Trace element partitioning between ilmenite, armalcolite and anhydrous silicate melt: Implications for the formation of lunar high-Ti mare basalts

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Abstract

We performed a series of experiments at high pressures and temperatures to determine the partitioning of a wide range of trace elements between ilmenite (Ilm), armalcolite (Arm) and anhydrous lunar silicate melt, to constrain geochemical models of the formation of titanium-rich melts in the Moon. Experiments were performed in graphite-lined platinum capsules at pressures and temperatures ranging from 1.1 to 2.3 GPa and 1300–1400 °C using a synthetic Ti-enriched Apollo ‘black glass’ composition in the CaO–FeO–MgO–Al 2O 3–TiO 2–SiO 2 system. Ilmenite–melt and armalcolite–melt partition coefficients (D) show highly incompatible values for the rare earth elements (REE) with the light REE more incompatible compared to the heavy REE (D Ilm–melt La 0.0020 ± 0.0010 to D Ilm–melt Lu 0.069 ± 0.010 for ilmenite; D Arm–melt La 0.0048 ± 0.0023 to D Arm–melt Lu 0.041 ± 0.008 for armalcolite). D values for the high field strength elements vary from highly incompatible for Th, U and to a lesser extent W (for ilmenite: D Ilm–melt Th 0.0013 ± 0.0008, D Ilm–melt U 0.0035 ± 0.0015 and D Ilm–melt W 0.039 ± 0.005, and for armalcolite D Arm–melt Th 0.008 ± 0.003, D Arm–melt U 0.0048 ± 0.0022 and D Arm–melt W 0.062 ± 0.03), to mildly incompatible for Nb, Ta, Zr, and Hf (e.g. D Ilm–melt Hf 0.28 ± 0.05 and D Arm–melt Hf 0.76 ± 0.07). Both minerals fractionate the high field strength elements with D Ta/D Nb and D Hf/D Zr between 1.3 and 1.6 for ilmenite and 1.3 and 1.4 for armalcolite. Armalcolite is slightly more efficient at fractionating Hf from W during lunar magma ocean crystallisation, with D Hf/D W = 12–13 compared to 6.7–7.5 for ilmenite. The transition metals vary from mildly incompatible to compatible, with the highest compatibilities for Cr in ilmenite (D ∼7.5) and V in armalcolite (D ∼8.1). D values show no clear variation with pressure in the small range covered.

Crystal lattice strain modelling of D values for divalent elements prefer to substitute for Fe while armalcolite data suggest REE replacing Mg. Tetravalent cations appear to preferentially substitute for Ti in both minerals, with the exception of Th and U that likely substitute for the larger Fe or Mg cations. Crystal lattice strain modelling is also used to identify and correct for very small (<0.3 wt.%) melt contamination of trace element concentration determinations in crystals.

Our results are used to model the Lu–Hf–Ti concentrations of lunar high-Ti mare basalts. The combination of their subchondritic Lu/Hf ratios and high TiO 2 contents requires preferential dissolution of ilmenite or armalcolite from late-stage, lunar magma ocean cumulates into low-Ti partial melts of deeper pyroxene-rich cumulates.

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1. INTRODUCTION

The elemental and isotopic compositions of the main rock suites on the lunar surface are commonly interpreted in the general framework of the lunar magma ocean (LMO) model (Smith et al., 1970; Wood et al., 1970). This
model invokes the presence of a compositionally and mineralogically layered interior early in the evolution of the Moon, formed by cooling and crystallisation of a global magma ocean (e.g. Snyder et al., 1992; Shearer et al., 2006; Elardo et al., 2011).

In the context of the LMO model, lunar mare basalts are thought to be partial melts of layered mantle cumulates. For example, trace element depleted basalts are interpreted to originate from deep, early-formed olivine- and pyroxene-bearing cumulates that sank to the bottom of the LMO (e.g. Münker, 2010; van Kan Parker et al., 2011 and references therein). Uniquely Ti-rich basalts, with TiO₂ contents up to ~14 wt.% (e.g., Neal and Taylor, 1992; Shearer et al., 2006), have also been interpreted in the framework of the LMO model, by invoking a role for late-stage LMO cumulates rich in the Ti-rich mineral ilmenite (nominally (Fe,Mg)TiO₃) and/or armalcolite ((Fe,Mg)₂TiO₅) in their genesis (e.g. Longhi, 1992; Snyder et al., 1992; Shearer et al., 1996, and references therein). Ilmenite is also a possible candidate for causing the observed fractionation of W from Hf during lunar magma ocean crystallisation (e.g. Shearer and Papike, 1999; Lee et al., 2002; Klemme et al., 2006).

Petrological modelling and high-pressure experiments show that ilmenite and armalcolite are indeed expected to become stable phases during the latest stages of LMO crystallisation (Snyder et al., 1992; Thacker et al., 2009). Their presence at relatively shallow levels combined with their relatively high density (e.g. Tronche et al., 2010) is thought to have resulted in a gravitationally unstable mineral stratification in the lunar mantle, inducing a mantle overturn that triggered significant mare basalt formation (e.g. Elkins-Tanton et al., 2002; Hess and Parmentier, 1995; de Vries et al., 2010).

Although the involvement in ilmenite and/or armalcolite in high-Ti basalt generation is fully accepted, the processes leading to the Ti enrichment are subject to debate (e.g. Shearer and Papike, 1999; Elkins-Tanton et al., 2002; Münker, 2010). Some models propose direct melting of ilmenite-rich cumulates after convective mantle overturn (e.g. Ringwood and Kesson, 1976; Hess and Parmentier, 1995; Beard et al., 1998). Other scenarios involve hybridization of low-Ti melts by assimilation of ilmenite/armalcolite and clinopyroxene-rich cumulates (e.g., Hubbard and Minear, 1975; Wagner and Grove, 1997; Liang et al., 2007; Liang and Hess, 2008).

