# The effect of titanium on the partitioning behavior of high-field strength elements between silicates, oxides and lunar basaltic melts with applications to the origin of mare basalts

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## ARTICLE INFO

## ABSTRACT

A specific feature of some basaltic lunar rocks is that their $TiO_2$ contents can reach concentrations as high as 16 wt.%. The high-field strength elements (HFSE) group, which includes Ti, may provide valuable information of the processes that occurred in the lunar mantle to generate high-Ti mare basalts. To assess the effect of such high $TiO_2$ concentrations on the partitioning of Zr, Hf, Nb, Ta, U, Th, Mo and W between major silicate and oxide phases and silicate melts, we present results from experiments at one atmosphere and 1100 °C–1305 °C, under controlled oxygen fugacity. With the exception of Nb, all $D_{HFSE}^{cpx/melt}$ show a strong negative correlation with the $TiO_2$ content of the silicate melt. Olivine/Silicate melt partition coefficients for Zr, Hf, Nb, Ta and Th decrease slightly from 0 to ca. 5 wt.% $TiO_2$, above which they remain constant up to ca. 20 wt.% $TiO_2$ in the silicate glass. In addition, redox sensitive elements, i.e. U, Mo, and W show clearly distinct $D_M^{silicates/melt}$ at different $fO_2$, implying that these elements are relatively more compatible at reduced (ca. IW − 1.8) than at oxidized (FMQ and air) environments. Iron-rich and Mg-rich armalcolite show contrasting patterns of $D_M^{crystal/melt}$, with the latter exhibiting slightly higher values of partition coefficient for all analyzed elements, except Th, which is equally incompatible in both end-members. Finally, the new dataset of $D_{HFSE}^{crystal/melt}$ was used to perform simple melting models of the lunar mantle cumulates. Results indicate that to reproduce the fractionation of W from the HFSE, as well as U and Th observed in lunar mare basalts, metal saturation and the presence of Fe–Ti oxides in the mantle sources is required.

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## 1. Introduction

Titanium is generally considered to be a minor element in the Bulk Silicate Earth (BSE: 1265 μg/g – Palme and O'Neill, 2014), with an average of 1.6 wt.% $TiO_2$ for mid-ocean ridge basalts (Gale et al., 2013) and a maximum reported concentration of 5.5 wt.% (Arndt et al., 1995). On the Moon, however, mare basalts show a bimodal distribution with respect to their $TiO_2$ contents, and are subdivided into low- and high-Ti groups, the latter of which can reach concentrations as high as 16 wt.% of $TiO_2$ (e.g., Marvin and Walker, 1978; Meyer, 2012). The main hypotheses that are invoked to account for this extreme $TiO_2$ enrichment include: 1) the assimilation of Fe–Ti bearing minerals when low-Ti basaltic magmas ascended to the Moon's surface (e.g., Liang and Hess, 2006; Liang et al., 2007; Münker, 2010; Dygert et al., 2013) or; 2) mantle overturn after crystallization of a magma ocean, with addition of ilmenite from late-crystallizing mafic cumulates to early, ultramafic–harzburgite cumulates, generating a mixed cumulate source (e.g. Ringwood and Kesson, 1976; Beard et al., 1998). Despite distinct theories for their origin, lunar basalts are thought to be partial melts of a peridotite mantle. As such, understanding their formation may contribute to a better understanding of planetary evolution processes, like the differentiation of the Moon, lunar mantle dynamics, composition and phase stability (Bence et al., 1980; Shearer and Papike, 1993). Therefore, it is crucial to have precise knowledge of how major and trace elements fractionate under different conditions. In particular, it is necessary to understand how the melt composition, namely at high $TiO_2$ contents, may affect trace element partitioning during lunar differentiation and mantle melting.

