Potts, N. J., Bromiley, G., & Brooker, R. A. (2021). An experimental investigation of F, Cl and H₂O mineral-melt partitioning in a reduced, model lunar system. *Geochimica et Cosmochimica Acta*, 294, 232-254. <https://doi.org/10.1016/j.gca.2020.12.003>

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[10.1016/j.gca.2020.12.003](https://doi.org/10.1016/j.gca.2020.12.003)

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An experimental investigation of F, Cl and H₂O mineral-melt partitioning in a reduced, model lunar system.

Nicola J. Potts¹, Geoffrey D. Bromiley^{1,2*}, Richard A. Brooker³

¹School of GeoSciences, Grant Institute, University of Edinburgh, Edinburgh, UK.

²Centre for Science at Extreme Conditions, University of Edinburgh, UK.

³School of Earth Sciences, University of Bristol, Bristol, UK

*corresponding author: geoffrey.bromiley@ed.ac.uk

Abstract

It is believed that the Moon formed following collision of a large planetesimal with the early Earth. Over the ~4 Gyr since this event the Moon has been considerably less processed by geological activity than the Earth, and may provide a better record of processes and conditions in the early Earth-Moon system. There have been many studies of magmatic volatiles such as H, F, Cl, S and C in lunar materials. However, our ability to interpret variable volatile contents in the lunar sample suite is dependent on our understanding of volatile behaviour in lunar systems. This is currently constrained by limited experimental data. Here, we present the first experimental mineral-melt partitioning coefficients for F, Cl and H₂O in a model lunar system under appropriately reduced conditions (log f_{O_2} to IW-2.1, i.e. oxygen fugacity down to 2.1 log units below the Fe-FeO buffer). Data are consistent with structural incorporation of F, Cl and OH⁻ in silicate melt, olivine and pyroxene under conditions of the lunar mantle. Oxygen fugacity has a limited effect on H₂O speciation, and partitioning of H₂O, F and Cl is instead largely dependent on mineral chemistry and melt structure. Partition coefficients are broadly consistent with a mantle source region for lunar volcanic products that is significantly depleted in F, Cl and H₂O, and depleted in Cl relative to F and H₂O, compared to the terrestrial mantle. Partitioning data are also used to model volatile redistribution during lunar magma ocean (LMO) crystallisation. The volatile content of lunar mantle cumulates is dependent upon proportion of trapped liquid during LMO solidification. However, differences in mineral-melt partitioning during LMO solidification can result in significant enrichment on F relative to Cl, and F relative to H₂O, in cumulate phases relative to original LMO composition. As such, Cl depletion in lunar volcanic products may in part be a result of LMO solidification.

1. Introduction

The presence of ‘water’ or related H-bearing species, i.e. H₂O, OH⁻, H₂ etc, in the interior of the Earth has a controlling influence on a range of mantle properties from melting behaviour to rheology (Peslier, 2010, and references therein). The additional role of water in sustaining life means that the origin of Earth’s volatiles and the timing of their delivery are key areas of study in Earth and planetary sciences. However, many geological processes have modified the Earth since its initial formation, redistributing these volatiles and masking geochemical signatures of their origin. If it is accepted that the Earth and Moon share some common history, the question is when did their compositions diverge and to what extent (Albarède, 2009). According to the canonical “Giant Impact” hypothesis, the Moon formed following collision of

a Mars-sized planetesimal with the early Earth (Canup and Agnor, 2000; Canup, 2004). This catastrophic heating event was previously believed to be consistent with an anhydrous lunar interior and lunar sample suite (Lucey et al., 2006; Taylor et al., 2006). The subsequent detection of water and other volatiles in volcanic lunar glasses (Saal et al., 2008) has heralded a new era of lunar research and reinvestigation of the lunar sample suite. This has revealed the presence of 'water' in volcanic lunar glasses (Saal et al., 2008, 2013; Greenwood, 2018), in apatites in mare basalts (Boyce et al., 2010; McCubbin et al., 2010a; McCubbin et al., 2010b; Greenwood et al., 2011; Barnes et al., 2013; Greenwood, 2018), in olivine-hosted melt inclusions in mare basalts (Chen et al., 2015; Hauri et al., 2011; Hauri et al., 2015; Ni et al., 2017; Ni et al., 2019), in plagioclase from lunar anorthosites (Hui et al., 2013; 2017), as well as halogens in mesostasis in lunar basalts (Greenwood et al., 2020). It is now clear that various lunar mantle source regions contain appreciable H, in addition to Cl, F, C and S. As the Moon shares a common origin with the Earth, the logical conclusion is that a similar process may have been involved in volatile delivery to both components of the early Earth-Moon system. Volatiles were either delivered to the Earth prior to the Moon-forming event or delivered to the Earth-Moon system shortly after the Moon-forming event, whilst the newly-formed Moon was still in a largely molten state. As the Moon has remained less affected by large-scale geological processes since its formation, the lunar volatile budget may provide much needed insight into the early Earth-Moon system, and ultimately, provide constraints on the origin of Earth's hydrosphere.

The lunar sample suite is consistent with a high temperature origin for the Moon. For example, the lunar anorthositic crust probably represents a plagioclase floatation crust formed during lunar magma ocean (LMO) solidification (Warren, 1985). The later mare basalts most likely formed by partial melting of deeper mantle cumulates, also produced by the same LMO solidification process, following late-stage cumulate overturn (Ryder, 1991). As a result, the volatile content of mare basalts and associated volcanic glasses provides insight into the volatile budget of the lunar mantle melts and the LMO solidification products (e.g. Hauri et al. 2011; Saal et al. 2008). With the detection of 'water' in lunar materials and inferred 'water' contents in parental lunar magmas, it is tempting to make direct comparison with terrestrial magmas. For example, Hauri et al. (2011) noted that volatile contents of melt inclusions in lunar olivine are similar to those in terrestrial mid-ocean ridge basalts, implying similar volatile budgets in terrestrial and lunar mantle source regions. However, any such comparison can be misleading because of differences in magmatic conditions between evolved terrestrial and lunar systems. Mare basalts and associated volcanic glasses are reduced compared to terrestrial volcanic materials, with mineral assemblages and direct oxygen fugacity (fO_2) measurements indicating fO_2 below that of the iron-wüstite (IW, i.e. Fe-FeO) solid buffer, and either at or near Fe-metal saturation (Longhi, 1992; Shearer et al., 2006). The reduced nature of lunar magmas implies melting of a similarly reduced lunar interior (Longhi, 1992), with the oxidation state of the source region for mare basalts and volcanic glasses generally assumed to be at least 2 log units lower than Earth's upper mantle (Rutherford and Papale, 2009; Sato, 1976). Oxygen fugacity has a fundamental control on 'water' or H incorporation in silicate materials. In terrestrial systems at high mantle temperatures and pressures 'water' is incorporated into nominally anhydrous minerals such as olivine and pyroxenes as interstitial H associated with underbonded O atom sites (e.g. Skogby et al., 1990; Smyth et al., 1991; Ingrin and Skogby, 2000; Stalder and Skogby, 2003; Bromiley et al., 2004; Bromiley and Bromiley, 2006; Smyth et al., 2006), forming various O-H defects (Lemaire et al., 2004; Matveev et al, 2005; Grant et al, 2007). In terrestrial silicate melts, water is incorporated initially

as OH⁻, with molecular H₂O becoming more dominant at higher total water contents, at least under more oxidising conditions (e.g. Stolper, 1982; Pandya et al., 1992; Dixon et al., 1995). This has recently been contested by Cody et al. (2020) who suggest that H₂O dominates at low H abundances, at least in highly polymerised silicate melts, although whether this is true in less polymerised, basaltic melts remains unclear. Under reducing conditions H₂O becomes unstable as a species, and other H-related defects such as H₂ and CH₄ are observed in spectroscopic investigations of melts at the expense of OH⁻ (Kadik et al., 2006; Mysen et al., 2011; Hirschmann et al., 2012; Ardia et al., 2013). Magmas are commonly used as probes of planetary interiors as they represent escaped partial melts that transport information about source regions. The ‘water’ content of magmas is controlled in part by mineral-melt partitioning during partial melting of the mantle source. Any change in speciation of ‘water’ as a function of fO_2 could result in significant changes in partitioning. The ‘water’ content of a magma will likely depend on both the H concentration and the fO_2 in its mantle source region, and any comparison between lunar and terrestrial magmas must take this into account. Kadik et al. (2006) noted that at high pressure in silicate melts at fO_2 below IW, H₂ becomes increasingly important at the expense of more oxidised species. Hirschmann et al. (2012) noted that the proportion of H₂ in lunar magmas is low under the low total water contents of the lunar interior. However, in reduced lunar systems over a range of inferred bulk ‘water’ contents (Elkins-Tanton and Grove, 2011) the proportion of H₂/H₂+H₂O could range up to 20-50%. In solid phases under similarly reducing conditions, Yang et al. (2016) demonstrated that mantle silicates can also incorporate some molecular H₂, in addition to OH defects. The effects of any change in speciation on volatile behaviour remain unclear. Newcombe et al. (2017) demonstrated that degassing mechanisms in lunar melts over a range of highly reducing conditions (below the IW buffer) are strongly controlled by H speciation, although they noted that diffusion is dominated by flux of OH⁻ rather than H₂. Recently, Lin et al. (2019) demonstrated that fO_2 has a strong control on H₂O partitioning between plagioclase and silicate melt, but aside from that study there is an absence of data on the effect of fO_2 on volatile partitioning in lunar systems. Here we present the first experimental data on partitioning of H₂O, F and Cl in a reduced, model lunar mantle lithology system. F and Cl are important tracers in lunar materials (e.g. Hauri et al., 2011; Chen et al., 2015), and are increasingly used to provide insight into volatile redistribution during terrestrial geological processes (e.g. Urann et al., 2017; Klemme and Stalder, 2018). Furthermore, isotopic variations of Cl in lunar materials provide significant additional insight into lunar magmatic processes (McCubbin et al., 2011; Potts et al., 2018; Boyce et al., 2018). Therefore, combined study of F, Cl and H₂O distribution during magmatic processes provides a powerful tool for reinvestigating the importance of measured volatile concentrations in lunar samples, and for drawing inferences on volatile delivery to the early Earth-Moon system.