Geochemical models attempting to identify the roles of these different processes in high-Ti basalt formation (e.g. Münker, 2010) require accurate knowledge of major and trace element partitioning between ilmenite, armalcolite, and lunar melts during partial melting and crystallisation processes at high pressure (P) and temperature (T) conditions. Previously published studies reporting ilmenite–melt and/or armalcolite–melt partition coefficients (D, defined as the ratio by weight between elemental concentrations in mineral and co-existing melt) show large variations in measured D values, varying up to three orders of magnitude for ilmenite and one order of magnitude for armalcolite (Green et al., 1971; McKay and Weill, 1976; Palme and Wlotzka, 1977; Irving et al., 1978; Fujimaki and Tatsumoto, 1984; McKay et al., 1986; Nakamura et al., 1986; Candela and Bouton, 1990; LaTourrette et al., 1991; Stimac and Hickmott, 1994; Zack and Brumm, 1998; Righter and Shearer, 2003; Klemme et al., 2006).

These variations, that must be related to a combination of the range of natural and synthetic compositions (x) used, and differences in the P, T and oxygen fugacity (fO₂) conditions applied, make it very difficult to identify appropriate D values for petrogenetic modelling of lunar melting and crystallisation processes involving these minerals. The lack of systematic data specifically tailored to lunar P–T–x conditions also precludes development of predictive partitioning models for use in studies of lunar petrogenesis. Here we present a series of ilmenite–melt and armalcolite–melt partition coefficients for large ion lithophile elements (LILE) Li and Ba; rare earth elements (REE), La, Ce, Nd, Sm, Eu, Er, Tm, Y, Yb, and Lu; high field strength elements (HFSE) Zr, Nb, Hf, Ta, Th and U; and transition metals Sc, V, Mn, Co, Cu, and Mo, derived from experiments performed in a synthetic lunar basaltic composition at temperatures between 1300 and 1400 °C, P between 1.1 and 2.3 GPa and relatively reducing conditions. The wide range of trace elements that were added allows us to assess the applicability of the crystal lattice strain model (Blundy and Wood, 1994) to ilmenite–melt and armalcolite–melt partitioning data, providing a step towards the development of fully predictive partitioning models. We illustrate the relevance of our new data by assessing the roles of ilmenite and armalcolite in determining the Lu–Hf–Ti concentrations of high-Ti lunar mare basalts.

2. METHODS

2.1. Experimental and analytical techniques

Experiments were performed in the CaO–FeO–MgO–Al₂O₃–TiO₂–SiO₂ system (CFMATS). The starting mixture and experimental P–T conditions were guided by the study of Beck and Hess (2004), who mapped the solubility of ilmenite in a synthetic high-Ti Apollo red glass. Our starting mixture (Table 1) was chosen to be a synthetic Ti-enriched high-Ti Apollo black glass equivalent (Delano, 1986).

The starting material was prepared by mixing appropriate amounts of high purity (99.5–99.99%, Alfa Aesar) powdered oxides (MgO, Fe₂O₃, Al₂O₃, TiO₂, SiO₂) and CaCO₃ (99.5–100.05%, Alfa Aesar). The oxides MgO, Al₂O₃, TiO₂ and SiO₂ were fired overnight at 1000 °C prior to use to drive off residual moisture, and subsequently stored at 110 °C, as were Fe₂O₃ and CaCO₃. After mixing the starting material under ethanol in an agate mortar for 1 h, it was dried in air and decarbonated in a Pt crucible in a box furnace by gradually raising T from 650 to 1200 °C over 7.5 h. The Pt crucible had previously been iron-saturated to minimize Fe loss during starting composition preparation. The mixture was subsequently melted at 1550 °C for 10 min and quenched by immersing the bottom of the Pt crucible in water. A small chip of the resulting glass was embedded in epoxy, polished, carbon coated and analysed for homogeneity by electron microprobe.
The glass was ground under ethanol in an agate mortar for 1 h and doped with varying amounts of the LILE Li and Ba; the REE La, Ce, Nd, Sm, Eu, Er, Tb, Y, Yb, and Lu; the HFSE Zr, Nb, Hf, Ta, Th and U; and transition metals Sc, V, Mn, Co, Cu, and Mo, using 1000 ppm atomic absorption spectroscopy (AAS) standard solutions. The total amount of added trace elements was <0.25 wt.% for all other experiments. The resulting mixture was remelted for 10 min at 1550 °C to promote starting material homogeneity for major and trace elements. The starting material was ground under ethanol one final time for 1 h in an agate mortar, dried in air and stored at 110 °C.

Table 2 gives an overview of experimental conditions used in this study. High P–T experiments were conducted in an end-loaded piston-cylinder (PC) at the Faculty of Earth and Life Sciences, VU University Amsterdam, using a ½ in. diameter talc-Pyrex cell assembly. The assembly was calibrated via the albite to jadeite plus quartz and fayalite to ferrosilite plus quartz transitions at 1000 °C, resulting in a pressure correction due to friction of 3% and pressure uncertainty of 0.1 GPa. A hand-machined graphite bucket, with an ID of 0.7 mm, OD of ~1.7 mm and length of 3–4 mm, was filled, closed with a graphite lid and inserted in a Pt capsule, with an ID of 1.7 mm, OD 2.0 mm, and length of 5–7 mm. The bottom of the Pt capsule was triple cramped, flattened and welded shut at one end, after the graphite capsule was inserted the other end was cramped and welded shut using a Lampert PUK 3 welder. Before closing and welding shut, the capsules were held at 575 °C for ~10 min to drive off residual moisture.

A Pt-graphite double capsule was chosen to impose a relatively low oxygen fugacity (fO2) of approximately 1.5 log units above the iron–wüstite buffer (IW + 1.5, Médard et al., 2008), reasonably close to fO2 estimates for the lunar mantle (~ IW-0.6, Nicholls and Rutherford, 2009). Oxygen fugacity has been shown to affect phase relations in lunar mantle compositions (e.g. Krawczynski and Grove, 2008), and can influence mineral–melt partitioning behaviour by affecting the dominant valence state of multivalent elements such as Eu, Fe, Cr, Ti, and V (e.g. Papke et al., 2005), by enabling or disabling coupled substitutions that accompany heterovalent substitutions in mineral structures (for example those involving Fe3+).

