

TRACE ELEMENT EVOLUTION DURING LUNAR MAGMA OCEAN CRYSTALLISATION. Mirjam van Kan Parker¹, Paul Mason², Axel Liebscher^{3,4}, Dirk Frei^{4,5}, Jelle van Sijl¹, Jon Blundy⁶, Gerhard Franz³, Wim van Westrenen¹. ¹Faculty of Earth and Life Sciences, VU University Amsterdam, The Netherlands, ²Faculty of Geosciences, Utrecht University, The Netherlands, ³Institut für Angewandte Geowissenschaften, Technische Universität Berlin, Germany, ⁴GFZ German Research Centre for Geosciences, Germany, ⁵Geological Survey of Denmark and Greenland (GEUS), Denmark, ⁶CETSEI, Department of Earth Sciences, University of Bristol, United Kingdom. (mirjam.van.kan@falw.vu.nl).

Introduction: The presence of a lunar magma ocean (LMO) [1] early after lunar accretion has important implications for the subsequent thermal and chemical evolution of the Moon. Quantifying major and trace element incorporation behaviour of minerals at different conditions during lunar magma ocean (LMO) crystallisation is essential to constrain lunar evolution models. Depending on the initial lunar bulk composition [2, 3] the crystallisation sequence of the LMO is thought to be: olivine, orthopyroxene, plagioclase, clinopyroxene, and ilmenite.

The mineral-melt partitioning behaviour for most of these minerals has been studied experimentally over the past decades, but most studies focused on applications to terrestrial rather than lunar compositions. In addition, although it is well known that trace element partitioning between equilibrium phases depends on pressure, temperature, composition and oxygen fugacity (P - T - x - fO_2), currently available mineral-melt partitioning data often do not systematically consider these parameters. As a result, no predictive model for the lunar interior evolution of major and trace elements is available. We have obtained new experimental results on orthopyroxene-melt and ilmenite-melt partitioning of direct relevance to LMO crystallisation.

Orthopyroxene (Opx) is the second phase crystallising from the LMO after olivine. Although in terrestrial applications its contribution is often thought to be minor because of its relative low partition coefficients compared to clinopyroxene, it plays an important role in early LMO crystallisation.

Trace element partitioning between Opx and anhydrous silicate melts was studied by a combination of experiments and computational techniques [4]. Experiments were performed in air at atmospheric pressure and temperatures ranging from 1,326 to 1,420 °C in the system CaO-MgO-Al₂O₃-SiO₂ and subsystem CaO-MgO-SiO₂. Additional experiments in the Cr₂O₃-CaO-FeO-MgO-Al₂O₃-TiO₂-SiO₂ (CCFMATS) were carried out, using graphite-lined Pt capsules, at elevated pressure ranging from 1.0 to 2.8 GPa and temperatures from 1,400 to 1,600 °C (Fig. 1). We determined D 's for a wide range of trace elements (LILE, REE, HFSE and transition metals). In the CMAS system, REE partition coefficients increase from

$D_{La}^{opx-melt} \sim 0.0005$ to $D_{Lu}^{opx-melt} \sim 0.109$, D values for highly charged elements vary from $D_{Th}^{opx-melt} \sim 0.0026$ through $D_{Nb}^{opx-melt} \sim 0.0033$ and $D_U^{opx-melt} \sim 0.0066$ to $D_{Ti}^{opx-melt} \sim 0.058$, and are all virtually independent of temperature. The partitioning behaviour of Opx is also found to be generally unaffected by pressure.

To elucidate charge-balancing mechanisms for incorporation of REE into Opx, and to assess the possible influence of Fe on Opx-melt partitioning, we compared our experimental results with computer simulations. In these simulations we examined major and trace element incorporation into the Opx end-members enstatite (Mg₂Si₂O₆) and ferrosilite (Fe₂Si₂O₆). Calculated solution energies show that R²⁺ cations are more soluble in Opx than R³⁺ cations of similar size, consistent with experimental partitioning data. In addition, simulations suggest that charge-balancing of R³⁺ cations by coupled substitution with Li⁺ on the M1 site is energetically favoured over coupled substitution involving Al-Si exchange on the tetrahedrally coordinated site. To test this model we are performing experiments with identical experimental conditions and starting compositions, where one of the compositions is doped with Li and the other one is Li-free.



Figure 1. BSE images of Opx-melt partitioning experiments, producing Opx, olivine and melt (1.1 GPa and 1430 °C), a) was doped with Li and b) was not.

Using the Blundy and Wood [5] lattice strain model of mineral-melt partitioning, we derived best-fit values for ideal ionic radii r_0 , maximum partition coefficients D_0 , and apparent Young's moduli E for substitutions onto the Opx M1 and M2 lattice sites. Simulations indicate that ferrosilite r_0 values are systematically larger by ~ 0.05 Å for both M1 and M2 lattice sites. The latter is opposite to experimental data, which appear to show a slight decrease in r_0^{M2} in the presence of Fe (Fig. 2 [4]).

