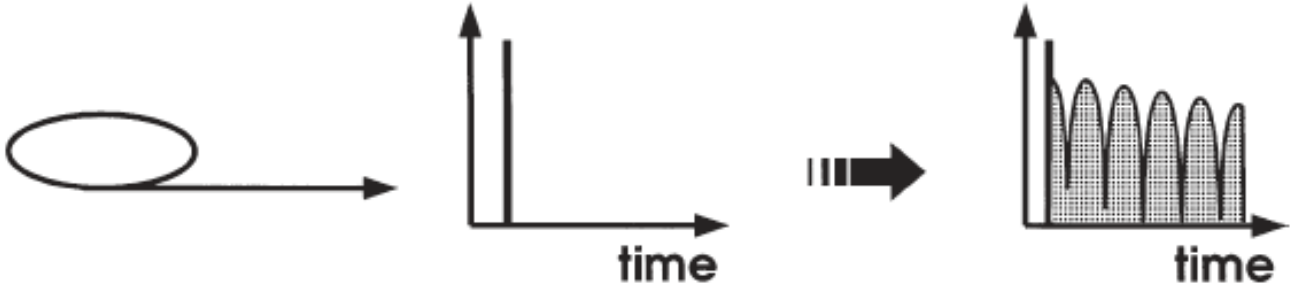


Figure 1. Reciprocal properties of radioactive sources (top) and synchrotron radiation (bottom) lead to reciprocal experimental techniques. The center panels illustrate the source characteristics averaged over a time period needed for data collection.

Sturhahn et al. 98 Hyp. Interact.

Experimental setup

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Undulator: High resolution monochrometer
Pulse (Bunch mode)
APD: Avalanche photodiode detector
High resolution monitor of time decay

Inelastic Nuclear Resonance X-ray Scattering (INRXS)