T was monitored and controlled during experiments using a W57Re3-W25Re75 (type D) thermocouple and Eurotherm 2404 controller, with a resulting T uncertainty of ±3°C. The centre of the sample was located in the hotspot of the assembly, ~2 mm away from the thermocouple tip end. This ensured T in all parts of the samples to remain within 10 °C of the thermocouple readings (Watson et al., 2002). The ‘hot piston in’ technique was used to bring the sample to the desired P–T conditions. Experiments were terminated by shutting off the power to the furnace.

Experimental run products were mounted in epoxy resin, polished and carbon coated for electron microprobe analysis. Glasses and crystals were analysed for major elements with a JEOL JXA 8800M electron microprobe at VU University Amsterdam. The accelerating voltage was 15 kV at a beam current of 25 nA. For the glass analysis we used a defocused beam of 10 μm diameter. A focused beam of 0.5 μm diameter was used for the mineral phases. Analyses were calibrated against primary standards diopside (Mg, Si, Ca), ilmenite (Ti, Fe), and corundum (Al). A natural MORB glass (for Mg, Al, Si, Ca and Fe), diopside (for Mg, Ca, and Al) and ilmenite (for Ti) were used

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dependence of log(D) of isovalent elements on cation radius, as first observed by Onuma et al. (2005).

Trace element concentrations in crystals and glasses in experiments that contained >50% by mass of silicate melt were determined by laser ablation inductively coupled mass spectrometry (LA-ICP-MS) at Utrecht University. The LA-ICP-MS system consists of a 193-nm GeoLas 200Q Excimer laser ablation system (Günther et al., 1997) coupled to a Thermo Finnigan Element 2 sector field ICP-MS instrument, operated in low-resolution mode. Samples were ablated to produce 20 or 30 µm diameter craters, dependent on crystal size. Trace element concentrations of the glasses were measured in 5–8 different spots. Five or six laser ablation spots were located on Ilm–Gk crystals and four or five on Arm crystals. Mixing between mineral and melt phases during laser ablation analysis was monitored using LREE concentrations and results that were clearly affected by mixing (due to poor targeting of the laser beam) were discarded. Measurements were also discarded when crystals could only be analysed for less than 10 s, i.e. when crystals proved to be too thin and too few laser scans could be used for averaging the values, resulting in large standard deviations for individual measurements.

A constant fluence of 5 J cm⁻² was used with a pulse repetition rate of 5 Hz for both glass and co-existing minerals. Calibration was performed against NIST SRM 610 glass using the published values of Pearce et al. (1997). Ti concentrations as obtained by electron microprobe were used as internal standard. The following isotopes were measured: ⁴⁰Sc, ⁴¹Ti, ⁵¹V, ⁵³Cr, ⁵³Mn, ⁵⁹Co, ⁶¹Cu, ⁸⁸Y, ⁹⁰Zr, ⁹³Nb, ⁹⁵Mo, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴⁵Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁶⁷Yb, ¹⁷⁵Lu, ¹⁷⁹Hf, ¹⁸¹Ta, ¹⁸²W, ²³⁵Th and ²³⁸U, with typical ablation times of 60 s. Background intervals of 60 s were measured before and after ablation of the sample. Trace element concentrations determined for the USGS glass external standard Columbia River Basalt BCR2-G during our analytical sessions were typically within 20% of recommended values, as suggested in the GeoBCR2-G during our analytical sessions were typically within 20% of the concentrations reported by Dorrit et al., 2009 (Fig. 1). Both Fe/Mg and Ti lattice sites are sixfold coordinated. Armalcolite (space group: Bbmm) is a solid solution between ferropseudobrookite (FeTi₂O₅) and karrooite (MgTi₂O₅). Armalcolite has the pseudobrookite structure, made up of bands of distorted edge-sharing octahedra (e.g. Smyth, 1974) and is also characterised by two lattice sites referred to as the M₁ site (occupied by Mg/Fe) and the M₂ site (occupied by Ti), which are both sixfold coordinated. Sixfold coordinated radii of all elements were taken from Shannon (1976). Experimental results for nominally M⁵⁺, M⁶⁺ and M⁷⁺ cations were fitted to Eq. (1), using a non-linear least square Levenberg–Marquardt fitting routine (Press et al., 1992). Data were weighted using the standard deviation on D as weighting factor and minimising χ² = ∑[(Dᵢ - Dᵢ) / Dᵢ]².

3. RESULTS

3.1. Run products and evidence for equilibrium

Run products are listed in Table 2, and major element compositions of the co-existing mineral and melt phases are given in Table 3. An overview of the resulting phase assemblages at run conditions is shown in Fig. 1, with back-scattered electron images of run products shown in Fig. 2. Armalcolite co-exists with ilmenite and orthopyroxene at 1.1 GPa – 1300 °C and 1.4 GPa – 1305 °C (Fig. 1). Consistent with previous studies (Friel et al., 1977; Thacker et al., 2009) we find that at P > 1.4 GPa armalcolite is no longer stable. In five of the eight experiments (at pressures of 1.1 and 2.3 GPa) either no Ilm or Arm crystals were present (with rutile becoming the stable high-Ti phase towards higher P and T), or temperatures were so close to the solidus for this composition that the resulting low melt fraction (<15 wt.%) was mostly present in small melt pockets, precluding reliable D determinations.

With increasing P rutile co-exists with Ilm, orthopyroxene (Opx) and/or clinopyroxene. In the experiments at 2.3 GPa at T > 1325 °C clinopyroxene and Ilm are no longer stable. At T > 1350 °C the modal abundance of rutile decreases significantly and at 1400 °C Ti is distributed between the silicate melt and co-existing Opx.