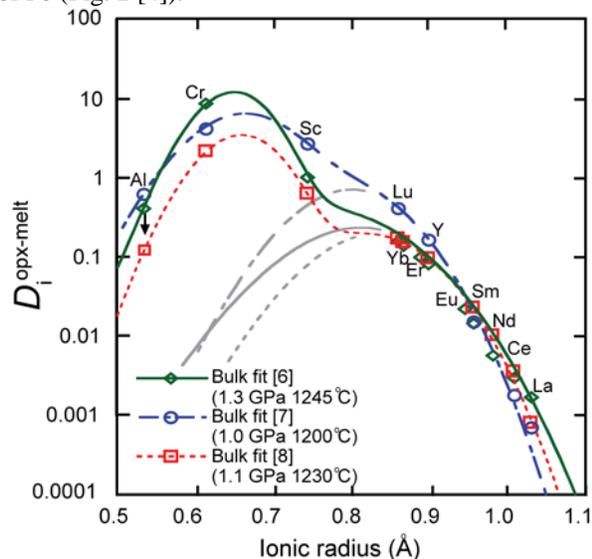


Figure 2. Comparison of Opx-melt partition coefficient data of two Fe-bearing studies [6, 7] with an experiment in the Fe free system [8] under similar conditions. Coloured lines show fits of the data to the lattice strain model [5].

Ilmenite (Ilm) is the main titanium-bearing, oxide mineral on the Moon and plays a relatively minor role in terrestrial magmatic processes. However, it did play a crucial role in the late stages of LMO crystallisation and subsequent mare basalt formation [2, 3].

We performed systematic high-pressure, high-temperature ilmenite-melt partitioning experiments in the CaO-FeO-MgO-Al₂O₃-TiO₂-SiO₂ (CFMATS) system to study the mineral-melt partitioning behaviour of Ilm. Starting materials were doped with a wide range of trace elements (LILE, REE, HFSE and transition metals). Experiments were carried out at elevated pressures, ranging from 1.0 GPa to 1.7 GPa, using graphite-lined Pt capsules (Fig. 3).

Our results show that transition metals are generally compatible at pressures between 1.0 and 1.7 GPa and 1565 ± 23 K, with Cr having the highest partition coefficient ($D \sim 6$), followed by V ($D \sim 3.5$). Mn and Co have D values near 1. The HFSE are moderately incompatible at elevated pressures, with partition coefficients of 0.11-0.54. The REE are all incompatible,

with HREE D values of 0.06 ± 0.03 , and LILE D values are all < 0.004 . No clear pressure effect on D values is identified in this pressure range for any element, with the possible exception of uranium.

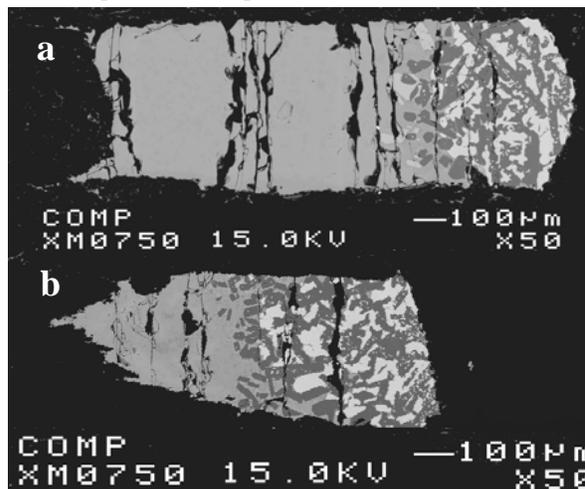


Figure 3. BSE images of Ilm-melt partitioning experiments, a) producing Ilm, Opx, armalcolite and melt (1.4 GPa and 1305 °C), b) producing Ilm, Opx and melt (1.7 GPa and 1315 °C).

Our experiments show that ilmenite is efficient at fractionating 'geochemical twin' HFSE pairs, with $D_{\text{Ta}} > D_{\text{Nb}}$ and $D_{\text{Hf}} > D_{\text{Zr}}$. Contrary to major terrestrial mantle minerals garnet and cpx, D_{Nb} and D_{Ta} are higher than D_{Zr} and D_{Hf} by a factor of ~ 3 . Ilmenite fractionates Hf from W, to the same extent as cpx ($D_{\text{Hf}} / D_{\text{W}} \sim 5$), but with lower absolute D values. Our data are used to model the evolution of HFSE budgets in the main lunar reservoirs during the later stages of magma ocean crystallisation and subsequent mare basalt formation.

During the meeting implications of our new data sets for Opx-melt and Ilm-melt partitioning will be discussed, focusing on the HFSE and REE evolution of the LMO during progressive fractional crystallisation.

References: [1] Warren P. H. (1985) *An. Rev. Earth Planet. Sci.*, 13, 201-240. [2] Synder G. A. et al. (1992) *Geoch. Et Cosm. Acta*, 56(10), 3809-3823. [3] Shearer C. K. and Papike J. J. (1999), *AM*, 84, 1469-1494. [4] van Kan Parker et al. M, (2009) *Contrib. Mineral. Petrol. Online only*. [5] Blundy and Wood (1994) *Nature* 372, 452-454 [6] McDade et al. P. (2003) *Am Miner* 88, 1825-1831. [7] Klemme S. et al. (2006) *Chem. Geol.* (234), 251-263. [8] Frei D. et al. (2009) *Contrib. Mineral. Petrol.* (157), 473-490.