monochromatic

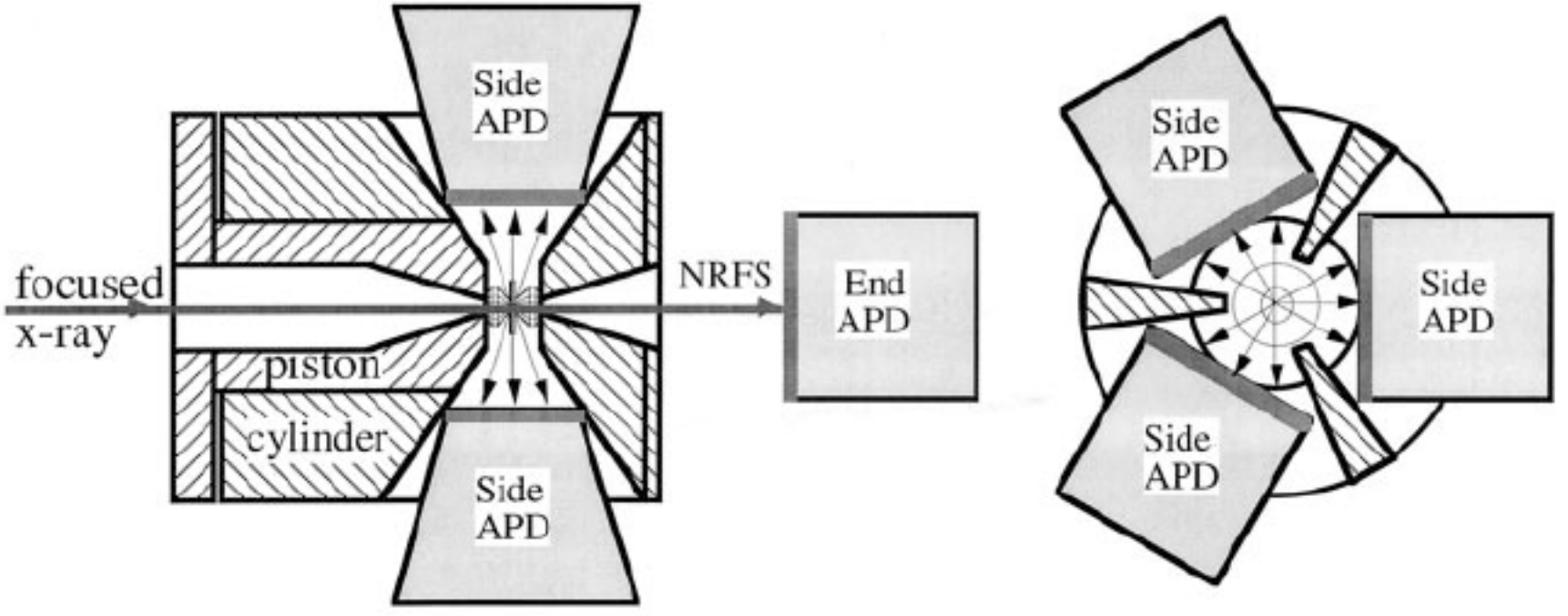


Fig. 1. Wide-angle diamond cell optimized for NRIXS at ultrahigh pressures (left, side view; right, end view). Long piston-cylinder configuration assures the alignment stability critical for reaching ultrahigh pressures. Three windows, each with a 105° equatorial and 68° azimuthal opening [resembling cells developed for neutron diffraction (*36*)], allow the collection of Fe fluorescence through the high-strength Be gaskets (*19*) over a huge (40% of the $4\pi r^2$) spherical area by tailor-fitting three APD on the side. The fourth APD at the end records the coherent nuclear forward scattering and monitors the instrument resolution function.

Mao et al., 01, Science

Determination of fractionation factor

- Partial vibrational (phonon) densities of states (PVDOSs)

0.8 meV resolution

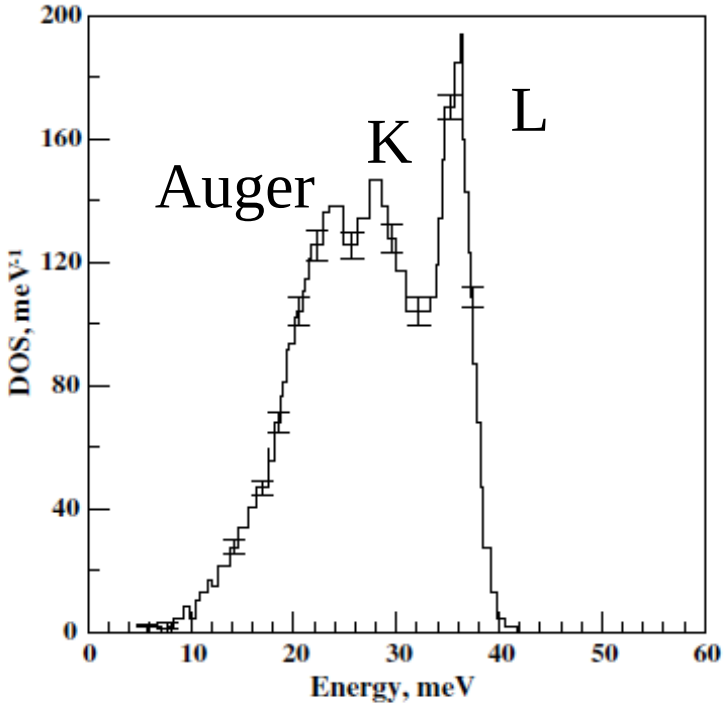


Fig. 1. The phonon DOS of metallic iron (α-Fe) (Alp et al., 2001). Typical uncertainties in the phonon DOS values are shown by error bars.