Titanium-rich crystals are euhedral to subhedral and varied considerably in size within and between experiments with diameters between 10 and 100 µm. Orthopyroxene
Summary of microprobe analyses (wt.%) of selected experiments, \( n \) is number of microprobe analysis. Other abbreviations are as in Table 2. Rutile was not analysed.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Mineral</th>
<th>( n )</th>
<th>SiO(_2)</th>
<th>TiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ilm</td>
<td>8</td>
<td>0.03(2)</td>
<td>57.9(2)</td>
<td>0.66(2)</td>
<td>32.3(1)</td>
<td>10.2(1)</td>
<td>0.11(3)</td>
<td>101.2(2)</td>
</tr>
<tr>
<td></td>
<td>Arm</td>
<td>11</td>
<td>0.14(1)</td>
<td>73.3(5)</td>
<td>2.30(11)</td>
<td>15.8(1)</td>
<td>8.9(8)</td>
<td>0.17(7)</td>
<td>100.6(4)</td>
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<tr>
<td></td>
<td>Opx</td>
<td>9</td>
<td>55.0(4)</td>
<td>1.69(17)</td>
<td>1.69(25)</td>
<td>13.2(3)</td>
<td>28.1(4)</td>
<td>1.52(17)</td>
<td>102.1(1)</td>
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<td>2</td>
<td>Melt</td>
<td>21</td>
<td>35.9(6)</td>
<td>20.0(7)</td>
<td>6.21(29)</td>
<td>20.4(3)</td>
<td>8.9(27)</td>
<td>9.6(27)</td>
<td>101.1(2)</td>
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<td>57.0(2)</td>
<td>0.78(2)</td>
<td>32.3(2)</td>
<td>10.4(1)</td>
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<td>2.65(3)</td>
<td>16.0(3)</td>
<td>8.9(11)</td>
<td>0.13(9)</td>
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<tr>
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<td>54.3(7)</td>
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<td>1.97(23)</td>
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<td>7.17(88)</td>
<td>9.68(20)</td>
<td>100.1(6)</td>
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</tbody>
</table>

Numbers in parentheses indicate one standard deviation (1σ) of replicate analyses in terms of last significant numbers: 0.03(2) should be read as 0.03 ± 0.02.

crystals generally also enclosed minute Ilm crystals, and showed poorly defined crystal faces.

Electron microprobe analyses of core–rim transects across grains revealed no major or minor element zonation. Small standard deviations of measurements in both minerals and melts (Table 3) show insignificant crystal-to-crystal compositional variations. The ilmenite crystals formed in the experiments were solid solutions between compositional end-members ilmenite (FeTiO\(_3\)) and geikielite (Gk; MgTiO\(_3\)) and are hereafter referred to as Ilm–Gk. Most lunar ilmenites are also Ilm–Gk solid solutions (e.g. Lucey et al., 2006). Mineral major element compositions do not vary significantly across the relatively limited \( P–T \) range covered in this study. At \( P = 1.1 \) GPa, \( T = 1300 \) °C, Ilm–Gk with composition Ilm\(_{64.6}\)Gk\(_{36.0}\) coexists with Opx, En\(_{76.6}\)Fs\(_{20.2}\)Wo\(_{3.0}\). At \( P = 1.4 \) GPa, \( T = 1305 \) °C, Ilm\(_{63.6}\) Gk\(_{36.4}\) coexist with En\(_{73.5}\)Fs\(_{21.0}\)Wo\(_{5.5}\) and finally at \( P = 1.7 \) GPa, \( T = 1315 \) °C, Ilm\(_{61.2}\)Gk\(_{38.8}\) coexists with En\(_{73.5}\)Fs\(_{22.1}\)Wo\(_{4.4}\).

Glasses were transparent and free of inclusions and bubbles. Locally the melt showed a slightly quenched texture (darker areas/spots in Fig. 2). Multiple laser ablation analyses both within larger individual Ilm–Gk and Arm grains, and in different crystals in a single run product resulted in comparable trace element concentrations, with no significant core to rim variations or within-sample heterogeneity, suggesting a close approach to equilibrium.

Additional evidence for major and trace element equilibration in our experiments comes from the results of a preliminary experiment identical in run conditions and run duration to experiment 3, that used a starting composition identical in major and minor element abundances to the composition used in experiments 1–8, but doped with lower concentrations of trace elements. Laser ablation analysis of the phases in this preliminary experiment revealed that concentrations of most trace elements in the resulting Ilm–Gk and Arm crystals were below detection limit, causing us to repeat the experiment at the higher doping levels reported here. However, doping levels in the preliminary experiment were sufficient to obtain precise Arm–melt \( D \) values for V, Cr, Zr, Nb and Ta. Resulting major, minor and trace element partition coefficients in this experiment are identical within 1–2σ to the results of experiment 3, providing strong evidence for equilibration.

This result is consistent with the results of previous time series studies of silicate mineral–silicate melt partitioning performed in several laboratories. Mysen et al. (2004) and Mysen and Shang (2005) showed that 24 h is sufficient to reach equilibrium for both major and trace elements at 1350–1400 °C in olivine–melt systems at 1 atm. Pertermann et al. (2004) reported no significant difference in garnet–melt trace element partitioning data in experiments at 1350 °C lasting 4, 15 or 24 h in a similar synthetic system at a pressure of 3 GPa.

### 3.2. Partition coefficients and lattice strain models

Major element partition coefficients show a minor decrease with increasing pressure in \( D_{\text{Ilm}} \) for both Ilm–Gk, from 2.9 ± 0.1 (Exp. 1, 1.1 GPa) to 2.5 ± 0.1 (Exp. 3, 1.4 GPa) to 2.4 ± 0.1 (Exp 4, 1.7 GPa) and Arm, from 3.7 ± 0.1 (Exp. 1, 1.1 GPa) to 3.2 ± 0.1 (Exp. 3, 1.4 GPa).
Mg is compatible in both Ilm–Gk ($D = 1.1–1.3 \pm 0.1$) and Arm ($D = 1.0 \pm 0.1$), whereas Fe is compatible in Ilm–Gk ($D = 1.5–1.6 \pm 0.1$) and slightly incompatible in Arm ($D = 0.76–0.78 \pm 0.01$).

All trace element concentrations in minerals and co-existing melts are summarised in Table 4. We were unable to use any of the analysis performed on Ilm–Gk minerals of experiment 4 at 1.7 GPa and 1315°C since the mineral analyses were clearly affected by mixing, but for completeness the average glass composition for this experiment is given in Table 4.

