High volatile abundances in lunar samples are also problematic for our basic understanding of the Moon, such as its formation in a giant impact event and the crystallization of a lunar-wide magma ocean. The giant impact event provides the necessary energy for melting a large portion of the Moon, but a severe depletion of the most volatile elements is generally an expectation of this fantastic event (Albarède et al., 2015). Crystallization of the lunar magma ocean (LMO) predicts that the last liquids would be enriched in incompatible elements, such as K, REEs, and P (KREEP) (Warren and Wasson, 1979). Volatile elements are also incompatible in the anhydrous minerals expected to crystallize from the magma ocean, and thus water, fluorine, and chlorine should have been highly enriched in the original KREEP component (urKREEP). If water contents were 1000 ppm in the lunar magma ocean, such as found in olivine hosted melt inclusions of 74220 (Hauri et al., 2011), this would lead to 5 wt.% H₂O in urKREEP (Elkins-Tanton and Grove, 2011). This much water would lead to water saturation at the base of the lunar crust (a likely place for the KREEP liquid to reside at the end of LMO crystallization). To prevent extensive water in the KREEP liquid, water contents of the initial magma ocean likely should have 100 ppm water or far less (Elkins-Tanton and Grove, 2011).

INTRODUCTION

Our understanding of lunar volatiles has undergone a revolution since 2008 with the dual discoveries of water in Apollo samples (Saal et al., 2008) and its remote detection on the lunar surface (Pieters et al., 2009). Earth-like abundances for the volatiles water, fluorine, chlorine, and sulfur were found in apatite (Boyce et al., 2010; McCubbin et al., 2011) and olivine-hosted melt inclusions (Hauri et al., 2011), while volatile isotopic compositions were decidedly extraterrestrial for hydrogen (Greenwood et al., 2011; Saal et al., 2013), chlorine (Sharp et al., 2010) and zinc (Paniello et al., 2012). A recent model has shown that lunar apatite volatile compositions are probably evidence for low volatile contents of magmas (Boyce et al., 2014), which leaves only one sample, 74220, with high, earth-like, volatile abundances (Albarède et al., 2015). This, coupled with a complete dearth of fluid inclusions (Roedder and Weiblen, 1970) or hydrous minerals (McCubbin et al., 2015) in lunar samples, seems to indicate that the Moon likely possesses less volatiles than the Earth.

High volatile abundances in lunar samples are also problematic for our basic understanding of the Moon, such as its formation in a giant impact event and the crystallization of a lunar-wide magma ocean. The giant impact event provides the necessary energy for melting a large portion of the Moon, but a severe depletion of the most volatile elements is generally an expectation of this fantastic event (Albarède et al., 2015). Crystallization of the lunar magma ocean (LMO) predicts that the last liquids would be enriched in incompatible elements, such as K, REEs, and P (KREEP) (Warren and Wasson, 1979). Volatile elements are also incompatible in the anhydrous minerals expected to crystallize from the magma ocean, and thus water, fluorine, and chlorine should have been highly enriched in the original KREEP component (urKREEP). If water contents were 1000 ppm in the lunar magma ocean, such as found in olivine hosted melt inclusions of 74220 (Hauri et al., 2011), this would lead to 5 wt.% H₂O in urKREEP (Elkins-Tanton and Grove, 2011). This much water would lead to water saturation at the base of the lunar crust (a likely place for the KREEP liquid to reside at the end of LMO crystallization). To prevent extensive water in the KREEP liquid, water contents of the initial magma ocean likely should have 100 ppm water or far less (Elkins-Tanton and Grove, 2011).
Two recent studies have attempted to estimate the volatile element content and character of the urKREEP component and these differ wildly in Cl content. One estimate, based mainly on magma ocean crystallization simulations, suggests that urKREEP is enriched in Cl, and predicts that urKREEP should contain 1100–1350 ppm Cl, 660 ppm F, and 300–1250 ppm H₂O (McCubbin et al., 2015). Another estimate of the urKREEP fluorine and chlorine component, based on geochemical element correlations in KREEP samples, gives 660 ppm F and only 150 ppm Cl (Treiman et al., 2014). Here we report analyses of late-stage glasses and apatite in KREEP basalts 15382,17 and 15386,60 using a combination of electron and ion microscopy, and then use these measurements to estimate the F and Cl content of urKREEP and the lunar magma ocean.

