LARGE MASS FRACTIONATION OF IRON ISOTOPES IN COSMIC SPHERULES COLLECTED FROM DEEP-SEA SEDIMENTS

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Clayton *et al.* [1] reported the oxygen isotopic compositions of several grain size fractions of 100-500 μm diameter silicate (S-type) and magnetite (I-type) deep-sea spherules of extraterrestrial origin. They found that the I-type spherules contain isotopically heavy oxygen that plots on the terrestrial fractionation line on a three-isotope plot with $\delta^{18}O$ = 39.9 to 47.1 ‰. S-type spherules lie off the terrestrial fractionation line along a line joining bulk C2 and C3 chondrites with the I-type spherules at $\delta^{18}O$ = 22.5 to 25.1 ‰. The I-type spherules are thought to have originally been Fe-Ni metal interplanetary dust particles (IDPs) that were oxidized and melted during entry into the earth's atmosphere. The S-type spherules are thought to be melted chondritic IDPs. As the oxygen in the I-type particles is of terrestrial origin, Clayton *et al.* concluded that the spheres sampled the atmosphere at an altitude of ~100 km and that oxygen at these altitudes is isotopically heavy. S-type spheres appear to contain a mixture of terrestrial and extraterrestrial oxygen. Recent experiments on the evaporation of molten Mg_2SiO_4 in a vacuum furnace show that evaporation follows a Rayleigh process in which the gas/liquid isotopic fractionation factors are close to the values calculated from the inverse square root of the masses of the evaporating species, Mg, SiO_2 and O (or O_2) [2]. This raised another possible explanation for the heavy oxygen in the I-type spherules: that the metal grains experienced significant evaporative mass loss while molten, enriching the residue in the heavy isotopes of oxygen. Models of the physics of atmospheric entry of IDPs also suggest that significant evaporative and ablative mass loss occurs for sub-mm spheres [3] and analyses of platinum metal nuggets in magnetite spheres show volatility fractionation indicating evaporation [4]. If the heavy oxygen is due to evaporative mass fractionation, Fe in the spheres should also be isotopically heavy.

We analyzed 7 ~250 μm S-type spheres for Mg isotopes and 4 ~250 μm I-type spheres for Fe isotopes using a modified AEI IM-20 ion microprobe. Major elements were also determined on each sphere by ion microprobe. Mg isotopes and chemical compositions were determined by standard techniques. The Fe isotopic analyses were made at low mass resolution (M/ΔM = 300). In order to avoid molecular isobaric interferences, such as CaO and Si_2 on ^{56}Fe, analyses were limited to samples and standards with low concentrations of Mg, Ca and Si. ^{54}Fe was corrected for ^{54}Cr interference by measuring ^{52}Cr and assuming that Cr is of normal isotopic composition. ^{58}Fe, the least abundant Fe isotope, is interfered with by ^{58}Ni, the most abundant Ni isotope. As all of the magnetite spheres contain significant Ni (2-5 wt% NiO), the interference was too large to correct for precisely and ^{58}Fe was not measured. No corrections were made to ^{56}Fe and ^{57}Fe. The data are reported in Table 1 and Figure 1 as $\delta^{56}Fe$ and $\delta^{57}Fe$, normalized to the average for magnetite. The primary standard used was a synthetic magnetite prepared from J. T. Baker® reagent-grade Fe metal and hematite. It was assumed that this material was of normal (=terrestrial) Fe isotopic composition. For comparison, Fe-Ni metal in a chondrule in the Mighei CM2 chondrite was measured and found to be of near-normal isotopic composition. Large differences in instrumental isotopic mass fractionation of Fe isotopes in different matrices have been reported [5,6]. Relative to magnetite, Hutcheon *et al.* [5] gave fractionations of 0.0, +1.5 and +11.4 ‰/amu for metal, Fe sulfide and titanomagnetite and Fahey and Zinner [6] gave -5.2, -3.4 and +10.5 ‰/amu for metal, pyrite and augite, respectively.