Polyakov et al., 07 GCA

Kinetic energy of thermal vibration

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

Einstein function for energy of the single harmonic oscillator

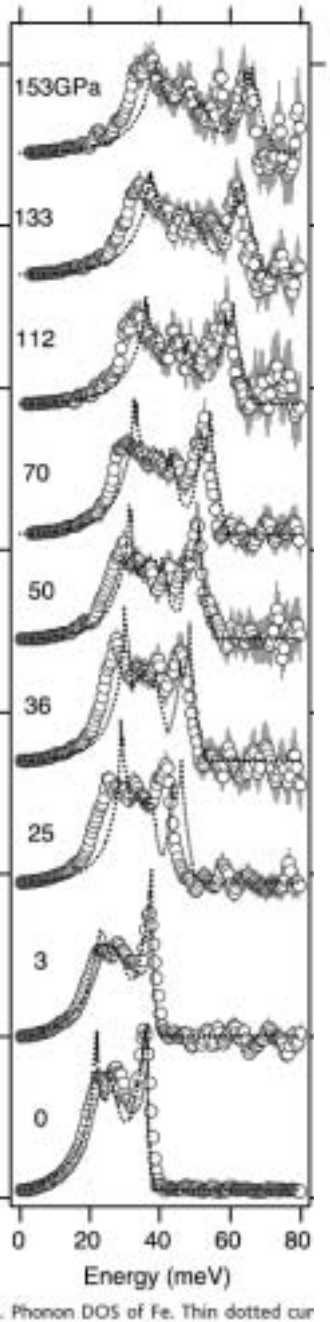
