

Supporting online materials.

S1. Iron isotope compositions of basalts from different planetary bodies.

Poitrasson et al. (S1) found that terrestrial and lunar basalts are enriched in heavy iron isotopes relative to Martian basaltic shergottites, Vesta basaltic eucrites and chondrites, undifferentiated meteorite. Subsequent studies (S2 - S6) generally confirmed this observation (Fig S1). However, the difference between iron isotope compositions of lunar and terrestrial basalts is still a controversial subject (S4 - S6). Different interpretations (S1, S2, S4-S6) of iron isotope compositions of lunar and terrestrial samples are presented below (see also Fig. S2):

1. Poitrasson et al. (S1, S5) argue the enrichment of Moon's rocks in heavy iron isotope relative to those from the Earth based on their measurements of iron isotope composition of lunar and terrestrial samples. Poitrasson et al. (S1) obtained 0.206‰ for the averaged $\delta^{57}\text{Fe}$ value of $N = 14$ lunar samples (Fig S2). (Hereafter, all iron isotope compositions are given relative to the Institute for Reference Materials and Measurements 014 (IRMM-014) standard). The standard deviation (SD) of the lunar sample set measured by Poitrasson et al. (S1) is 0.051‰; the standard error (SE) is 0.014‰. Appropriate values for the Earth samples investigated by Poitrasson et al. (S1) are following: $N=13$; $\delta^{57}\text{Fe} = 0.102\text{‰}$; $\text{SD} = 0.053$; $\text{SE} = 0.015$. Poitrasson et al. (S1) showed that averaged $\delta^{57}\text{Fe}$ values of iron isotope compositions of lunar and terrestrial samples they studied are distinctly different at the $> 99\%$ confidence level based on the Student t -test. There are five lunar Ti-rich ($>8\%$) basalts among samples investigated by Poitrasson et al. The averaged $\delta^{57}\text{Fe}$ value of iron isotope composition of these high-Ti basalts ($\delta^{57}\text{Fe} = 0.242\text{‰}$, $\text{SD} = 0.029\text{‰}$) is somewhat greater than that of other lunar basalts ($\delta^{57}\text{Fe} = 0.188\text{‰}$, $\text{SD} = 0.061\text{‰}$). Nevertheless, the average $\delta^{57}\text{Fe}$ value of lunar samples without high-Ti basalts is greater than that of terrestrial mafic rocks, according to Poitrasson et al. (S1) measurements (Fig S2).

2. Weyer et al. (S2, S6) believe that lunar and terrestrial basalts have identical bulk Fe-isotope compositions. According to Weyer et al. (S2) measurements, the averaged $\delta^{57}\text{Fe}$ value of lunar basalts is 0.158‰ (SD = 0.099‰; SE = 0.026‰; N= 15). Weyer et al. (S2) also found that Ti-rich lunar basalts have the heavier Fe isotope composition in comparison with other lunar basalts. The averaged $\delta^{57}\text{Fe}$ of four high-Ti mare basalts samples is 0.301‰ (SD = 0.013‰; SE = 0.008‰). Non-Ti-rich basalts have significantly easier lower Fe isotope compositions: the averaged $\delta^{57}\text{Fe}$ = 0.106‰; SD = 0.049‰; SE = 0.015‰; N = 11. Fe isotope compositions of Earth basalts were investigated by Weyer and Ionov (S7): the averaged $\delta^{57}\text{Fe}$ = 0.169‰; SD = 0.086‰; SE = 0.024‰; N=14 (Fig. S3).
3. Beard and Johnson (S4) suggested to use Fe compositions of low-Ti mare lunar basalts for interplanetary comparisons (Fig. S2). According to their compilation based on data from (S2, S8), the averaged $\delta^{57}\text{Fe}$ of low-Ti mare lunar basalts to be converted to IRMM-014 standard is 0.15‰ (SD = 0.06‰; N=14). Using data from (S1, S2, S8), they found the average $\delta^{57}\text{Fe}$ = 0.27‰ (SD = 0.045‰; N=9) for high-Ti mare basalts. The average $\delta^{57}\text{Fe}$ for Earth basalts (S9) is 0.143 (SD = 0.066‰; SE = 0.012‰; N = 30).