2. Methods

2.1 System and bulk composition

To constrain volatile mineral-melt partitioning during lunar mantle melting, a synthetic starting material was used with a composition similar to lunar low-Ti, picritic, green volcanic glass beads. These pyroclastic glasses are believed to be amongst the most primitive lunar samples (Delano, 1979) and suggested to represent partial melts from lunar mantle cumulates formed at around 1.5 to 2.5 GPa (Shearer et al., 2006). A composition, corresponding to an average green lunar glass from Saal et al. (2008) was chosen (Table 1). This composition is close to

that of Apollo 15A green glasses that best represent primitive lunar melts with minimal mantle cumulate assimilation (Barr and Grove, 2007).

A homogenous, reduced starting material was made by first grinding high-purity oxides (SiO_2 , Al_2O_3 , MgO , TiO_2 , Fe_2O_3 , Cr_2O_3) and carbonates (Na_2O , CaCO_3 , K_2CO_3), under isopropanol in an agate pestle and mortar for 40 minutes. Prior to weighing, SiO_2 , TiO_2 , MgO , and Al_2O_3 were fired at 1000 °C in a box furnace for 24 hours. These were then stored in a 110 °C oven with the other powders. After grinding, the mixture was transferred to an Fe-saturated Pt crucible and decarbonated in a box furnace from 600 to 900 °C over eight hours. The mixture was removed from the furnace and stored in a 110 °C oven while the furnace was raised to 1550 °C. The mixture was then inserted into the hot spot of the furnace for 30 minutes. The mixture was removed and quenched to a homogenous glass by inserting the bottom of the Pt crucible in water, and then reground. The resulting fine powder was placed in an Fe-saturated Pt crucible and reduced in a 1 atmosphere furnace at 1200 °C for 24 hours using a $\text{CO}_2\text{-H}_2$ gas mix equivalent to two log units below the iron-wustite buffer (IW-2; $\log f\text{O}_2 = -14.6$). After regrinding, halogens and water were added as CaF_2 and CaCl_2 and $\text{Al}(\text{OH})_3$. Al and Ca proportions prior to glassing were calculated so that addition of volatiles resulted in the final, desired bulk composition.

2.2 High-pressure experiments

Encapsulation techniques for highly reduced, high pressure experiments are challenging with a high failure rate resulting from a loss of capsule integrity (physical or chemical; see section 3). After much trial and error, two capsule designs were used for these high-pressure volatile-bearing experiments. To ensure that $f\text{O}_2$ remained below IW we developed a capsule consisting of a 4 mm diameter high-purity (99.99%+) Fe metal outer capsule with hammer-fit lid. This capsule acts as a sink for any excess O_2 present in the starting mix or introduced during loading and also ensures that melts remain at/near Fe metal saturation. This use of high-purity iron follows pioneering experiments on mare basalts (e.g. Longhi, 1992; Walker et al., 1975). The starting mix was loaded into the capsule along with a welded 2mm diameter inner Pt capsule containing a solid $\text{Cr-Cr}_2\text{O}_3$ buffer. During high pressure/temperature experiments the reaction:

within the Pt capsule buffers $f\text{O}_2$ at several log units below the IW buffer (Holzheid and O'Neill, 1995) at least while both Cr metal and Cr_2O_3 are present. In theory, H diffusion through the thin (0.1 mm thick) Pt inner capsule allows $f\text{O}_2$ conditions within the inner capsule to be transmitted to the outer capsule and sample, as in other double capsule techniques. However, under reducing conditions Cr metal reacts with Pt to form a mixed Pt-Cr phase, implying reaction [1] describes oxidation of the Cr component in a binary alloy, rather than an end-member reaction. However, the success of this technique has been demonstrated by Stokes et al. (2019) who used Fe XANES spectra to demonstrate that a Cr-based buffer can maintain reducing conditions below IW, and this is further verified here by the presence of metallic iron in run products, as described below. A second capsule design was used to purposely buffer $f\text{O}_2$ closer IW and to allow direct comparison with previous studies. This design involved loading the starting material into a graphite capsule with press fit lid which was then loaded

into a welded Pt outer capsule. The graphite bucket in this standard double capsule design buffers fO_2 at C-CO, which in hydrous systems equates to roughly IW+2 to IW-1 depending on run temperature, pressure and nature of sample (e.g. Armstrong et al., 2015).

Experiments were performed in an end-loaded piston cylinder apparatus. For Pt+graphite runs (Pt_C), experiments were pressurised to ~0.5 GPa before simultaneously heating while pressurising, until run values were reached. For Fe capsule runs (Fe), experiments were fully pressurised before heating to ensure the capsules were closed (pressure welded). All runs were heated at ~100°C/min, taken to the final run temperature and held for 24 hours. Rapid, isobaric quenching was achieved by turning off power to the system whilst maintaining run pressures. A fuller description of high-pressure experiments is given in Bromiley et al. (2017). Experimental conditions were chosen to mimic near-liquidus experiments in lunar systems, and synthesize mantle phases in equilibrium with high fraction silicate melt (e.g Longhi, 1992).

2.3 Sample preparation and analysis

Recovered capsules were sectioned using a 2 μ m diamond wire saw. Both halves of capsules were mounted in crystal bond, then ground and polished with diamond suspensions. Samples were removed from crystal bond by dissolving in high-purity acetone, mounted in indium, and C coated for visual inspection and analysis using a Scanning Electron microscope fitted with quantitative Energy Dispersive Spectrometer (SEM-EDS). After SEM-EDS analysis, the C coat was carefully removed from samples by buffing surfaces with a 0.25 μ m diamond suspension. At this stage one half of the capsule was removed from the indium mount, glued onto a glass slide with crystal bond polished side down, and ground down to produce 300 μ m thick section. These were then removed from the glass slide with acetone and thoroughly cleaned in ethanol for investigation by Fourier Transform Infrared (FTIR) spectroscopy. However, due to the friable nature of run products only a limited number of experimental charges could be successfully prepared in this way. Experiments run in graphite-lined platinum capsules did not survive wafering. Instead, polished run products in mounts were analysed using a Raman Imaging microscope to identify absorption due H-related species. For all experiments, the remaining half of the capsule was gold coated and used for determination of F, Cl, H and C contents by Secondary Ion Mass Spectrometry (SIMS) analysis.

F, Cl, H and C contents of samples were determined by secondary ion mass spectrometry (SIMS) using a Cameca 4f instrument at The University of Edinburgh NERC Ion Microprobe Facility. Prior to analysis, samples were kept in a vacuum oven for at least a week to reduce H backgrounds. Samples were then gold coated before immediately being loading into the relevant instruments vacuum chamber, and kept under vacuum ($<5 \times 10^{-8}$ mbar) for at least 48h prior to analysis. A 5 nA negative ^{16}O ion beam accelerated to 10 kV was used for all measurements. Secondary ions were accelerated to 4500 V minus a 75 eV energy offset for F, Cl and H measurements, and 50 eV offset for C. Beam diameter was approximately 20 μ m. Each analysis area was pre-sputtered for 3 minutes with a 30 μ m rastered beam, then spots were analysed using a 10 μ m small field aperture, avoiding any cracks, crystal edges and inclusion within samples. Depth of analysis pits was <2 μ m, and after SIMS analysis all samples were imaged again using the SEM to ensure that analysis pits did not reveal presence of any source of contamination. Each measurement consisted of 10 cycles, although the first 5 cycles for H₂O measurements were discounted to minimise surface contamination. CO₂ was

measured first with high mass resolution sufficient to resolve interference by $^{24}\text{Mg}^{2+}$ on the $^{12}\text{C}^+$ peak. CO_2 and H_2O -bearing experimental basaltic glasses (ST) from Shishkina et al. (2010) were used as primary standards for both CO_2 and H_2O , with anhydrous San Carlos olivine standard additionally used to determine H_2O backgrounds, and NIST-SRM610, BCR-2G and KL2-G used as secondary standards. Presence of volatile-bearing inclusions was discounted by monitoring $^1\text{H}/^{30}\text{Si}$ signals. F and Cl concentrations were normalised to the ^{30}Si count rate and calibrated using VG-2 (basaltic glass, Juan de Fuca ridge, #111240/52), VG-A99 (basaltic glass, Makaopuhi lava lake, Hawaii, #113498/1), GSD-1G (basaltic glass, USGS), and BIR-01G (basaltic glass) standards (Jochum et al., 2005). NIST-SRM610 and BCR-2G glasses were used as a secondary standard and San Carlos olivine as a background blank.

