STABLE NICKEL ISOTOPE ABUNDANCES IN TYPE I DEEP-SEA SPHERES AND IN NICKEL-RICH ALBERTA (CANADA) SPHERULES.

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Introduction - Type I spheres comprise a significant fraction of the small extraterrestrial objects isolated magnetically from deep-sea sediments [1]. Most type I deep-sea spheres consist mainly of oxides of iron and nickel; their radii seldom exceed a few hundred μm. A few incorporate sizable eccentric cores of pure iron-nickel and tiny nuggets rich in the platinum group elements. Published analyses [2-4] show large, mass-dependent isotopic fractionations, Φ, of Fe and Ni in favor of the heavier isotopes, and an anti-correlation between Φ and nickel content. An earlier attempt to identify spheres with and without metal cores on the basis of surface morphology gave ambiguous results [4]. We report here nickel isotope abundances of cores and/or oxide shells separated physically from three type I spheres. In related work, Bi et al. [5] reported compositional and petrographic analyses of a suite of spheres collected from oil sands in Alberta, Canada. These objects typically have radii of 40-60 μm. Morphology and large concentrations of nickel are similar to those of other groups of particles thought to be extraterrestrial. In particular, the similarity to cores of type I spheres made it seem worthwhile to measure nickel isotope abundances in nickel-rich Alberta spherules.

Experimental methods - Gentle crushing of a number of type I spheres between two glass slides eventually yielded three Type I spheres with diameters of 300 μm (Table 1) that separated into metal cores and powdery oxide. Alberta spheres were taken intact; their masses were estimated from their diameters and an assumed density of 8 g/cm^3. Nickel was separated and analyzed isotopically by ICP/MS as described by [3] but with a different nebulizer and sample and skimmer cones.

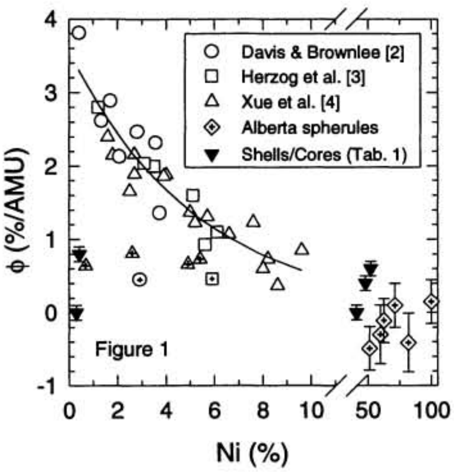
Table 1. Ni isotopic abundances in nickel-rich cores (-C) and oxide shells (-S) of type I deep-sea spheres.

	Mass (μg)	Ni (%)	δ^{60}Ni (‰)	δ^{61}Ni (‰)	δ^{62}Ni (‰)	Φ (‰/AMU)
KK1-1			28±2	40±5	48±3	13±1
KK1-1 [3]		5.0	30±3	38±11	55±8	14±1
KK1A-C	28	41	1±2	1±8	2±5	0±1
KK1A-S	56[1]	0.29	0±4	0±14	-7±8	0±1
KK2A1-C	34	48	10±3	12±12	15±7	4±1
KK2A1-S	52[1]	0.44				
KK1B-C	13	52	8±2	17±8	20±5	6±1
KK1B-S	66[1]	0.43	14±3	16±10	19±6	8±1

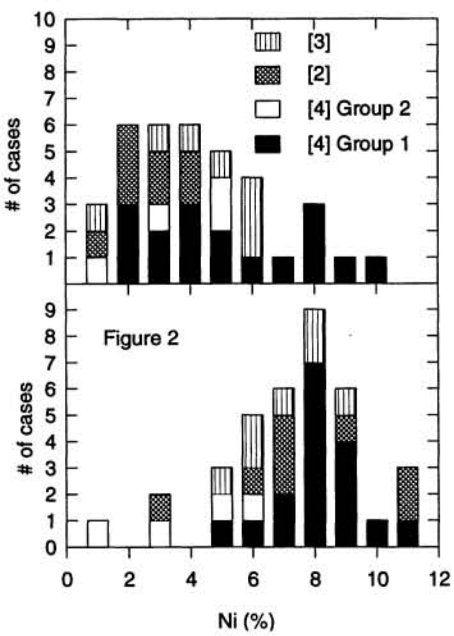
1) Estimated with an uncertainty of ±30% from initial sphere diameter, diameter of core, and densities of 5.3 and 8.0 g/cm^3 for oxide and metal.

