MAGMATIC FRACTIONATION AND DEGASSING OF SIDEROPHILE VOLATILE ELEMENTS IN LUNAR MAGMATIC ROCKS. P. Gleißner<sup>1</sup>, J. Salme<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 volatile element inventory of the Moon and the leading processes of volatile loss and/or gain (e.g., degassing and late accretion) are key aspects for our understanding of the Earth-Moon system. Since the era of the Apollo missions the Moon was thought to be highly depleted in volatile elements relative to Earth and chondrites. The proposed volatile abundance pattern of the bulk silicate Moon (BSM) is often interpreted as a consequence of large-scale volatile loss during the Moon-forming giant impact and subsequent lunar disk stage [1-3]. The notion of a strongly volatiledepleted BSM was recently challenged by the detection of elevated concentrations of volatile elements and water in various types of lunar materials [4-6]. The new estimates of the BSM composition suggest only moderate depletion when compared to the bulk silicate Earth (BSE). In these models the BSM inventory is dominated by volatiles partially preserved during the giant impact and/or replenished to the Moon during late accretion [4-6]. However, in order to balance the proposed model of a less volatile-depleted lunar interior with the strongly volatile-depleted nature of most analyzed lunar samples, strong magmatic degassing is required [4-6].

Here we present a different approach to the study of the volatile inventory of lunar rocks. Mass fractions of siderophile volatile elements (SVE) have been determined by isotope dilution methods from the same aliquot of representative pristine highland rocks and mare basalts. The results yield a coherent picture of SVE behavior in lunar igneous rocks, which formed at different depths, and allow us to constrain the influence of magmatic and secondary processes onto their SVE inventory. Following this, more robust constraints on the extent of volatile loss during magmatic differentiation and formation of mantle source regions are possible.

Samples and methods: The analyzed Apollo 12 low-Ti olivine basalts (MgO 11.6-16.7 wt.%) likely belong to a single magma body and are related to each other by fractional crystallization and accumulation of olivine [7]. Similarly, Apollo 15 low-Ti olivine-normative basalts (MgO 8.2-11.2 wt.%) are believed to belong to a single suite dominated by fractional crystallization of olivine [8]. The Apollo 17 high-Ti basalts (type B and C) with MgO contents from 7.9 to 10.5 wt.%. are not co-genetic, but evolved from similar depleted mantle sources and underwent similar fractional crystallization processes [9]. Many mare

basalt samples display abundant vesicles, indicative of degassing during ascent and/or eruption. Magnesian suite samples are characterized by variable modal abundances of cumulate plagioclase and low-Ca pyroxene and/or olivine with minor interstitial phases, which crystallized from intercumulus melt [10]. Ferroan anorthosite samples are mainly monomict breccias of coarse-grained precursor anorthosites. After their formation, most highland samples experienced various degrees of shock due to impacts, but all are considered as pristine [11].

Samples were digested in HF-HNO<sub>3</sub> and equilibrated with spike solutions in Parr bombs for 3 days. After conversion to chloride form, Cu, Ag, Te, Se, S, Cd, In and Tl were separated from the matrix and collected according to the separation protocol of [12]. Isotope ratios were determined using the Element XR sector-field ICP-MS at Freie Universität Berlin.

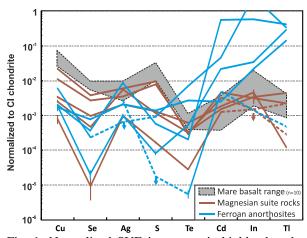


Fig. 1. Normalized SVE in magmatic highland rocks compared to mare basalts (dotted lines when neighboring elements are b.d.l.). Elements are displayed in the order of decreasing 50% condensation temperature from a gas of solar composition [13].

**Results and discussion:** Mass fractions of SVE in all studied samples are in the lower ng/g range except for Se, Cu and S. With these new data we provide the first comprehensive data set for SVE in lunar samples, including Cu and S, determined by isotope dilution from the same digestion aliquot. Furthermore, in comparison to older data, uncertainties on mass fractions, and hence element ratios, are significantly reduced, leading to a better distinction between different processes.