Electron probe microanalysis (EMPA) was used to determine mineral and melt major element composition using a Cameca SX100 instrument running at 15 keV and the following conditions/standards/analysing crystals: for glass, 2 nA and an 8 μm beam for Na (jadeite, LTAP), Mg (spinel, LTAP), Al (spinel, LTAP), Fe (fayalite, LLIF), Ca (wollastonite, PET and LPET), Si (wollastonite, TAP), and a 8 nA, 80 μm beam for Ti (rutile, PET and LPET), Cl (NaCl, PET and LPET), F (SrF_2 , TAP and LTAP), Cr (metal, LLIF) and Mn (metal, LLIF). For orthopyroxene and olivine a 4 nA, 2 μm beam was used for Fe (fayalite, LLIF), Mg (forsterite, LTAP) and Si (forsterite, TAP), and a 100 nA, 2 μm beam for Ca (wollastonite, PET), Ti (rutile, PET), Na (jadeite, LTAP), Cr (metal, LLIF) and Al (spinel, LTAP). For clinopyroxene analyses a 4 nA, 2 μm beam was used Mg (spinel, LTAP), Si (wollastonite, TAP), Al (spinel, LTAP), Fe (fayalite, LLIF), Ca (wollastonite, PET), and a 100 nA, 2 μm beam for Ti (rutile, PET), Na (jadeite, LTAP) and Cr (metal, LLIF).

FTIR and Raman spectroscopy was used to provide information on H and C speciation and bonding environment in recovered samples. Spectra were obtained from polished, sectioned samples in transmission mode using a Thermo-Nicolet iN10MX IR microscope at the School of Earth Sciences, University of Bristol. Samples were placed on thin BaF_2 plates, and unpolarised spectra collected over the range 4000-450 cm^{-1} at a 4 cm^{-1} spectral resolution, using a variable shaped aperture to avoid cracks and inclusions within grains. Background spectra were obtained through the BaF_2 plate prior to each transect, and automatically subtracted from sample spectra. Raman spectra were obtained using a Thermo Scientific DXRxi Raman Imaging microscope, also at the School of Earth Sciences, University of Bristol, using a 532nm (green) doubled Nd:YVO₄ DPSS excitation laser, a 400 lines mm^{-1} extended range grating, a 50x objective, a 25 μm confocal pinhole and EMCCD detector. Approximately 1550 data points were acquired from 50-6000 cm^{-1} , typically at a laser power of 9 mW for between 0.3 and 4s, averaged over 600-1000 scans.

3. Results

3.1 Phase and melt relations in recovered samples.

Most experiments were conducted at 2 GPa as this is an approximate pressure for multiple mineral saturation in low-Ti picritic lunar systems, and within the range of estimates for the pressure of formation of mare basalts and associated picritic glasses (Elkins-Tanton et al., 2003; Shearer et al., 2006). Run products consisted of quenched glass with some minor growth of quench crystals, and coexisting crystals of olivine, orthopyroxene, and pigeonite. There was no evidence of a fluid phase in any experiment. This is consistent with the relatively

low amount of volatiles loaded (or derived from the graphite) which is below fluid saturation in the melt for most of the expected species at these pressures. Experimental details and run products are listed in Table 2, and SEM images representative of run products are shown in Figure 1. High failure rate was noted in initial experiments, in part because the effect of low fO_2 under H-rich conditions appears to stiffen and embrittle many metals, including Pt and Fe capsules, which ensure the integrity of the experiment.

Run Fe_2 is an example of an earlier experimental design where sample charge and buffer were separated by Pt foil. As evident in Figure 1A, melt from the experimental charge leaked and partially reacted with the buffer during the experiment. Reaction resulted in Cr-enrichment of the experimental charge and precipitation of a Cr-spinel phase not seen in other experiments. The experimental charge also contains an Fe-rich metal phase, common with all experiments conducted using Fe capsules, and attesting to Fe-saturated, reducing conditions. In subsequent experiments the buffer mix was sealed within a welded Pt capsule (Figure 1B), a design with a significantly higher success rate despite Pt embrittlement under run conditions. However, glass compositions (Table 3) demonstrate that high run temperatures still result in Cr gain in the silicate run products due to solid state diffusion and/or alloying of Cr with the Pt capsule. Various experimental designs were trialed to circumvent this issue, including alternative capsule materials and solid buffers. However, alloying remained an issue in all designs, and other designs had higher failure rates. Therefore, we adopted the Fe-Pt-Cr-Cr₂O₃ design for the limited number of subsequent experiments described here.

Use of Fe capsules and reduced starting materials results in reducing, Fe-saturated run conditions at or below IW. Run fO_2 is further buffered by reaction of Cr and Cr₂O₃, although this is complicated by alloying of Cr with Pt. A lack of thermodynamic data on the Pt-Cr system means that fO_2 cannot readily be calculated from the sample assembly. However, the presence of a free Fe phase in run products using Fe capsules means that fO_2 can be estimated based on the exchange of Fe between silicate melt and the Fe-phase:

The equilibrium constant for [2] can be expressed as:

$$\log K = \log(a_{FeO}^{melt}/a_{Fe}^{metal}) - \frac{1}{2}\log fO_2 = \log(X_{FeO}^{melt} \cdot \gamma_{FeO}^{melt} / X_{Fe}^{metal} \cdot \gamma_{Fe}^{metal}) - \frac{1}{2}\log fO_2 \quad [3]$$

where a_{FeO}^{melt} and a_{Fe}^{metal} are the activities of FeO in silicate melt and Fe in Fe metal, respectively, where fO_2 is oxygen fugacity under experimental conditions, and X and γ corresponding mole fractions and activity coefficients for each. For pure Fe metal and pure FeO, i.e. the IW buffer, activities are unity and [3] can be expressed as:

$$\log K = \frac{1}{2} \log fO_2^{IW} \quad [4]$$

where fO_2^{IW} is the oxygen fugacity of the IW buffer under experimental conditions. Combining (3) and (4):

$$2 \log(X_{FeO}^{melt} \cdot \gamma_{FeO}^{melt} / X_{Fe}^{metal} \cdot \gamma_{Fe}^{metal}) = \Delta \log fO_2^{IW}$$

demonstrates that concentrations of FeO in the melt phase, and Fe in the metal phase can be used to determine fO_2 under run conditions relative to the IW buffer. Data from O'Neill and Eggins (2002) was used to estimate γ_{FeO}^{melt} . Assuming that the Fe phase in experiments is pure Fe implies fO_2 in run products varying from 1.2 to 2.1 log units below the IW buffer. The low FeO content of experiment Fe_13 gives a much lower fO_2 of 4.4 log units below the IW buffer. Experiments Fe_13 and Fe_14 used an Fe-free starting mix, and Fe_13 may have failed to attain equilibrium between the Fe capsule and experimental charge (see below), so this value is likely unreliable. The FeO content of melt in Fe_14 is higher and comparable to experiments performed using the FeO-rich starting mix, suggesting that full equilibrium was attained. Fe_14 was performed at 160°C higher temperature, providing an explanation as to why this experiment achieved equilibrium and Fe_13 did not.

Calculations of fO_2 presented in Table 2 assume that the metal phase is pure Fe. Compositions of exsolved Fe in run products were not determined here, although it is unlikely that the material is pure Fe, and may contain variable amounts of O, Si, Cr and other elements. The effect of such impurities on the calculation of fO_2 can be estimated using the model of activity coefficients in liquid Fe metal by Wade and Wood (2005). The effect of adding significant amounts ($X=0.1$) of Si, Cr etc to the Fe phase only results in an increase in $\Delta \log fO_2^{IW}$ of ≈ 0.1 . As such, estimated fO_2 based on melt compositions in table 2 provides a reasonable lower bound. As expected, values lie well within the range imparted by the sample assembly (IW and Cr-Cr₂O₃ buffers). This range overlaps conditions assumed for lunar mantle source regions, and allows us to assess the effect of reducing conditions on volatile partitioning.

In contrast, Pt_C experiments do not contain a Fe-phase, and fO_2 cannot be estimated. The absence of an Fe-rich phase in the experimental charge is consistent with a slightly higher fO_2 imparted from the sample assembly, i.e. fO_2 at approximately IW or higher. However, the presence of an Fe-phase in experiments using Fe capsules might represent a dynamic process of Fe dissolution at the edge of the capsule and exsolution of an Fe-rich solid within the sample volume. Experiments Fe_13 and Fe_14 used Fe-free starting materials to test the extent of equilibration between Fe capsules and run products. For the higher temperature Fe_14, comparable Fe melt contents with other experiments strongly indicates attainment of equilibrium, implying that exsolution of Fe in run products is not simply a transport process, but a reflection of chemical equilibration under run conditions. Experiments Fe_6 and Fe_10, which produced 100% melt with no evidence for the presence of crystalline (silicate) phases, have melt FeO contents substantially lower than that of the Fe-rich starting composition used, implying that melt FeO contents are, similarly, not simply reflective of the crystallisation of more Fe-rich solid phases. Instead, melt composition is reflective of the equilibrium given in [2]. Lack of exsolved Fe in Pt-C experiments implies more oxidising conditions above the IW buffer. More broadly, capsule-sample exchange noted in experiments Fe_13 and Fe_14 supports attainment of equilibrium in experiments, aside from the FeO content in Fe_13. Demonstrating chemical equilibrium in high pressure/temperature experiments is notoriously difficult. However, the fact that experiments described here are performed at high temperatures, have high melt fractions favouring melt-crystal exchange throughout experimental charges, and that run products typically consist of euhedral, unzoned crystal phases supports attainment of equilibrium, or at least development of steady state conditions. Cr₂O₃ contents of run products are variable between experiments, although this likely reflects variations in capsule morphology rather than disequilibrium.