One should stress that all investigators (S4 -S6) agree that similar rock types must be compared when considering possible inter-planetary Fe isotope differences and that basalt-basalt correlation mirrors differences in iron isotope compositions of silicate portions of interplanetary bodies.

S2. Main concepts and quantities of the stable isotope fractionation theory.

An isotope fractionation factor between two samples *A* and *B* is defined as ratio of isotopic compositions of these samples. According to this definition, one can write for the $^{57}\text{Fe}/^{54}\text{Fe}$ isotope fractionation factor: $\alpha_{A-B} = ([^{57}\text{Fe}]/[^{54}\text{Fe}])_A / ([^{57}\text{Fe}]/[^{54}\text{Fe}])_B$, where $[^{57}\text{Fe}]$ and $[^{54}\text{Fe}]$ denote the concentration of ^{57}Fe and ^{54}Fe isotopes, respectively. Along with the isotope fractionation factor,

one uses the isotopic shift (Δ) usually expressed in per mill (‰) and defined as: $\Delta_{A-B} = (\alpha_{A-B} - 1) \times 1000$ (‰). Since the deviation of the isotope fractionation factor from unity is not significant for iron isotope substitution, it is convenient to use the $10^3 \ln \alpha_{A-B}$ instead of the isotopic shift due to the relationship: $10^3 \ln \alpha_{A-B} \approx 10^3 (\alpha_{A-B} - 1) = \Delta_{A-B}$, which is fulfilled with the high accuracy.

The β -factor or the reduced isotopic partition function ratio is the main concept of the stable isotope fractionation theory (S10). At given temperature and pressure, one defines the β -factor in terms of

free energies of two isotopologues as: $\ln \beta = -\frac{G^*(T, P) - G(T, P)}{zRT} - 1.5 \ln \frac{m^*}{m}$, where β is the β -

factor; $G(T, P)$ is the Gibbs free energy at given pressure and temperature; z is the multiplicity of the isotope substitution; R is the universal gas constant; m is the mass of the isotope; the asterisk stands

for the minor isotopologue. Equilibrium fractionation factor between two substances A and B is

directly expressed through the β -factors: $\ln \alpha_{A-B} = \ln \beta_A - \ln \beta_B$. For equilibrium isotopic shift, one

can write: Δ_{A-B} (‰) = $10^3 \ln \alpha_{A-B} = 10^3 \ln \beta_A - 10^3 \ln \beta_B$. The β -factor of a given substance determines the distribution of isotopes in equilibrium processes.

S3. Evaluation of anharmonic corrections at high pressures and temperatures.

Evaluation of anharmonic effects is the principal subject of the stable isotope fractionation theory.

According to the technique developed by P. Gillet with his collaborators (S11), the effect of anharmonicity can be written as a sum of the quasi-harmonic term describing explicit dependence of normal frequencies on molar volume (density) and the intrinsic anharmonic term expressing normal frequencies as explicit functions of temperature. As it was shown (S12), the intrinsic anharmonicity does not affect the β -factor significantly and can be neglected. For this reason, the quasi-harmonic approximation is used in the present evaluation of the anharmonic correction. If the $\ln \beta$ at higher

temperature (T) is calculated in the harmonic approximation using the PDOS obtained at room temperature (T_0) and pressure P , this means that $\ln\beta$ is calculated at high temperature (T) and volume V_0 corresponding to temperature T_0 and pressure P according to the equation of states (EOS). To evaluate the anharmonic correction to the value of the $\ln\beta$, one must calculate the change of the $\ln\beta$ caused by the change of volume from V_0 to V (V is the molar volume at temperature T and pressure P), *i.e.*, $\ln\beta(T,V) - \ln\beta(T,V_0)$.

