LOW ABUNDANCES OF HIGHLY SIDEROPHILE ELEMENTS IN THE LUNAR MANTLE: EVIDENCE FOR PROLONGED LATE ACCRETION.

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), [2]Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd., Washington DC 20015 [3]Institute of Meteoritics, Department of Earth & Planetary Sciences, University of New Mexico, Albuquerque, NM 87131.

Introduction: The highly siderophile elements (HSE: including Re, Au, Ir, Os, Ru, Pt, Pd, Rh) are strongly partitioned into metal relative to silicates. In the terrestrial planets these elements are concentrated in metallic cores. Earth's mantle has sufficiently high abundances of the HSE (~0.008 times CI abundances) that it has been hypothesized approximately 0.1-0.5% of the mass of the Earth was added following the last major interaction between the core and mantle [e.g. 1]. The additional material added to the Earth and Moon has been termed a "late veneer", and the process has often been termed "late accretion" [2].

The timing of the dominant late accretionary period of the Earth and Moon is still poorly known. The abundances of HSE in the lunar mantle could provide important constraints on when the late veneer was added. The material that ultimately became the silicate portion of the Moon was likely stripped of most of its HSE prior to and during coalescence of the Moon. Consequently the initial lunar mantle likely had very low concentrations of the HSE. Unlike Earth, the generation of permanent lunar crust by ~4.4 Ga prevented subsequent additions of HSE to the lunar mantle via continued accretion. Thus, if a substantial portion of the late veneer was added after 4.4 Ga, the lunar mantle should have retained very low HSE concentrations. Converesely, if the late veneer was mostly added prior to 4.4 Ga, HSE abundances in the lunar mantle may be rougly similar to abundances in the terrestrial mantle.

Because of the lack of direct samples of the lunar mantle, indirect methods for determining lunar mantle abundances of HSE have been previously employed and estimates of the HSE content of the lunar mantle have varied considerably from those similar to that of Earth's mantle, to those much lower [3-7]. As part of a continuing study, here we discuss Os isotopic composition/concentration data and corresponding Re, Ir, Ru, Pt and Pd concentration data for several size fractions of picritic Apollo 15 green (15421 and 15426) and Apollo 17 orange (74001 and 74220) glasses. The glasses from both sites are generally spherical in shape and are products of fire-fountaining on the lunar surface. For comparison to the glasses, we also examined Apollo 17 dunite 72415, which has a bulk MgO content of 43.6 wt. %. This rock is a member of the highlands magnesian suite [8] and formed as a cumulate from a pre-mare basaltic melt at about 4.45 Ga [9]. As a high MgO rock, it serves as a valuable comparison to similarly MgO-enriched terrestrial rocks.

Analytical Methods: Un-ground, hand purified glass samples were spiked for isotope dilution analysis and etched in Carius tubes in reverse *aqua regia* at 230°C for approximately 12 hours. Although the spherules visibly reacted with the acid, digestion was incomplete. To assess the quantity of HSE remaining in the residue, the residual solids were recovered from the digestion vessel, further leached in warm 6M HNO_3 and 5M HCl (to remove residual spike), 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.

Results: Concentratons of HSE are highly variable among the glass fractions. For almost all size fractions of both green and orange glasses, the etchates contain the highest abundances of HSE (e.g. Fig. 1). This could reflect the presence of at least some of the HSE as surface condensates on the glass spherules, as has been previously demonstrated for some volatile elements and Au [10]. Calculated bulk abundances of Os and Ir show a weak negative correlation between spherule size and concentration. However, the etchates also tend to have the least radiogenic $^{187}Os/^{188}Os$ ratios, with most approaching chondritic values. Residues generally have considerably suprachondritic $^{187}Os/^{188}Os$ ratios.
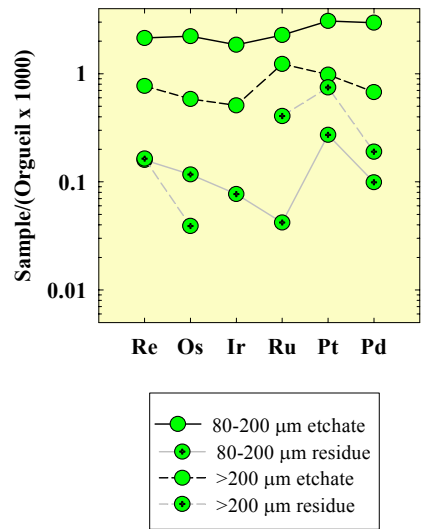
Discussion: The isotopic variability between etchates and residues indicates the presence of at least two components with distinct Re/Os ratios within the glass fractions. The fact that some etchates have generally high concentrations of HSE with chondritic relative abundances *and* approximately chondritic $^{187}Os/^{188}Os$ suggests that a significant portion of the Os contained in the glass concentrates is a meteoritic contaminant. This was probably added as micrometeorite influx to the soils after deposition [10]. If the indigenous HSE concentrations were low, as little as 0.01 wt % of a meteoritic contaminant will strongly affect both the Os isotopic composition and HSE concentrations in a mixture.

