LASER-ABLATION ICP-MS ANALYSES OF METEORITIC METAL GRAINS IN LUNAR IMPACT-MELT BRECCIAS.

R. L. Korotev[1], B. L. Jolliff[1], A. J. Campbell[2], and M. Humayun[2]. [1]Department of Earth and Planetary Sciences, Washington University, 1 Brookings Drive, Saint Louis MO 63130 (rlk@levee.wustl.edu), [2]Dept. of the Geophysical Sciences, The University of Chicago, 5734 S. Ellis Avenue, Chicago, IL 60637

Introduction: Lunar impact-melt breccias contain metal grains from the meteorites that formed the breccias. Because the breccias contain clastic material that may derive from older breccias, metal grains from earlier impacts may be present, too. The large subset of moderately mafic (8–12% FeO), KREEP-rich ("LKFM") melt breccias is particularly important because (1) these are the melt breccias most likely to have been produced in basin-forming impacts, (2) it is from these breccias that many of the ~3.9 Gyr ages that are so common in lunar samples derive, (3) the breccias contain large proportions of FeNi metal, more than 1% in some types of Apollo 16 breccias, and (4) the metal potentially provides information about the impactors causing the apparent cataclysm at 3.9 Gyr [1–9].

Early studies of lunar breccias noted that whole-rock ratios of siderophile elements, most notably Ir/Au, varied widely and that ratios clustered among samples from a given site, suggesting that the siderophile-element signature could be used to fingerprint the basin of origin [e.g., 7,8]. Because of (1) the high proportion of metal in the Apollo 16 breccias, (2a) the resemblance of the composition (Ni, Co, Ir, Au) of the metal, and (2b) of whole-rock siderophile-element ratios to group IAB irons (main group, low Ir of [10]), the metal of the Apollo 16 breccias (groups 1 and 2 [2,3]), appears to derive from an iron meteorite [2, 9]. Based on whole-rock ratios of siderophile-elements in the poikilitic impact-melt breccias of Apollo 17, the impactor appears to be an enstatite chondrite [9,6]. However, very little data for highly siderophile elements are available for individual metal grains to test whether a single type of meteorite dominates the siderophile-element signature or whether there were multiple impactors. We report here results of a feasibility study to test whether laser-ablation

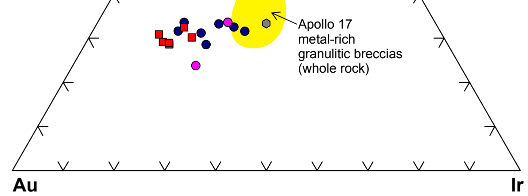

Figure 1. CI-normalized concentrations of Ni, Au, and Ir in metal grains (after [9]). The tie lie connects two portions of a single large grain. The yellow field represents whole-rock concentrations in metal-rich granulitic breccias from Apollo 17.

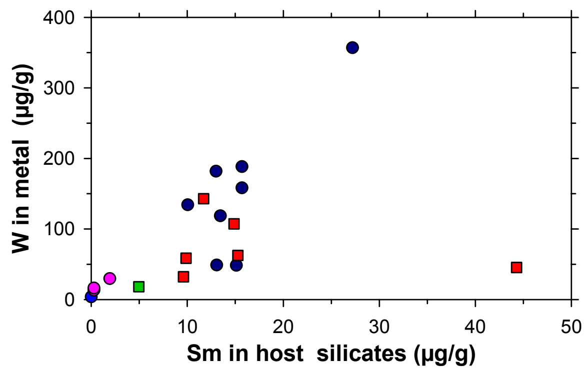

Figure 2. W in metal (LA-ICP-MS) and Sm of host silicates (whole-rock, INAA). The high-Sm point is for an anomalous alkai-rich impact-melt breccia from Apollo 16 that is vesicular, suggesting that it cooled too quickly to allow redistribution of W from silicates to metal.

(LA) inductively-coupled plasma (ICP) mass spectrometry (MS) is a useful tool for classifying metal grains in lunar impact-melt breccias.

