

**COMBINING S-SE-TE AND HIGHLY SIDEROPHILE ELEMENT ABUNDANCES IN ANCIENT LUNAR IMPACTITES – NEW CONSTRAINTS ON IMPACTOR COMPOSITION, MIXING AND LUNAR DIFFERENTIATION.** P.Gleißner<sup>1</sup> and H. Becker<sup>2</sup>, <sup>1</sup>Freie Universität Berlin, Institut für Geologische Wissenschaften, Malteserstr. 74-100, 12249 Berlin, Germany (gleissner@zedat.fu-berlin.de).

**Introduction:** Core-mantle differentiation largely depleted the silicate portion of planetary bodies in siderophile elements. Late accretion in the aftermath of the main accretion phase added back siderophile elements but, may also have influenced some important compositional parameters for the evolution of the terrestrial planets and minor bodies in the solar system (e.g., availability of volatiles like hydrogen, carbon and sulfur). Therefore, absolute and relative abundances of highly siderophile elements (HSE) and siderophile volatile elements (SVE) can be used to constrain the nature of late accreted material, but are also important to trace metal-silicate and sulfide-silicate fractionation processes during core formation and later mantle melting.

The HSE record of ancient lunar impactites may provide constraints on the composition of material accreted late to the terrestrial planets. However, the origin of variably fractionated HSE patterns in different lithologies and landing sites is still debated [1-3]. Impact rocks from different landing sites display broadly linear correlations of  $^{187}\text{Os}/^{188}\text{Os}$  (a measure of the long-term Re/Os ratio of the samples) and HSE ratios which range from chondritic to suprachondritic. The compositional range is either interpreted as signatures of distinct ancient impactors [1, 2] or resulting from mixing of several ancient impactor compositions [3]. In either case, the nature of the putative impactors and their formation remains poorly constrained.

The SVE budget of lunar impactites and crustal rocks is currently not well constrained by modern methods. Accurate determination of absolute and relative abundances of SVE such as Te, Se and S may help to better constrain the composition of late accreted material and its volatile content [4]. In addition, the geochemical properties of these elements may also yield constraints on lunar differentiation and crust formation processes.

**Analytical methods:** In order to distinguish impactor and target contributions we determined HSE, Te, Se, and S from the same aliquot of multiple subsamples of five impactites following the analytical procedures of [3] and [4]. Samples were crushed into coarse-grained chips and mixed  $^{185}\text{Re}$ - $^{190}\text{Os}$ ,  $^{191}\text{Ir}$ - $^{99}\text{Ru}$ - $^{194}\text{Pt}$ - $^{105}\text{Pd}$ ,  $^{77}\text{Se}$ - $^{125}\text{Te}$  and individual  $^{34}\text{S}$  spike solutions were added to sample aliquots of 60 to 120 mg. After digestion in reverse aqua regia 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. The rest of the HSE and SVE were separated by ion exchange chromatography from the matrix and analyzed by ICP-MS. Sample solutions were aspirated either via a Scott-type spray chamber (Re, Ir, Pt, Au, and S), an Aridus desolvation system (Ir, Ru, Pt, Rh, and Pd) or hydride generation (Te, Se).

**Results and Discussion:** The samples of this study are mafic KREEP-rich impact melt rocks and breccias from the Apollo 15 and 16 landing site and a crystalline matrix breccia from Apollo 14 (Fig. 1). All samples display increasingly suprachondritic HSE/Ir ratios from refractory to moderately volatile HSE and  $^{187}\text{Os}/^{188}\text{Os}$  ratios, in the range of Apollo 15 and 16 impact melt rocks [3, 5, 6]. In most samples Te, Se and S are depleted relative to the HSE and abundances overlap with the highest concentrations of these elements obtained on HSE-poor lunar crustal rocks (Fig. 1). Sample 61015 displays the highest SVE concentrations and yields average Se/Te of  $8.0 \pm 1.4$  and S/Se of  $2560 \pm 540$  overlapping with the range in carbonaceous chondrites (Se/Te = 6.6 to 8.5, S/Se = 2600 to 2750). In contrast, Se/Te ratios in other samples are chondritic to suprachondritic (11-72), whereas S/Se ratios are always suprachondritic (3760-6880). Sample 15405 displays lower absolute HSE but similar absolute and relative abundance of Te, Se and S as the other samples (Fig. 1).

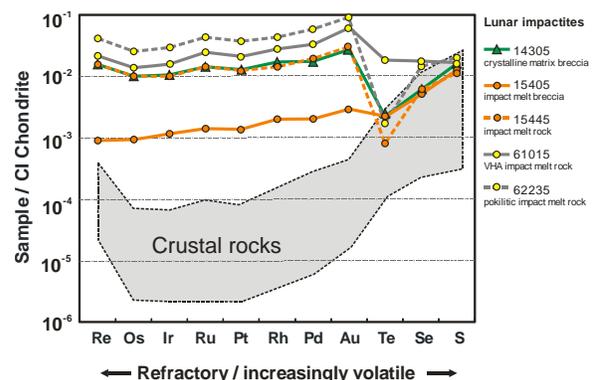


Fig. 1. HSE and SVE abundances of lunar impactites determined by ID-ICP-MS. All values are weighted averages of 5 rock aliquots of each sample. Range of HSE-poor lunar crustal rocks from ID-ICP-MS data [7] and RNAA data e.g., [8, 9].

