STABLE ISOTOPIC FRACTIONATION DURING FORMATION OF THE EARLIEST

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Introduction: Data afforded by recent advances in our ability to measure stable isotope ratios of major rock-forming elements have prompted an emerging hypothesis that collisions between rocky planetesimals, planetary embryos, and/or proto-planets caused significant losses of moderately volatile (e.g., K) and "common" (or moderately refractory) elements (e.g., Mg and Si). The primary evidence for these losses is in the form of heavy isotope enrichments in rock-forming elements relative to the values for various chondrite groups (Figure 1).

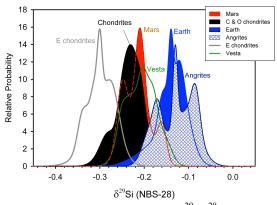


Figure 1. Literature compilation of ²⁹Si/²⁸Si for various solar system rocky bodies [1-4].

There is evidence for substantial mass losses in the bulk compositions of planets. For example, because Ca is highly referactory, and therefore largely retained in the melt during volatilization, the concentration of Ca can be used to estimate the masses of more volatile elements compared with their precursor values. In the case of Earth accreted from E chondrite like material, the mass of Earth's Mg compared with the E chondrite precursors is 1/3; evaporation removed 2/3 of the mass of Mg from the building blocks of Earth. However, the isotopic data require equilibrium between melt and vapor in this scenario [1].

The evaporation hypothesis has numerous implications for the our interpretations of the isotopic compositions of meteoritical materials. Here we focus on the implications for the iron isotopic compositions of iron meteorites.

Fe Isotopes of Iron Meteorite Parent Bodies: Our Fe isotope ratio data for carbonaceous chondrites and IIIAB iron meteorites are similar to the overall trend reported in the literature: the iron meteorites are high in 57 Fe/ 54 Fe relative to chondrites by ~ 0.1 ‰ (Figure 2).

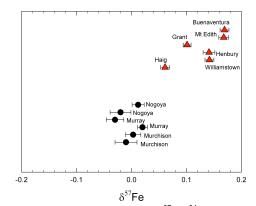


Figure 2. Comparison between ⁵⁷Fe/⁵⁴Fe for IIIAB iron meteorites and CM carbonaceous chondrites at UCLA. The difference is similar to that seen in other studies of various chondrite groups and iron meteorites.

Literature Fe isotope ratio data comparing iron meteorites to various other chondritic reservoirs are shown in Figure 3 for comparison to Figure 2. One commonly invoked explanation for high ⁵⁷Fe/⁵⁴Fe of metal is equilibration between metal and silicate during core formation.

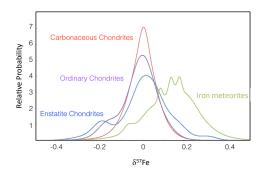


Figure 3. Literature compilation of 57 Fe/ 54 Fe for iron meteorites and chondrites.

Metal-silicate fractionation factor. Combining the measured Fe isotope fractionation between metal and silicate in aubrites obtained at UCLA together with experimental calibrations of the effects of substitutions for iron in metals from the Geophysical Laboratory [5]

results in a model for metal-silicate Fe isotope fractionation: Δ^{57} Fe_{metal-silicate} = 5.56×10^4 /T² + 0.0112(x-5.1) where x is the atom% of elements substitutiong for iron in the metal (Ni + S in this case). We estimate values for Δ^{57} Fe_{metal-silicate} for magmatic temperatures using observed Ni concentrations in magmatic iron meteorites and previous estimates of S concentrations of the metal parental melts.