Samples and Analysis: As this was a feasibility study, we selected 2–4-mm lithic fragments from Apollo 16 and 17 regolith samples that we knew to be rich in metal because we had analyzed them by INAA [11,12]. We examined a thin or thick section of each fragment by optical microscopy and electron microprobe to obtain major element compositions and to select metal grains for analysis by LA-ICP-MS. A CETAC LSX-200 laser ablation peripheral (Nd:YAG 266 nm) was used for solid sample introduction into a magnetic sector ICP-MS, the ThermoFinnigan Element [13,14]. Isotopes monitored were ^{31}P, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{95}Mo, ^{102}Ru, ^{103}Rh, ^{105}Pd, ^{182}W, ^{185}Re, ^{192}Os, ^{193}Ir, ^{195}Pt, and ^{197}Au. In most cases 3–6 points were measured on each grain. Each analyzed point was ablated by ~25 laser pulses at 10 Hz with laser apertures of 40–140 µm, depending upon the size of the metal grain. Pit depths were 10–15 µm. The mass range was scanned repeatedly while the ablated material was carried by Ar gas from the sample chamber into the mass spectrometer. The signal from the transient laser ablation pulse was integrated over a period of 16 s; this was sufficient time for the pulse to reach a peak intensity and then decay almost to background levels. All signals were blank-corrected, and instrumental sensitivity factors for each isotope were determined by measuring signal intensity from Filomena IIA, which has known concentrations of the elements of interest [14]. The corrected intensities were converted to elemental abundances by normalization to [Fe]+[Co]+[Ni] = 100 wt%. Typical analytical uncertainties for each spot were about 16% based on repeat measurements of the standard.

Results: One grain, from an Apollo 17 aphanitic impact-melt breccia, is not of meteoritic origin (high-Ni point of Fig. 1). All of the meteoritic grains are enriched in W by factors up to several hundred over concentrations expected in meteoritic metal. There is a tendency for the concentration of W in the metal to correlate with concentration of incompatible elements in the host (Fig. 2) because W originally in the silicate melt partitions into the metal during crystallization [15,16].

A grain of free metal (16% Ni) with minor attached lunar silicates from Apollo 17 appears to be a fragment from an ordinary chondrite. A metal grain from an Apollo 16 regolith breccia probably also derives from an ordinary chondrite.

All of the remaining Apollo 16 metal grains are from mafic, KREEP-bearing impact-melt breccias (10–44 µg/g Sm; Fig. 2). Despite that the breccias span a wide range of compositions and belong to different compositional grouping, based on lithophile elements [2,3], the metal compositions are all similar. This metal is the carrier of the low-Ir/Au signature of "ancient meteorite group 1" that is characteristic of Apollo 16 samples [7,8]. Although the metal of Apollo 16 rocks has been likened to that of group IAB irons [2,9] on the basis of Ni, Co, Ir, and Au, the match to Odessa IAB is not great (Fig. 3). However, irons of group IAB are highly variable in composition [10].

Compositions of the metal grains from Apollo 17 poikilitic impact-melt breccias are more variable in composition than those of Apollo 16 (Fig. 3). On the basis of plots such as Fig. 2, we have previously speculated that the Apollo 17 melt breccias have intermediate Ir/Au ratios because they contain siderophile elements from two sources: (1) impact melt with low-Ir/Au metal such as that of the Apollo 16 breccias (red squares, Fig. 2) and (2) clasts with high Ir/Au ratios [17]. The Apollo 17 poikilitic melt breccias contain clasts of feldspathic granulitic breccias, and a subset of these breccias are rich in siderophile elements with ~chondritic Ir/Au ratios from an earlier impact (yellow field). The samples of this study were not chosen to optimally test the hypothesis, and the results neither support or refute it. It is not clear whether any of the three metal grains from granulitic breccias that we analyzed are those of metal-rich breccias, which we found to be common among lithic fragments in the Apollo 17 regolith [11].

Conclusions: For any given metal grain, uncertainties in the concentrations of most trace siderophile elements (95% confidence limits, based on multiple spots per grain) were ~50% in this study, indicating heterogeneity within the grains. The Apollo 16 results probably reflect well the uncertainty associated with sampling of lunar metal grains of similar meteoritic origin by LA-ICP-MS. It is likely necessary to measure many grains in several breccias of a given compositional type to address the question of impactor types. We have not yet investigated the likelihood of obtaining usable data from grains that are small with respect to the laser pit size. Nevertheless, our preliminary results suggest that LA-ICP-MS can produce new and valuable information about the source of metal grains in lunar impact-melt breccias. For future work, W (and perhaps Mo) may be replaced by several volatile siderophiles (Ga, Ge, As, Sb) in the analytical protocol to improve the diagnostic capabilities of the LA-ICP-MS technique.

Acknowledgment: This work was funded by NASA grants NAG5-4172 (L. A. Haskin) and NAG5-9800 (MH).