The indigenous lunar component in the glass fractions can be estimated from mixing curves connecting the residues with radiogenic $^{187}Os/^{188}Os$ to the etchates with chondritic ratios (Fig. 2). For green glass 15426, we conclude the indigenous lunar component contains ≤0.020 ng/g of Os. For orange glass 74220, the indigenous component likely contains ≤0.009 ng/g of Os (Fig. 2). These abundances are considerably lower than the corresponding concentrations of the bulk glass fractions (Fig. 3). When compared to trends defined by terrestrial rocks with variable MgO [7], the Os concentration estimates for the indigenous components are ≥20 times lower. The offset of the high MgO dunite from the terrestrial trend is also consistent with this estmate(Fig.3).
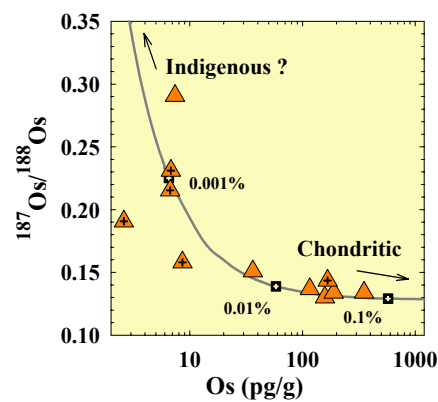
We suggest that the mantle sources of the orange and green glasses were depleted in the HSE by at least a factor of 20 relative to the terrestrial mantle. This in turn suggests that the lunar mantle did not receive a late accretionary component proportionally consistent with the Earth. Presumably the "missing" HSE reside in the lunar crust. If it is assumed that crustal formation prevented the missing late accreted materials from incorporation into the lunar mantle, then >90% of the late veneer must have been added after ca. 4.4 Ga for both the Earth and Moon.

Conclusions: These new results indicate that a significant portion of the late veneer was added relatively late in the evolution of the solar system (>100 Ma after formation of the solar system), long after planetary accretion was initiated. It remains unknown whether this late-accreted material was progressively added as an exponentially decaying function during the period from 4.4 to 3.9 Ga, or was largely added during a relatively short time interval, i.e., during a "terminal cataclysm". The latter has been proposed as a means of generating the relatively uniform isotopically reset ages at 3.8 to 3.9 Ga for lunar impact breccias [11].

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Fig. 2. Plot of $^{187}Os/^{188}Os$ versus Os concentration. Curve shows mixing between a hypothetical indigenous orange glass composition and an ordinary chondrite. The parameters used in the calculations for the indigenous endmember are 3 pg/g Os, $^{187}Os/^{188}Os = 0.5$. The parameters for the chondrite are: 580 ng/g Os, $^{187}Os/^{188}Os = 0.128$. The mixing curve is shown in dark gray. Data for orange glass etchates (open triangles) and residues (triangles with crosses). Percentages (by mass) of the chondritic component are labeled and denoted as black boxes with white crosses.
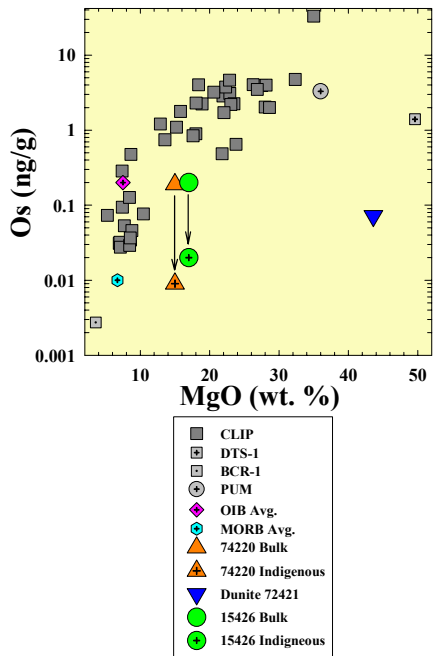
Fig. 3. MgO (in wt. %) versus Os (in ng/g) for terrestrial rocks and lunar glasses and dunite 72421. The terrestrial array for rocks from the Caribbean Large Igneous Province (CLIP) are from [12]. The averages for MORB and ocean island basalts are compiled from the literature.

Fig. 1. CI chondrite normalized abundances (x1000) of HSE for green glass 15426 etchates and residues.