OSMIUM ISOTOPE AND HIGHLY SIDEROPHILE ELEMENT COMPOSITIONS OF LUNAR ORANGE AND GREEN GLASSES. R. J. Walker[1], M.F. Horan[2], C. K. Shearer[3] and J. J. Papike[3], [1]Department of Geology, University of Maryland, College Park, MD 20742 (rjwalker@geol.umd.edu), Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd., Washington DC 20015 [3]Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131.

Introduction: The absolute and relative abundances of the highly siderophile elements (HSE) present in planetary mantles are primarily controlled by: 1) silicate-metal partitioning during core-mantle differentiation, 2) the subsequent addition of HSE to mantles via continued planetary accretion [1-3]. Consequently, constraints on the absolute and relative abundances of the HSE in the lunar mantle will provide unique insights to the formation and late accretionary history of not only the Moon, but also Earth.

Determining the HSE content of the lunar mantle, however, has proven difficult, because no *bona fide* mantle rocks have been collected from the moon. The only materials presently available for constraining mantle abundances are lunar volcanic rocks. Lunar basalts typically have very low concentrations of HSE and highly fractionated HSE patterns [4]. Because of our extremely limited understanding of mantle-melt partitioning of the HSE, even for terrestrial systems, extrapolations to mantle compositions from basaltic compositions are difficult, except possibly for the less compatible HSE Pt and Pd [5].

Primitive, presumably less fractionated materials, such as picritic glasses are potentially more diagnostic of the lunar interior [6]. Here we report Os isotopic composition data and Re, Os, Ir, Ru, Pt and Pd concentration data for green glass (15426,164) and orange glass (74001,1217). As with previous studies utilizing neutron activation analysis, we are examining different size fractions of the spherules to assess the role of surface condensation in the generation of the HSE abundances.

Materials: The Apollo 15 green and Apollo 17 orange glasses represent the best and most voluminous examples of the sampled lunar pyroclastic deposits [e.g. 6]. The glasses from both sites are generally spherical in shape and are products of fire-fountaining on the lunar surface. The *ca*. 3.4 Ga [7] green glasses represent near-primary very low-TiO_2 basalts (≈0.2 to 0.7 wt.% TiO_2) with Mg# as high as 0.68. The *ca*. 3.6 Ga [8] orange glasses represent near-primary high-TiO_2 basalts (≈8.4 to 9.4 wt.% TiO_2) with Mg# as high as 0.54. High pressure experiments and extensive geochemical-isotopic data for both compositions have been interpreted as indicating that these magmas were derived through the melting of lunar magma ocean cumulate assemblages in the deep lunar interior (> 400 km) leaving behind a residuum of olivine and orthopyroxene [e.g. 6].

Analytical Methods: Glass samples were purified on a laminar flow bench using a binocular microscope, polystyrene petri dishes, sieves, and clean utensils. Because of the high initial purity of the samples, the purification of the glass beads was done by hand picking non-glass contaminants under a binocular microscope. These non-glass contaminants consisted primarily of small rock fragments and individual mineral grains. The purified samples were then split based on bead size using nylon cloth sieves with polypropylene frames.

Un-ground samples were spiked for isotope dilution analysis and digested in Carius tubes in reverse *aqua regia* at 230°C. Although the spherules visibly reacted with the acid, digestion was incomplete. To assess the quantity of HSE remaining in the residue, the residual solids of orange glass sample 74001-1217 (180-325 mesh) were recovered from the digestion vessel, leached in 6M HNO_3 and 5M HCl, finely-ground, then re-spiked and digested. Separation/purification of the HSE was accomplished via solvent extraction (Os) and anion exchange chromatography (Re, Ir, Ru, Pt, Pd). Osmium analysis was done via negative thermal ionization mass spectrometry. The remaining elements were analyzed via ICP-MS. Average blanks for Os, Ir, Ru, Pt and Pd were 0.5, 3.3, 13, 94, and 13.5 pg, respectively. Analytical uncertainties are highly variable, with the greatest uncertainty resulting from high blank/sample ratios, with Os and Ir uncertainties of approximately 50% for sample 74001-1217 (75-180 mesh) Uncertainties in isotopic composition are also highly dependent on the blank/sample ratio (Table 1). Again, the greatest uncertainty is for sample 74001-1217 (75-180 mesh). The quantities of Re liberated by the digestions were generally at blank levels, so Re concentrations are estimated based on the age of the material and assuming a chondritic initial $^{187}Os/^{188}Os$ at the time of formation. This assumption is likely valid for at least the orange glasses based on the generally chondritic initial $^{187}Os/^{188}Os$ ratio determined for lunar orange glass 74220 [9].