References: [1] James (1980) *PLSC11*, 365–393; [2] Korotev (1994) *GCA* **58**, 3931–3969; [3] Korotev (2000) *JGR* **105**, 4317–4345; [4] Wasson et al (1975) *The Moon* **13**, 121–141; [5] Ryder (1989) *Trans. Am. Geophys. Union* **71**, 313–323; [6] Norman et al. (2002) *EPSL* **202**, 217–228; [7] Anders et al. (1973) *The Moon* **8**, 3–24; [8] Hertogen et al. (1977) *PLSC8*, 17–45; [9] James (2002) *LPS XXXIII*, #1210; [10] Wasson & Kallemeyn (2002) *GCA* **66**, 2445–2473; [11] Jolliff et al (1996) *M&PS* **31**, 116–145; [12] Korotev et al. (1997) *LPSXXVIII*, 753–754; [13] Campbell & Humayun (1999) *Anal. Chem.* **71**, 939–946; [14] Campbell et al. (2002) *GCA* **66**, 647–660; [15] Wlotzka et al. (1972) *PLSC3*, 1077–1084; [16] Wlotzka et al. (1973) *PLSC4*, 1483–1491; [17] Haskin et al. (1998) *M&PS* **33**, 959–975; [18] Anders & Grevesse (1989) *GCA* **53**, 197–214.

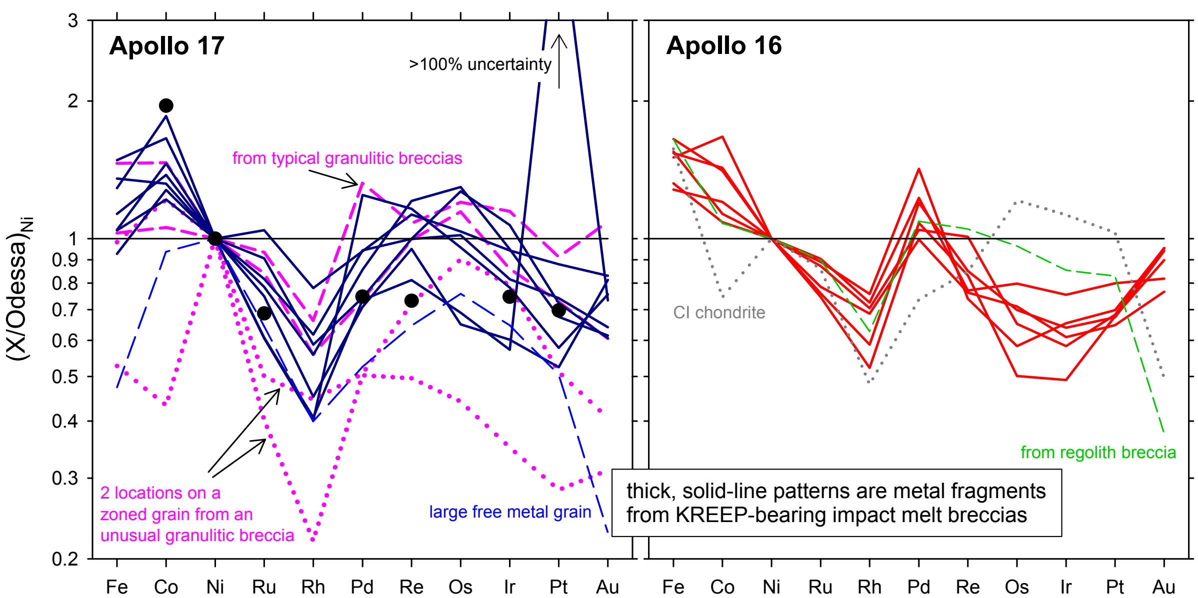

Figure 1. Comparison of siderophile-element concentrations in metal grains from Apollo 16 and 17 samples. The data are normalized to Odessa IAB (Campbell, unpubl. data) and to Ni. Most of the Apollo 17 grains are from poikilitic impact-melt breccias (solid, thick lines), 2 (dotted) are from 2 locations on a large fragment in an unusual ferroan granulitic breccia, 2 (short dash) are from more typical granulitic breccias, and 1 (long dash) is a large (~2-mm) grain of free metal. The black circles are the whole-rock data for poikilitic impact-melt breccias of Norman et al. [6]. For Apollo 16, 1 grain (dash) is from a regolith breccia, the others (solid) are from KREEP-bearing impact-melt breccias of compositional groups 1 and 2 [2,3]. For reference, the CI chondrite [18] pattern is also shown.