$$E(e) \equiv \frac{e}{\exp(e/kT) - 1} + 0.5e \qquad (2)$$

Fe β factor

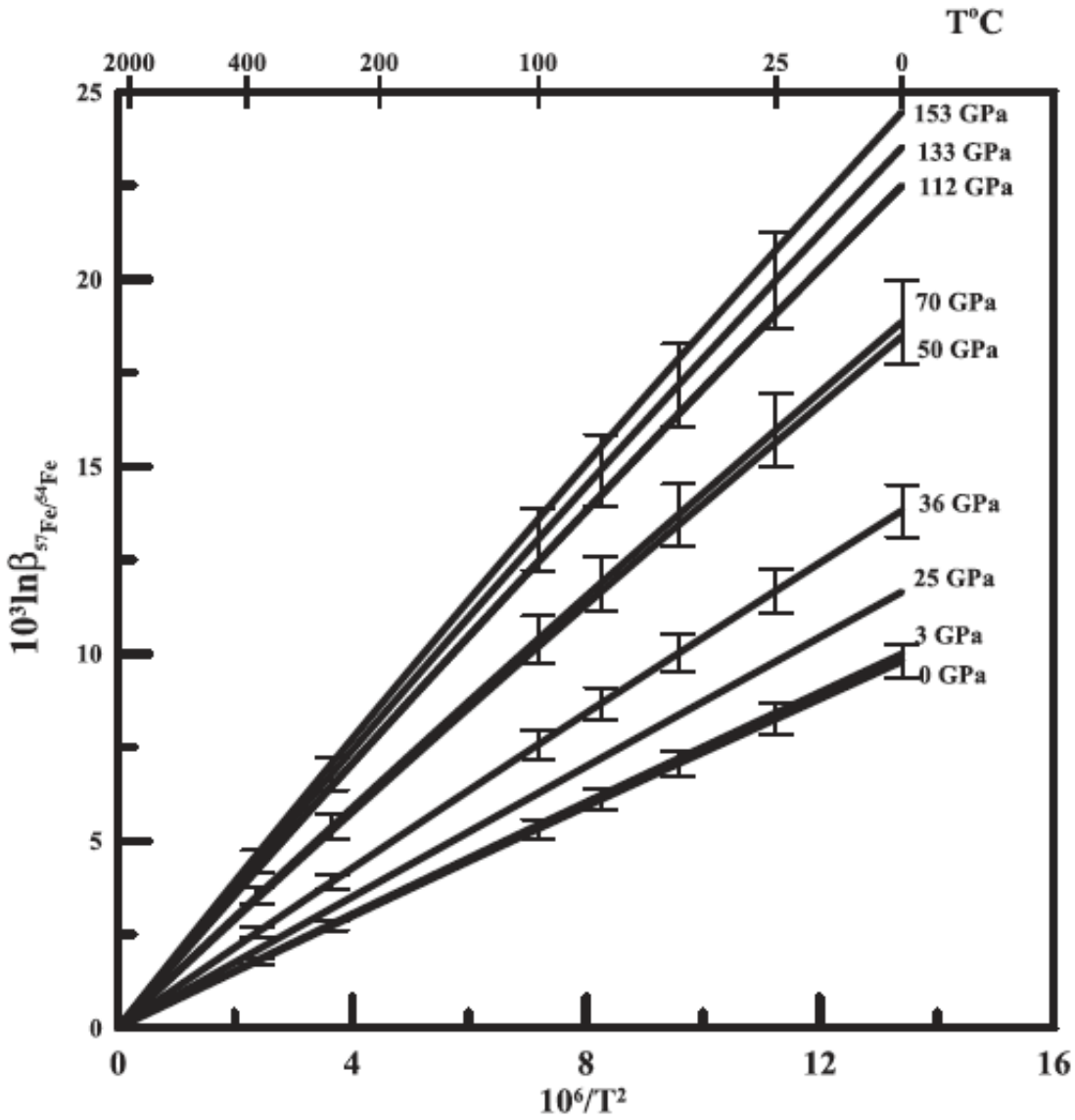
$$\ln\beta = -\left(\frac{K_{^{57}\mathrm{Fe}}}{kT} - \frac{3}{2}\right)\frac{\Delta m}{m}$$

