HIGHLY SIDEROPHILE ELEMENT FRACTIONATIONS IN APOLLO 16 IMPACT MELT ROCKS: LARGE-SCALE FRACTIONATION PROCESSES.

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Introduction: Early work on ancient lunar impact rocks from Apollo and Luna landing sites has shown that significant quantities of highly siderophile elements (HSE) were added to the lunar crust after core formation and magma ocean crystallization [e.g. 1&2]. Hence, their compositional record provides constrains on the composition and timing of the impact flux to the Moon, with important implications for the inner solar system dynamics and late accretion history of the terrestrial planets [e.g. 3&4]. The composition of lunar impactites might also hold the key to understand the observed slight deviation from chondritic ratios of highly siderophile elements in the Earth's mantle and the [4&5].

Precise HSE and osmium isotope data are now available for ancient lunar impact melt rocks but the origin of observed differences in composition is debated [6-9]. Key points of the discussion are on one hand the interpretation of small-scale fractionations observed in multiple aliquots of the same sample and on the other hand large-scale fractionations between samples from different lithologies and landing sites.

Based on HSE data for mineral separates from Apollo 16 impact melt rocks Gleißner and Becker [10] suggest that the small-scale fractionation processes are due to solid metal-liquid metal partioning during cooling and crystallization. Differences in abundances and ratios of the HSE between metal separates are controlled by the abundances of light elements like sulfur and phosphorous. However, the unanswered key question is whether the large differences between samples from different landing sites represent the signatures of distinct ancient impactors [6&8], mixing of several ancient impactor compositions [7] or large-scale fractional crystallization of metal within large impact melt pools, similar to processes in some terrestrial impactites [11].

Analytical techniques: In general we followed the analytical procedure of [7] and [12]. The samples were crushed into coarse-grained chips and mixed ^{185}Re-~Os and ^{191}Ir-^{99}Ru-^{194}Pt-^{105}Pd and individual ^{34}S spike solutions were added to aliquots of ~100 mg.

After digestion in 1 ml conc. HCl + 2 ml conc. HNO_3 for 16 h at 320°C in a high-pressure asher, Os was extracted by solvent extraction and back extraction into HBr followed by microdistillation. Os isotopic ratios were measured by negative TIMS (ThermoFinnigan Triton) on an electron multiplier or faraday cups. Measured ratios were corrected for isobaric oxide interferences and mass fractionation. The rest of the HSE and S were separated by cation exchange chromatography from the matrix and analyzed by ICP-MS (Element XR). Total analytical blanks contributed generally less than 0.5 % for Os, Ir and Ru, <3 % for Au and Rh, <5 % for Re, Pd and Pt and <20 % for S.

Results and Discussion: Many Apollo 16 Impact melt rocks display more strongly fractionated HSE patterns compared to samples from other landing sites, which tend to be closer to chondritic compositions (Fig. 1&2). The main questions in lunar impact melt rock studies is whether the impacting bodies were of primitive or differentiated composition and whether or not these are similar to known meteorite groups.

According to recent studies of components in unequilibrated ordinary and enstatite chondrites [13&14] primitive impactor compositions 10-30 % more fractionated than known chondrite groups are viable. Based on available data, HSE patterns observed in Apollo 14 and 17 impact melt rocks could be theoretically explained by such hypothetical primitive impactor compositions, however, for the more fractionated Apollo 15 and 16 samples this seems rather unlikely. In addition, none of the known chondrite components display ^{187}Os/^{188}Os ratios (i.e. long term Re/Os ratios) as high as most Apollo 16 impact melt rocks [13&14] and therefore a fractionation mechanism different from volatility-controlled fractionation processes during chondrite component formation is required.

Fractionated HSE pattern as observed in Apollo 16 impact melt rocks could also be generated if crystallizing solid metal is gravitationally removed from an initially chondritic impact melt composition [11]. The recently documented example of a coarse-grained cumulate rock formed by fractional crystallization in a lunar impact melt sheet [15] seems to further promote this prediction. However, the majority of Apollo 16 impact melt rocks display fine-grained subophitic to intersertal textures, often referred to as basaltic. The large-scale fractional crystallization scenario would further demand huge amounts of segregated Fe-Ni metal to be produced. The unique HSE compositional characteristics (high absolute concentrations and relative enrichment of refractory HSE) of such metal would make it relatively unlikely to overlook. However, such an early-crystallized metal component has never been sampled on the lunar surface and is also not detectable in lunar meteorites. In contrast, impact melt rocks display usually high iron contents in metal spherules [7&9] and samples with the most fractionated HSE patterns usually display the highest HSE contents.