Compositional data for quenched melt was obtained in regions distal from quench crystals, but as close to analysed solid phases as possible. Aside from Fe_13, where Fe exchange with the capsule did not reach equilibrium, Fe contents in all run products are variable, with melt compositions ranging from 7.5 to 18.4 weight %. Fe_5 is the exception, where silicate melt FeO content, 29.5%, exceeds that of the starting mix. Melt composition is additionally dependent on phase relations, although in this experiment only olivine and quenched melt were identified, and olivine has a similarly high FeO content. The reason for this discrepancy cannot be fully explained. Olivine in Fe_4 is also relatively FeO rich and in equilibrium with melt with a substantially lower FeO content. However, the lower temperature Fe_4 contains additional orthopyroxene, which has a much lower FeO content. Higher FeO melt contents in Fe_5 imply $\Delta\log fO_2^{IW} \approx -1.3$, which is less reducing than other experiments with Fe capsules. As such, this may have resulted in net dissolution of FeO into the melt from the capsule, as opposed to exsolution of variable Fe from the melt, as noted in other samples.

Melt in Pt_C experiments has FeO contents of 9.9 and 14.0 weight %, comparable to experiments with Fe capsules. However, in this instance there is no obvious exsolution of Fe metal from the experimental charge which might explain reduction in FeO content compared to the starting bulk composition. Similarly, coexisting orthopyroxene in these experiments has similarly low FeO. Fe loss to Pt is common in high pressure experiments, which might explain observed compositions if parts of the experimental charge were in contact with the outer Pt capsule. Although examination of run products suggests that inner graphite capsules retained integrity, this possibility cannot be discounted. Alternatively, it is possible that the presence of some additional Fe-rich phase, such as small quantities of a spinel-type phase, accounts for lower than expected melt Fe contents. SEM examination of run products provides no evidence for this, although the possibility cannot be discounted.

Phase relations in run products vary with experimental conditions and capsule type. For the most reduced Fe-bearing experiments with Fe capsules, olivine comes onto the liquidus below 1550°C followed by orthopyroxene below 1400°C, with significant amounts of melt still present (Figures 1B, C). This is broadly consistent with previous studies using low-Ti ultramafic lunar glass bulk compositions at 2 GPa and under reducing conditions (e.g. Barr and Grove, 2013; Chen and Lindsay, 1982; Chen et al., 1983; Elkins-Tanton et al., 2003). From experiment Fe_2 it is apparent that enrichment in Cr₂O₃ stabilises Cr-rich spinel in run assemblages, and orthopyroxene at the expense of olivine. Previous studies indicate that clinopyroxene is stabilised at lower temperatures, sometimes at the expense of olivine, and/or at slightly higher pressures (e.g. Barr and Grove 2013; Elkins-Tanton et al., 2003). Indeed, the lowest temperature (1340°C) experiment, Fe_13 which was run with an initial Fe-free bulk composition that was then allowed to equilibrate with the Fe capsule did result in large intergrowths of orthopyroxenes and pigeonite in equilibrium with the melt phase. In the higher temperature 1500°C run for the same design, substantial reaction of the experimental charge with the Fe capsule occurred, implying attainment of Fe saturated conditions during the experiment. However, unlike the olivine+melt assemblage of run Fe_5 also at 1500°C, Fe_14 consisted of small pigeonite crystals disseminated throughout a glass/melt phase. Stabilisation of pigeonite in these experiments might be due to Fe-Mg exchange in the run products, and/or some effect of small variations in fO_2 . An fO_2 dependence on melt relations in more Ti-rich systems was noted by Krawczynski and Grove (2012) and Brown and Grove (2015), due to its effect on Fe-Mg exchange, Ti valence and Fe-Ti coordination. In particular,

Brown and Grove (2015) noted that a decrease in fO_2 resulted in an increase in the multiple saturation point, and stabilisation of pigeonite. As such, varying bulk Fe contents during experiments here might explain the presence of pigeonite rather than olivine. An additional complication here is the effect of run conditions on SiO_2 activity. Lower FeO abundance in experiments results in an increase in the ratio $SiO_2/(FeO+MgO)$. An increase in this ratio could conceivably stabilise pyroxene over olivine as a liquidus phase.

Experiments Pt_hal 1 and Pt_hal 2 were less reduced due to the use of graphite lined Pt capsules. Run products contain smaller orthopyroxene crystals in equilibrium with a melt phase instead of the liquidus olivine formed at more reduced conditions. Replacement of orthopyroxene for olivine was noted by Barr and Grove (2013) as characteristic of higher-pressure conditions. Given these experiments were consistently run at 2.0 GPa, a change in phase relations instead implies some effect of capsule design. For Pt_C experiments, melt FeO contents are again towards the lower range of compositions measured in this study. As such, a similar effect of Si activity in lower FeO systems might stabilise pyroxene, and/or it is again possible that fO_2 influences Fe (and Ti) coordination and phase stability. Melt H_2O contents in Pt_C experiments are also higher than other experiments (Table 3), implying either that water was better retained during these experiments or that H-related species in the more reduced runs are less soluble in silicate melt. In this capsule design most water should be retained in the experimental charge, although it is evident from stiffening of Pt that some H diffuses into the outer capsule material. In contrast, with the Fe+Pt capsule design one might expect H diffusion into the buffer mix to give lower 'water' contents in the melt. A difference in melt 'water' content may also affect near-liquidus phase stability, as OH is a melt network modifier.

3.2 H_2O , F, Cl, and CO_2 composition data.

F, Cl and H_2O contents of all phases are listed in Table 3. F and Cl contents of melts were determined using both EMPA and SIMS. As shown in Figure 2 and Table 3, there is reasonable consistency between SIMS and EMPA data. For F there is a general linear correlation with some scatter. There is a consistent offset between SIMS and EMPA data such that SIMS F contents are between 0.5 and 1 wt% higher. This could be related to a matrix mismatch between these samples and the standards in SIMS analysis, although it might equally relate to a systematic error arising from the EMP calibration. For Cl data, aside from Pt_hal1, there is good consistency between SIMS and EMPA data and a close to 1:1 linear correlation. When determining partition coefficients (concentration in mineral/concentration in melt), SIMS melt data have been used. Cl and F contents of all mineral phases were below the detection limit for EMPA, and H_2O contents cannot be determined by EMPA. Therefore, use of only SIMS data for determining partition coefficients ensures consistency.

The loaded water content of all experiments at 2 wt% is well below saturation for the melt. H_2O contents in mineral phases in all samples are subsequently low, from a few 10s to 100s ppm by weight, compared to other fluid-saturated experiments. H_2O contents of melt are higher, although significantly lower than the loaded 2 wt% in the Fe+Pt capsule runs (Table 3). This implies that a significant fraction of 'H' is lost from charges during these experiments, possibly relocated to the buffer capsule, but also into Fe and Pt capsule materials under reducing conditions. This contrasts with the higher water contents in the Pt-C experiments. F and Cl

are also incompatible and concentrated in the melt phase, and measured concentrations suggest no loss during the experiment. In fact, for samples Fe_6 and Fe_10, which are 100% melt, F contents of the melt phase are higher than the starting composition. It cannot be discounted that these experiments did produce small amounts of an additional solid phase not observed in sections. However, this would also be explained by systematic over determination in measured F by SIMS, or by weighing errors in starting mix preparation.

SIMS analysis of both mineral and melt in Fe capsule experiments suggests heterogeneous distribution of small amounts of C, measured as CO₂ (Table 3). Fe capsule experiments are nominally C-free. However, contamination of experimental charges during loading and during preparation of starting mixes would provide a source for the detected C. C ingress from the graphite furnace is another possibility (Brooker et al., 1998). For Pt-C experiments, the use of an inner capsule results in graphite saturation and a ready source for C, C-O, C-H species during experiments. CO₂ contents of melt in these experiments are notably higher.

Representative FTIR spectra obtained from glass and mineral phases are shown in Figure 3. Glass spectra contain a broad, asymmetric absorption feature over the wavenumber range 3000-4000 cm⁻¹ that is characteristic of O-H stretching. Absence of molecular H₂O bending absorption bands at 1630 cm⁻¹ and 5200 cm⁻¹ suggests this species is largely absent, consistent with the low total 'water' concentration (Stolper, 1982). Even under reduced conditions, water is dominantly incorporated as OH⁻ in glass, either as isolated OH⁻ or as clusters of OH⁻ groups, or in accordance with Cody et al. (2020), possibly even as H₂O. Only one spectrum contains the broad absorption feature around 4000-4500 cm⁻¹ which Kadik et al. (2006) assigned to molecular H₂. This sample also has an unassigned broad feature at 2600 cm⁻¹. There is no H₂ specific calibration for silicate melt which would allow estimation of an equivalent 'H₂O' content corresponding to the 4000-4500 cm⁻¹ band, although it is likely that the concentration of H₂ in Fe-10 glass is small in comparison with concentration of O-H. This H₂ band is not noted in other spectra implying that H₂ is either absent or below detection limit. Sample Fe_10 was synthesised at higher pressure than other samples (3 GPa compared to 2 GPa) but still failed to display evidence of significant H₂. It might be expected that higher pressure would stabilise a small proportion of 'water' as H₂, in accordance with Hirschmann et al. (2012). Attempts to access conditions higher than 3 GPa resulted in a 100% failure rate with this capsule design.