m: the mass of an iron isotope

Metallic iron



. Phonon DOS of Fe. Thin dotted cur
tic theory; circles with error bars, NI

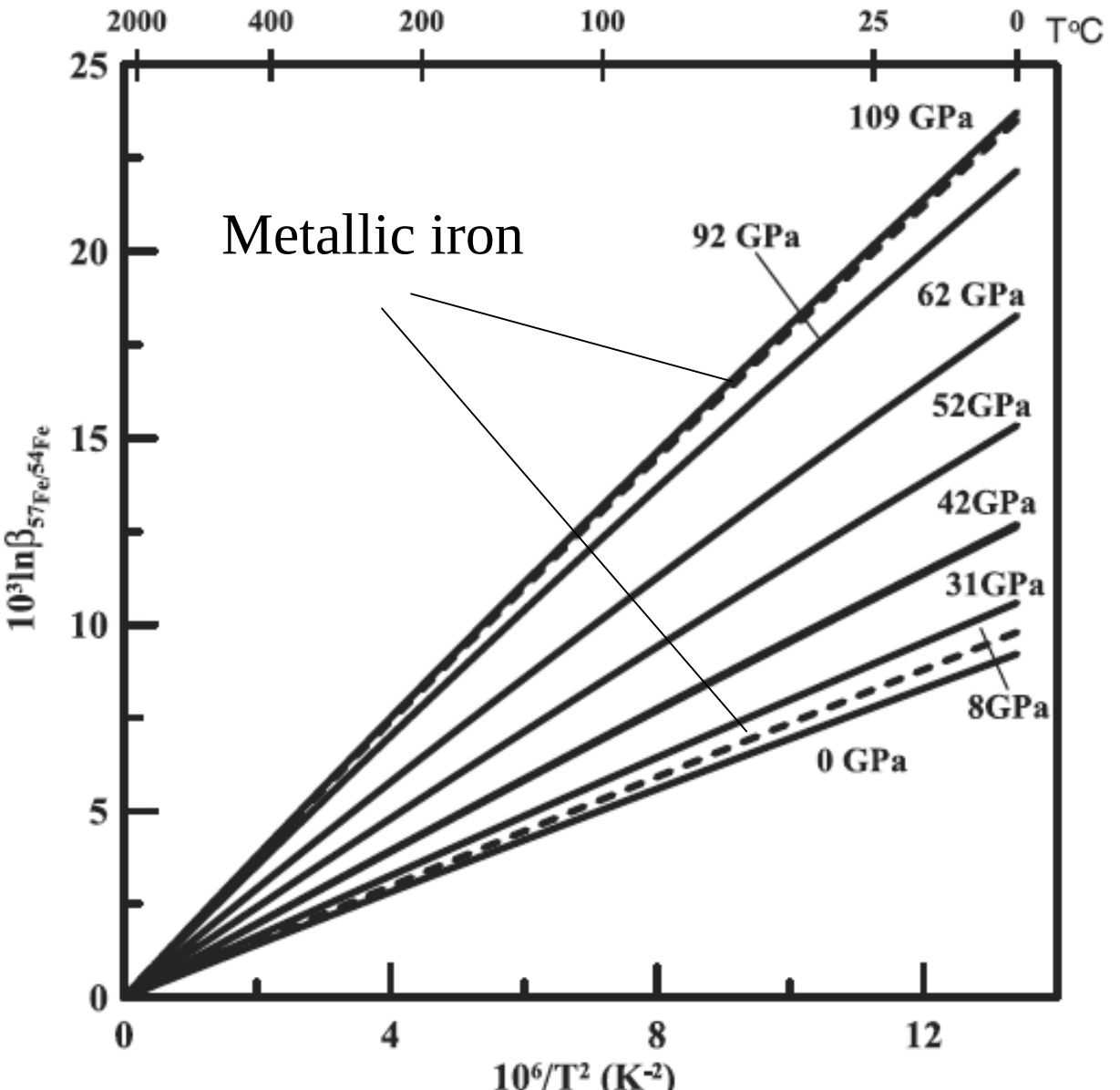


Mao et al., 01, Science

Fig. 1. Temperature and pressure dependence of the $^{57}Fe/^{54}Fe$ β factor for metallic Fe. The $^{57}Fe/^{54}Fe$ β factor of Fe metal is computed from the ^{57}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 lnβ are calculated from the experimental uncertainties in the ^{57}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 β factor with increasing pressure to ultrahigh pressures is not a unique feature of Fe metal (see text and Figs. 2 and 3

