Highly siderophile element depletion in the Moon

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A B S T R A C T

Coupled $^{187}Os/^{188}Os$ and highly siderophile element (HSE: Os, Ir, Ru, Pt, Pd, Re) abundance data are reported for Apollo 12 (12005, 12009, 12019, 12022, 12038, 12039, 12040), Apollo 15 (15555) and Apollo 17 (70135) mare basalts, along with mare basalt meteorites La Paz icefield (LAP) 04841 and Miller Range (MIL) 05035. These mare basalts have consistently low HSE abundances, at $\sim 2 \times 10^{-5}$ to 2×10^{-7} the chondritic abundance. The most magnesian samples have broadly chondrite-relative HSE abundances and chondritic measured and calculated initial $^{187}Os/^{188}Os$. The lower abundances and fractionated HSE compositions of more evolved mare basalts can be reproduced by modeling crystal–liquid fractionation using rock/melt bulk-partition coefficients of ~ 2 for Os, Ir, Ru, Pt and Pd and ~ 1.5 for Re. Lunar mare basalt bulk-partition coefficients are probably higher than for terrestrial melts as a result of more reducing conditions, leading to increased HSE compatibility. The chondrite-relative abundances and chondritic $^{187}Os/^{188}Os$ of the most primitive high-MgO mare basalts cannot be readily explained through regolith contamination during emplacement at the lunar surface. Mare basalt compositions are best modeled as representing ~ 5–11% partial melting of metal-free sources with low Os, Ir, Ru, Pd (~ 0.1 ng g^{-1}), Pt (~ 0.2 ng g^{-1}), Re (~ 0.01 ng g^{-1}) and S (~ 75 μg g^{-1}), with sulphide-melt partitioning between 1000 and 10,000.

Apollo 12 olivine-, pigeonite- and ilmenite normative mare basalts define an imprecise ^{187}Re–^{187}Os age of 3.0 ± 0.9 Ga with an initial $^{187}Os/^{188}Os$ of 0.107 ± 0.010. This age is within uncertainty of ^{147}Sm–^{143}Nd ages for the samples. The initial Os isotopic composition of Apollo 12 samples indicates that the source of these rocks evolved with Re/Os within $\sim 10\%$ of chondrite meteorites, from the time that the mantle source became a system closed to siderophile additions, to the time that the basalts erupted. Similarity in absolute HSE abundances between mare basalts from the Apollo 12, 15 and 17 sites, and from unknown regions of the Moon (La Paz mare basalts, MIL 05035), indicates relatively homogeneous and low HSE abundances within the lunar interior. Low absolute HSE abundances and chondritic Re/Os of mare basalts are consistent with a late accretion addition of ~ 0.02 wt.% of the Moon's mass to the mantle, prior to the formation of the lunar crust. Late accretion must also have occurred significantly prior to cessation of lunar mantle differentiation (> 4.4 Ga), to enable efficient mixing and homogenization within the mantle. Low lunar HSE abundances are consistent with proportionally 40 times more late accretion to Earth than the Moon. Disproportional late accretion to the two bodies is consistent with the small ^{182}W excess (~ 21–28 ppm) measured in lunar rocks, compared to the silicate Earth.

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1. Introduction

Derivative melts of the Moon's interior, sampled as mare basalts, pyroclastic glass beads, and crustal rocks, represent the only available materials for establishing the lunar mantle composition. Pyroclastic glasses are believed to represent primitive (13–20 wt.% MgO), high-degree partial melts sourced from the deep mantle (>400 km depths; Shearer and Papike, 1993), whereas mare basalts have witnessed more complex petrogenetic histories, including variable extents of both partial melting and crystal–liquid fractionation (e.g., Neal and Taylor, 1992; Longhi, 2006). In terrestrial igneous systems, high-MgO melts, such as picrites and komatiites have highly siderophile element (HSE: Os, Ir, Ru, Rh, Pt, Pd, Re, Au) abundances broadly similar to their mantle sources, because they result from high degree partial melting, with (nearly) all sulphide host minerals in the parent mantle being incorporated into the melt (e.g., Barnes et al., 1985; Rehkämper et al., 1999). Early studies showed that