Spectra from large orthopyroxene crystals also show broad absorption features in the O-H stretching frequency range 3000-3800 cm⁻¹ (e.g. Stalder, 2004; Bromiley and Bromiley, 2006). The double absorption feature between 2300-2400 cm⁻¹ noted to varying degrees in all spectra is due to failure to correct for atmospheric CO₂ within the spectrometer beam path. There is no indication that this CO₂ is intrinsic to samples. Spectra do, however, contain multiple absorption features around 2900 cm⁻¹. 3 distinct, sharp bands are noted in spectra, reminiscent, although at slightly different wavenumbers, to a cluster of small, sharp absorption bands which Kadik et al. (2006) assign to either CH₄ or C-H related species. Although samples were re-cleaned in solvent, spectra still displayed these features. Despite this, it cannot be discounted that these bands represent contamination from organic material, such as resin used in sample preparation. Raman examination of quenched melt in samples Pt_hal1 and Pt_hal2 (which could not be prepared as IR wafers) revealed the presence of a broad hump at a Raman shift of approximately 3500 cm⁻¹ due to OH⁻, with no characteristic sharp absorption band around 4100 cm⁻¹ due to H₂. Raman spectra show no evidence for the

presence of C-H related species, despite the higher C content of these samples, although this could be due to higher fO_2 imparted by this capsule design. As expected, higher fO_2 in these experiments means that all 'water' is incorporated as OH^- in the melt. Any H and C related species in the crystalline phases would be below the detection limit of Raman spectroscopy in these samples.

F, Cl, H_2O and CO_2 mineral/melt partition coefficients ($D_{F/Cl/H_2O/CO_2}^{mineral/melt}$) calculated using SIMS data are included in Table 3. Even for a limited dataset, D_{H_2O} , D_F and D_{Cl} data show promising consistency, except for sample Fe_13 which has a larger $D_{H_2O}^{opx/melt}$ than other samples. This is also the sample which has the most prominent C-H absorption bands in FTIR spectra and a low bulk FeO content. In contrast, there is a much larger scatter for the $D_{CO_2}^{min/melt}$ data both within and between samples, with values also scattered around 1. Although previous studies demonstrate that C can be incorporated into reduced silicate melts (Kadik et al., 2006; Hirschmann et al., 2012; Ardia et al., 2013), it is likely that measured CO_2 contents here largely reflect contamination; therefore, CO_2 partitioning is not considered further.

4. Discussion

4.1 Controls on H_2O , F, and Cl mineral/melt partitioning in reduced lunar systems.

Figure 4 shows F, Cl and H_2O partition coefficients from this and previous studies as a function of temperature. This new data for reduced lunar conditions confirms all three volatiles are incompatible, consistent with previous studies. There is a general trend $D_F > D_{H_2O} > D_{Cl}$, except for limited olivine data, which suggest $D_{Cl} > D_{H_2O}$. H_2O is slightly more incompatible than F for all phases, but Cl is much more incompatible than F. This would be predicted based on the significantly larger ionic radius of Cl relative to F, assuming similar incorporation mechanisms. For F partition coefficients, pigeonite > orthopyroxene > olivine, which is again consistent with observed halogen partitioning in natural, terrestrial samples (Urann et al., 2017). For H, pigeonite > orthopyroxene > olivine, and for Cl, pigeonite > orthopyroxene = olivine. Data from Hauri et al. (2006) is from reanalyses of experimental products from numerous previous studies in terrestrial systems, under various conditions. Rosenthal et al. (2015) conducted experiments using a model tholeiitic composition and either graphite-lined Pt capsules (similar to experiments Pt-hal1 and Pt-hal2 here, but not with reduced starting mixes) or Fe-saturated Pt capsules (more oxidising). Dalou et al. (2012) used model basaltic and peridotitic compositions that were nominally H-free and more oxidised than this study, as their use of graphite capsules probably buffered fO_2 between FMQ+1 and FMQ-2. Beyer et al. (2012) performed experiments in simplified $CaO-MgO-Al_2O_3-SiO_2 \pm Na_2O$ systems using Pt capsules; fO_2 was not controlled, but probably lay close to the more oxidising Ni-NiO (NNO) buffer considered 'intrinsic' in solid-media apparatus (Stokes et al., 2019; Matjuschkin et al., 2015). Joachim et al. (2015, 2017) also performed experiments in a simplified $CaO-Al_2O_3-MgO-SiO_2$ system under water absent and water present conditions, respectively, also under unbuffered but presumably more oxidising conditions. O'Leary et al. (2011) performed experiments using a natural high- Al_2O_3 basalt starting mix and nominally Al-free synthetic analogue, and used olivine-Ni composite capsules with a Ni-NiO buffer. As such, comparison of experimental partition coefficients demonstrates that fO_2 has little discernible influence on halogen or H_2O partitioning, at least down to fO_2 of approximately IW-2 at these pressures. Importantly, this

implies that partitioning data from studies under model terrestrial conditions provide insight into the behaviour of volatiles under lunar conditions.

Temperature has little effect on H₂O and halogen partitioning, except possibly for Cl. Joachim et al. (2015) noted a temperature dependence of $D^{\text{mineral/melt}}_{\text{Cl}}$ in a simple model system. However, the same study also noted a strong effect of temperature on F partitioning which is not supported by examination of data across other studies (Figure 4). In Figure 5 there is a clear correlation between D_{F} and $D_{\text{H}_2\text{O}}$, (excluding sample Fe_13) as noted by Joachim et al. (2017). There is a weaker correlation between D_{F} and D_{Cl} , and possibly also a correlation between D_{Cl} and $D_{\text{H}_2\text{O}}$. Joachim et al. (2017) suggested a negligible effect of H₂O on Cl partitioning, and suggested that correlations between F and H₂O partition coefficients implied the presence of clumped F and H defects in olivine, as proposed by Creppisson et al. (2014). Olivine partitioning data in this study is too limited to test this, although from Figure 5 it is clear that D_{F} and $D_{\text{H}_2\text{O}}$ are correlated across all data for olivine, orthopyroxene and pigeonite.

It has been repeatedly observed that H₂O pyroxene-melt partitioning, and possibly olivine-melt partitioning is dependent on mineral Al₂O₃ content, and in particular, on the extent of Al substitution into tetrahedral sites in mineral structures (^{IV}Al³⁺) (e.g. Hauri et al., 2006; Tenner et al., 2009; O'Leary et al., 2011). Figure 6 shows a broad trend of increasing $D^{\text{pyroxene/melt}}_{\text{H}_2\text{O}}$ with increasing ^{IV}Al³⁺, consistent with previous studies. Data here fit this broad trend, implying that a coupled substitution of Al³⁺ for tetrahedral Si⁴⁺ charge-balances H incorporation in ortho- and clinopyroxene under relatively reducing conditions. The obvious out-lying sample is Fe_13, the lower temperature experiment performed using an Fe-free starting mix. Either this sample is not fully equilibrated, or low bulk Fe content has a marked influence on H₂O partitioning. The effect of increasing ^{IV}Al³⁺ on $D^{\text{clinopyroxene/melt}}_{\text{F}}$ for data here is broadly in accordance with the trend noted by O'Leary et al. (2011) in high and low alumina basalts. Scatter in the wider dataset implies additional controls on F incorporation, although from Figure 6 it is apparent that coupled substitutions involving Al³⁺ are also an important control on F pyroxene-melt partitioning.

Mosenfelder and Rossman (2013a,b) similarly proposed that F incorporation in pyroxene is coupled to both Al³⁺ and Fe³⁺ substitution onto tetrahedral sites, and to monovalent cation substitutions onto the M2 site. No effect of mineral Fe content on F partitioning is noted here, although this is expected due to the low *f*O₂ used which excludes the presence of Fe³⁺. However, we observe clear positive correlations between mineral F content and mineral TiO₂, Al₂O₃, and Cr₂O₃ contents (Figure 7). Correlation between F (and H₂O) and TiO₂ across mineral phases could indicate F incorporation via Ti-clinohumite/Ti-humite type planar defects, although this is not supported by detailed TEM analysis (e.g. Joachim et al., 2015). However, in these reduced conditions it is likely that a fraction of Ti is incorporated in pyroxenes as Ti³⁺, consistent with XANES measurements which demonstrate that pyroxenes and olivine equilibrated at similar *f*O₂ can contain up to 25% Ti as Ti³⁺ (Leitzke et al., 2018). Coupled Ti³⁺ and OH⁻ defects have been noted in other nominally anhydrous minerals such as rutile and its high-pressure polymorph TiO₂ (II) (Bromiley et al., 2004b; Bromiley and Hilairret, 2005) under more oxidising, high-pressure conditions. As such, all trends in Figure 7 likely result from F incorporation charge-balanced by M³⁺ substitutional defects, as discussed in detail in Dalou et al. (2012). In agreement with Dalou et al. (2012) and Mosenfelder and Rossman (2013b) there is also an additional weak correlation between mineral Na content and F. Correlations are generally weaker for Cl due to greater scatter in a smaller data set. However, it is possible that

there is a similar correlation between $^{IV}Al^{3+}$ on $D_{\text{clinopyroxene/melt}}^{Cl}$ (Figure 6). It is difficult to assess the extent to which Al-Si substitution into olivine could charge-balance F and Cl incorporation, although a wider comparison of data (Figure 6) possibly supports a positive correlation between olivine Al_2O_3 content and $D_F^{\text{olivine/melt}}$.

Both Dalour et al. (2012) and Urann et al. (2017) observed that melt polymerisation has an effect of mineral-melt partitioning of F and to a lesser extent, Cl. Melt polymerisation can be represented by the ratio of non-bridging oxygen to tetrahedral sites (NBO/T) using major element melt data, and is included in Table 3 and compared to partition coefficients in Figure 8. Within scatter, D_F appears to generally decrease with increasing NBO/T in accordance with previous studies, and there is a similar, stronger control of NBO/T on D_{H_2O} . Any such relationship in the Cl dataset is less clear.