In the quasi-harmonic approximation, the volume derivative of the $\ln\beta$ is written as (S13, Eq. 9):

$$\left(\frac{\partial \ln \beta}{\partial \ln V}\right)_T = \gamma T \left(\frac{\partial \ln \beta}{\partial T}\right)_V \quad (\text{S3.1})$$

$$\gamma = \frac{\sum_i \gamma_i [u_i \coth(u_i / 2) - u_i^* \coth(u_i^* / 2)]}{\sum_j [u_j \coth(u_j / 2) - u_j^* \coth(u_j^* / 2)]} \quad (\text{S3.2})$$

where $u_i = h \nu_i / kT$ is the dimensionless frequency; γ_i is the modal Grüneisen parameter; "*" denotes minor isotopologue quantities. The parameter γ coincides with the Grüneisen γ_{th} constant in the case of single-element (simple) substances.

At high temperatures, $\ln\beta \sim T^{-2}$, Eq. S3.1 can be rewritten as:

$$\left(\frac{\partial \ln \beta}{\partial \ln V}\right)_T = -2\gamma \ln \beta \quad (\text{S3.3})$$

One can get from Eq. S3.3 after simple transformations:

$$\frac{\Delta \ln \beta}{\beta} = -2\gamma \Delta \ln V \quad (\text{S3.4})$$

The change of the volume is caused by the thermal expansion and can be calculated by the following formula:

$$\Delta \ln V = \int_{T_0}^T \alpha_T dT = \bar{\alpha}_T \Delta T \quad (\text{S3.5})$$

Eq. S3.5 is the subject of Lagrange's theorem. In this equation, α_T is the thermal expansion coefficient; $\bar{\alpha}_T$ is the value of the thermal expansion coefficient at some temperature T_1 , $T_0 < T_1 < T$. As $T_0 \ll T$, then $\Delta T \approx T$. The thermal expansion coefficient increases with temperature. Since, the following expression somewhat overestimates the $\Delta \ln V$, if α_T relates to temperature T :

$$\Delta \ln V \approx \alpha_T T \quad (\text{S3.6})$$

Substituting this to (S3.4), one gets:

$$\frac{\Delta \ln \beta}{\ln \beta} = -2\gamma\alpha_T T. \quad (\text{S3.7})$$

For the quantitative estimate of the anharmonic correction, it is convenient to transform Eq. S3.7:

$$\frac{\Delta \ln \beta}{\ln \beta} = -2\gamma\alpha_T T = -\frac{2\gamma\gamma_{th}C_V T}{VK_T} = -\frac{6\gamma\gamma_{th}RT}{VK_T} \quad (\text{S3.8})$$

where $\gamma_{th} \equiv \frac{\alpha K_T V}{C_V}$; K_T is the isothermal bulk modulus; C_V is the molar heat capacity at constant volume; $C_V \approx 3Rn$ at high temperatures; n is the number of atoms in a chemical molecular unit.

The most simple evaluation can be done for iron, because $\gamma = \gamma_{th} \approx 1$ in this case. This gives

$\Delta \ln \beta / \ln \beta \sim -0.87$ at 2000 K and ~ 0.175 at 4000 K and low pressure, if literature data of $K_T = 161.6$

GPa and $V = 6.89 \text{ cm}^3/\text{mole}$ are used. For non-single-element substances, γ is significantly lower

than unity (S13), one can expect that the anharmonicity effect will be lower. The anharmonic

correction to the $\ln \beta$ is always negative. One can expect that the anharmonic correction to $\ln \alpha$

between post-perovskite and iron does not exceed 9% at 2000 K and 18% at 4000 K at low

pressures.