Trace element concentrations show very small variations within the different run product phases with standard deviations typically ~10% of the average value (Table 4). Higher concentrations (e.g. >10 ppm) on average correlate with smaller standard deviations (~10%), while low concentrations (e.g. <1 ppm) show standard deviations of ~30%. Uncertainties for the HREE and Th can be higher, with standard deviations of up to 65% for Th in Ilm–Gk (Experiment 1).

Resulting mineral–melt partition coefficients for Ilm–Gk and Arm are listed in Table 5. In Fig. 3 our results are compared to literature data for both Ilm–Gk and Arm. Our Ilm–Gk $D$ values are generally towards the lower end of the wide range in reported literature values, in particular for the HFSE. Armalcolite values are also generally at the lower end of the reported literature data range, however, there is less agreement and the literature $D$ range is smaller, due to the limited number of studies dealing with the partitioning behaviour of Arm. Our results are consistent with the recent study of Ilm–Gk/melt partitioning by Dygert et al. (2011), who show a decrease in HFSE (Zr, Hf, Nb, Ta) $D$ values with increasing melt TiO$_2$ content. Dygert et al. (2011) attribute this decrease in terms of HFSE substitutions for tetravalent Ti (charge-balanced by trivalent cations in case of Nb and Ta) in high-Ti melts. In this case,
HFSE melt activities increase with increasing TiO₂ content, lowering partition coefficients, as also observed in rutile–melt systems (e.g. Horng et al., 2000). Fig. 3 illustrates the necessity to use appropriate compositions and conditions in order to obtain reliable D values for lunar petrogenetic modelling.

The small set of D values presented by Dygert et al. (2011) was obtained at conditions and bulk compositions similar to ours, using starting material pre-conditioned at a more reducing O₂ of IW-1. The close similarity between our Ilm–Gk/melt partition coefficients and the Dygert et al. (2011) data suggests that there is no significant difference in D values between our experiments at F/O₂ = 1 + 1.5 and experiments at F/O₂ close to that of the lunar mantle (~IW-0.6, Nicholls and Rutherford, 2009).

Ilm–Gk/melt and Arm/melt partition coefficients, shown together in Fig. 4, are comparable but not identical. The LREE, Th and U are all preferentially incorporated into Ilm–Gk, while Mn is incompatible. Both minerals preferentially incorporate U, Th, Ilm–Gk and Arm and can fractionate the HFSE as incompatible, whilst Hf, Zr, Nb and Ta are only mildly incompatible. Both minerals incorporate Cr and V strongly incompatible, whilst Hf, Zr, Nb and Ta are only mildly incompatible. Both minerals preferentially incorporate U over Th. Ilm–Gk and Arm can fractionate the HFSE as D<sub>Hf</sub> = 0.24–0.25 for the produced Ilm–Gk and D<sub>W</sub> = 0.24–0.25 for Arm.

Table 4

<table>
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<tr>
<th>Exp. Phase</th>
<th>Melt</th>
<th>Ilm/Gk</th>
<th>Arm</th>
<th>Melt</th>
<th>Ilm/Gk</th>
<th>Arm</th>
<th>Melt</th>
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<td>V</td>
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<td>133(9)</td>
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<td>267(21)</td>
<td>440(32)</td>
<td>66(7)</td>
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<td>Cr</td>
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<td>428(28)</td>
<td>38(37)</td>
<td>58(7)</td>
<td>451(60)</td>
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<td>123(13)</td>
<td>132(33)</td>
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<td>Co</td>
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<td>61(9)</td>
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<td>Y</td>
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<td>Nb</td>
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<td>23(1)</td>
<td>94(11)</td>
<td>38(1)</td>
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<tr>
<td>Mo</td>
<td>39(4)</td>
<td>36(8)</td>
<td>34(5)</td>
<td>170(24)</td>
<td>10(1)</td>
<td>117(23)</td>
<td>194(19)</td>
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<td>Ba</td>
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<td>1.1</td>
<td>3.3(10)</td>
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<td>1.7(1)</td>
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<td>432(44)</td>
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<td>BD &lt; 0.19</td>
<td>0.67(16)</td>
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<td>BD &lt; 0.30</td>
<td>236(27)</td>
<td>0.61(21)</td>
<td>BD &lt; 0.8</td>
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<tr>
<td>Eu</td>
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<td>0.21(8)</td>
<td>0.58(14)</td>
<td>247(33)</td>
<td>0.38(16)</td>
<td>0.63(20)</td>
<td>323(33)</td>
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<tr>
<td>Er</td>
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<td>1.1(4)</td>
<td>0.54(6)</td>
<td>186(23)</td>
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<td>2.3(5)</td>
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<tr>
<td>Tm</td>
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<td>4.6(10)</td>
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<td>181(17)</td>
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<td>Yb</td>
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<td>4.8(10)</td>
<td>2.3(4)</td>
<td>199(17)</td>
<td>8.9(11)</td>
<td>4.6(6)</td>
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<td>Lu</td>
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<td>3.5(12)</td>
<td>182(17)</td>
<td>11(1)</td>
<td>5.8(2)</td>
<td>252(28)</td>
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<td>Hf</td>
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<td>29(1)</td>
<td>93(8)</td>
<td>58(7)</td>
<td>81(5)</td>
<td>103(10)</td>
</tr>
<tr>
<td>W</td>
<td>126(19)</td>
<td>5.5(10)</td>
<td>8.2(13)</td>
<td>458(53)</td>
<td>16(1)</td>
<td>27(4)</td>
<td>604(49)</td>
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<tr>
<td>Th</td>
<td>396(69)</td>
<td>0.82(54)</td>
<td>2.8(13)</td>
<td>963(103)</td>
<td>0.42(22)</td>
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<td>1369(95)</td>
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<tr>
<td>U</td>
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<td>2.5(7)</td>
<td>334(35)</td>
<td>0.63(15)</td>
<td>1.5(3)</td>
<td>445(23)</td>
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</tbody>
</table>

Numbers in parentheses indicate one standard deviation (1σ) of replicate analyses in terms of last significant numbers: 27(2) should be read as 27 ± 2. When a value lacks 1σ then only 1 measurement was above the detection limit. BD = below detection limit.

Indicates that 1 measurement was discarded, e.g. when n = 5 and a number is marked by 'a' only 4 measurements could be used.