In summary, fO_2 has no discernible influence on F, Cl and H_2O partitioning. Partition coefficients for all 3 volatiles are broadly comparable between the reduced model lunar system used here and model terrestrial systems under more oxidised conditions. Volatile incorporation mechanisms are also similar, implying that ‘water’ is structurally incorporated in silicate melt, pyroxenes and olivines dominantly as OH^- . Kadik et al. (2006) concluded that at $fO_2 = IW-2.4$ ‘water’ in silicate melts is largely incorporated as OH^- , with H_2 and C-H groups dominating at more reduced conditions, although their experiments were conducted at higher pressure (4 GPa). Hirschmann et al. (2012) suggested that pressure significantly increases the proportion of H_2 in silicate melts. It is possible that at more reducing conditions at higher pressures, the proportion of H_2 in both mineral and melt phases increases, potentially influencing H partitioning in some way yet to be explored. However, for fO_2 estimates for the lunar interior, and at the relatively low pressures where melting is likely to have occurred, it appears that most ‘water’ will be incorporated as OH^- .

4.2 Volatile redistribution during lunar magmatic processes

Partition coefficients can be used to estimate the volatile content in mantle source regions for lunar volcanic products. For example, Zhang et al. (2019) used a batch melting calculation (4 and 8% partial melting of a lunar cumulate consisting of 50% olivine, 25% pigeonite and 25% orthopyroxene) to estimate a source region for lunar volcanic glasses with 6-22 ppm H_2O . By comparison, the water content of Earth’s mantle is estimated to be 290 ppm, or 100 ppm for the depleted uppermost mantle, implying significant depletion of ‘water’ in the Moon relative to Earth (Zhang et al., 2019). The same calculation using average $D_{H_2O}^{\text{min/melt}}$ values determined here (excluding Fe₁₃) gives a slightly lower maximum H_2O content of the lunar mantle of 15 ppm. Applying the same calculation to F and Cl contents of mare basalt olivine-hosted melt inclusions of 34-77 and 1.7-3.0 ppm, respectively (Chen et al., 2015), gives lunar mantle volatile contents of 2.4-8.4 ppm for F, and 0.07-0.3 ppm for Cl. For comparison, Ni et al. (2019) estimated a lunar mantle source region based on melt inclusion data with H_2O of 84 ppm, F of 5 ppm and Cl of 0.39 ppm. Estimated terrestrial halogen contents are variable, as recently summarised by Klemme and Stalder (2018), with proposed primitive mantle F and Cl contents ranging from 18-25 ppm, and 1.4-35 ppm, respectively, depleted upper mantle F and Cl contents ranging from 11-16 ppm, and 0.5-1 ppm, respectively, and bulk silicate Earth F and Cl contents of approximately 15 ppm, and 17 ppm, respectively. As such, partitioning data here imply a lunar mantle source region which is both significantly volatile-depleted relative to

the terrestrial mantle, and depleted in Cl relative to F and H₂O. As previously noted (e.g. Hauri et al. 2015; McCubbin et al. 2015; Boyce et al., 2015), depletion of Cl compared to both F and H₂O is characteristic of the lunar mantle.

As noted by McCubbin et al. (2015), however, calculation of lunar mantle volatile contents from geochemical characteristics of volcanic products can give a misleading impression of bulk lunar composition. The lunar mantle is likely heterogenous with respect to water and other volatiles (McCubbin et al., 2015), and high volatile contents promote mantle melting. As such, calculated volatile contents from mare basalt and volcanic glass data may not be representative of the ‘average’ lunar mantle, and may be overestimates. Following accretion of the Moon, cooling and progressive crystallisation of the Lunar Magma Ocean (LMO) would have resulted in partitioning of F, Cl and H₂O between mantle cumulates and the remaining magma. The incompatible nature of all three volatiles means that they would have been increasingly concentrated in the final products of LMO solidification. Differences in incompatibility may have also resulted in relative fractionation of F, Cl and H₂O. McCubbin et al. (2015) argued that depletion of Cl relative to F and H₂O in lunar volcanics implies sourcing from a lunar mantle whose composition largely reflects mineral-melt partitioning of volatiles during LMO solidification.

Elkins-Tanton and Grove (2011) used published, i.e. ‘terrestrial’, H₂O partition coefficients to model distribution of H₂O during LMO crystallisation, and suggested an initial LMO ‘water’ content of approximately 1000 ppm H₂O. McCubbin et al. (2015) used published or estimated partition coefficients for F, Cl and H₂O, corrected for varying mineral chemistry, to model sequential solidification of the LMO using the crystallisation model of Elardo et al. (2015), and constrained volatile concentration and relative fractionation. Here we adopt a similar approach, incrementally solidifying a LMO over 100 steps using the crystallisation sequence of Rapp and Draper (2018) (Table 4). At each step we use $D^{\text{min/melt}}$ values for H₂O, F and Cl based on data from this study, and a fractional crystallisation calculation to determine volatile contents in remaining magma and newly-formed cumulate (Table 4, and supplementary material). McCubbin et al. (2015) derived models for the effect of ^{IV}Al³⁺ on volatile partition coefficients to account for variations in $D_{\text{H}_2\text{O}/\text{F}/\text{Cl}}$ due to changes in mineral chemistry during the various stages LMO solidification. However, due to uncertainties in the correlations between $D_{\text{H}_2\text{O}/\text{F}/\text{Cl}}$ and ^{IV}Al³⁺, especially for Cl, and variations in $D_{\text{H}_2\text{O}/\text{F}/\text{Cl}}$ due to other compositional effects (including the extent of melt polymerisation), here we use specific $D_{\text{H}_2\text{O}/\text{F}/\text{Cl}}$ for samples with broadly similar compositions to those in the experiments of Rapp and Draper (2018). $D_{\text{H}_2\text{O}/\text{F}/\text{Cl}}^{\text{olivine/melt}}$ are taken from Fe_5. During comparable stage 1 experiments, Rapp and Draper (2018) note variations in olivine composition from Al₂O₃ of 0.04-0.13 wt%, compared to 0.1 wt% for olivine in Fe_5. Orthopyroxene ^{IV}Al³⁺ varies from 0.08 to 0.128 apfu in experiments here, overlapping compositions for orthopyroxene in stage 2 (0.096-0.124) in experiments of Rapp and Draper (2018). Therefore, for stage 2 we use average D values for orthopyroxene from experiments here, not including Fe_13. For stage 3, orthopyroxene in experiments of Rapp and Draper (2018) is slightly more aluminous, with ^{IV}Al³⁺ varying from 0.128-0.184. Any increase in $D^{\text{orthopyroxene/melt}}$ for F and H₂O due to this increase in ^{IV}Al³⁺ is small, and possibly minor compared to other compositional changes. Furthermore, because of a lack of data on how $D^{\text{orthopyroxene/melt}}$ varies for Cl we use the same partition coefficients as used for stage 2. $D_{\text{H}_2\text{O}/\text{F}/\text{Cl}}^{\text{clinopyroxene/melt}}$ are taken from Fe_14. Clinopyroxene ^{IV}Al³⁺ for this sample is 0.14, and CaO content 16.6 wt%, compared to ^{IV}Al³⁺ =0.18 and CaO=13.45 wt% for clinopyroxene in stage 3 crystallisation experiments of Rapp

and Draper (2018). For plagioclase we use an average $D_{\text{H}_2\text{O}}^{\text{plag/melt}}$ from Lin et al. (2019), who measured H_2O partitioning between plagioclase and melt in a model lunar system. Due to a lack of data on plagioclase/melt partitioning of F and Cl, and the similarity of H_2O partition coefficients for plagioclase from Lin et al. (2019) to pigeonite data here, we use pigeonite Cl and F partition coefficients to tentatively model plagioclase-melt partitioning. Rapp and Draper (2018) note formation of an intermediate Ca-content plagioclase during stage 4 experiments, with $^{\text{IV}}\text{Al}^{3+} = 0.05$ to 0.09 . To model crystallisation of this phase we use orthopyroxene partitioning data from Pt_hal1 ($^{\text{IV}}\text{Al}^{3+} = 0.08$).

LMO solidification was modelled up to 97% crystallisation. Later stages of crystallisation involve formation of more complex cumulate assemblages, including mineral phases for which no partitioning data is available. Furthermore, the effect of progressive increases in melt polymerisation are not considered here; these may have a considerable influence during the latter stages of LMO solidification. The purpose of modelling here is, instead, to test the extent to which new data allow trends in volatile abundance in LMO cumulates to be identified. There are, however, two additional complications in using such an approach to model lunar mantle volatile abundances. Firstly, cumulates formed during LMO solidification will contain a proportion of trapped liquid. Elkins-Tanton and Grove (2011) argued for a proportion of trapped intercumulate liquid (ICL) of 5-10%, which would have a strong influence on bulk cumulate incompatible element chemistry. Given that all volatiles are highly incompatible, this degree of liquid retention would dominate cumulate volatile content. McCubbin et al. (2015) argue that because of this, geochemical observations imply that the amount of intercumulate liquid (ICL) was likely low (below 1%). Here, we model ICL contents of 0 and 1% using the approach of McCubbin et al. (2015), by instantaneously trapping liquid at each stage of cumulate formation.

An additional complication is cumulate overturn and hybridisation during the latter stages of LMO solidification, which acts in effect to partially homogenise the lunar mantle (Shearer et al., 2006). One important effect of cumulate overturn is partial melting within overturned, hybridised cumulates, resulting in formation of mare basalts and associated volcanic products. As such, regions of the lunar interior ‘sampled’ by volcanic activity have any signature of LMO solidification ‘overprinted’ by cumulate overturn and associated processes. Despite this, modelling progressive crystallisation provides insight into the distribution of volatiles in the products of LMO solidification, including various cumulate sequences and later stage liquids (>99% crystallisation) which eventually form a proposed urKREEP component enriched in volatiles (Taylor et al., 2006).