the Ir concentrations in lunar picritic, high-Ti orange and low-Ti green glasses were depleted by factors of two to four, compared to similarly-evolved terrestrial rocks (Ganapathy et al., 1973; Morgan and Wandless, 1979). This observation led to the conclusion that HSE concentrations in the lunar mantle sampled by picritic glasses are similar to those in the terrestrial mantle (Ringwood, 1992). However, significant doubt has been cast on such elevated HSE abundances in the lunar interior. Pristine pyroclastic picritic glasses contain elevated volatile and siderophile abundances that are surface-correlated (e.g., Chou et al., 1975; Krähenbühl, 1980), and surface-correlated, elevated HSE abundances have been ascribed to meteoritic contamination on the outer surfaces of the glass beads, after their formation and emplacement (Walker et al., 2004).

In contrast to their exteriors, the interiors of the lunar pyroclastic glass beads are characterized by much lower abundances of the HSE (Walker et al., 2004), and the interior abundances are similar to abundances determined for mare basalts from the Apollo 15 and 17 sites (Day et al., 2007). Utilizing the relationship of HSE abundance variations with indices of fractionation (e.g., MgO) in mare basalts (e.g., Warren et al., 1999) it is possible to perform regression analysis to assess the lunar mantle composition. The mantle abundances obtained by Day et al. (2007) using this method (0.01 ng g^{-1} Re, 0.1 ng g^{-1} Os, Ir, Ru, Pd and 0.2 ng g^{-1} Pt) are $\sim$40 times lower than HSE abundances estimated for Earth's primitive mantle (Becker et al., 2006). An interpretation of low abundances of the HSE in the lunar mantle is supported by similarly low HSE abundances measured in pristine lunar crustal rocks (Warren and Wasson, 1980; Day et al., 2010).

Three aspects of lunar mare basalt genesis currently limit our ability to more accurately estimate lunar mantle HSE composition. First, contamination of mare basalt lavas by even minor amounts ($<$0.1% by mass) of HSE-rich impactor material present in regolith would lead to increased HSE contents, flatter chondrite-normalized HSE patterns, and chondritic ^{187}Os/^{188}Os. Such contamination could potentially lead to an overestimate of lunar mantle HSE abundances. Second, metal in the source of mare basalts after melt-extraction could be problematic to understanding lunar mantle composition. At low fO$_2$ conditions in the lunar mantle, stable metal phases could strongly control the HSE, leading to low and fractionated abundances of these elements in mare basalt parental melts. Third, while there is clear evidence for mineralogical heterogeneity and fractionation of stable isotopes and long-lived radiogenic lithophile isotope systems in mare basalt source regions (e.g., Warren and Taylor, 2014), the degree to which the lunar mantle is heterogeneous with respect to the HSE is not well constrained. Understanding the distribution of the HSE is important since it is possible that magma ocean differentiation, possibly accompanied by late accretion, led to large variations in HSE abundances, as well as strong HSE fractionations in the lunar mantle. In turn, these observations can affect interpretation of the isotopic composition of other siderophile elements, such as W, measured in mantle-derived lunar materials (Walker, 2014). In this contribution, new data are reported for Apollo 12, 15 and 17 mare basalts, as well as two lunar meteorites, to improve understanding of HSE abundances in the lunar interior.