Two measurements were discarded.
In Fig. 5, Ilm–Gk/melt and Arm/melt partition coefficients for nominally di- tri- and tetravalent elements are shown as symbols in Onuma diagrams (Onuma et al., 1968) of \( \log(D) \) values versus trace element radii (sixfold coordinated values from Shannon, 1976). Best-fit values for lattice strain parameters \( D_0, r_0 \) and \( E \) (Eq. (1)) are given in Table 6, and resulting crystal lattice strain model fits are shown as curves in Fig. 5.

4. DISCUSSION

4.1. Lattice strain models

Application of the lattice strain model (Table 6; Fig. 5) enables us to elucidate the substitution mechanism for some of the trace elements involved, and identify and correct for minor contamination issues affecting measured \( D \) values for highly incompatible elements. Fig. 5b shows that Ilm–Gk/melt and Arm/melt partitioning data for many nominally M\(^{3+} \) elements conform to the near-parabolic shape predicted from the lattice strain model. Partition coefficients for Cr and V are higher than expected for a purely M\(^{3+} \) element, consistent with both being multivalent (e.g. Papike et al. 2005). Deviations from the curves for the LREE \( D \) values are discussed below. Previous work has suggested that even the smallest M\(^{3+} \) cation considered here (Al) substitutes onto the Fe/Mg site in armalcolite (Smyth, 1974), not onto the smaller Ti site, and fits to the M\(^{3+} \) partitioning data are consistent with this suggestion for both Ilm–Gk and Arm.

The fits to our M\(^{3+} \) data reveal a minor contamination issue with our data. The LREE show higher partition coefficients than expected from the lattice strain model (Fig. 5b). As discussed by van Westrenen et al. (2001a) very small (<1 wt.%) amounts of glass contamination during trace element analysis of crystals can lead to significant overestimation of \( D \) values for highly incompatible elements. In Fig. 6 we show the effect of the addition of different percentages of glass to the Ilm–Gk mineral analysis for the 1.1 GPa experiment. The difference between observed and predicted \( D \) values for the LREE can be explained by as little as 0.1–0.3 wt.% amounts of glass contamination during trace element analysis of crystals can lead to significant overestimation of \( D \) values for highly incompatible elements. In Fig. 6 we show the effect of the addition of different percentages of glass to the Ilm–Gk mineral analysis for the 1.1 GPa experiment. The difference between observed and predicted \( D \) values for the LREE can be explained by as little as 0.1–0.3 wt.% amounts of glass contamination of our mineral analyses. Fig. 6 also shows that the effect of such minor addition on \( D \) values is minimal for the HREE. The LREE \( D \) values listed in Table 5 are therefore maximum values, and petrogenetic models involving LREE partitioning in the presence of Ilm–Gk and Arm should make use of \( D \) values calculated from the curves in Fig. 5b (using the parameters listed in Table 6).

The smaller group of partition coefficients for the divalent cations conforms partly to the lattice strain model (Fig. 5a). Comparing best-fit lattice strain model parameters shows that \( r_0 \) for divalent cations in Ilm–Gk is very close to the sixfold radius of Fe (0.78 Å, Shannon, 1976).
whereas $r_0$ for Arm is closer to that of Mg (0.72 Å). This indicates substitution of M$^{2+}$ into the Fe/Mg site. $E$ values for divalent cations are identical within error for Ilm–Gk and Arm, suggesting the elastic properties of the sites in these two minerals are similar. $E$ values are high compared to values for M$^{2+}$ replacing divalent major cations in other minerals, which are generally in the range of 100–250 GPa (e.g. Blundy and Wood, 1994), suggesting the Fe/Mg sites in Ilm–Gk and Arm impose larger fractionations between divalent elements than these other minerals.

The minor contamination during laser ablation analysis identified from M$^{3+}$ partitioning data also explains the discrepancy between the measured values of Ilm–Gk/melt and Arm/melt $D$ values expected from lattice strain modelling. Glass contributions of 0.3–0.7 wt.% to the ilmenite–geikielite and armalcolite concentration measurements are sufficient to explain these unexpectedly high values. Copper and Co $D$ values do not conform to the M$^{2+}$ curve, as observed previously in both computer simulations and experiments on olivine–melt partitioning of M$^{2+}$ cations (Purton et al., 2000). This is possibly due to Jahn–Teller effects in the case of Cu, and crystal field stability energy effects in crystals and melts in the case of Co, which affect overall partitioning energetics (Purton et al., 2000).

For both minerals $r_0$ for the tetravalent cations Si, Ti, Hf and Zr is close to that of Ti (0.605 Å), indicating that these elements preferentially substitute for Ti$^{4+}$ (Fig. 5c). The
Fig. 5. Onuma diagrams showing mineral–melt partitioning data for the ilmenite–geikielite (left) and armalcolite (right) bearing experiments. (a) Nominally divalent elements; (b) nominally trivalent elements and (c) nominally tetravalent elements.
measured partition coefficients for U and Th are 3–4 orders of magnitude higher than expected from extrapolation of the lattice strain models for the other M⁴⁺ elements. The minor contamination issue discussed above cannot explain this large difference. This suggests that Th and U are incorporated into the larger Mg/Fe site in Ilm–Gk and Arm, rather than replacing Ti, similar to the situation in Ti-rich garnets (Van Westrenen et al., 2001b).

Most best-fit lattice strain parameters show little or no variation across the pressure range covered in these experiments. The only exceptions are the observed slight decreases in $r_0$ for divalent cations with increasing pressure for both Ilm–Gk and Arm, accompanied by small decreases in apparent site Young’s moduli $E$. Decreases in $r_0$ with increasing $P$ have been observed in partitioning data for other minerals (most notably garnet, e.g. Draper and van Westrenen, 2007; van Westrenen and Draper, 2007) and are consistent with the measured decreases in the Mg/Fe site volumes with increasing compression (e.g. Trombe et al., 2010). Although decreases in $r_0$ are often accompanied by increases in $E$, interpreting $E$ values is notoriously difficult (e.g. Hill et al., 2000; van Westrenen et al., 2000) and our data set is too small to draw definitive conclusions about the relation between $r_0$ and $E$ for divalent cations in Arm and Ilm–Gk.