To model the effects of LMO crystallisation on volatile distribution we use bulk silicate moon (BSM) volatile estimates from McCubbin et al. (2015). These are based on their LMO crystallisation model and estimates for the proportion of residual liquid trapped within cumulates formed during LMO solidification. LSHA* is a BSM composition which McCubbin et al. (2015) derive from modelled F abundances in lunar soil and highlands apatite. This BSM composition has an upper volatile content of 13.1 ppm H_2O , 7.1 ppm F and 13.8 ppm Cl. CFHA* is a BSM composition which McCubbin et al. (2015) derive from Cl chondritic and highlands apatite F abundances. This BSM has upper volatile concentrations of 114 ppm H_2O , 60 ppm F and 123 ppm Cl. As such, these models provide volatile-poor and relatively volatile-rich estimates of bulk lunar composition, although with a markedly lower H_2O content than that proposed by Elkins-Tanton and Grove (2011).

Figure 9 shows the results of LMO solidification modelling using the CFHA* BSM composition (additional information, and results using both CFHA* and LSHA* compositions is given in supplementary material). All three volatiles are highly incompatible, and as expected early formed cumulates are essentially volatile-free. Once orthopyroxene crystallises and solidification exceeds 60% there is a marked increase in cumulate volatile content, and importantly, a marked change in volatile ratios (Figure 6C). The slightly higher compatibility of F means that, despite overall volatile concentrations, F/H₂O in cumulate is initially >2, but following formation of pyroxene-rich cumulates, decreases sharply, and stays at slightly above 1 during latter stages of LMO solidification. Formation of pyroxene also results in a marked increase in the ratio F/Cl, which approaches 3 during latter stages of LMO solidification. Addition of inter-cumulate liquid (ICL) masks these signatures of mineral-melt partitioning. However, even the addition of 1% ICL still results in marked trends in F/H₂O, which increases to 0.8 during LMO solidification, and F/Cl which approaches 1.

Results of modelling are in good agreement with McCubbin et al. (2015), despite differences in approach used. Cumulate volatile contents are low and largely dependent on the original LMO composition, but with enrichment of F relative to H₂O and F relative to Cl within cumulates. During latter stages of LMO solidification volatiles contents of cumulates approach a few 10s ppm for a CFHA* composition, and a few ppm for a LSHA* composition, even with additional 1% ICL. As such, regardless of differences in LMO crystallisation sequence used, or in choice of partition coefficients and the dependence of these on composition, there are clear trends arising from LMO solidification. For low estimates of the extent of trapped intercumulate liquid, lunar mantle cumulates are enriched in F relative to Cl, and in F relative to H₂O compared to the original LMO composition. As all volatiles are highly incompatible there is, correspondingly, a marked increase in volatile content of remaining liquid during LMO solidification (Figure 9A), which approaches 1000s ppm for each when the CFHA* composition is used, and 100s ppm for each with an LSHA* composition (supplementary material). However, there are only relatively minor changes in volatile ratios in the liquid, even during the latter stages of LMO solidification (Figure 6F). F/H₂O and F/Cl both remain close to 0.5, reflecting the original composition of the LMO.

5. Implications for volatiles in the early Earth-Moon system.

New partitioning data for H₂O, Cl and F presented here demonstrate that volatile incorporation in a reduced, model lunar system is comparable to more oxidised, terrestrial systems. At fO₂ down to approximately IW-2, H remains dominantly incorporated in nominally anhydrous mantle minerals as OH⁻, at least at relatively low pressures of the lunar interior. Comparison of limited F, Cl and H₂O mineral-melt partitioning data demonstrates that all three volatiles are highly incompatible, although F is slightly less incompatible, and Cl considerably more incompatible. Incorporation of all three volatiles is likely coupled to substitution of other minor elements in mantle minerals, and likely dependent on melt composition and structure.

New partitioning data supports previous work where coefficients from model and actual terrestrial systems are used to investigate volatile behaviour during lunar processes. Partition coefficients can be used to estimate volatile content of lunar mantle source regions from, for example, melt inclusion data. Results are consistent with estimates based on incompatible element ratios, implying a lunar interior which is depleted in volatiles relative to BSE, and importantly, strongly depleted in Cl relative to F. Forward modelling of LMO solidification using

new partitioning data supports the model of McCubbin et al. (2015). Cumulate phases have elevated F/H₂O and F/Cl relative to the original LMO composition, although the extent of any signature is dependent on the proportion of intercumulate liquid trapped during solidification. McCubbin et al. (2015) argue that a clear signature of Cl depletion in lunar material is consistent with a lunar mantle volatile abundance largely dependent of mineral-melt partitioning, implying low proportions of intercumulate liquid. However, although the lunar mantle can have an elevated F/Cl inherited from LMO solidification, mineral-melt partitioning is unable to fully account for the elevated F/Cl of lunar materials compared to chondritic and terrestrial abundances (Hauri et al., 2015).

Acknowledgements

Work was supported by the UK National Environmental Research Council via NE/M000346/1 (to Bromiley) and award of instrument time at the Edinburgh Ion Microprobe facility, IMF597/0516. Brooker was funded by the NERC Thematic Grant consortium NE/M000419/1. Dr Amrei Baasner is thanked for preparing starting mixes, and Dr Chris Hayward and Dr Richard Hinton for assistance in conducted EMPA and SIMS analyses, respectively. The authors thank Prof. Youxue Zhang and two anonymous reviewers whose comments and suggestions improved this manuscript considerably.

839 Table 1. Target model lunar compositions used for partitioning experiments. Target
840 composition is an Apollo green glass composition based on average glass bead analyses by
841 Saal et al. (2008), but discounting K and P.
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Oxide	Saal et al. (2008)*	Volatile free mix	Volatile-bearing mix
SiO ₂	45.67	45.59	44.07
TiO ₂	0.40	0.40	0.38
Al ₂ O ₃	7.79	7.77	7.52
Cr ₂ O ₃	0.63	0.63	0.61
FeO	19.75	19.72	19.06
MgO	16.81	16.78	16.22
MnO	0.27	0.27	0.26
CaO	8.73	8.72	8.42
Na ₂ O	0.12	0.12	0.12
K ₂ O	0.01	0.00	0.00
P ₂ O ₅	0.02	0.00	0.00
H ₂ O			1.98
F ₂			0.58
Cl ₂			0.78
<i>Total</i>	<i>100.21</i>	<i>100.00</i>	<i>100.00</i>

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845 Table 2: Experimental conditions and run products (successful runs only). Key: opx=orthopyroxene (low Ca pyroxene), Cr-sp=Cr-rich spinel
846 (due to buffer contamination), melt=quenched melt/glass, ol=olivine, pig=pigeonite.
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Run.	Capsule	Initial T (°C)	Final T (°C)	Pressure (GPa)	Duration (h)	Log fO ₂ range constrained from assembly ²	Estimated experimental log fO ₂ ³	Products
Fe_2	Fe+Pt foil	1500	1350	2	24	0 to -5.0	-2.1	opx+Cr-sp+melt
Fe_4	Fe+Pt	1500	1400	2	24	0 to -4.8	-1.7	ol+opx+melt
Fe_5	Fe+Pt		1500	2	24	0 to -4.4	-1.3	ol+melt
Fe_6	Fe+Pt		1550	2	24	0 to -4.2	-2.1	melt
Fe_10	Fe+Pt		1500	3	24	-0 to 4.4	-2.5	melt
Fe_13 ¹	Fe+Pt		1340	2	24	0 to -5.0	(-4.4)	opx+pig+melt
Fe_14 ¹	Fe+Pt		1500	2	24	0 to -4.4	-2.0	pig+melt
Pt_hal1	Pt_C		1500	2	72	-1 to +2	-	opx+melt
Pt_hal2	Pt_C		1450 ⁴	2	72	-1 to +2	-	opx+melt

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849 ¹ Starting mix is Fe-free but Fe is gained from the capsule

850 ² Relative to Fe-FeO (IW) buffer based on Fe capsule and Cr-Cr₂O₃ buffer, or estimated for use of graphite inner capsule.

851 ³ relative to IW, determined from FeO content of silicate melt in equilibrium with Fe metal (see text for details).

852 ⁴ Thermocouple failure during experiment, estimated temperature based on transformer output (±30°C)

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Table 3. Compositions of run products determined by electron microprobe and SIMS and corresponding mineral-melt partition coefficients.