The results (Table 1) show that all four I-type spherules measured have substantial enrichments in the heavy isotopes of Fe. They range from 8.7 to 23.5 ‰/amu heavier than the magnetite standard. In contrast, the S-type spheres show little Mg isotopic fractionation. Also shown in Table 1 are the chemical compositions of the spheres and the magnetite standard. Figure 1 shows that the Fe isotopic data lie along the slope 2/3 line expected from isotopic mass fractionation. ^{57}Fe was not corrected for the hydride ^{56}FeH. If this interference is significant, it is the same for both standard and sample, as the data lie along the slope-2/3 line. Small deviations from this line may be due to variable hydride interference in samples or standards. Metal from the Mighei chondrule shows no significant fractionation relative to the standard. The samples and standards are very similar in chemical composition, so the large fractionation effects are not due to matrix effects. Furthermore, the fractionations are up to twice as large as the entire range reported for terrestrial materials of much more widely varying composition.

The discovery of large isotopic mass fractionation of Fe in deep-sea spherules suggests that the oxygen in them is also mass fractionated and that the high $\delta^{18}O$ of the spherules **does not** imply a high $\delta^{18}O$ of the upper atmosphere. The average Fe fractionation for the four spherules is 14.6‰/amu. Iron meteorite fusion crusts show an average $\delta^{18}O$ of 15.2 ‰ and are isotopically lighter than the atmosphere from which they obtained their oxygen [1]. We will assume that the fractionation during iron meteorite oxidation is given by the 8.3 ‰ difference between the $\delta^{18}O$ values of iron meteorite fusion crusts and the lower atmosphere (23.5 ‰). If the upper atmosphere has the same isotopic composition as the lower atmosphere, $\delta^{18}O$ = 23.5 ‰, the $\delta^{18}O$ of oxidized spherules should start out the same as iron meteorite fusion crust, 15.2 ‰. The difference between this value and the measured $\delta^{18}O$ of 240-340 μm spherules, 42.7 ‰, can be attributed to evaporative mass fractionation and corresponds to a heavy iso-

tope enrichment of 13.8 ‰/amu. This value is remarkably close to the Fe fractionation value and suggests that both oxygen and Fe evaporate together as iron-oxygen compounds. If the evaporating species is FeO, the amount of evaporation calculated from the Rayleigh equation is 87% for the average of the 4 spheres and ranges from 71 % to 96 %.

Given the large isotopic fractionation of Fe, it is surprising that there is so little fractionation of Mg. From a simple inverse-square root of mass dependence of gas/liquid isotopic fractionation, the 14.6 ‰/amu fractionation of Fe and a similar extent of evaporation would imply an Mg fractionation of 42 ‰/amu, assuming FeO and Mg are the evaporating species. Si isotopes are also unfractionated in the S-type spheres: composite samples KK1-84A, B and D (see [1]) have $\delta^{30}Si$ values of -0.7, -0.5 and -0.1, which are indistinguishable from the average bulk chondrite value of -0.5. The chemical compositions of the S-type spheres also lack evidence for evaporative fractionation: they are generally chondritic [7] and do not show the enhancement in refractory elements expected for evaporation of more than 70 % of the initial mass. There are two possible explanations for the unfractionated nature of the S-type spheres. (1) Diffusion rates in silicate liquids are slower than those in Fe oxide. Slow diffusion would prevent internal equilibration of the molten bead during the ~1 sec evaporation period, so that the isotopically heavy skin of the sphere is immediately ablated or evaporated away. (2) It has recently been reported that the evaporation of Mg_2SiO_4 is kinetically hindered, so that it evaporates at only one tenth of the rate expected if the vapor phase species were those predicted by equilibrium thermodynamics [8]. Hashimoto [pers. comm.] suggests that Fe oxide could evaporate more rapidly.

References: [1] Clayton R. N. *et al.* (1986) *EPSL* **79**, 235-240. [2] Davis A. M. *et al.* (1990) *Nature* **347**, 655-658. [3] Love S. G. and Brownlee D. E. (1991) *Icarus*, in press. [4] Brownlee D. E., *et al.* (1984) *Nature* **309**, 693. [5] Hutcheon I. D. *et al.* (1987) *GCA* **51**, 3175-3192. [6] Fahey A. and Zinner E. (1987) *LPS XVIII*, 277-278. [7] Blanchard M. B. *et al.* (1978) *EPSL* **46**, 178. [8] Hashimoto A. (1990) *Nature* **347**, 53.

