

**IRON AND NICKEL ISOTOPIC MASS FRACTIONATION IN DEEP-SEA SPHERULES;** Andrew M. Davis<sup>1</sup> and Donald E. Brownlee<sup>2</sup>; <sup>1</sup>Enrico Fermi Institute, University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637; <sup>2</sup>Department of Astronomy, University of Washington, Seattle, WA 98105.

Magnetite-wüstite spherules collected from deep-sea sediments are thought to have originally been Fe-Ni metal particles at the top of the atmosphere that were oxidized and melted during entry into the earth's atmosphere. Some likely sources for the metal particles are Fe-Ni interplanetary dust particles (IDP's) and metal or sulfide from stony IDP's that separated after melting. Davis *et al.* [1] reported that four of these spherules are enriched in the heavy isotopes of iron, with enrichments of 8–23 ‰/amu. Herzog *et al.* [2] analyzed a separate collection of spherules and found enrichments in the heavy isotopes of nickel of 10–25 ‰/amu. We have developed a technique for analysis of both iron and nickel isotopes on the same ion microprobe spot and have applied this technique to a number of deep-sea spherules in order to better understand the processes leading to isotopic mass fractionation. Eight spherules show iron and nickel isotopic mass fractionation, with iron and nickel enriched in the heavy isotopes by 10 to 19 ‰/amu and 4 to 32 ‰/amu, respectively. If the mass fractionations are due to Rayleigh fractionation during evaporation, these spherules lost 76 to 94% of their original mass.

We analyzed the four magnetite-wüstite spherules for which iron isotopic data were reported by Davis *et al.* [1] as well as four new spherules. The spherules range in diameter from 170 to 600  $\mu\text{m}$ . Iron and nickel isotopic analyses were made at low mass resolution ( $M/\Delta M = 300$ ) using a modified AEI IM-20 ion microprobe.  $^{54}\text{Fe}$  was corrected for  $^{54}\text{Cr}$  interference by measuring  $^{52}\text{Cr}$  and assuming that chromium is of normal isotopic composition.  $^{58}\text{Ni}$  is interfered with by  $^{58}\text{Fe}$ . A correction was made assuming that  $^{56}\text{Fe}/^{54}\text{Fe}$  and  $^{58}\text{Fe}/^{54}\text{Fe}$  fractionate in nature and in instrumental mass fractionation in the same way and that the fractionation factor follows an inverse square-root of mass relationship. There are a number of molecular interferences that can occur in samples high in lithophile elements:  $\text{Mg}_2$  interferes with  $^{52}\text{Cr}$ ;  $\text{Al}_2$  with  $^{54}\text{Cr}$ ;  $\text{CaO}$  with  $^{56}\text{Fe}$ ,  $^{58}\text{Ni}$  and  $^{60}\text{Ni}$ ;  $\text{Si}_2$  with  $^{56}\text{Fe}$ ,  $^{57}\text{Fe}$ ,  $^{58}\text{Ni}$  and  $^{60}\text{Ni}$ ; and  $\text{TiO}$  with  $^{62}\text{Ni}$  and  $^{64}\text{Ni}$ . We analyzed only samples low in magnesium, aluminum, silicon, calcium and titanium. Molecular interferences were suppressed by operating under energy-filtering conditions. Energy-filtering decreases secondary ion current, but molecular ion intensities fall off more rapidly with increasing energy than do monatomic ion intensities. When the ion microprobe is tuned for maximum secondary beam intensity for  $\text{Fe}^+$ , machine fractionation of iron and nickel isotopes is quite large,  $\sim -30$  and  $\sim -15$  ‰/amu, respectively. In addition to cutting down on molecular interferences, use of energy-filtering has the added benefit of lowering the machine fractionation for iron and nickel isotopes to  $\sim -10$  and  $\sim -4$  ‰/amu, respectively. The primary standards used were synthetic magnetite and NiO. Data are reported as  $\delta$  values, for example,  $\delta^{56}\text{Fe} = \{[(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^{56}\text{Fe}/^{54}\text{Fe})_{\text{std}}] - 1\} \times 1000$ .  $^{54}\text{Fe}$  and  $^{60}\text{Ni}$  were used as reference isotopes. For comparison, the Cape of Good Hope iron meteorite was analyzed and found to be of near-normal iron and nickel isotopic composition. An example of the data collected is shown in Fig. 1, where  $\delta$  values are plotted vs. mass. The error bars are  $\pm 1\sigma$ , for clarity; uncertainties in  $F_{\text{Fe}}$  and  $F_{\text{Ni}}$  (see below) are  $\pm 2\sigma$ . It can be seen that isotopic compositions of iron and nickel in spherule KK191D-8 follow a mass fractionation relationship, whereas Cape of Good Hope shows no fractionation. In some samples, including both plotted in Fig. 1, there appears to be excess  $\delta^{57}\text{Fe}$ , presumably due to  $^{56}\text{FeH}$ .

For each spherule analyzed, the average iron and nickel mass fractionation,  $F_{\text{Fe}}$  and  $F_{\text{Ni}}$ , are plotted in Fig. 2. The error bars shown are  $\pm 1\sigma$ .  $F_{\text{Fe}}$  is based on  $\delta^{56}\text{Fe}$  alone, because of hydride interferences on  $\delta^{57}\text{Fe}$ . Most  $F_{\text{Ni}}$  values are based on all five nickel isotopes, but for a few samples there is excess  $\delta^{61}\text{Ni}$ , due to  $^{60}\text{NiH}$ . Two spherules are high in titanium ( $\sim 0.5\%$

**FE AND NI ISOTOPES IN COSMIC SPHERULES;** Davis A. M. & Brownlee D. E.

TiO<sub>2</sub>), so <sup>64</sup>Ni was not used. There is a good correlation between F<sub>Fe</sub> and F<sub>Ni</sub>. It appears that iron evaporates first, up to F<sub>Fe</sub> = 8–10 ‰/amu, then F<sub>Ni</sub> increases with increasing F<sub>Fe</sub>. The maximum F<sub>Fe</sub> and F<sub>Ni</sub> values observed so far are 19 and 37 ‰/amu, respectively.

Davis *et al.* [1] inferred that iron evaporated as FeO from the spherules, based on the agreement between the amount of isotopic mass fractionation of iron and oxygen. We calculated the fraction of iron and nickel evaporated from each spherule, assuming Rayleigh fractionation and using FeO and NiO as the gas phase species involved in the evaporation reaction. The fraction of iron evaporated ranged from 76 to 94%, the fraction of nickel evaporated ranged from 52 to 99.2 % and ratio of original mass to present mass ranged from 4 to 18. Most of the spheres

were two to three times as large in diameter prior to evaporation. No relationship was found between present spherule diameter and F<sub>Fe</sub> or F<sub>Ni</sub>.

F<sub>Ni</sub> vs. NiO content are plotted in Fig. 3. The error bars shown are ±1σ. There is an inverse correlation between these parameters, indicating that nickel evaporates more rapidly than does iron.

References. [1] Davis A. M. *et al.* (1991) *LPS XXII*, 281. [2] Herzog G. F. *et al.* (1992) *LPS XXIII*, 527.