	Fe_2		Fe_4			Fe_5		Fe_6	Fe_10
	<i>melt</i>	<i>opx</i>	<i>melt</i>	<i>ol</i>	<i>opx</i>	<i>melt</i>	<i>ol</i>	<i>melt</i>	<i>melt</i>
¹ n=	4/4/9	5/4/5	5/4/10	1/-/4	5/5/8	4/4/9	4/4/7	6/6/11	4/4
EMP data (wt%)									
Na ₂ O	0.41(3)	0.03(1)	0.27(2)	n.d.	0.02(0)	0.21(2)	n.d.	0.23(2)	0.24(2)
Al ₂ O ₃	9.82(27)	3.58(55)	9.11(22)	0.12(3)	3.88(55)	7.43(28)	0.10(0)	7.94(19)	8.06(12)
FeO	11.30(43)	11.55(74)	18.44(29)	22.35(172)	13.93(74)	29.48(32)	28.86(71)	11.71(14)	7.52(24)
MgO	11.71(28)	27.52(75)	14.77(15)	38.76(150)	26.74(75)	13.79(24)	34.36(37)	17.48(10)	18.26(26)
CaO	13.88(20)	1.83(6)	9.37(19)	0.21(1)	1.39(6)	7.29(15)	0.22(0)	7.94(9)	8.24(4)
SiO ₂	43.72(63)	53.35(66)	42.75(33)	37.77(22)	52.49(66)	38.65(41)	36.91(15)	44.51(65)	46.37(49)
Cr ₂ O ₃	3.02(1)	3.03(23)	1.56(1)	1.00(5)	1.96(16)	0.52(0)	0.30(1)	7.18(40)	6.10(17)
TiO ₂	0.72(1)	0.09(3)	0.56(1)	0.01(0)	0.07(1)	0.42(1)	0.01(0)	0.43(1)	0.44(1)
MnO	0.31(1)	0.22(3)	0.30(1)	0.22(1)	0.20(1)	0.24(1)	0.18(1)	0.26(1)	0.24(1)
F	3.88(31)	-	2.41(19)	-	-	1.71(11)	-	2.19(21)	2.27(4)
Cl	2.35(23)	-	0.83(1)	-	-	1.05(1)	-	1.17(1)	0.93(1)
<i>Total</i>	99.47(169)	101.20(35)	99.46(138)	100.44(45)	100.69(30)	100.52(103)	100.94(54)	101.25(60)	98.67(56)
NBO/T ²	1.44		1.65			2.08		1.83	1.61
Al _T (pfu)		0.110			0.123				
SIMS data (ppm)									
H ₂ O	2230(130)	39(12)	4120(170)	-	63(8)	3840(150)	4(4)	1410(80)	1230(150)
CO ₂	25(5)	30(10)	19(2)	-	20(3)	27(23)	18(5)	41(38)	37(5)
F	53800(1500)	1240(120)	37500(1600)	160(-)	1048(58)	27460(690)	98(16)	30500(2400)	28100(900)
Cl	28180(880)	38(5)	9400(640)	n.d	41(22)	11470(550)	34(14)	12220(1120)	9100(260)
Mineral/melt partition coefficients³									
D _{min/melt} ^H		0.018(6)		-	0.015(2)		0.0011(10)		
D _{min/melt} ^F		0.023(2)		0.004(0)	0.028(2)		0.0036(1)		
D _{min/melt} ^{Cl}		0.001(0)		-	0.004(0)		0.003(0)		
D _{min/melt} ^C		1.25(49)		-	1.06(18)		0.67(59)		

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	Fe_13			Fe_14		Pt_hal1		Pt_hal2	
	<i>melt</i>	<i>opx</i>	<i>pig</i>	<i>melt</i>	<i>pig</i>	<i>melt</i>	<i>opx</i>	<i>melt</i>	<i>opx</i>
¹ n=	4/3	4/3/6	2/2/2	5/5	1/1/4	5/4/4	5/4/5	4/4/12	5/54
EMP data									
Na ₂ O	0.33(5)	0.02(1)	0.20(1)	0.32(5)	0.23(1)	0.45(2)	0.03(1)	0.35(4)	0.02(0)
Al ₂ O ₃	15.42(21)	3.68(108)	10.79(56)	13.16(13)	7.29(59)	10.52(19)	4.11(110)	10.27(2)	2.89(27)
FeO	0.83(17)	1.81(30)	0.59(3)	12.69(28)	4.77(180)	12.97(67)	14.00(0.38)	8.96(26)	9.91(124)
MgO	8.03(11)	32.65(157)	15.95(44)	7.30(13)	17.50(96)	11.45(18)	26.79(53)	15.05(13)	30.06(34)
CaO	12.51(12)	1.23(26)	13.47(92)	12.12(13)	16.55(192)	14.20(17)	1.63(10)	11.39(12)	1.14(5)
SiO ₂	50.25(41)	54.99(138)	50.89(90)	46.43(40)	50.85(90)	41.62(81)	52.31(113)	44.22(45)	54.21(39)
Cr ₂ O ₃	4.09(10)	0.15(4)	7.31(60)	0.58(2)	1.61(30)	0.18(1)	1.14(9)	0.35(0)	0.98(16)
TiO ₂	0.49(1)	0.15(4)	0.57(2)	0.66(2)	0.30(3)	0.79(4)	0.07(1)	0.53(0)	0.05(1)
MnO	0.21(0)	0.27(4)	0.37(4)	0.19(1)	0.26(3)	0.28(1)	0.22(2)	0.23(1)	0.18(1)
F	4.95(8)	-	-	4.27(8)	-	3.92(5)	-	2.97(7)	-
Cl	1.08(1)	-	-	0.97(1)	-	2.87(5)	-	2.08(1)	-
<i>Total</i>	98.26(45)	99.82(54)	100.15(59)	98.73(32)	99.34(76)	99.33(36)	100.30(64)	96.28(78)	99.43(53)
NBO/T ²	0.65			0.89		0.93		1.31	
Al _T (pfu) ³		0.09	0.136		0.141		0.128		0.08
SIMS data									
H ₂ O	660(10)	61(32)	44(21)	4400(590)	144(-)	10200(670)	156(16)	28300(500)	287(40)
CO ₂	61(23)	69(1)	81(9)	33(0)	n.d.	122(50)	50(0)	2986(62)	47(3)
F	48300(3400)	1383(58)	-	47000(5400)	3397(-)	31300(2800)	1160(125)	29500(100)	689(136)
Cl	8500(670)	69(1)	-	9000(1500)	70(-)	11000(1000)	40(9)	20300(800)	39(9)
Mineral/melt partition coefficients³									
D _{min/melt} ^H		0.09(5)	0.07(3)		0.033(5)		0.015(2)		0.010(1)
D _{min/melt} ^F		0.029(2)	-		0.072(8)		0.037(5)		0.016(4)
D _{min/melt} ^{Cl}		0.003(0)	-		0.008(0)		0.004(0)		0.002(0)
D _{min/melt} ^C		1.13(42)	1.3(5)		-		0.41(17)		0.016(1)

¹Number of analysis for SIMS (F+Cl) /SIMS (H+C)/ EMP (major elements), one analysis per crystal;

²ratio of non-bridging oxygens to tetrahedral sites as a measured of melt polymerisation;

³Calculated atoms of Al on the tetrahedral site in pyroxene (per formula unit);

⁴Based on melt SIMS data.

861 Table 4: input data used to model volatile distribution during lunar magma ocean solidification. Steps during solidification and phase
862 assemblages are from Rapp and Draper (2018).
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Stage/% solidification	Phase assembly (mineral proportions)	D ^{ol/melt}			D ^{opx/melt}			D ^{cpx/melt}			D ^{plag/melt}		
		H ₂ O	Cl	F	H ₂ O	Cl	F	H ₂ O	Cl	F	H ₂ O	Cl	F
1 (0-52%)	ol	0.001	0.003	0.004	-	-	-	-	-	-	-	-	-
2 (52-74%)	opx	-	-	-	0.015	0.002	0.03	-	-	-	-	-	-
3 (74-88%)	0.3 ol + 0.15 cpx + 0.15 opx + 0.4 plag	0.001	0.003	0.004	0.015	0.002	0.03	0.03	0.007	0.08	0.03	0.007	0.08
4 (88-97%)	0.6 opx + 0.4 plag	-	-	-				-	-	-	0.03	0.007	0.08

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867 Figure 1. Backscattered electron images (SEM) of selected run products.

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Figure 2: Comparison of SIMS and EMPA data for F (top) and Cl (bottom) concentrations in glass (quenched melt). Error bars are standard deviations on mean values for each sample based on repeat analyses. Dashed lines are 1:1 relationships.

877 Figure 3. Unpolarised FTIR spectra from selected run products, offset vertically for clarity,
 878 and obtained from samples with consistent thicknesses, although not thickness corrected.
 879 No background correction has been applied due to complex and contrasting backgrounds.

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883 Figure 4. Effect of temperature on F, H₂O and Cl partitioning between silicate melt and orthopyroxene (squares), pigeonite/clinopyroxene (high
884 Ca pyroxenes) (circles) and olivine (triangles). Black symbols: this study, Grey: Hauri et al. (2006), Red: Joachim et al. (2017), Yellow: Joachim
885 et al. (2015), White: Rosenthal et al. (2015), Blue: Beyer et al. (2012), Hatched: Dalou et al. (2012), Green: O’Leary et al. (2010).

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888 Figure 5. Relationship between F and H₂O mineral-melt partition coefficients (top) and Cl
889 and F partition coefficients, with relationship between Cl and H coefficients shown in insert).
890 Key as for Figure 4.

Figure 6. Top: F, H₂O and Cl pyroxene-melt partition coefficients as a function of atoms per formula unit (APFU) Al³⁺ on the tetrahedral site in ortho- and clinopyroxene structures. Bottom: F and Cl olivine-melt partition coefficients as a function of olivine Al₂O₃ content (ppm by weight).

Figure 7. Variation in F content in minerals (measured by SIMS) with mineral chemistry determined by EMPA (TiO₂ contents x10 for clarity).

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901 Figure 8. Effect of melt polymerisation, defined by the calculated ratio NBO/T, on volatile
 902 partitioning. Key as for Figure 4.

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905 Figure 9: Results from modelling F, Cl and H₂O distribution during progressive solidification of a model LMO, using crystallisation sequence of
 906 Rapp and Draper (2018) (grey boxes, from 0-97% solidification), based on CFHA* LMO model of McCubbin et al. (2015). A-B: solidification with
 907 no inter-cumulate liquid. D-E: solidification with 1% intercumulate liquid. A and D show volatile content of liquid (magma) during progressive
 908 solidification; F = black squares, H₂O = dark grey squares, Cl = light grey circles. B and E show volatile abundances in cumulate (same key). C
 909 shows corresponding volatile ratios for cumulates with no intercumulate liquid (dashed lines) and 1% intercumulate liquid (solid lines): grey =
 910 F/Cl, black = F/H₂O. F shows volatile ratios in remaining liquid.

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