**MATERIALS AND METHODS**

**Materials**

KREEP basalt lunar thin-sections 15382,17 and 15386,60 were carefully studied using optical and electron microscopy at Wesleyan University to find apatite and glass suitable for electron and ion microprobe analyses. 15382,17 is an old lunar thin-section, that has been analyzed by several other groups in the last 40 years. 15386,60 is a new thin-section prepared at Johnson Space Center, and we were the first group to use this thin-section. Also studied were JSC lunar thin-sections low-Ti mare basalts 15555,171 and 12039,42, 12039,42 was made for us in 2009 by JSC. We mounted rock chip 15555,1055a in low-temperature liquid metal in the Wesleyan University Lunar Laboratory with standards, to minimize contamination of terrestrial volatiles during ion microbeam analyses, especially hydrogen. This sample was prepared without the use of water or oils. All samples were carbon-coated for electron and ion microscope analyses. Minimal electron beam study is implemented, only enough to map samples and quickly identify minerals and glasses using the Wesleyan University JEOL SEM.

**Electron microprobe**

We used the JEOL JXA-8530F ‘Hyperprobe’ Field Emission Gun electron microprobe at Yale University for electron microprobe quantitative spot analyses, as well as semi-quantitative WDS mapping, utilizing five spectrometers. We employed special techniques to try to measure low levels of fluorine and chlorine, while not damaging the glasses by electron irradiation. We generally used a defocused beam, and a low beam current. Beam diameter and beam current are shown in Table 1. We varied these parameters on a spot-by-spot basis, due to the need to analyze glass areas free of crystals. We always analyzed F and Cl first, on separate spectrometers, for 300 s on peak. Most other elements were 20 s on peak. We also monitored count rates to check for time-dependent effects, such as loss or gain of fluorine. Our typical
Chlorine-rich glasses in KREEP basalts

Detection limit for F was 450 ppm, and 90 ppm for Cl. Detection limit for P2O5 is 0.04%.

Secondary Ion Mass Spectrometry (SIMS)

The new Cameca ims 1280-HR ion microprobe at Hokkaido University was used to analyze Cl in lunar glasses. We analyzed 35Cl, 30Si, and 18O. A two minute pre-sputter was used. We used 35Cl/18O instead of 35Cl/30Si as there was a much smaller range in our electron microprobe calculated oxygen content vs. silicon content of glasses. Terrestrial natural and synthetic glasses were used for standardization. We determined Cl contents via electron microprobe, using the methods outlined above, for JFR (383 ppm), NBS 610 (380 ppm), and NBS 612 (145 ppm). We used SIMS calibration of these three glasses to determine the Cl content of K2292 (20 ppm). For analyses of lunar glasses we used K2292 and JFR for Cl calibration, as we had these mounted in 15555,1055a lunar sample mount. Raw data are shown in Fig. 1 for Cl. A 10% error is assessed due to counting statistics. Apatite measurement methodology followed our published protocol (Greenwood et al., 2011).

RESULTS

Apatite H2O and δD

We were only able to find one apatite grain large enough for our SIMS analytical technique in 15382,17. Due to technical difficulties, we were not able to analyze apatite in 15386,60 for this study. The petrographic context of the apatite grain we analyzed in 15382,17 and its coexisting glass can be seen in Figs. 2–4. In Fig. 2, the subophitic texture of KREEP basalt 15382 can be seen. 15382 is dominated by plagioclase and pyroxenes, with subordinate ilmenite, silica, and large patches of mesostasis glass (Dowty et al., 1976). A higher magnification view of this apatite grain is shown in Fig. 3, where it can be seen that this apatite grain is rimmed by merrillite. This apatite grain is mostly fluorine-rich, with 3.5 wt.% fluorine and only 0.03 wt.% Cl. A Cl-rich area, assumed to be the last crystallizing part of the grain, can
be seen in Fig. 3. Analyses of this Cl-rich area were difficult, but the Cl-rich area of this apatite grain could be as high as 0.9 wt.% Cl. SIMS spot measurement of the F-rich part of this apatite grain in 15382,17 has 300 ppm OH and $^4$D = +1364 ± 96‰ ($^2_\sigma$), among the lowest water contents and highest D/H of lunar apatite (Tartèse et al., 2014; Robinson and Taylor, 2014).