Ferropericlase $(Mg_{0.75}\,Fe_{0.25})O$

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



Data from
Lin et al., 06, GRL

Post-perovskite and perovskite $(Mg_{0.6}Fe_{0.4})SiO_3$

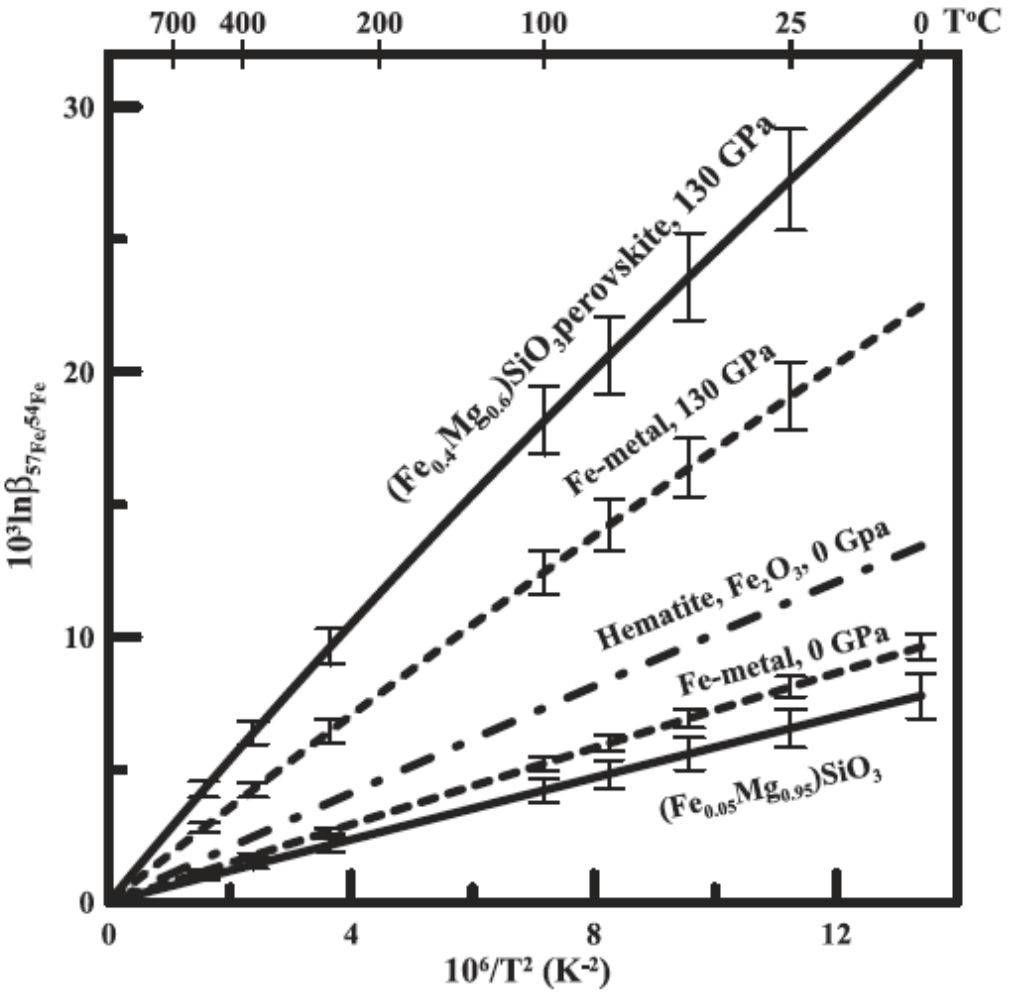


Fig. 3. The Fe β factor for the post-perovskite and perovskite phases at CMB and ambient pressures, respectively. The Fe β factor for $(Fe_{0.4}Mg_{0.6})SiO_3$–post-perovskite at 130 GPa was calculated from the ^{57}Fe PVDOS obtained by the synchrotron INRXS (*15*). Error bars are calculated from experimental uncertainties using the Monte-Carlo technique (*17*) (SOM text). The β factor for $(Fe_{0.05}Mg_{0.95})SiO_3$-perovskite was calculated from the Mössbauer second-order Doppler shift (*27*) by a method described elsewhere (*10*, *18*). The β factors for metallic Fe (Fig. 1) and hematite (*10*, *11*) are also shown for comparisons. The β factor for hematite at ambient pressure from (*10*) was used as an analog for the perovskite phase by Georg *et al.* (*13*).