Figure 1. Fe isotopic compositions of magnetite-rich I-type deep-sea spherules lie along the shaded Rayleigh fractionation curve. The numbered circles give the % evaporated assuming that the gas/liquid isotopic fractionation factor is given by the inverse square root of the masses of the isotopes of evaporating FeO.
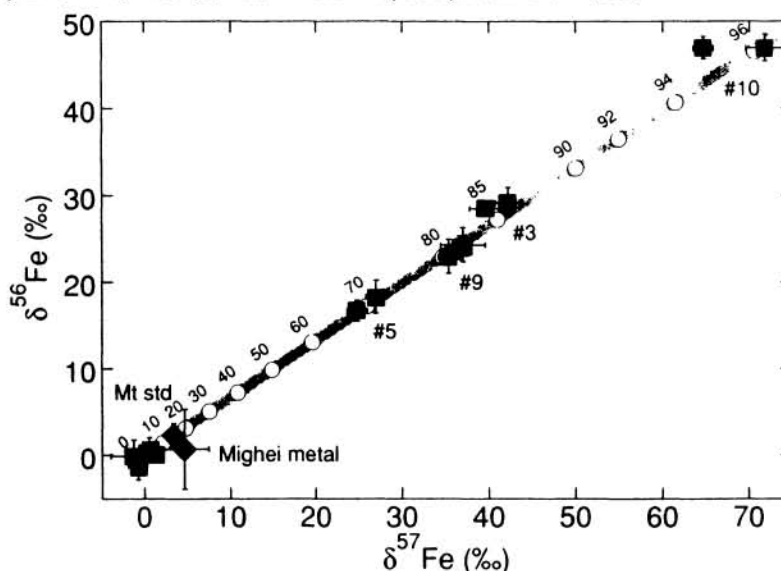

Table 1. Isotopic and chemical compositions of I- and S-type deep-sea spheres of the KK1-90B series.

	Fe₃O₄ std	3	5	9	10	Fe-Ni[1]	1	2	4	6	7	8	11
MgO (wt%)	0.0032	0.019	0.0013	0.095	0.0043		23.0	23.5	18.8	23.5	25.6	26.5	23.4
Al₂O₃ (wt%)	0.056	0.38	0.0007	0.76	2.1		2.60	2.82	3.88	3.21	3.62	3.21	1.75
SiO₂ (wt%)	0.010	0.0066	0.0059	0.18	0.061		33.4	31.5	23.4	35.7	38.1	36.7	26.5
CaO (wt%)	0.083	0.22	0.0019	0.19	2.8		0.23	0.95	0.29	2.51	2.64	2.20	2.81
Cr₂O₃ (wt%)	0.0069	0.023	1.26	0.029	0.053		0.38	0.36	0.031	0.41	0.21	0.24	0.42
FeO (wt%)[2]	99.5	96.0	94.1	92.8	94.0		38.9	38.5	52.5	31.7	28.4	28.9	46.0
NiO (wt%)	0.025	3.0	4.2	5.4	0.6		0.78	1.79	0.11	2.24	0.84	1.66	0.61
δ²⁵Mg (‰)[3]							4.0	2.5	7.0	3.1	2.1	2.3	2.8
δ²⁶Mg (‰)[3]							7.8	5.6	12.6	6.6	3.9	5.2	6.6
δ⁵⁶Fe (‰)[4]	≡0.0	28.8	17.5	23.7	46.9	1.5							
δ⁵⁷Fe (‰)[4]	≡0.0	41.0	25.9	36.4	68.3	4.0							

[1]From a chondrule in the Mighei CM2 chondrite. [2]Total FeO + Fe₂O₃ reported as FeO.

[3]$\delta^{25}Mg = [[(^{25}Mg/^{24}Mg)_{sample}/(^{25}Mg/^{24}Mg)_{std}] - 1] \times 1000$; $\delta^{26}Mg$ defined similarly.

[4]$\delta^{56}Fe = [[(^{56}Fe/^{54}Fe)_{sample}/(^{56}Fe/^{54}Fe)_{std}] - 1] \times 1000$; $\delta^{57}Fe$ defined similarly.