Results: Absolute and relative abundances of HSE are highly variable (Tables 1-2; Fig. 1). Green glass 15426,164 (75-180 mesh) has approximately 2x higher abundances of Os and Ir than has been previously reported [10]. The elemental ratios of the HSE are within the range defined by chondritic meteorites [11]. Orange glass 74001,1217 (180-325 mesh) has Os and Ir concentrations a minimum of 2-3 time higher than reported for earlier neutron activation analyses [12-13]. The HSE pattern for this sample is moderately fractionated with higher normalized abundances of Pt and Pd compared with Os and Ir. The slightly supra-chondritic $^{187}Os/^{188}Os$ ratio is similar to the ratio reported for an orange glass concentrate from 74220 (0.1339, [9]). This is likely indicative of a modestly fractionated Re/Os relative to chondritic. The leached and ground re-analysis of the residue of this sample yielded higher abundances of all elements (notably Os) except Re. The isotopic composition of the residue was considerably less radiogenic than the un-ground sample. Orange glass 74001,1217 (75-180 mesh) has a highly fractionated HSE pattern with major depletions in Os and Ir. The rather supra-chondritic $^{187}Os/^{188}Os$ of this aliquant requires a substantially fractionated Re/Os since its formation. Ruthenium, Pt and Pd abundances are similar to the finer, un-ground fraction. The Os and Ir abundances are similar to those determined previously by neutron activation analysis [12-13].

Discussion: The chondrite-normalized HSE pattern for green glass 15426,164 is relatively flat, indicating that the HSE abundances of this aliquant of green glass were likely dominated by a meteoritic contaminant. The chondritic $^{187}Os/^{188}Os$ is also strongly suggestive of a meteoritic component. This sample can probably provide little information about the lunar interior, but may provide useful information about the types of meteorites impacting the lunar surface. The moderately fractionated pattern for 74001,1217 (180-325 mesh) is not a result of fractionation during condensation. This conclusion is based on the similarities in normalized abundances between Pt and Pd, two elements with highly disparate volatilities. Instead this pattern could reflect primary melt concentrations. These concentrations are a factor of 3-4 lower than abundances for terrestrial volcanic rocks with similar MgO. Alternately, the pattern may represent a mixture between an indigenous primary melt composition and a meteoritic contaminant. The latter interpretation is more consistent with the results from the coarser fraction (below). The results for the leached residue are difficult to interpret, particularly the very high concentration of Os. We are exploring the possibility that this sample was contaminated in the reprocessing. The very low abundances of Os and Ir in the coarser fraction of 74001,1217 (75-180 mesh) most likely reflect a dominantly indigenous signature. Abundances of Pt and Pd are factors of 5-10 less than terrestrial rocks with similar MgO and may indicate somewhat lower abundances of HSE in the lunar mantle relative to the terrestrial mantle.

Conclusions: It remains difficult to assess the HSE content of the lunar mantle. Orange and green volcanic glasses may provide valuable insights, but the effects of meteoritic contamination must be carefully removed.

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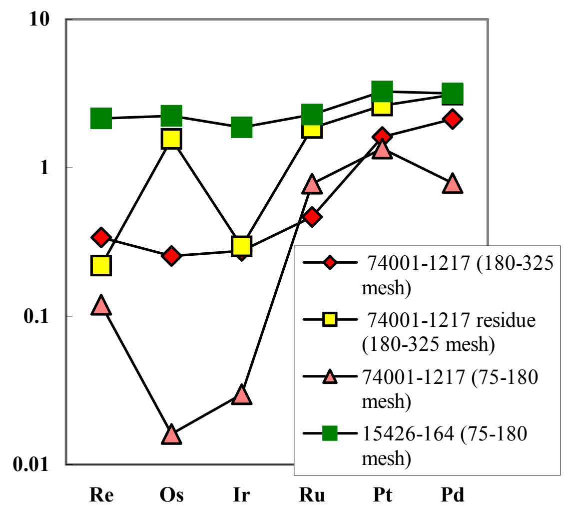

Figure 1. Abundances of HSE in lunar glasses normalized to CI chondrites x 1000.

Table 1. Concentrations of highly siderophile elements in pg/g. Re* calculated from Os isotopic composition assuming chondritic initial ratio at 3.6 Ga (74001) and 3.4 Ga (15426) and using $\lambda = {}^{187}$Re of 1.666 x $10^{-11}a^{-1}$.

Sample	Weight (g)	$^{187}Os/^{188}Os$	Re*	Os	Ir	Ru	Pt	Pd
74001-1217 (180-325 mesh)	0.090	0.1368±30	13	116	125	301	1387	1194
74001-1217 (180-325 mesh) residue	0.010	0.1182±8	8.4	718	135	1197	2257	1740
74001-1217 (75-180 mesh)	0.112	0.291±40	4.6	7.39	14	509	1152	445
15426-164 (75-180 mesh)	0.116	0.1280±3	82	1020	854	1481	2789	1783

Table 2. Highly siderophile element concentrations normalized to CI chondrite Orgueil x 1000. Orgueil concentrations used for normalization: Re - 38.31, Os – 458.5, Ir – 455.6, Ru – 649.6, Pt – 859.2, Pd – 562.9, all in ng/g, from [11].

Sample	Re*	Os	Ir	Ru	Pt	Pd
74001-1217 (180-325 mesh)	0.339	0.253	0.275	0.464	1.61	2.12
74001-1217 (180-325 mesh) residue	0.219	1.57	0.296	1.84	2.63	3.09
74001-1217 (75-180 mesh)	0.120	0.0161	0.0297	0.784	1.34	0.790
15426-164 (75-180 mesh)	2.14	2.22	1.87	2.28	3.25	3.17