In a chondrite-normalized diagram, SVE in two different low-Ti mare basalt suites display sub-parallel patterns and increasing depletions in the order of S\leq In\leq Se\leq Ag\leq Tl\leq Cd\leq Te when compared to Cu (the least volatile SVE in our study; Fig. 1). Apollo 17 high-Ti mare basalts are higher in S, Se, and Cd, but follow the depletion pattern observed in low-Ti basalts. In general, mass fractions of Cd, In, and Tl in mare basalts are more variable than other SVE, most likely reflecting more volatile behavior. Mass fractions of most SVE in magnesian suite rocks are more variable due to accumulation of silicate phases, but fractionation patterns are very similar to mare basalts, except for Cd, Tl, and sometimes Ag. On average ferroan anorthosites display lower mass fractions of Cu, Se, and S, but are increasingly enriched in Te<Ag<Cd<In<Tl.

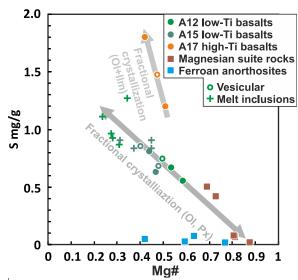


Fig. 2. Mg# (molar Mg/(Mg+Fe) ratio) vs. mass fractions of S in magmatic highland rocks and mare basalts. Olivine hosted melt inclusion data from the literature [6].

Most SVE in magnesium suite rocks and mare basalts display clear relations to indicators of fractional crystallization. For example, the negative correlation of S with Mg# (Fig. 2) can be explained by fractional crystallization of mainly low-Ca pyroxene (magnesian suite), olivine (low-Ti basalts), and olivine + ilmenite (high-Ti basalts). This observation is entirely consistent with the incompatible behavior of SVE in these processes and the notion that lunar mantle-derived magmas did not reach S-saturation during magmatic differentiation [14]. However, these correlations are in conflict with the proposed strong volatile loss of S and other SVE from such magmas [4-7]. Significant degassing of S during ascent and eruption should disturb correlations with lithophile major elements in mare

basalts. Instead, we observe a coherent correlation of S with Mg# in vesicular basalts, non-vesicular basalts, and olivine-hosted melt inclusions (Fig. 2). This observation strongly argues against significant degassing of S, consistent with the limited variability of  $\delta^{34}$ S [15]. Furthermore, a more or less continuous fractional crystallization trend from volcanic low-Ti basalts to plutonic magnesian suite rocks can be explained if sulfur contents in the sources of initial mantle melts were similar. Copper and Se display similar relations between fractional crystallization trends in low-Ti mare basalts and magnesian suite rocks. In mare basalts, mass fractions of Ag, Cd, and partially In, follow similar fractional crystallization trends. Therefore, we argue that depletion of most SVE in mare basalts must have occurred before fractional crystallization.

In ferroan anorthosites mass fractions of SVE are apparently unrelated to fractional crystallization (Fig. 2). Together with the generally much stronger variability of these elements in magmatic highland rocks (Fig. 1), this argues for significant post-magmatic re-enrichment of Cd, In, and Tl in many, and presumably also Ag and Te in some highland samples.

These results demonstrate that precise and accurate SVE data obtained by isotope dilution can reveal important insights into magmatic fractionation processes, some of which are not constrained by lithophile trace elements. Such data also places limits on the magnitude of magmatic degassing of SVE, which might constrain fractionation processes which occurred in the source regions of the magmas or before the mantle sources were formed.

**Acknowledgments:** This work is funded by the German Research Foundation (Project-ID 263649064, TRR 170). Samples were provided by NASA JSC and CAPTEM.

**References:** [1] O'Neill H. S. C. (1991) GCA, 55, 1135-1157. [2] Albarède F. et al. (2015) MAPS, 50, 568-577. [3] Wang K. & Jacobsen S. B. (2016) Nature, 538, 487-490. [4] Chen et al. (2015) EPSL, 427, 37-46. [5] Hauri et al. (2015) EPSL, 409, 252-264. [6] Ni et al. (2019) GCA, 249, 17-41. [7] Bombardieri D. J. et al. (2005) MAPS, 40, 679-693. [8] Ryder G. & Schuraytz B. C. (2001) JGR, 106, 1435-1451. [9] Snyder G. A. et al. (2000) Origin of the Earth and Moon., Canup and Righter (eds), 361-208. [10] Shearer C. K. et al. (2015) Am. Min., 100, 294-325. [11] Warren P. H. (1993) Am. Min., 78, 360-376. [12] Wang Z. et al. (2015) GGR., 39, 185-208. [13] Wood B. J. et al. (2019) Am. Min., 104, 844-856. [14] Day J. M. D. (2018) Am. Min., 103, 1734-1740. [15] Wing B. A. & Farquhar J. (2005) GCA, 170, 266-280.