Chlorine content of late stage glasses
The late-stage glasses in 15382 and 15386 are the last remnants of the crystallization of these two basalts and are associated with minerals typically found in the late-stage areas of lunar basalts, such as apatite, merrillite, tranquilliityite, K-,Ba-rich alkali feldspar, armalcolite, baddelyleite and ferrohedenbergite (Dowty et al., 1976). Figure 4 shows a high magnification BSE image and Ca K$\alpha$ and Cl K$\alpha$ WDS maps of a mesostasis area adjoining the apatite grain analyzed via SIMS (above) in 15382,17. The Cl K$\alpha$ WDS map shows enhancement of Cl in the glass over the surrounding plagioclase and hedenbergite. Two electron microprobe analyses of glasses in this area are listed in Table 1. The Cl contents of these electron microprobe analyses and their locations are shown in Fig. 4. We also analyzed a number of other mesostasis glasses in 15382,17 and 15386,60 for chlorine using SIMS, and the results of those analyses are listed in Table 2. We find the highest Cl values yet reported for a lunar glass in the late-stage areas of KREEP basalts 15382 and 15386 (243 ± 24 to 1016 ± 102 ppm; Tables 1 and 2). Our results are consistent with high chlorine reported for KREEP-rich soils (Reed et al., 1972; Reed and Jovanovic, 1973). The K-,Si-,Al-rich late-stage glasses of the KREEP basalts are similar in major element chemistry to late-stage glasses of low-Ti mare basalts 12039 and 15555 (Table 1). The KREEP samples and the two mare basalts have all experienced extensive fractional crystallization of phosphate during late-stage crystallization of these basalts on the lunar surface, as evidenced by phosphorus at or below detection levels in the late stage glasses of basalts 15382, 12039, and 15555 (Table 1). Late-stage glasses from 12039 and 15555 basalts are low in fluorine (<100 ppm F) and chlorine (Table 2), suggesting that extreme fractional crystallization of apatite depleted the 12039 and 15555 parent magmas in fluorine and chlorine, as recently predicted in the Lunar Apatite Paradox model (Boyce et al., 2014). The depletion of chlorine in the low-Ti basaltic glasses of 12039 and 15555 could be explained as loss due to apatite crystallization or degassing of chlorine. One complication for comparing the KREEP basalts to the low-Ti mare basalts is that the KREEP basalts have a substantial portion of their phosphate as the mineral merrillite, which is volatile-free; merrillite is rare in 12039 and 15555.
We determined the apatite/merrillite of 15382,17 (see below), and find that apatite abundance is higher in the KREEP basalts than in the low-Ti mare basalts, showing that the high Cl in the late-stage glasses is not due to a low volume of apatite crystallization, but is a result of high Cl in the KREEP component of the Moon, as predicted during the Apollo program (Reed et al., 1972; Reed and Jovanovic, 1973).