2. Samples

Mare basalts from the Apollo 12 mission (12005, 12009, 12019, 12022, 12038, 12039, 12040) that have crystallization ages of 3.2 ± 0.1 Ga, span a range in MgO contents from 6.7 to 20 wt.% and include olivine-, pigeonite-, ilmenite-, and feldspar-normative basalts, were analyzed for Re–Os isotopic systematics and HSE abundances. A summary of petrology, mineralogy, ages and compositions for these samples is provided in Table S1. Analyses

of Apollo 12 samples are complemented by new analyses of two evolved, low-Ti mare basalt meteorites from Antarctica: La Paz (LAP) 04481 ($\sim$7 wt.% MgO) and Miller Range (MIL) 05035 (7.4 wt.% MgO). LAP 04481 is paired with LAP 02205, 02224, 02226, 02436 and 03632, and these stones collectively crystallized at $\sim$3 Ga and have possible affinities to low-Ti, low-Al Apollo 12 mare basalts (e.g., Righter et al., 2005; Day et al., 2006). By contrast, MIL 05035 is a 3.8 Ga coarsely-crystalline meteorite that is unusual for a lunar basalt in that it lacks a pronounced Eu-anomaly (Liu et al., 2009). Powder splits of basalts 15555 and 70135 that were measured in the study of Day et al. (2007) were also measured for inter-laboratory comparison.

3. Analytical methods

Samples were requested from the Curation and Analysis Planning Team for Extraterrestrial Materials (CAPTEM), and from the Meteorite Working Group (MWG), as freshly-split interior portions of main sample masses. None of the received samples had adhering materials or metal markings when examined under a high-powered binocular microscope. Samples were disaggregated to a fine powder using an alumina mortar and pestle dedicated to processing lunar mare basalts, in a clean laboratory environment. To obtain the most precise Os isotope and HSE abundance data using isotope dilution, we used data previously obtained for mare basalts by Day et al. (2007) for guidance. Up to three separate digestions of each sample were made, with masses ranging from 0.26 to 1.34 g.

Osmium isotope and HSE abundance analyses were performed at the University of Maryland (UMd). Samples were sealed in 10- to 20-cm long borosilicate Carius tubes, or in 50 mL quartz high-pressure asher (HPA) digestion vessels, with isotopically enriched multi-element spike (^{99}Ru, ^{106}Pd, ^{185}Re, ^{190}Os, ^{191}Ir, ^{194}Pt), and 4 to 11 mL of acid mixture (1 part 12 M HCl and 2 parts 15.7 M HNO$_3$). All reagents were Teflon distilled multiple times. Samples were digested in Carius tubes at a maximum temperature of 270 °C in an oven for $>$72 hrs, or for 6 hrs in an *Anton Paar* HPA device at a maximum temperature of 320 °C and $>$150 bar. Osmium was triply extracted from the acid phase into CCl$_4$ (Cohen and Waters, 1996) and then back-extracted from the solvent into concentrated HBr, followed by purification by micro-distillation (Birck et al., 1997). The remaining HSE were recovered and purified from residual solutions using an anion exchange separation technique. We deliberately refrained from using an HF digestion-step on residual solutions, as has been proposed by recent studies (Ishikawa et al., 2014). An HF digestion-step has been reported to access up to 9 to 15% more Re from within silicate phases, compared with standard Carius tube/HPA digestion (Li et al., 2014), at least in some instances. Release of additional Re by a second-stage HF digestion would result in measured Re/Os that does not reflect the ratio in equilibrium with measured ^{187}Os/^{188}Os. This is particularly disadvantageous for obtaining chronological information, where Re/Os may be increased significantly, leading to younger apparent ages.

Osmium isotopic compositions were measured as OsO$_3$$^-$ ions using a secondary electron multiplier in negative ion mode using a *ThermoFisher* Triton thermal ionization mass-spectrometer (TIMS), and Re, Pd, Pt, Ru and Ir were measured using an *Aridus II* desolvating nebuliser coupled to a *ThermoFisher* Element 2 inductively coupled plasma-mass spectrometer (ICP-MS) in low-resolution mode, using identical methodologies for measurement and data correction as described previously (Day et al., 2010). External precision of ^{187}Os/^{188}Os, determined from individual measurements of 3.5 to 35 pg Os standards (UMCP Johnson and Matthey) during the analytical campaign using the Triton TIMS, was better than $\pm$0.2% (^{187}Os/^{188}Os = 0.11373 $\pm$ 9; $n = 19$; 2σ). External reproducibility (2σ) on standard solutions analyzed by ICP-MS were better than