FRACTIONATION AND REMOBILIZATION OF SIDEROPHILE ELEMENTS IN METAL GRAINS OF APOLLO 16 LUNAR IMPACT-MELT BRECCIA 67095.
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Introduction: Impact-generated melts commonly incorporate exogenic impactor materials, in some cases evinced by the appearance of metal and troilite in the resulting melt rocks (Fig. 1). Because potential impactors, such as chondrites and iron meteorites [1, 2], are typically enriched in siderophile elements relative to planetary crusts, such as the lunar crust [3], siderophile element patterns in impact melt breccias are highly leveraged towards the impactor compositions. Yet, when employing the siderophile element data of impact-melt breccias to determine the compositions of impactors that formed them, it is critical to evaluate the degree to which the siderophile elements might have been fractionated or remobilized during formation and subsequent cooling of the melt [4]. To revisit this question, we have used laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to determine the surface to interior compositions of, and range in patterns between, metal and troilite grains separated from Apollo 16 basaltic melt breccia 67095.

Samples: Lunar impact melt breccia 67095 is a basaltic impact melt rock that was collected from the rim of the North Ray Crater at the Apollo 16 landing site. We were allocated sample 67095, 125. This sample contains substantial metal globules and troilites, which are relatively rich in siderophile elements. The rock is friable and easily broken into pieces using ceramic tweezers. Sizable (50-350μm) metal globules and troilite grains (Fig. 1) were carefully separated for LA-ICP-MS study, and some of them were subsequently digested individually for the measurement of Os isotope compositions and highly siderophile element (HSE) concentrations. The remaining bulk rocks were split into ten sub-samples that were also dissolved and analyzed for Os isotope compositions and HSE concentrations [5].

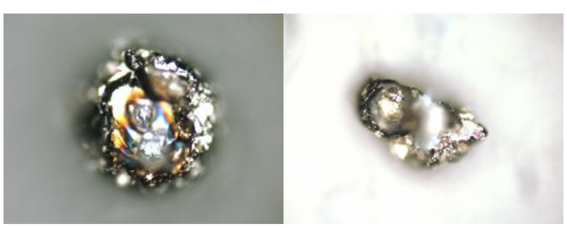

Fig. 1. The left image shows the rugged surface of a typical metal globule in sample 67095, 125. The right image shows an irregular shape for a troilite in 67095, 125. The width of field of each image is 675 μm.

Analytical Methods: The separated metal and troilite grains were carefully attached to a glass slide using double-sided sticky tape. Sample grains were analyzed by LA-ICP-MS using a New Wave Research UP-213 laser-ablation system coupled to a Thermo-Finnigan ICP-MS (*Element 2*). Ablated material was transported from the ablation cell by a 1 L/min He gas flow, mixed with a 0.6 L/min Ar gas flow, and then introduced to the ICP torch. The ablation spot sizes ranged from 55 to 80 μm. The laser power was controlled to 2.0 to 2.3 Jcm^{-2}, and the repetition pulse rate was 7 Hz. Isotope masses were measured for 5 ms per cycle with 180 cycles per analysis. No ablation occurred in the first 20 seconds of each analysis for background count determination. The system was flushed with He for 2 minutes between analyses. Isotopes monitored and reported here were: ^{57}Fe, ^{59}Co, ^{61}Ni, ^{71}Ga, ^{74}Ge, ^{99}Ru, ^{103}Rh, ^{105}Pd, ^{121}Sb, ^{185}Re, ^{189}Os, ^{193}Ir, ^{195}Pt, and ^{197}Au. Data reduction was performed using *Lamtrace*, with the iron meteorites Hoba, Filomena and Coahuila utilized as reference materials. Concentrations were calculated based on an assumed Fe concentration that yielded a sum of Fe+Ni+Co of 100 % for metals (Table 1), and an assumed Fe concentration of 60 % for all troilites analyzed.

Table 1. Concentrations of Fe, Co and Ni (mg/g) in metal globules from sample 67095, 125.

Sample/Spot	Fe	Co	Ni
M1 rim	899	2.8	98.5
M1 core	947	4.1	49.2
M3	849	1.7	150
M6 rim	865	1.4	133
M6 core	952	3.9	43.6
M9	968	4.3	28.0
M10	870	1.4	128

Note: Metal grains M1 and M6 were both ablated twice on the same spot with the first analysis labeled “rim” and the second labeled “core”, while other grains were ablated only once.

Results: Five metal grains and six troilite grains were analyzed. The siderophile elements of interest in troilites were generally near or below the detection limits. Our analyses for Fe, Co and Ni of the five metal grains are listed in Table 1; chondrite-normalized siderophile element patterns are plotted in Fig. 2, in which Fe and Co are not included because their concentrations can be greatly affected from mixing of lunar endogenous metals into the meteoritic metals.

