FRACTIONATION AND VOLATILE REDISTRIBUTION OF SIDEROPHILE ELEMENTS IN METAL GRAINS FROM LUNAR IMPACT-MELT BRECCIA 76215.

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Introduction: Some impact melts incorporate material derived from the impactor when they form. In order to use siderophile-element data for impact-melt breccias to determine the compositions of the impactors that formed them, it is important to assess the extent to which the relatively volatile siderophile elements might have been remobilized during formation and subsequent crystallization of the melt. To investigate this question, we have used laser-ablation inductively-coupled-plasma mass spectrometry (LA ICP-MS) to analyze the surfaces of meteorite-derived metal and other particles exposed in broken vesicles in Apollo 17 poikilitic impact-melt breccia 76215.

Samples: We performed LA ICP-MS analyses on the surfaces of metal and troilite particles in two chips of 76215, which we designated J and A. The surface of a vesicle in chip J contained an exposed metal globule adjacent to a euhedral metal crystal with striated surfaces (Fig. 1 left). The surface of a vesicle in chip A contained an exposed metal globule like that in J and a hexagonal plate of troilite (Fig. 1 right). The globules were derived from the impactor and their spherical shapes indicate that they were molten while they were enclosed within the impact melt. The euhedral shapes of the metal and troilite crystals indicate that they precipitated from the vapor that formed the vesicles. After the laser analyses, the bulk chips J and A were dissolved and analyzed by conventional ICP-MS [1].

Figure 1. The left image shows a vesicle surface in chip J: the metal globule is at left and the euhedral metal crystal (striated) is at right. The right image shows a vesicle surface in chip A: the metal globule is at right and the euhedral troilite crystal is at left. Both globules are ~ 100 µm across.

Analytical techniques: Samples were analyzed by LA ICP-MS using an Element 2 (magnetic sector MS, Thermo Electron Corp.) coupled to a UP193He (New Wave Research) ArF excimer laser. Ablated material was removed from the ablation cell (3 cm^3) to the MS via a 1 L/min He stream, which was mixed, immediately before the entry into the plasma torch, with a 0.6 L/min Ar stream. Spot sizes for the ablation ranged from 4 to 55 µm, depending upon the geometry and size of the sample. Laser output power was maintained to 60% (ca. 8-10 Jcm^{-2}) and the repetition flash rate varied from 5 to 10 Hz, depending upon sample size. Isotope masses were measured for 5 ms per cycle with 180 cycles performed per analysis. Isotopes monitored and reported herein were: ^{57}Fe, ^{59}Co, ^{61}Ni, ^{73}Ge, ^{101}Ru, ^{105}Pd, ^{121}Sb, ^{187}Re, ^{192}Os, ^{193}Ir, ^{194}Pt, ^{195}Pt and ^{197}Au. Data reduction was carried out using Lamtrace, with NIST 612, Hoba and Coahuila used as standard reference materials. Concentrations were based on an assumed Co concentration that yielded a sum of Fe+Ni of about 100%.

Results: Our analyses for Fe, Co and Ni are listed in Table 1; chondrite-normalized data are plotted in Fig. 2. Fe and Co are not plotted because their concentrations can be greatly affected by indigenous lunar metal mixed into the meteoritic metal.

Table 1. Concentrations of Fe, Co, and Ni (mg/g) in globules and euhedral crystal of metal analyzed herein

	Fe	Co	Ni
globules			
J	936	7.4	77.2
J repeat	877	7.7	107
A	945	5.6	54.5
crystal			
J	954	8.0	59.7
J repeat	880	5.4	b.d.

Discussion: The Fe-Co-Ni data for the metal particles are consistent with electron-microprobe data for metal from the same rock [2]. Data for the euhedral metal crystal are consistent with this crystal having precipitated from vapor containing significant concentrations of volatile siderophiles. In the crystal, siderophile elements less volatile than Fe are below detection limits, but significant concentrations of the more volatile elements Ni, Pd, Au, and Ge are present. The globules show fractionated chondrite-normalized siderophile-element patterns (Fig. 2): Ni, Pd, Au, Sb and Ge are high; Ru and Pt are somewhat lower; and the refractory siderophiles Re, Os and Ir are lowest, with chondrite-normalized Os significantly lower than Ir. Patterns such as these are characteristic of some types of magmatic iron meteorites (e.g., Fig. 3), in which fractionally crystallized metal has removed the refractory siderophiles.

