Supplementary Material

Assessment of matrix effects associated with Fe isotope analysis using 266 nm femtosecond and 193 nm nanosecond laser ablation multi-collector inductively coupled plasma mass spectrometry

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Laser ablation substrates

Magnetite standard 08BI-12 was collected from the Biwabik iron formation from the Thunderbird mine (Minnesota, USA). Magnetite standards 90LP5 and 90LP12 were picked from polymetamorphosed, granulite-facies marble collected at the Weston Mine within 100 m of the contact with the Marcy Anorthosite massif, Adirondack Mountains, New York. Similar magnetite grains were collected from the same locality, and previously used for study of oxygen isotopes.^{1, 2} Magnetite standard 98LH7 was picked from Rhyodacite from dome B of Chaos Crags, Lassen Volcanic National Park, California,³ and magnetite standard P2-670 was picked from carbonatites from the Bond zone from Oka (Canada).⁴ Pyrite standard Bal-4-13B was from the Balmat Mine (New York, USA). Pyrrhotite standard North Bend was purchased from Wards Science. Siderite standard was from a department collection. Pure Fe metal was purchased from Alfa Aesar.

Estimation of ablation volume

Ablation crater depths were measured by white light interferometry at University of Wisconsin Materials Research Science and Engineering Center. For raster ablation by fs-laser, the volume of material consumed during fs-LA was calculated using the equation reported in our previous work.⁵ For spot analysis by fs-LA, because the crater shape was a circular truncated

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cone (Fig. A1), the volume of material being removed (V) was calculated using the following equation (Eq. A1):

$$V = \frac{1}{3} \times \pi \times \left(r_{top}^2 + r_{bottom}^2 + r_{top} \times r_{bottom} \right) \times h \quad (Eq. A1)$$

where r_{top} is the top radius of crater on the sample surface, and r_{bottom} is the bottom radius of crater, *h* is the ablation depth (Fig. A1).

When r_{top} , r_{bottom} , and h can be directly measured by white light interferometry, the measured values were used in Eq. A1 to calculate volume. White light interferometry, however, was not able to measure depths of some craters produced by fs-laser spot ablation, because aspect ratios of those craters were probably too high to allow for the light to penetrate to the bottom of crater to produce the interference patterns. In these cases, spot ablations were carried out to produce a series of craters with a range of depths, using a range of laser dosages at a fluence and laser spot size identical to that used for the crater whose depth was not possible to directly measure. The volume of the target crater was inferred by the extrapolation of volumes determined for the series of craters produced at lower total laser shots (Fig. A2).

Modeling hydride interferences on the measured Fe isotope ratios

A mass resolving powder of >7000 is required to resolve Fe hydrides (⁵⁶FeH⁺) from ⁵⁷Fe⁺, so any potential ⁵⁶FeH⁺ interference cannot be fully resolved during our analysis where resolving powder was typically ~6000-7000. However, we concluded that such interference on the measured δ^{57} Fe values was entirely negligible during our analysis.

We modeled the potential impact of ⁵⁶FeH⁺ on δ^{57} Fe, and found that such an influence depends on two factors (1) amount of ⁵⁶FeH⁺ generated relative to Fe intensity, and (2) the difference in true ⁵⁷Fe/⁵⁴Fe ratios between sample and bracketing standard. If sample and bracketing standard has the same ⁵⁷Fe/⁵⁴Fe ratio, ⁵⁶FeH⁺ would have no influence on the measured δ^{57} Fe values. We modeled deviations of the measured δ^{57} Fe from true value as a function of hydride generation rates and differences in ⁵⁷Fe/⁵⁴Fe ratios between sample and bracketing standard (Fig. A3). Under an extreme case where a hydride generation rate (⁵⁶FeH^{+/56}Fe⁺) was assumed to be 1‰, which is several times higher than previously reported hydride generation rates of a few hundred ppm on ICP-MS,^{e.g., [6]} and a ⁵⁷Fe/⁵⁴Fe difference between sample and bracketing standard was assumed to be 7.5‰, which covers almost the entire ⁵⁷Fe/⁵⁴Fe variability in nature, the measured δ^{57} Fe value would only deviate from the true value by 0.1‰.

Manganese hydrides (⁵⁵MnH⁺) can interfere ⁵⁶Fe⁺, but typical mass resolving power used during our analysis (~6000-7000) was able to resolve this interference (required resolving power 5116) during our analysis. Moreover, ⁵⁵MnH⁺ interferences were negligible in our study, because Mn contents in all substrates ablated in our study were low (<9.25 wt. %, see Appendix Table A1 and A2). Assuming an extreme hydride generation rate (⁵⁵MnH⁺/⁵⁶Fe⁺) of 1‰, Mn ion intensity needs to be ~10% of Fe intensity to result in a ~0.1‰ shift in the measured δ^{56} Fe. Our measurements typically had Mn/Fe intensity ratios <1%.

Moreover, ⁵⁶FeH⁺ and/or ⁵⁵MnH⁺ interferences would result in the measured δ^{57} Fe and δ^{56} Fe values deviated from the expected mass-dependent fractionation relation in a three-isotope (δ - δ) plot, but such a deviation was not observed in our results.



Fig. A1 A typical profile of the crater created by fs-laser using spot ablation, as measured by white light interferometry. Note the circular truncated cone shape of the crater.



Fig. A2 Three series of craters produced by spot ablation using fs-laser. Each series used different total laser shots, but kept pulse energy and spot size identical to that used for the crater whose depth cannot be measured directly by white light interferometry. The target craters were produced by 455 shots, so the target crater volumes were obtained by extrapolating the measured data to 455 shots.



Fig. A3 The modeled deviations of the measured δ^{57} Fe from its true value (Δ^{57} Fe_{measured-true}) due to ⁵⁶FeH⁺ interference as a function of the hydride formation rate (56 FeH⁺/ 56 Fe⁺) and δ^{57} Fe difference between sample and bracketing standard (Δ^{57} Fe_{sample-standard}).

Reference

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