A variety of factors affect the partitioning of trace elements between crystals and silicate melts. These include crystal composition and structure (e.g., Blundy and Wood, 1994); pressure and temperature (e.g., Adam and Green, 1994); the oxidation state of the magma (e.g., Borisov, 2012; Mallmann et al., 2015); melt structure and

composition (e.g., Mysen, 1990; Prowatke and Klemme, 2005; Dygert et al., 2013). Of all these factors, the effect of melt composition is the least well-constrained, despite of its potential importance in affecting trace element behavior during magmatic processes (cf., Watson, 1976; Ryerson and Hess, 1978). The $TiO_2$ melt content has been shown to affect the exchange of Fe and Mg between olivine and silicate melt ($Kd_{ol-liq}^{Fe-Mg}$ – Longhi et al., 1978; Jones, 1988; Xirouchakis et al., 2001). As $TiO_2$ contents increase, $Kd_{ol-liq}^{Fe-Mg}$ decreases, mostly due to the formation of Fe–Ti–O melt species (e.g., Ferropseudobrookite) which bind Fe and prevent it from substituting into other phases like olivine (Xirouchakis et al., 2001). In this regard, Longhi et al. (1978) expected that this effect would show and influence not only on the partitioning behavior of network forming cations, but also elements that are geochemically similar to Ti, i.e., the extended high-field strength elements group (HFSE – Nb, Ta, Hf, Zr, as well as Mo and W), U and Th. In this sense, Dygert et al. (2013) demonstrated that $D_{HFSE}^{oxide/melt}$ decreases with increasing $TiO_2$ in the melt. However, this effect was observed only for melt $TiO_2$ lower than ca. 7 wt.%. Of particular interest is the behavior of Mo and W, due to the fact that they are simultaneously refractory and moderately siderophile and, hence, are important tracers for planetary evolution including studies of core formation processes (Kleine et al., 2004; O'Neill et al., 2008). Furthermore, both Mo and W, as well as U, are thought to change oxidation state under reducing conditions (e.g., O'Neill and Eggins, 2002; Danielson et al., 2011), which has been shown to dramatically affect their trace element partitioning behavior (Fonseca et al., 2014). Additionally, variations in oxidation state are known to affect phase stability in the lunar mantle sources of mare basalts (e.g., Krawczynski and Grove, 2012; Brown and Grove, 2015), which supports the necessity of further study.

Several studies have been carried out on the partitioning of the HFSE between Fe–Ti oxides (e.g. ilmenite, rutile and armalcolite) and basaltic melts (e.g., McCallum and Charette, 1978; Klemme et al., 2006; Dygert et al., 2013). Nevertheless, a scarcity of data exists for how the HFSE partition between silicates (ol, cpx and opx) and lunar mare basaltic melts as a function of melt composition, namely their $TiO_2$ content. To address this gap in our knowledge, several experiments have been carried out to investigate the partitioning behavior of the HFSE, Mo, W, U and Th between silicates and realistic lunar basaltic melts.

## 2. Experimental methods

### 2.1. Starting materials

Starting compositions were based on the work of Longhi (1987) and Mallmann and O'Neill (2009) (Table 1). At one atmosphere, the base mixture of each composition, which contains around 1 wt.% $TiO_2$, results in silicate melt, olivine (forsterite) and an additional phase, either cpx (1), opx (5), chromite or Cr-diopside (7) and plagioclase or Al-spinel (8) (Mallmann and O'Neill, 2009). Several compositional series were carried out in either the CMAS + $TiO_2$ or the CFMAS + $TiO_2$ systems, modifying the base compositions by adding ca. 1 to 20 wt.% $TiO_2$. In four series, Fe was only added in trace amounts (ca. 0.1 to 0.5 wt.%), while in a fifth series, FeO contents similar to those observed in lunar basalts (ca. 20 wt.% - Meyer, 2012) were added to the starting compositions. The rationale behind this strategy was to test whether a Fe–Ti complex was indeed responsible for the reported differences in HFSE behavior (Dygert et al., 2013). Moreover, the CMAS + $TiO_2$ system was chosen as an analogue for lunar basalts to avoid, at an initial stage, any potential redox interaction between FeO and $TiO_2$ during quenching (Borisov et al., 2013). In addition, the CMAS + $TiO_2$ system is thought to be a good proxy for most known basaltic compositions as it stabilizes major mineral phases of the upper mantle (Liu and O'Neill, 2007). The proportion $SiO_2/TiO_2$ for the compositions with 5, 10 and 20 wt.% $TiO_2$ was established in relation to the binary anorthite-diopside as in O'Neill et al. (2008), while the ratio between

other major elements and $SiO_2$ remained constant in order to decrease the effect of other variables.