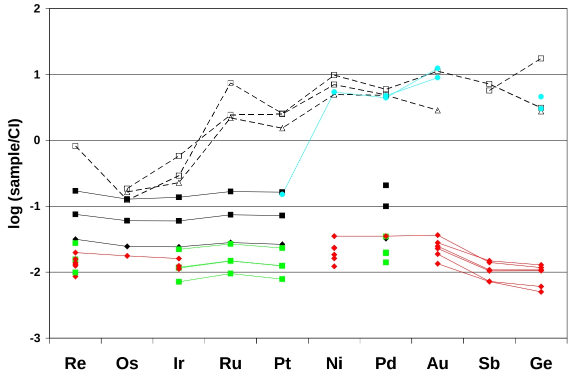

Figure 2. Siderophile-element concentrations normalized to the composition of CI chondrites [3]. Condensation temperatures of elements plotted decrease from left to right. Our data for globules are shown by open symbols connected by dashed lines; analyses of the bulk samples containing the globules [1] are shown by black filled symbols connected by solid lines. Our data for the euhedral metal crystal in chip J are shown in turquoise. Other samples from the same melt-breccia boulder as 76215 were analyzed by ICP-MS by [4] (data shown in green) and by RNAA by [5-7] (data shown in red).

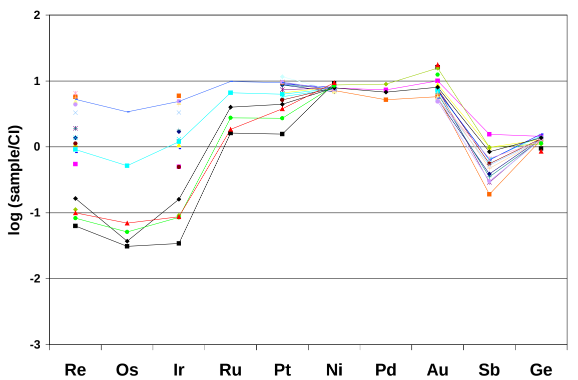

Figure 3. Siderophile-element analyses of chemically evolved group IIIAB magmatic iron meteorites.

The bulk samples that contain the globules, however, do not show fractionated patterns like the globules (Fig. 2). The bulk samples instead show fairly flat, "chondritic" chondrite-normalized siderophile-element patterns from Re to Au and slightly lower chondrite-normalized Sb and Ge (Au, Sb and Ge only by RNAA). Thus, the bulk samples must also contain metal that is enriched in refractory siderophiles to balance the refractory-depleted globule metal we have analyzed. The simplest explanation for this discrepancy is that our analyses do not represent the bulk globules. The spherical shapes of the globules indicate that they were largely or wholly molten after they were incorporated in the impact melt breccia. As the globules crystallized, the crystallized metal would have extracted much of the refractory siderophiles, but, since the crystal-liquid distribution coefficient for Ni appears to be close to 1 (Fig. 3), both the crystals and the liquid would have had much the same Ni concentrations. The laser analyses were at the surfaces of globules, so these analyses might have sampled only later-crystallized metallic liquid, if the earliest metal crystals formed in the globule interiors. At the globule surfaces, the chondrite-normalized abundances of the volatile siderophiles Pd-Ge are relatively high and similar to the abundances in the euhedral metal crystal. The similarity probably reflects equilibrium of both types of metal with vapor in the vesicles.

The presence of the euhedral troilite crystal demonstrates that S was also present in the vapor in the vesicles. The troilite we analyzed is virtually free of the siderophile elements discussed herein.

Conclusions: 1) The globules, which are relicts of the impactor, were molten within the impact melt and fractionated internally as they crystallized. Because of this fractionation, laser analysis is on too fine a scale to determine the bulk siderophile-element composition of the meteoritic impactor. 2) The vapor in the vesicles in the melt rocks was enriched in Fe and more volatile siderophile elements, as is indicated by the abundance of Fe, Ni, Pd, Au and Ge in the euhedral metal crystal, which crystallized from that vapor; the vapor was also rich in S (indicated by the presence of a vapor-deposited troilite crystal). 3) The presence of vapor rich in volatile siderophiles during crystallization of the impact melt indicates that there was some redistribution of the more volatile siderophile elements in 76215. We cannot determine, however, if there was any bulk loss of volatile siderophiles from the impact melt or whether the volatile siderophiles were simply redistributed within the melt and its crystallization products.

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References: [1] Puchtel I.S. et al. (2007) *LPS XXXVII*, this vol. [2] Misra K.C. et al. (1976) *PLSC7*, 2251. [3] Anders E. and Grevesse N. (1989) *GCA, 53,* 197. [4] Norman M.D. et al. (2002) *EPSL, 202,* 217. [5] Higuchi H. and Morgan J.W. (1975) *PLSC6*, 1625. [6] Gros J. et al. (1976) *PLSC7*, 2403. [7] Morgan J.W. et al. (1974) *PLSC5*, 1703.