

**MULTIPLE CAUSES OF SIDEROPHILE VOLATILE ELEMENT VARIATIONS IN LUNAR MARE BASALTS.** P. Gleißner<sup>1</sup> and H. Becker<sup>1</sup>, <sup>1</sup>Freie Universität Berlin, Institut für Geologische Wissenschaften, Malteserstr. 74-100, 12249 Berlin, Germany (gleissner@zedat.fu-berlin.de).

**Introduction:** The mantle of the Moon has many compositional and isotopic similarities to the mantle of the Earth, but is believed to be considerably more depleted in volatile elements than Earth's mantle. Therefore, volatile loss (e.g., degassing) and delivery processes (e.g., late accretion) are keystones to our understanding of the Earth-Moon system.

Because they cover a large range in relative volatility, moderately volatile elements are considered of great relevance to constrain the accretion and differentiation history of Earth and Moon [e.g., 1,2]. Many moderately volatile elements display siderophile and/or chalcophile behavior, thus their abundances are also controlled by metal-sulfide-silicate partitioning processes. However, for lunar samples we still rely on older mass fraction data (mainly RNAA), which have not been tested by isotope dilution ICP-MS methods. Furthermore some key elements like S and Cu were often not included in early studies of lunar rocks. Recent studies of the moderately volatile element inventory and stable isotope compositions of lunar samples reveal contrasting results and interpretations for the lunar mantle ranging from only moderately depleted [1,3] to strongly depleted [2,4] when compared with bulk silicate Earth. Here we present new isotope dilution data for mass fractions of siderophile volatile elements (SVE) in lunar mare basalts. Together with available data from the literature we discuss their behavior during magmatic processes and possible constraints on magmatic degassing and the composition of mantle sources.

**Samples and methods:** Representative samples of Apollo 12 and Apollo 17 mare basalts were studied. The Apollo 12 samples are porphyritic to ophitic low-Ti olivine basalts with MgO contents between 11.6 and 16.7 wt.%. Previous petrographic and melt inclusion studies revealed that they likely belong to a single magma body and are related to each other by fractional crystallization and accumulation of olivine [5,6]. The Apollo 17 samples are porphyritic to subophitic high-Ti basalts (type B and C) with MgO contents from 7.9 to 10.5 wt.%. Although the different high-Ti mare basalts types are not cogenetic, they come from similar depleted mantle sources [7] and underwent similar fractional crystallization processes [8]. Some samples display abundant vesicles indicative of degassing during ascent and/or eruption.

Samples were digested in HF-HNO<sub>3</sub> and equilibrated with spike solutions in Parr bombs for 3 days. After

conversion into HCl solution, Cu, Ag, Te, Se, S, Cd, In and Tl were separated from the matrix and collected in groups according to the separation protocol of [9]. Isotope ratios were determined using the Element XR sector-field ICP-MS at Freie Universität Berlin.

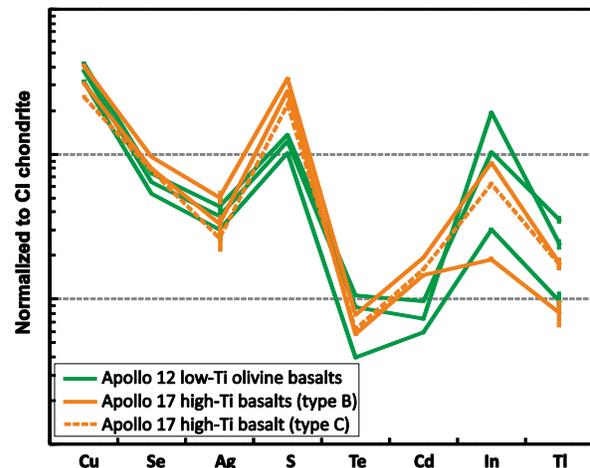


Fig. 1. Normalized SVE in lunar mare basalts determined by isotope dilution ICP-MS. Elements are displayed in the order of decreasing 50% condensation temperature from a gas of solar composition [10].

**Results and discussion:** Mass fractions of SVE in the studied samples are in the lower ng/g range except for Se (105-189 ng/g), Cu (3.18-5.42 µg/g) and S (552-1800 µg/g). When compared to available data from other methods, similar mass fractions were obtained for most SVE from RNAA and for S from XRF. In contrast, Cu values determined by external standardization ICP-MS are 3 to 10 times higher than our values. For our new concentration data, propagation of blank contributions and measurement statistics yield 2σ uncertainties of <1% for S, Cu, Se, <5% for Cd, In, Te and <20% for Ag and Tl. When compared to other methods uncertainties on concentration values are considerably decreased which makes variations between samples distinguishable. Furthermore, we determined SVE (including S and Cu) from the same aliquot which further reduces the uncertainties on element ratios.