Determination of Fe β factor

Equilibrium isotopic shift

$$\Delta_{A-B}(‰) \approx 10^3 \ln \alpha_{A-B}$$

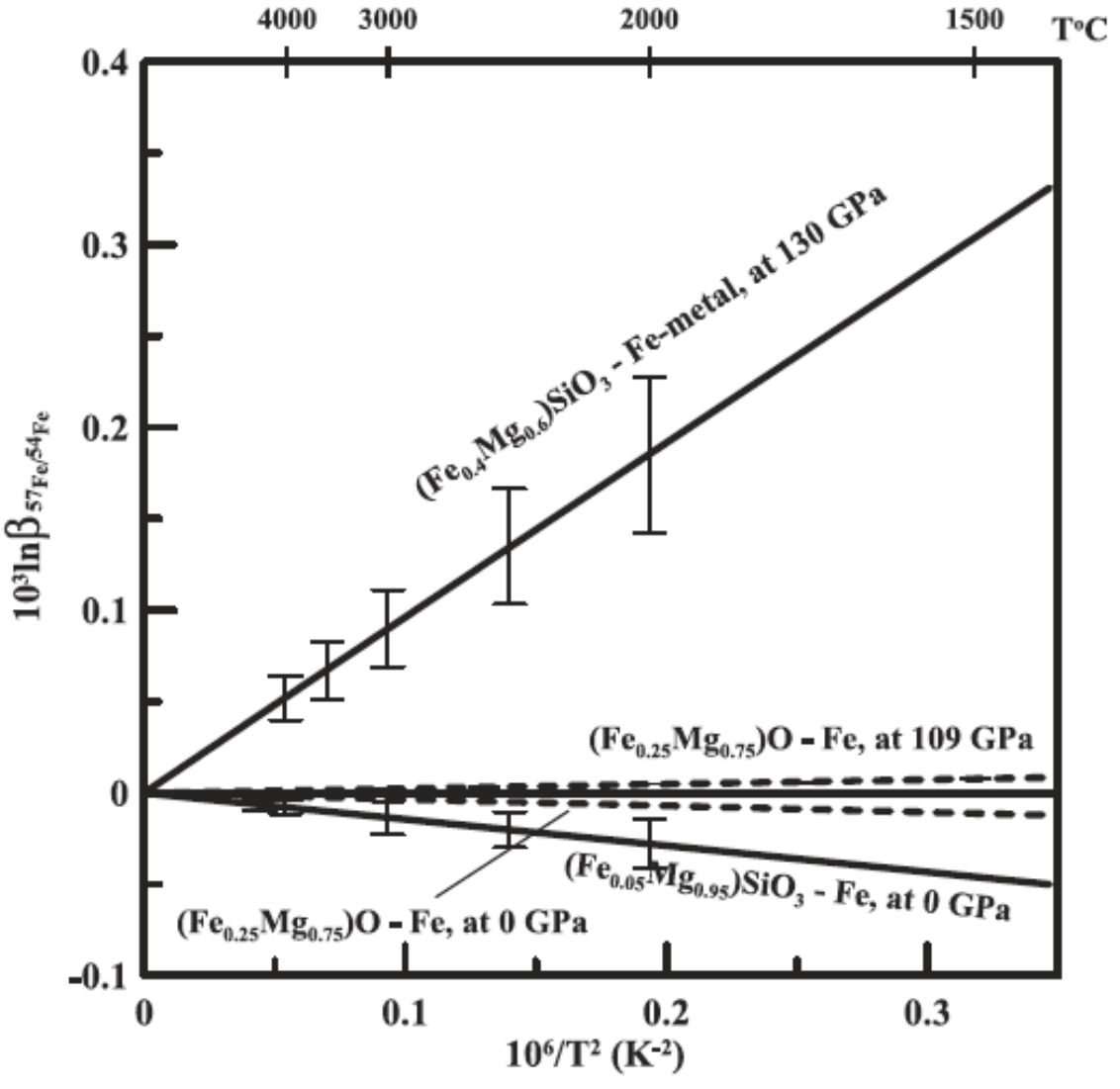
$$= 10^3 \ln \beta_A - 10^3 \ln \beta_B \qquad (4)$$

$$\alpha_{A\text{-}B} = ([^{57}Fe]/[^{54}Fe])_A/([^{57}Fe]/[^{54}Fe])_B$$

Equilibrium Fe isotope fractionations

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 β factors presented in Figs. 1 to 3 using Eq. 4. One can see the different directions of the equilibrium Fe isotope fractionation between ferrous (Fe^{2+}) lower mantle minerals and metallic Fe (Fe^{0}) at ambient and CMB pressures.

Dashed line: FP-Fe



Summary

- The equilibrium Fe isotope fractionation becomes positive at ~100 GPa.
- The enrichment of terrestrial basalts in heavy Fe isotopes relative to those from Mars, Vesta and chondrite was caused by core-mantle differentiation in Earth occurring mainly at high pressure.

  Mars, Vesta: core formation at low pressure

  Moon: Earth's core-mantle differentiation before "giant impact"