High-purity oxide powders ($SiO_2$, MgO, $Al_2O_3$, $Fe_2O_3$ and $TiO_2$) were ground with $CaCO_3$ under acetone in an agate mortar until homogenized. Chromium was added as Specpure plasma standard solution of 10,000 µg/mL $Cr(NO_3)_3$ in 5% $HNO_3$ and P was added as 1000 µg/mL solution in 5% $HNO_3$. Starting powder mixes were subsequently dried, pressed into pellets and placed in a corundum crucible inside a vertical tube furnace to decarbonate overnight in air at 1 bar and 950 °C. All pills were then re-ground under acetone and trace elements were added to the powders, in amounts of 500 to 1000 µg/g, as oxides (Nb, Ta, Zr, Hf) as well as using 1000 µg/mL PlasmaCal standard solutions in $HNO_3$ (U and Th) and $H_2O$ (Mo and W). Barium (as $BaCO_3$ - 1000 µg/g) and Mn (as MnO - ca. 1 wt.%) were also added to some of the starting compositions. Barium was added as a tracer for evaluating the presence of melt inclusions in the crystals during LA-ICP-MS analysis (e.g., Lundstrom et al., 1994; Mollo et al., 2013). Manganese was added for use as an internal standard during LA-ICP-MS analysis (following Dygert et al., 2013). Crystal seeds were added to some starting compositions (labeled "S", i.e. "seeded") to promote crystal growth at run conditions. These seeds consist of pyroxene grains (Wo: 50%, En: 34% and Fs: 16%) collected at the summit of Vesuvius, Italy. Finally, two extra mixtures were produced using as a starting point the composition labeled "T1", with 0% and 10% $TiO_2$ and doped with rare-earth elements (La, Nd, Sm, Y and Lu) in addition to the HFSE, to constrain the crystal lattice strain model for olivine.

### 2.2. Experimental setup

Loops were made from either Pt or Re wire for experiments carried out using Fe-poor and Fe-rich compositions, respectively. Sample powders were mixed with water and polyethylene glycol to form a slurry that was placed on the loops. The metal loops + slurry were then hung in the hot spot of a furnace and fused at high-temperature. Loops were then suspended inside a vertical tube muffle furnace at temperatures between 1350 and 1400 °C, i.e., around 50 °C to 100 °C above the expected supraliquidus and under redox conditions imposed by a gas atmosphere (CO–$CO_2$ – Supplementary Table 1). Each sample remained at supraliquidus conditions for 3 to 5 h to ensure that powders were completely molten and homogenized. Cooling ramps were chosen, via trial and error, to maximize crystal growth, so that they were suitable for LA-ICP-MS analysis, to avoid any chemical zonation and to mitigate the development of skeletal crystals.

To address the potential role that $fO_2$ plays in affecting the partitioning behavior of elements like Mo, W, U, and Ti in the experiments, $fO_2$ was varied between the value of air (i.e., around log $fO_2 = -0.7$) and to ca. two orders of magnitude more reducing than the iron-wüstite redox equilibrium ($\Delta IW -2$, Myers and Eugster, 1983). These low $fO_2$ values for are in agreement to what is expected for the lunar mantle, which varies from IW +0.2 to −2.5 (Papike et al., 2005). Oxygen fugacity of each experiment was established by mixing CO–$CO_2$ in different proportions using Mykrolis mass flow controllers. The amount in SCCM (Standard Cubic Centimeters per Minute) required for the equilibrium gas species fugacities at 1 bar was calculated using an Excel macro as described in Kress et al. (2004) at the target temperature of each run. The effective values of $fO_2$ inside the furnaces were checked and calibrated using a $CaO-Y_2O_3$-stabilized $ZrO_2$ electrolite cell (see Chase, 1998; Laurenz et al., 2010). The determined $fO_2$ values were found to be within 0.6 log-bar units of the calculated values.

A significant challenge in carrying out experiments with FeO-bearing silicate melts is the loss of Fe into a metal wire or capsule (Borisov and Palme, 2000). To avoid this issue we pre-saturated Pt loops with Fe by pre-equilibrating them with a FeO-rich silicate melt (a K-rich lava from the Eastern Mediterranean – Kirchenbaur et al., 2012) at the relevant $fO_2$ of the experiment. Under more reducing