In a chondrite normalized diagram (Fig. 1), SVE in Apollo 12 low-Ti olivine basalts display almost parallel patterns with variable depletions when compared to Cu (the least volatile SVE in our study). Mass fractions of In and Tl are more variable, reflecting their higher volatility and mobility during magmatic processes. On

average studied Apollo 17 high-Ti mare basalts are somewhat higher in S, Se and Cd, but display a pattern of increasing depletions in the order of  $\text{Cu} < \text{S} < \text{Se} < \text{In} < \text{Ag} < \text{Tl} < \text{Cd} < \text{Te}$ , similar to low-Ti mare basalts. The observed element distribution is apparently neither correlated with condensation temperatures of these elements from a gas of solar composition (Fig. 1) nor correlated with their differential volatility during vaporization experiments [11]. The analyzed elements are characterized by variable metal-sulfide-silicate partition coefficients, ranging from  $10^1$  to  $10^3$  [12-14] and the observed distribution most likely reflects a combination of partition and volatility driven processes.

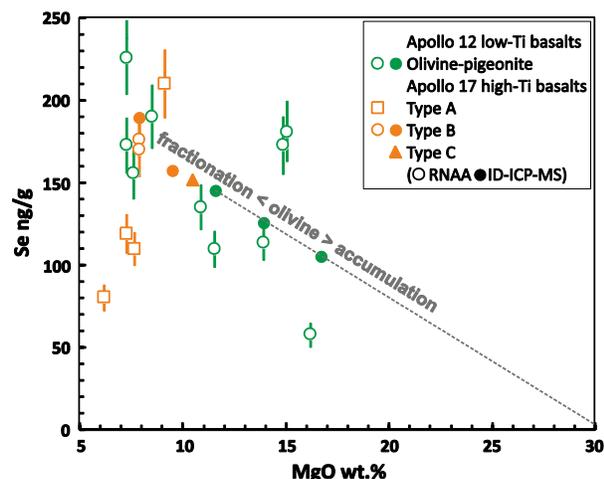


Fig. 2. Mass fractions of Se compared to MgO and RNAA data (LSC; uncertainties 1sd external reproducibility [15]).

In Apollo 12 olivine basalts and Apollo 17 type B basalts SVE are inversely correlated to indicators of fractional crystallization of mafic silicates  $\pm$  oxide phases (Fig. 2). Available data for Apollo 17 type A basalts display an opposite trend, indicative of sulfide saturation [14] and fractionation of sulfides. The distribution observed for the other basalt suites demonstrates that SVE behave incompatible during lunar mantle melt differentiation and suggests that any SVE depletion must have happened before near-surface fractional crystallization. Therefore, we argue that, degassing during eruption did not leave a measurable imprint on the mass fractions of most SVE in studied mare basalt samples. This interpretation is consistent with limited variability in stable isotope ratios of S and Zn in mare basalts [e.g., 3,4,16]. Thus, the SVE depletions in mare basalts can reveal insights into fractionation processes which occurred in the source regions of the magmas or even before the mantle sources were formed.

Tellurium displays the strongest depletion which cannot be easily reconciled with degassing, because the

more volatile elements In and Tl are less depleted (Fig. 1). On the other hand, Te is the most siderophile and chalcophile of the SVE. When compared to highly siderophile elements in mare basalts [17], Te is 10 times less depleted, which broadly agrees with the differences of their partition coefficients in metal-sulfide-silicate systems [14,18]. Therefore, the Te depletion and corresponding high Se/Te ratios might reflect a signature of lunar core formation or residual metal and/or sulfide during mantle melting. In contrast, Cu and Ag are only mildly fractionated from each other during metal-sulfide-silicate partitioning [12,13] and thus, the Cu/Ag ratios cannot be related to core formation or residual metal and/or sulfides. Within uncertainties the low-Ti and high-Ti mare basalts display indistinguishable Cu/Ag ratios. The average Cu/Ag ratio of  $6000 \pm 500$  is considerably higher than in the bulk silicate Earth ( $3500 \pm 1200$  [19]) and suggests the strong depletion of Ag most likely occurred by volatilization prior to the solidification of mare basalt source regions. These results demonstrate how SVE ratios in the lunar mantle can be constrained from their abundances in lunar mare basalts. The results so far are consistent with variable loss of some SVE, presumably by early degassing of the Moon, but also discernible signatures of metal-sulfide-silicate partitioning for others.

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