The fractionation factors constrain the fraction of the iron meteorite parent bodies composed of metal cores assuming metal-silicate equilibration. The constraints come from the δ^{57} Fe of the iron meteorites given the δ^{57} Fe of the bulk parent bodies: δ^{57} Fe_{metal} = δ^{57} Fe_{bulk} + $x_{\text{Fe,silicate}} \Delta^{57}$ Fe_{metal-silicate} and δ^{57} Fe_{silicate} = δ^{57} Fe_{metal} - Δ^{57} Fe, comprising two equations in three variables (δ^{57} Fe_{bulk}, $x_{Fe,silicate}$, and Δ^{57} Fe for specificied metal compositions), where $x_{\text{Fe,silicate}}$ is the fraction of the total Fe residing in silicate. The latter can be converted to the core fraction using estimates of iron concentrations prescribed by the oxygen fugacity relative to the iron-wüstite buffer: $\Delta IW = 2 \log(XFeO^{silicate}/$ XFe^{metal}) for ideal activity coefficients (realistic deviations from unit γ are negligible for this calculation) where Xi^{j} are mole fractions for iron species *i* in phase *j*. For our applications, ΔIW values near -2.3 to -2.7are most appropriate [6].

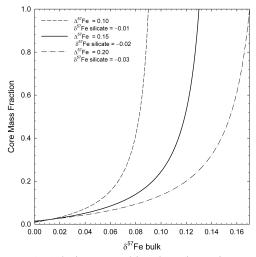


Figure 4. Solutions matching iron isotopic compositions of iron meteorites and silicates (e.g., HEDs) in the solar system in terms of bulk δ^{57} Fe and fraction of parent body composed of a metallic core.

Estimates for the core sizes of iron meteorite parent bodies: Figure 4 shows solutions to the equations in which silicate δ^{57} Fe values are within error of zero (e.g., as for the HED meteorites), where δ^{57} Fe of iron metal is within error of 0.13 ‰ (e.g., Figures 2,3), and where ΔIW values are near -2.5 ± -0.2 . Results are shown for a range of plausible metal-silicate fractionation factors representing a range in parental melt S concentrations from a low of 3.5 atom % to a high of 12.5 atom % [7] at an equilibration temperature of 1800 K (e.g., minimum liquid core-mantle boundary of Vesta). Results are not critally dependent on the temperature within several hundred degrees.

The results suggest that for parent bodies that were chondritic in δ^{57} Fe (wthin ~ 0.06 ‰ of zero), the mass fractions of IIIAB parent body cores were exceptionally small (~ < 0.1, or smaller than the lowest values of 0.16 estimated for Vesta [8]). In order for core fractions to be more typical (e.g., between 0.16 and 0.33, for example, representing a range for Vesta [8] and including the terrestrial value), the bulk δ^{57} Fe of the parent bodies of the iron meteorites must have been > 0.06 ‰ and could have been as high as 0.12 ‰. These results therefore suggest that evaporation attended the formation of the parent bodies of the iron meteorites (and the IIIAB parent bodies(s) in particular).

Conclusions: The high δ^{57} Fe values of iron meteorites in the solar system are not consistent with chondritic δ^{57} Fe values for the parent bodies unless core fractions were exceptionally (unrealistically) small. Evaporation of Fe during the formation of the parent bodies, as suggested for Si and Mg isotope ratios, may offer a solution to this conundrum. If so, the early formation of the non-carbonaceous iron meteorite parent bodies considered here (within < 2 Myr of CAI for the IIIABs [9]) suggests that the evaporation was occurring during the very earliest phases of planet formation, and not only during the latest giant impacts.

While it is possible that iron isotope fractionation between metal and silicate was not a controlling factor for the observed δ^{57} Fe values in iron meteorites, excluding this possibility leads to the same conclusion that 57 Fe/ 54 Fe is elevated in the metals due to evaporation.

The iron meteorites may be the last vestiges of some of the earliest-formed planetesimals that carry the isotopic signatures of evaporation.

References: [1] Hin R.C. et al. (2017) *Nature* 549, 511-515. [2] Savage P.S. and Moynier F. (2013) *EPSL* 361, 487-496. [3] Zombardi T. et al. (2013) *GCA* 121, 67-83. [4] Pringle E.A. et al. (2013) *EPSL* 373, 75-82. [5] Elardo S.M. and Shahar A. (2017) *Nature Geoscience* 10, 317-321. [6] Seenstra E.S. et al. (2016) *GCA* 177, 48-61. [7] Chabot N.L. (2004) *GCA* 68, 3607-3618. [8] Toplis M.J. et al. (2013) *MAPS* 48, 2300-2315. [9] Kruijer T.S. et al. (2017) *PNAS* 114, 6712-6716.