Results - Nickel isotope ratios had the following 1-σ precision: ^{60}Ni/^{58}Ni, ± 3‰; ^{61}Ni/^{58}Ni, ± 8‰; ^{62}Ni/^{58}Ni, ± 5‰; ^{64}Ni/^{58}Ni, ± 20‰. The shell from KK1A contained too little nickel for us to measure. The uncertainty of the ^{64}Ni/^{58}Ni ratio is greater than in previous work because of increased interference at mass 64 due to ^{64}Zn. The extent of mass dependent fractionation for each sample, Φ, was obtained from the slope of a plot of δ^{Y}Ni (Y=60, 61, 62) against Y-58. Mass-dependent fractionations inferred from δ^{64}Ni were consistent with these results, but are not included because of the size of the uncertainties in δ^{64}Ni. The reproducibility of Φ is indicated by the results for sphere KK1-1 (Table 1). Figure 1 summarizes new and old results. Nickel isotope ratios for seven Alberta spheres are indistinguishable from terrestrial values within the uncertainties. In spheres KK1-A and KK1-B the Φ values for metal and oxide are the same within errors. Sphere KK1-A is the first type I object analyzed that has no detectable mass fractionation.

NI ISOTOPES IN DEEP-SEA SPHERES AND ALBERTA SPHERULES: Xue et al.



Discussion - Figure 1 suggests the existence of two groups of type I spheres. In group one, Φ values ranging from 0.4 to 4.0 %/AMU anti correlate with nickel contents (solid line) [2-4]. Xue et al. [4] used published values of Φ_{Ni} and Φ_{Fe} [2] to estimate an Fe/Ni ratio of 13 prior to evaporative loss for spheres in a selected compositional range. Figure 2 shows an extension of that analysis. The measured, post-lost distribution is broad (upper panel). The inferred pre-loss distribution (lower panel) appears to have a peak at 8±1% Ni (Fe/Ni = 11.5± 0.9) into which 1/2 to 2/3 of the spheres fall. Good matches to this Fe/Ni ratio are found in type IAB, IIIF, and IIIA iron meteorites and in the metal of mesosiderites and E-chondrites. However, the identification of any particular source material on this basis must be regarded as tentative because it assumes that only evaporative losses caused changes in composition. Many scenarios for sphere formation envision the possibility of core loss [1]. Further, studies of the somewhat larger, 1-mm diameter, Canyon Diablo spheroids [6] show that mechanical losses of iron oxides unaccompanied by isotopic fractionation occur in the terrestrial environment. Finally, we note that the 1/3 to 1/2 of the spheres that do not belong to the peak allow for compositional heterogeneity of the source. A second group of spheres (non-diamond symbols with cross hairs in Figure 1) has generally smaller values of Φ, from 0.4 to 0.8%/AMU, independent of the nickel content. Within the precision of the measurements, the core and shell of KK1-B have the same isotopic composition, which corresponds to a nickel loss of about 50%. If not due to chance or error, the similarity suggests that diffusive communication between oxide and metal remains good during the initial phases of evaporation. The absence of detectable mass nickel fractionation from sphere KK1A indicates little evaporative loss and hence makes the composition of special interest. From Table 1 we obtain a rough bulk nickel content of 14±4%.



Conclusions - The nickel isotopes in about 2/3 of the type I spheres analyzed to date are mass-fractionated by more than 1%/AMU. Most of these objects have low nickel contents and probably do not contain large Fe/Ni cores. A semi-empirical calculation of their compositions prior to evaporative losses gives Fe/Ni ratios that cluster near a value of 11.5. In contrast, the degree of mass fractionation in three spheres that have separable cores is less than 1%/AMU and in one of them is zero within errors. Nickel in Alberta spherules and Canyon Diablo spheroids, which are also rich in nickel, is fractionated at most only slightly. We conclude that the largest evaporative losses occur in the absence of large metal cores. Although we cannot rule out the possibility of non-evaporative losses associated with oxidation or loss of cores, the general agreement the bulk compositions of all spheres, with and without cores, makes such losses seem unlikely at present.

References: **[1]** (Brownlee D.E. (1981) in *The Sea 7*, 733-762; Brownlee, D.E. (1985) *Annu. Rev. Earth Planet. Sci.13*, 147-173; Brownlee et al. (1984) *Nature 309*, 693-694. **[2]** Davis and Brownlee (1993) *Lunar Planet. Sci. XXIV*, 373-374.; **[3]** Herzog et al. (1994) *Geochim. Cosmochim. Acta 58*, 5319-5323.. **[4]** Xue et al. (1994) *Meteoritics*, *29*, 553.. **[5]** Bi et al. (1993) *Geochim. Cosmochim. Acta* **57**, 4129-4136. **[6]** Kelly W.R. et al. (1974) *Geochim. Cosmochim. Acta 38*, 533-543; Mittlefehldt D.W. et al. (1994) *Lunar Planet. Sci. XXIV*, 995-996; Xue S. et al. (1993) *Lunar Planet. Sci. XXIV*, 1547-1548.