These observations in general support the mixing model proposed by [3] in which the HSE record of lunar impactites is controlled by variable mixing of chondrite-like impactor components with a differentiated metal component (presumably poor in SVE). Modeling of HSE partitioning suggests that the composition of the differentiated impactor material requires derivation from light element-rich planetesimal or embryo core material with a P/S ratio higher than in most magmatic iron meteorites [6].

Since the HSE record of all studied samples is dominated by the differentiated metal component the composition of the unfractionated impactor components is more difficult to access. The observed range in Se/Te and S/Se ratios require a mixture of different components and/or processes that fractionate these elements.

Sample 61015 is the subophitic portion of a dimict breccia sample which was interpreted as impact melt injected into the floor of an unknown crater. Its high SVE content made it relatively insensitive to target contributions and its intrusive nature most likely prevented large scale outgassing during cooling. Fractionated HSE in combination with SVE ratios and SVE/Ir ratios in the range of CI chondrites (Fig. 1) strongly suggest that it represents a mixture between a volatile-rich primitive impactor component (similar to CI-chondrite) and a differentiated impactor component (see discussion in [3] and [6]).

SVE abundances and Se/Te ratios determined in samples 14305 and 15405 (Se/Te of 19 and 24, respectively) can be explained by addition of roughly 1 wt. % of ordinary chondrite-like material. However, sulfur abundances and S/Se ratios are not well explained in this case. Observed Se/Te (62 and 72) and S/Se ratios in samples 15445 and 62235 exceed the ranges observed in non-carbonaceous chondrites and also cannot be explained as a mixture of them. Recent studies of components in highly unequilibrated ordinary and enstatite chondrites reveal that some slightly and non-magnetic fractions are similarly fractionated in Se/Te ratios when compared to their respective bulk compositions [10]. However, primitive compositions dominated by the latter components would be chondritic to subchondritic in their S/Se, in contrast to strongly suprachondritic ratios observed in the impactites.

Previous RNAA work indicates that more or less pristine lunar crustal rocks from the ferroan anorthosite and magnesium suite usually display very low concentrations and subchondritic Se/Te, whereas some magnesium suite samples, high-Al basalts and KREEP basalts generally yield suprachondritic Se/Te [8, 11]. We note that mafic and KREEP-rich lunar impactites with

suprachondritic HSE patterns also display suprachondritic Se/Te e.g., [8, 9]. Recent chronological work e.g., [12, 13] suggests that the Moon became chemically heterogeneous at an early stage in that mare and KREEP magmatism started soon after lunar formation. It appears that mafic highland lithologies older than 3.9 Ga contributed significant to the S-Se-Te budget of the impactites. This interpretation is consistent with the general magnesian composition and variable KREEP component of many impactites. Based on available data we argue that in some cases the significant contribution of highland rocks with fractionated S-Se-Te might camouflage primitive impactor components in mafic impactites. Thus, suprachondritic Se/Te ratios as observed in mafic KREEP-rich lunar impactites may be inherited from ancient mafic rocks which either require magmatic fractionation of Te from Se (e.g., by residual mantle sulfide or sulfide segregation) or widespread volatility-controlled losses of Te during lunar differentiation.

**Summary:** Whereas the HSE record of many studied samples is dominated by broadly chondritic or the differentiated impactor component, the observed range in Se/Te and S/Se ratios require a mixture of different meteoritic components and/or planetary processes that fractionated these elements. Se/Te ratios of three samples fall in the range of chondritic meteorites and are consistent with accretion of differentiated core metal along with chondrite-like material, including volatile-rich carbonaceous chondrite-like material. Se/Te ratios of two samples are strongly suprachondritic, suggesting that ratios in these samples were fractionated due to fractionation processes in the lunar crust or mantle.

**References:** [1] Puchtel I. S. et al. 2008. *GCA* 72: 3022-3042. [2] Sharp M. et al. 2014. *GCA* 131: 62-80. [3] Fischer-Gödde M. and Becker H. 2012. *GCA* 77: 135-156. [4] Wang Z. and Becker H. 2013. *Nature* 499: 328-332. [5] Liu J. et al. 2015. *GCA* 155: 122-153. [6] Gleißner P. and Becker H. 2016 *GCA* 200: 1-24. [7] Day J. M. D. et al. 2010. *EPSL* 289: 595-605. [8] Ebihara M. et al. 1992. *Proc. LPSC* 22: 417-426. [9] Hertogen J. et al. 1977. *Proc. LSC* 8: 17-45. [10] Kadlag Y. and Becker H. 2016. *GCA* 172: 225-246. [11] Wolf R. et al. 1979. *LPSC Proc.:* 2107-2130. [12] Sokol A. K. et al. 2008. *GCA* 72: 4845-4873. [13] Crow C. A. et al. 2016. *GCA* <http://dx.doi.org/10.1016/j.gca.2016.12.019>.

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