Modeling of fractional crystallization of Apollo 16 impact melt rocks indicates closed system crystallization of solid metal from already fractionated metal melt compositions [10]. The latter likely were formed by impacts of large fragments of planetary core material, similar to some iron meteorites. The broadly linear correlations of different HSE ratios (Fig. 1&2) and $^{187}Os/^{188}Os$ ratios [9] of impact rocks for different landing sites are consistent with a variable mixing of chondrite-like impactor components with suprachondritic iron meteorite-like impact composition(s), and subsequent homogenization by younger impacts [7].

Some non-chondritic Apollo 16 impact melt rocks share HSE compositional characteristics with fractionated members of the S-poor IVA iron meteorite group [7&9], however, none of the known meteorite compositions provide a full match to all HSE/Ir ratios of the Apollo 16 end member composition. In contrast, the compositions of S-rich IIIA irons are similarly fractionated in refractory HSE/Ir ratios (Fig. 1) but less fractionated in moderately volatile HSE/Ir and therefore do not provide a good match (Fig. 2). Regardless of the poor match with known iron meteorite composition, non-chondritic Apollo 16 impact melt rocks display HSE compositions typical to residual metallic melt after significant solid metal formation from metal melt initially rich in phosphorus and/or sulfur.

Constraints on late accretion: Ancient Apollo 16 impact melt rocks display no evidence for in situ large-scale fractional crystallization of metal in impact melt pools. During cooling of the impact melt, millimeter-scale fractionation processes occurred in the presence of P and S between solid metal and coexisting metallic melt. The HSE compositional record of lunar impactites is consistent with accretion of differentiated core metal along with chondrite-like material. Observed HSE patterns and Ru anomalies reflect large-scale fractionation processes during differentiation of the parent body of the impactors. Late accreted material on Earth may have delivered similar material (embryo core material? leftover material from the moonforming impact?).

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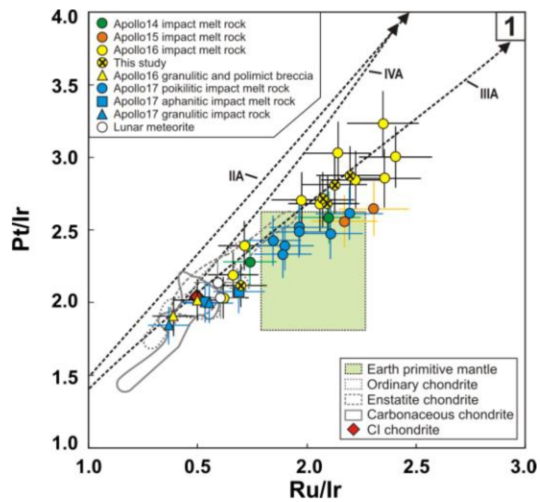

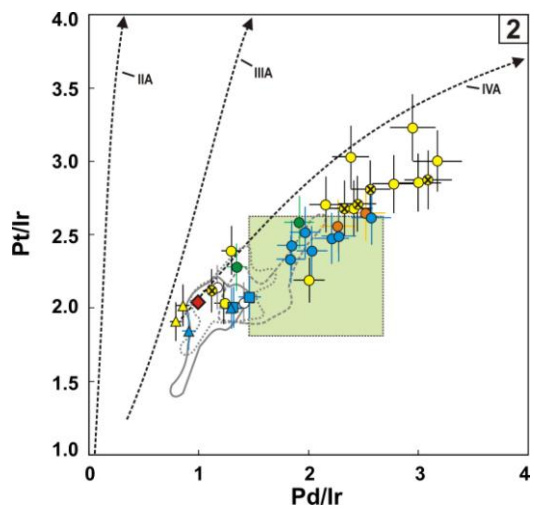

Fig. 1&2. HSE/Ir ratios calculated from weighted average values of multiple aliquots [6-10]. Uncertainties reflect the overall precision of concentration determinations. The range of the terrestrial primitive mantle, chondrite classes and fractionation trends of magmatic iron meteorite groups are given for comparison.

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