

**Crystal/silicate melt partitioning of HFSE, Mo, W, U and Th as a function of TiO<sub>2</sub>, with implications for the petrogenesis of lunar mare basalts**

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When compared to terrestrial rocks, some lunar mare basalts show, as specific feature, elevated TiO<sub>2</sub> bulk-rock content, which can reach concentrations as high as 16 wt. % [1,2]. Petrogenetic models that attempt to explain this enrichment require precise knowledge of major and trace elements fractionation under conditions similar to the ones that may have prevailed on the lunar mantle. Previous studies showed that the behavior of the high-field strength elements (HFSE) between Fe-Ti oxides and silicate melt is affected by the amount of TiO<sub>2</sub> in the silicate glass, possibly due to a melt complex consisted of Fe-Ti-O species [3]. Still, there is a scarcity of data on the behaviour of the HFSE between silicates and lunar mare basalts with different TiO<sub>2</sub> contents. To address this issue, the partitioning behaviour of Zr, Hf, Nb, Ta, U, Th, Mo and W between major silicate and oxide phases present in the lunar mantle and silicate melts, was derived from experiments at one atmosphere and 1100-1305 °C under controlled oxygen fugacity (air to IW -1.8). Starting compositions were based on the CFMAS + Ti system and mixed from high purity oxide and carbonate powders. Trace elements were added either as powder or solution to the starting composition in concentrations from 500 to 1,000 µg/g. Crystals and silicate melts were analyzed via EMP and LA-ICP-MS for their major and trace element contents respectively. Results show that  $D_M^{cpx/melt}$  have a strong negative correlation with the TiO<sub>2</sub> in the silicate melt. This behaviour is observed for  $D_{Zr}^{cpx/melt}$ ,  $D_{Hf}^{cpx/melt}$ ,  $D_{Ta}^{cpx/melt}$  and  $D_{Th}^{cpx/melt}$ , and is surprisingly less pronounced for  $D_{Nb}^{cpx/melt}$ . For the  $D_U^{cpx/melt}$ , this trend is also observed for the experiments where U<sup>4+</sup> predominates than U<sup>6+</sup>. The TiO<sub>2</sub> in the silicate glass is proportional to the TiO<sub>2</sub> in the cpx, which reaches concentrations up to 3.1 wt.% and substitutes both into the M1 and the T site. The <sup>IV</sup>Al is no higher than 0.07 apfu, indicating that Ca-Tschermak component was seldom present. Charge balance mechanism is defined by the substitution of Ti<sup>4+</sup> - 2Al<sup>3+</sup>, as already show for lunar pyroxenes [4]. Olivine/silicate melt partition coefficients for the HFSE and Th decrease slightly until ca. 5 wt. % TiO<sub>2</sub>, and after which they remain constant. Elements that are redox sensitive, such as U, Mo and W show a clear difference in their D values depending on fO<sub>2</sub>. These elements are less incompatible at reduced (ca. IW - 1.8) when compared to oxidized environments. Surprisingly,  $D_{HFSE}^{opx/melt}$  does not show any significant change over the range of TiO<sub>2</sub> in the glass in this study, apart from the same behaviour observed in olivine for heterovalent elements. i.e. relatively higher compatibility at lower fO<sub>2</sub>. Armalcolite/ melt partition coefficients show differences depending on the Mg# of armalcolite. For example, Mg-rich armalcolites exhibit higher D values for all elements analysed, with the exception of Th, which is equally incompatible in both end-members. Finally, our new dataset of partition coefficients was used for modeling the trace element pattern of low and high-Ti lunar mare basalts. Our models show that the HFSE elemental ratios and isotopic compositions are only satisfactorily reproduced once the TiO<sub>2</sub> content of silicate melt and oxygen fugacity prevalent during lunar mantle melting are taken into account. Further work is needed to investigate the transition between ilmenite and armalcolite as a function of melt composition, temperature, pressure and oxygen fugacity. This becomes particularly important considering the fact that armalcolite is known to take more Ti<sup>3+</sup> in its structure than ilmenite when found in lunar rocks [5]. One of the study's limitation is the scarcity of empirical data regarding lunar mare basalts, which may lead to a biased view of the TiO<sub>2</sub> contents in the Moon [6]. Nevertheless, our findings coupled with literature data, could be applied quite reliably to the petrogenesis of lunar mare basalts and can hopefully provide a better understanding of the evolution of the Moon.

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