One can also to estimate the anharmonic correction to $\ln \beta$ for iron at high pressures. Using $K_T = 746$

GPa and $V = 3.76 \text{ cm}^3/\text{mole}$ from Mao et al. (S14), one gets for iron: $\Delta \ln \beta / \ln \beta = 0.038$ at 2000 K

and 0.074 at 4000 K. It is difficult to estimate the anharmonic correction for complex, non-single-

element, substances because data on γ_i at high pressures are absent. However, if we suppose that γ is approximately the same at high and low pressures, one can estimate the ratio of anharmonic corrections at high and low pressures:

$$\left(\frac{\Delta \ln \beta}{\ln \beta}\right)_{P=P_{\text{low}}} \bigg/ \left(\frac{\Delta \ln \beta}{\ln \beta}\right)_{P=P_{\text{high}}} = \frac{(VK_T)_{P=P_{\text{high}}}}{(VK_T)_{P=P_{\text{low}}}}.$$

For iron, $\frac{(VK_T)_{130\text{GPa}}}{(VK_T)_{0\text{GPa}}} = 2.5$. For ferropericlase, $\frac{(VK_T)_{130\text{GPa}}}{(VK_T)_{0\text{GPa}}} = 2.45$ according to the EOS from

Westrenen et al. (S15); experimental value $\frac{(VK_T)_{80\text{GPa}}}{(VK_T)_{0\text{GPa}}} = 2.1$ (Crowhurst et al. S16) is in an

agreement with $\frac{(VK_T)_{80\text{GPa}}}{(VK_T)_{0\text{GPa}}} = 2.01$ given by Westrenen et al's EOS. For post-perovskite phase,

$\frac{(VK_T)_{130\text{GPa}}}{(VK_T)_{0\text{GPa}}} = 2.6$ according to the Oganov and Ono (S17) EOS for post-perovskite. One can see

that application of harmonic approximation to calculating the $\ln \beta$ at high pressure results in the smaller error than that at low pressure. The anharmonic correction to the $\ln \beta$ at ~ 4000 K and 130 GPa is equal to that at ~ 1600 K and ambient pressure. High pressures are a favorable condition for the application of the harmonic approximation to calculating the β -factor.

Errors about of 4% in $\ln \beta$ at 2000 K give errors < 0.02 in the $10^3 \ln \alpha$ value at 2000 K and errors 8% in $\ln \beta$ at 4000 K lead to errors < 0.01 at 4000 K.

S4. Propagation of experimental errors in ^{57}Fe PVDOS to $\ln\beta$.

Experimental uncertainties in the ^{57}Fe PVDOS for Fe-metal and (Mg,Fe)SiO₃-post-perovskite (S14, S18) allow evaluating errors in calculated $\ln\beta$. Unfortunately, authors of (S19) did not include data on experimental errors in the ^{57}Fe PVDOS of ferropericlase in their paper. One can expect that errors in $\ln\beta$ in the case of ferropericlase do not differ significantly from those calculated for Fe-metal and (Mg,Fe)SiO₃-post-perovskite. The propagation of error from the ^{57}Fe PVDOS to $\ln\beta$ is not a trivial task. Following the previous works (S20, S21), I have applied the Monte-Carlo technique to solve this task. The algorithm of calculations is as follows:

1. Using the computer program for the Gaussian distributed variable at a given mean value and dispersion, random values of $g_r(e)$ have been calculated at each experimental point of the PVDOS curve. (Mean values in this calculation are equal to experimental $g(e)$ values and dispersions are equal to the square of standard errors, *i.e.*, the one-side error bar length). One experimental curve contains about one hundred points.

2. The random $g_r(e)$ computed on the preceding stage has been normalized to unity:

$$\int_0^{e_{\max}} g_r(e) de = 1. \quad (\text{S4.1})$$

3. The random value of the $^{57}\text{Fe}/^{54}\text{Fe} \ln\beta_r$ has been computed by Eqs. 2 and 3 in the main text of this paper, using the $g_r(e)$ calculated on stages 1 and 2.
4. Computations according to items 1, 2 and 3 were repeated 250 times and the random sampling of the $\ln\beta_r$ was obtained.
5. The standard error in the $^{57}\text{Fe}/^{54}\text{Fe} \ln\beta$ was calculated as the square-root of the dispersion of the random sampling obtained in the previous step.