4.2. Implications for Lu–Hf–Ti concentrations of lunar high-Ti mare basalts

Because of the bulk composition and conditions used, the partition coefficients presented in this study are directly relevant to the Moon. A variety of models have been proposed to explain the high Ti contents of these basalts, including assimilation of late-stage ilmenite-bearing cumulates by low-Ti ultramafic liquids at shallow levels (e.g. Anderson, 1971; Hubbard and Minear, 1975; Wagner and Grove, 1997), sinking of late stage ilmenite cumulates to form a deep hybrid mantle source (e.g. Ringwood and Kesson, 1976; Hess and Parmentier, 1995) and shallow-level reaction and mixing of cumulates, followed by sinking of hybrid high-Ti material (Van Orman and Grove, 2000). In addition, Nakamura et al. (1986) and Beard et al. (1998) showed that the Lu/Hf ratios of high-Ti mare basalts (Lu/Hf = 0.12–0.17) are significantly lower than chondritic (Lu/Hf = 0.21, Lodders, 2003), requiring the addition of a mineral that preferentially incorporates Hf over Lu.

Ilm–Gk ($D_{Lu}/D_{Hf} = 0.24–0.25$) and Arm ($D_{Lu}/D_{Hf} = 0.05–0.06$) are such minerals, they are the only minerals involved in lunar magma ocean (LMO) crystallisation that preferentially incorporate Hf over Lu. Partitioning studies of other minerals that played a role during lunar magmatic processes all show $D_{Lu}/D_{Hf} > 1$. For example, olivine shows

---

### Table 6

<table>
<thead>
<tr>
<th>Exp.</th>
<th>P(GPa), T (°C)</th>
<th>Phase</th>
<th>Ilm–Gk</th>
<th>Arm</th>
<th>Ilm–Gk</th>
<th>Arm</th>
<th>Ilm–Gk</th>
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<td>1</td>
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<td>3</td>
<td>1.4, 1305</td>
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<td>4</td>
<td>1.7, 1315</td>
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<td>$D_0$</td>
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<tr>
<td>$2^+$</td>
<td>1.58(3)</td>
<td>1.00(2)</td>
<td>1.05(3)</td>
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<td>1.58(5)</td>
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<td>$3^+$</td>
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<td>0.904(43)</td>
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<tr>
<td>$4^+$</td>
<td>2.98(10)</td>
<td>3.87(13)</td>
<td>2.56(3)</td>
<td>3.32(4)</td>
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<td>$E$</td>
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<td>$2^+$</td>
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<td>382(11)</td>
<td>308(205)</td>
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<td>536(21)</td>
<td>429(10)</td>
<td>528(11)</td>
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<td>1260(38)</td>
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<td>$r_0$</td>
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<td>$2^+$</td>
<td>0.781(5)</td>
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<td>0.682(2)</td>
<td>0.696(1)</td>
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<td>$4^+$</td>
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<td>0.614(2)</td>
<td>0.621(2)</td>
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and Münker (2010) we assume 5

between super- and subchondritic, respectively (Fig. 7),

are predicted to be subchondritic in the range of 0.025–

Using our partition coefficients the Lu/Hf ratios of ilmenite

cumulates containing Ol ± Opx ± Cpx ± Plag show super-

are summarised in Table 7. Following Snyder et al. (1992)

is based on calculations using the olivine–plagioclase–silica

ternary phase diagram at 0.6 GPa derived from experiments

We calculated the Lu–Hf–Ti evolution of a crystallising

LMO and corresponding cumulates, assuming the LMO

crystallisation model of Snyder et al. (1992). This model

Table 7

Input parameters for trace element evolution modelling during LMO crystallisation assuming the crystallisation model of Snyder et al. (1992).

<table>
<thead>
<tr>
<th>Concentrations</th>
<th>LMO&lt;sup&gt;a&lt;/sup&gt;</th>
<th>High Ti&lt;sup&gt;b&lt;/sup&gt;</th>
<th>High Ti&lt;sup&gt;c&lt;/sup&gt;</th>
<th>High Ti&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Partition coefficients</th>
<th>$D_{DLu}$</th>
<th>$D_{DOPX}$</th>
<th>$D_{DCPX}$</th>
<th>$D_{DMOL}$</th>
<th>$D_{DILM}$</th>
<th>$D_{DSTM}$</th>
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<td>Lu (ppm)</td>
<td>0.119</td>
<td>1.0–1.1</td>
<td>2.4–2.6</td>
<td>0.5–1.5</td>
<td>0.041</td>
<td>0.052</td>
<td>0.74</td>
<td>0.0018</td>
<td>0.079</td>
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<tr>
<td>Hf (ppm)</td>
<td>0.575</td>
<td>6.4–7.0</td>
<td>14.7–15.9</td>
<td>5.1–10</td>
<td>0.013</td>
<td>0.0086</td>
<td>0.37</td>
<td>0.001</td>
<td>0.33</td>
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<tr>
<td>TiO$_2$ (wt.%)</td>
<td>12.5–13.7</td>
<td>9.1–9.7</td>
<td>10.1–14.2</td>
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<td>0.010</td>
<td>0.071</td>
<td>0.34</td>
<td>0.0446</td>
<td>2.9</td>
<td>3.7</td>
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<tr>
<td>Lu/Hf</td>
<td>0.21</td>
<td>0.16</td>
<td>0.16–0.17</td>
<td>0.13–0.17</td>
<td>3.2</td>
<td>6.1</td>
<td>2.0</td>
<td>1.8</td>
<td>0.24</td>
<td>0.06</td>
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</tbody>
</table>

<sup>a</sup> Initial values for the Lu and Hf concentrations in the LMO ($LOM_0 = 5^*CI$ chondrites) are derived using CI values of Lodders (2003).

<sup>b</sup> Lu–Hf and TiO$_2$ concentrations from Beard et al. (1998) for Apollo 17 basalts (b1) and Apollo 11 basalts (b2), and from Warner et al. (1979) for Apollo 17 basalts (b3).

<sup>c</sup> Partition coefficients for OPX from McDade et al. (2003).