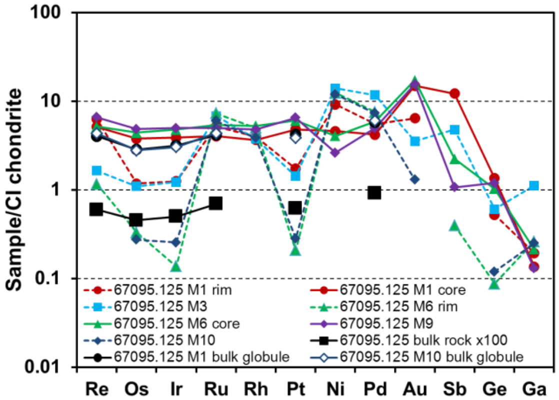

Fig. 2. Siderophile element concentrations normalized to CI chondrites [1] plotted as increasing condensation temperatures of elements from right to left [4]. Also plotted are the average (x100) of the bulk rock (black square [5]), and the results for bulk globules M1 and M10, which were dissolved individually. The bulk globules of M1 and M10 have intermediate HSE concentrations between the rims and cores. In general, the dashed lines represent the features for rims and the solid lines represent those for cores. Some areas of the surfaces may have lost the rim features during separation and processing, such as M9.

Discussion: As can be seen in Table 1, the rims (surfaces) of the metal globules tend to have lower Fe and Co contents, and higher Ni contents than their cores (interiors). This is inconsistent with crystal-liquid fractionation, as solid metal-liquid metal distribution coefficients for Ni typically approach unity [4]. The disparity implies disequilibrium between the rims and cores of the globules. The cores of the metal globules generally have essentially unfractionated (chondritic) patterns for the refractory siderophile elements (Re, Os, Ir, Ru, Rh, Pt and Pd) with enrichments in Au and depletions in volatile Ge and Ga (Fig. 2). Compared to the cores, the rims have rather fractionated patterns characterized by depletions of refractory (Re, Os, Ir and Pt) and volatile (Sb, Ge and Ga) siderophiles, but enrichments of Ru and Pd. The depletions of volatile siderophiles of the metal globules (both rims and cores) likely suggest that the siderophiles in these globules were largely derived from the impactor (assuming a nearly chondritic impactor) that lost volatile siderophiles in the impacting process.

The bulk globules have similar patterns and $^{187}Os/^{188}Os$ (i.e., Re/Os ratios) of siderophiles to the bulk rocks (Fig. 2), which is consistent with the observation that troilites and other phases have negligible siderophiles and that all grains were derived from a single source. The significant enrichments of Ru and Pd in the rims of the metal globules may lead to their relative enrichments in some bulk globules and some bulk rocks. The possibility of variable enrichments of Ru and Pd in bulk rock domains may be responsible for scatter and non-zero intercepts of correlations between Ir *vs.* Ru and Pd observed in some bulk rock sub-samples (e.g., [5]).

The chondrite-normalized siderophile element patterns of the rims in the metal globules are, in general, similar in shape to some types of magmatic iron meteorites [4], in which refractory siderophiles are stripped off into crystallized metals. The cores of the globules have siderophile element patterns within the range of crystallized metals seen in iron meteorites. Such contrasting and complementary results of siderophile element patterns in the rims and cores of the globules suggest that that the globules crystallized outward. However, the rims of the globules are rich in Ru and Pd, as well as Ni mentioned above, relative to their cores (Fig. 2). Similar correlations between Ni and these siderophiles (Ru, Rh and Pd) are seen in IVA Duel Hill (1854) and other IVA irons [6]. The cause for the enrichments of Ru, Pd and Ni relative to other refractory siderophiles in the rims of the globules compared to their cores is not well understood.

Conclusion: The similarity of highly siderophile element patterns of the bulk globules to the bulk rocks shows that the metal globules derived from the impactor are dominant carriers of the siderophile elements in these rocks. The complementary results of siderophile element patterns in the rims and cores of the metal globules suggest that that the globules crystallized outward. The disparity of Ni contents, as well as Ru and Pd, in the rims and cores implies disequilibrium between the rims and cores of the globules in the rapid cooling process. Similar positive correlations between these siderophile elements (Ni, Ru, Rh and Pd) are seen in some IVA irons. The cause for such fractionation of siderophile elements in the rims and cores of the globules is not well understood yet.

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References: [1] Horan M.F. et al. (2003) *Chem. Geol*. *196*, 5-20. [2] Fischer-Gödde M. et al. (2010) *GCA 74*, 356-379. [3] Day J.M.D. et al. (2010) *EPSL 289*, 595-605. [4] James O.B. et al. (2007). *LPSC XXXVIII*. 1094. [5] Liu J.G. et al. (2012) *LPSC XXXXII*. 2366 [6] Ash R. D. et al. (2007) *LPSC XXXVIII*. 2383.