A good agreement between the average value of the $\ln\beta_r$ random sampling and $\ln\beta$ computed using the function $g(e)$ is a criterion for the correctness of this algorithm. In present calculations average value of the $\ln\beta_r$ random sampling and $\ln\beta$ were different in the fourth significant digit only.

Calculated standard errors are presented on Fig. 1 and 3 as error bars. Standard errors of $^{57}\text{Fe}/^{54}\text{Fe}$ $\ln\alpha$ in Fig. 4 were calculated as a sum of standard errors of $^{57}\text{Fe}/^{54}\text{Fe}$ $\ln\beta$ for Fe-metal and for (Mg,Fe)SiO₃-post-perovskite which is divided by $\sqrt{2}$.

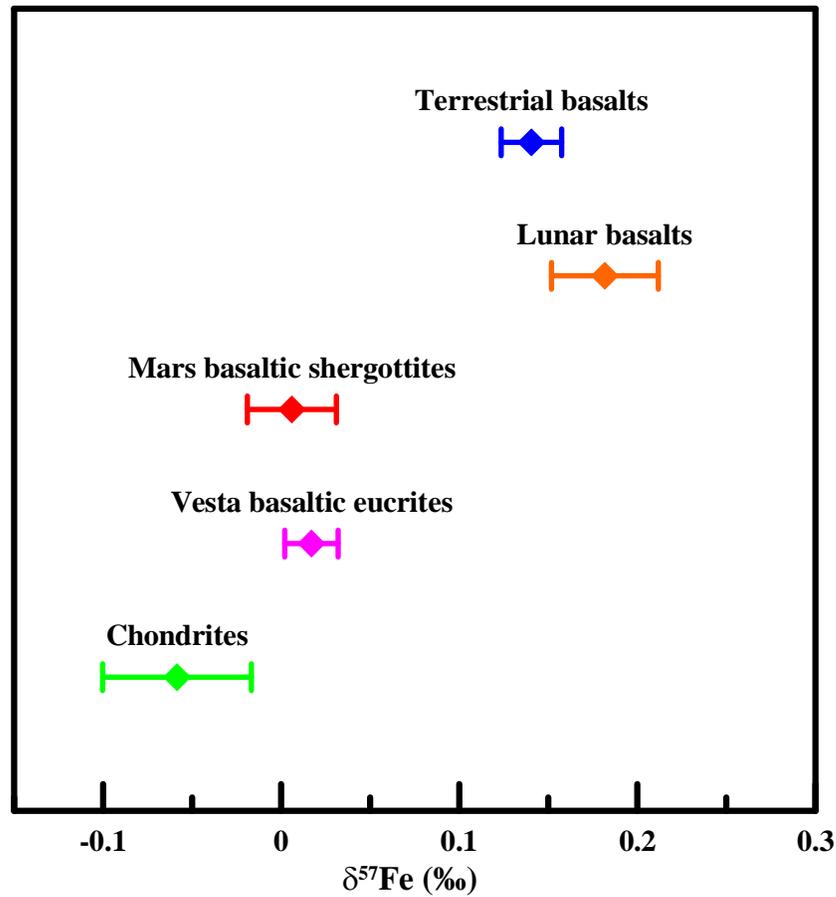


Fig. S1. Interplanetary differences in iron isotope compositions of basalts. Horizontal bars correspond to two-standard-error ranges. One can observe the enrichment of terrestrial and lunar basalts relative to those from the Mars, Vesta and chondrites samples at two-standard-error level. Parameters of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

	Averaged value, $\delta^{57}\text{Fe}$ (‰)	Standard deviation (‰)	Standard error (‰)	Number of samples	Literature sources
Chondrites	-0.059	0.072	0.021	13	S1, S3, S22
Vesta basaltic eucrites	0.017	0.031	0.007	19	S1, S2, S3
Mars basaltic shergottites	0.006	0.033	0.013	8	S1,S2
Lunar basalts	0.182	0.084	0.015	32	S1, S2, S8
Terrestrial basalts	0.140	0.070	0.008	69	S1, S2, S3, S7, S9

All original data are converted to $^{57}\text{Fe}/^{54}\text{Fe}$ isotope composition and IRMM-014 iron isotope standard.