<sup>d</sup> Partition coefficients for OPX from van Kan Parker et al. (2011).

<sup>e</sup> Partition coefficients for Plag from Tepley et al. (2010), with $D_{PL}$ fitted using the lattice strain model.

<sup>f</sup> Partition coefficients for Ilm-Gk and Arm are from Experiment 1 (this study).

$D_{DLu}/D_{DHf} = 3.2$ (McDade et al., 2003), clinopyroxene $D_{DLu}/D_{DHf} = 2.0$ (e.g. McDade et al., 2003), plagioclase $D_{DLu}/D_{DHf} = 1.8$ (e.g. Tepley et al., 2010) and orthopyroxene $D_{DLu}/D_{DHf} = 6.1 ± 2.5$ (van Kan Parker et al., 2011).

Fig. 7 shows predicted Lu–Hf–Ti concentrations for models whereby high-Ti basalts are generated by partially melting (10% fractional melting) the Opx cumulate formed from initial magma ocean crystallisation. Lu/Hf decreases in the residual liquids due to the high $D_{DLu}/D_{DHf}$ ratios of the crystallising minerals, and the corresponding cumulates containing Ol ± Opx ± Cpx ± Plag show superchondritic Lu/Hf ratios, between 0.36 and 1.2. Ilmenite and/or armalcolite start crystallising when the LMO has solidified for >95% (Snyder et al., 1992). We test models in which the Ti-rich minerals continue crystallising up to a total of 98% or 99% total LMO crystallisation. Consistent with Snyder et al. (1992) the late stage Ti-rich minerals crystallise together with clinopyroxene and plagioclase, producing a so-called ilmenite bearing cumulate layer (IBCL) or an equivalent armalcolite-bearing cumulate layer (ABCL). Using our partition coefficients the Lu/Hf ratios of ilmenite are predicted to be subchondritic in the range of 0.025–0.034, while armalcolite shows Lu/Hf ratios of 0.0068–0.0084. Lutetium/Hf ratios of bulk IBCL and ABCL vary between super- and subchondritic, respectively (Fig. 7), dependant on the total amount of crystallisation of the LMO. At ≥99% crystallisation, bulk Lu/Hf of IBCL and ABCL are not as subchondritic as the observed ratios in the high-Ti mare basalts.

Fig. 7. Comparison between observed (triangles, compilation from Beard et al., 1998 and Warner et al., 1979) and modelled (this study) Lu/Hf ratios and TiO$_2$ contents of high-Ti mare basalts. Curves show progressive dissolution of (a) ilmenite–geikielite or (b) armalcolite into 10% partial melts of early orthopyroxene cumulates. The Lu/Hf ratio of these initial melts decreases steeply with increasing Ilm (a) or Arm (b) addition. The Lu/Hf ratios of bulk ilmenite bearing cumulate (IBCL) and bulk armalcolite bearing cumulate (ABCL) are shown assuming Ti-rich mineral crystallisation up to either 98% or 99% total solidification of the LMO.
during early LMO crystallisation, followed by shallower-
level dissolution of Ilm–Gk or Arm from late-stage cumu-
late remnants. When we assume Ilm–Gk crystallisation up to
98% LMO solidification, a mixture of 17% of dissolved ilmenite with 83% of cumulate partial melt is required to
produce the observed Lu/Hf ratio of 0.16 in the high-Ti
mare basalts (Fig. 7a). If armalcolite would crystallise instead of ilmenite a mixture of 6.5% of armalcolite and
93.5% of cumulate partial melt is sufficient (Fig. 7b). If
Ti-rich mineral crystallisation from the LMO would con-
tinue up to 99% of solidification the required proportions reduce to 9% for ilmenite and to 3.5% if armalcolite dis-
solution is involved. A robust result from our modelling is
that bulk dissolution of the IBCL or the equivalent ABCL
including clinopyroxene and/or plagioclase cannot repro-
duce the observed subchondritic Lu/Hf ratios since their
Lu/Hf ratios are higher than observed in the basalts. Select-
tive dissolution of the Ti-rich phase is therefore required, consistent with the dissolution modelling of Wagner and
Grove (1997).

These scenarios reproduce the observed Lu/Hf ratio and the absolute TiO₂ concentrations in the high-Ti mare bas-
als. Absolute concentrations for Lu and Hf in these models are lower than the measured values. Simple late-stage oliv-
ine ± orthopyroxene fractionation at shallow levels, using the partition coefficients listed in Table 7, would result in
higher absolute values of both Lu and Hf at virtually un-
changed Lu/Hf ratios. However, TiO₂ concentrations would simultaneously increase to levels far exceeding those observed. Alternatively, shallow-level fractionation of oliv-
ine ± ilmenite, or olivine ± armalcolite (as suggested by,
e.g. Longhi, 1992) would lower TiO₂ concentrations to lev-
els below those observed.

Fractionation of olivine ± orthopyroxene ± ilmenite
would only change TiO₂ concentrations to a very minor ex-
tent while increasing the absolute Lu and Hf concentra-
tions. This latter scenario would also increase the Lu/Hf ratio slightly and therefore slightly more initial ilmenite dis-
solution would be required (18% at 98% crystallisation of
the LMO, or 10% at 99% crystallisation of the LMO).
We stress however that this analysis assumes that the partition coefficients listed in Table 7, chosen for their applica-
bility during high-pressure processes, are equally valid at
low pressure – an assumption that remains to be tested experimen-
tially.

5. CONCLUSIONS

We have experimentally determined the partitioning behaviour of a wide range of trace elements between ilmenite, armalcolite and anhydrous lunar silicate melt at high pressure and temperature in a Ti-rich system, to constrain geochemical models of the evolution of the interior of the Moon. Our data enable us to quantitatively model the Lu–Hf–Ti concentrations of lunar high-Ti basalt. We show that the combination of subchondritic Lu/Hf ratios and high TiO₂ contents requires preferential dissolution of ilmenite or armalcolite from late-stage lunar magma ocean cumulates into low-Ti partial melts of deeper pyroxene-rich cumulates, followed by shallow fractionation of olivine ± orthopyroxene ± ilmenite.

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