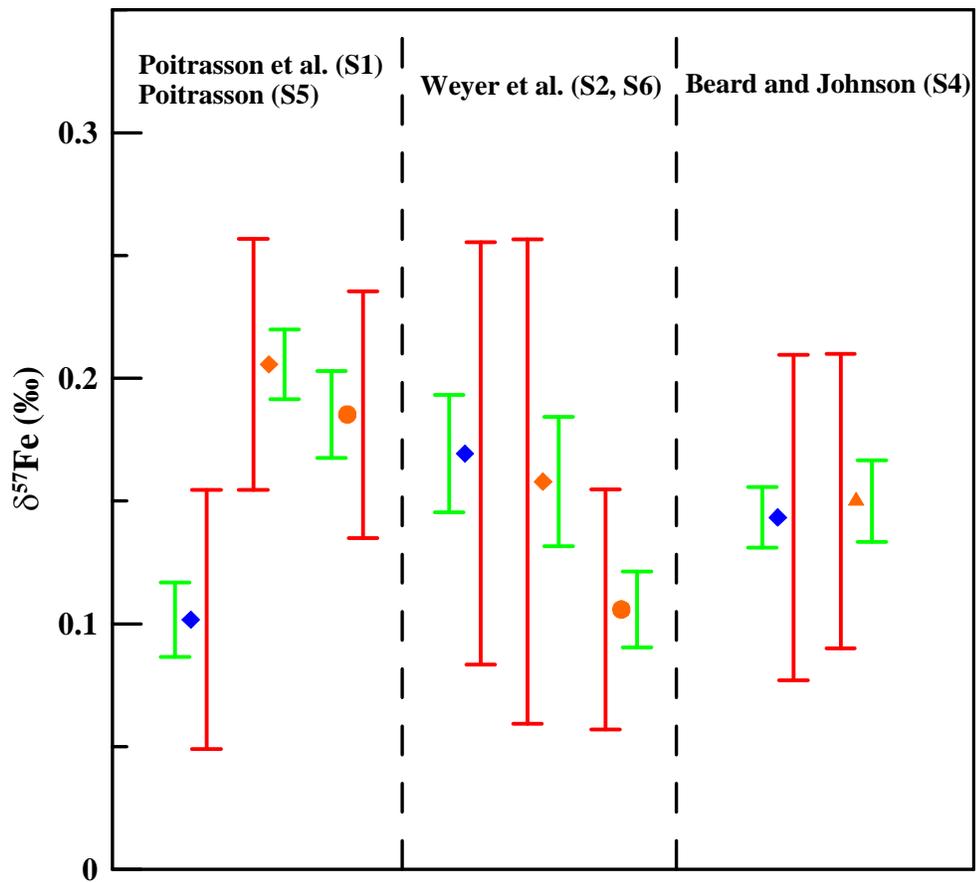


Fig. S2. Different estimates of the relationship between iron isotope compositions of lunar and terrestrial basalts. See also explanation in the chapter S1. Blue and orange diamonds relate to averaged $\delta^{57}\text{Fe}$ of terrestrial and lunar basalts respectively; orange circles relate to $\delta^{57}\text{Fe}$ of lunar basalts without high-Ti lunar basalts; an orange triangle relates to lunar low-Ti mare basalts. Red and green bars denote unbiased standard deviations and unbiased standard errors, respectively. Poitrasson et al's (S1) results include data on all rocks as this is done by authors (S1, S5). Weyer et al's estimate is presented using their data on Fe-isotope compositions of lunar basalts from (S2) and Weyer and Ionov (S7) measurements of Fe-isotope compositions of terrestrial basalts. Beard and Johnson's point of view is illustrated using their compilation of Weyer et al. (S2) and Wiesli et al (S8) data on low-Ti mare lunar Fe-isotope compositions and Beard et al. (S9) measurements of Fe-isotope compositions of terrestrial basalts. All data relate to IRMM-014 iron isotope standard.

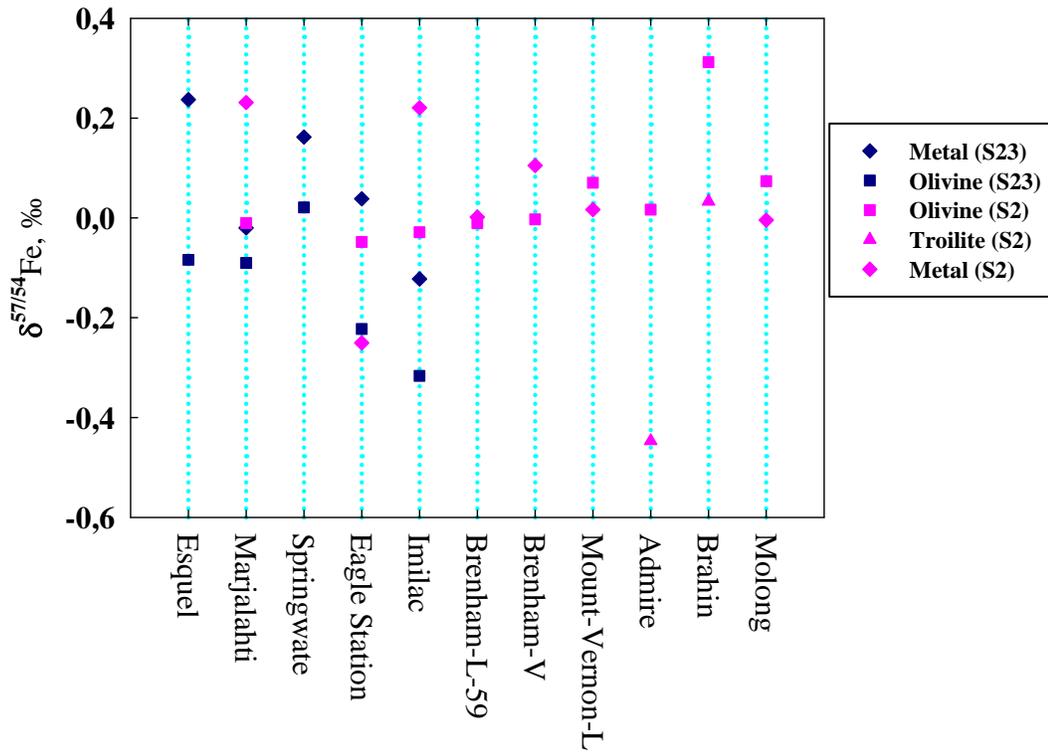


Fig. S3. Iron isotope fractionation between the silicate phase (olivine) and metallic phase (Fe-metal, troilite) in pallasite. One can see that the direction of silicate - Fe-metal isotope fractionations in pallasites coincides with those predicted by β -factors (S20, 24). Data for Molong and Mount-Vernon are within the uncertainty of measurements. Data for Eagle Station are controversial. Unfortunately, one cannot estimate the temperature of the metal-silicate differentiation using this data. "Isotopic" temperatures are too small to be realistic. Roskosz et al. (S25) noted that these "isotopic" temperatures reflect cooling history of meteorites. The kinetic (diffusional?) isotopic effects during cooling may be also occurred, for instance, in the case of Molong and Mount-Vernon (?). Troilite is always isotopically lighter than silicates as predicted by Moessbauer- and INRXS-derived β -factors.

References and notes

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