Modal amount of apatite in 15382,17 and 12039,3

To determine modal amounts of apatite, we used the program ENVI to distinguish apatite in elemental x-ray maps. For 15382,17, we used a Ca Kα WDS map obtained at Yale University using the JEOL FEG ‘Hyperprobe’ (Fig. 2). The Ca map was obtained at an accelerating voltage of 15 kV, a probe current of 5 nA, and dwell time of 100 ms. An 850 × 850 point matrix was used. Using the program ENVI, colors were ratioed to map out the distribution of apatite and merrillite in this map. This method provides a minimum estimate, as pixels on grain boundaries are generally not used, due to their mixed color properties. Our ENVI results, using 727,609 pixels, led to 1.596% being classified as phosphate; 0.894% as apatite, and 0.702% as merrillite. Chemically, 15382 has 0.55% P₂O₅ (Dowty et al., 1976), which trans-

![Fig. 4. Ca Kα WDS (wavelength-dispersive spectrometer) (top) and Cl Kα WDS x-ray maps (bottom) of Cl-rich glass area in 15382,17. The BSE (backscatter electron) image (middle) shows locations of electron microprobe analyses of Cl. Pl = plagioclase, Ap = apatite, Hd = hedenbergite, Gl = glass. Scale bar is 10 µm for all three images.](image)

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Chlorine-rich glasses in KREEP basalts

15555. We determined the apatite/merrillite of 15382,17 (see below), and find that apatite abundance is higher in the KREEP basalts than in the low-Ti mare basalts, showing that the high Cl in the late-stage glasses is not due to a low volume of apatite crystallization, but is a result of high Cl in the KREEP component of the Moon, as predicted during the Apollo program (Reed et al., 1972; Reed and Jovanovic, 1973).

Table 2. Ion microprobe analyses of Cl in the late-stage glasses of 15382,17, 15386,60, 12039,42, and 15555,1055a
lates to 1.1% modal apatite. 15386 is considered very similar to 15382, and has 0.7% P₂O₅ (Dowty et al., 1976) which gives 1.4% modal apatite. Our estimates of phosphorus appear on par with the chemical estimates, considering the small sample sizes and possible chemical heterogeneity to be expected for these samples (total sample mass of 15382 was 3.2 g).

The modal amount of apatite in 12039,3 was determined in a different manner. Hyperspectral image cubes of EDS data collected using the Wesleyan University JEOL SEM were imported into ENVI, so that raw data were used. The amount of merrillite in 12039 is trivial, and the published mode did not determine modal apatite. We find 0.09% P₂O₅ (Bunch et al., 1972). The published mode did not determine modal apatite. We find 0.27% modal phosphate in 12039,3. Chemical analyses of 12039 give 0.09% P₂O₅ (Bunch et al., 1972), which translates to 0.18% modal apatite. Thus we determine 0.894% apatite in 15382 and 0.27% apatite in 12039, by volume.

Calculation of the volatile content of KREEP
We find that the main carrier of chlorine in the KREEP basalts is late-stage glass, while fluorine is predominantly in apatite. By estimating the volumes of these two components, we calculate 313 ppm F and 27 ppm Cl in 15382 whole rock. Using P as a representative KREEP element, the fluorine and chlorine contents of 15382 extrapolate to 1159 ppm F and 101 ppm Cl for urKREEP (Jolliff, 1998). These fluorine and chlorine results are supported by recent estimates of these volatiles in KREEP that agree within a factor of 2 (Treiman et al., 2014). If urKREEP represents the last 1% of the LMO to crystallize, then our results would predict 12 ppm F and 1 ppm Cl for the bulk lunar magma ocean. Our estimates for the LMO are indistinguishable from estimates derived using the most volatile-rich glasses from the Moon (74220) (Hauri et al., 2011).

In 15382,17 and 15386,60, we find the main carrier of chlorine to be the late-stage glasses. The modal content of the glass has been determined to be 7.7% in 15382 (Crawford and Hollister, 1977). If we use 300 ppm Cl for the glass, this yields 23.1 ppm Cl for whole-rock 15382. Apatite is primarily F-rich in 15382. If we use an average Cl content of apatite of 350 ppm Cl for whole rock 15382. There are some Cl-rich hotspots in apatite, as well as a population of smallapatites that are more Cl-rich in mesostasis areas (e.g., Cl Kα WDS map of Fig. 4); these are too small for adequate quantitative analysis, but we have estimated that these areas may have 1000 ppm Cl, due to our best estimate of the Cl-rich area of the apatite grain shown in Fig. 3. If we assume an additional 0.1% of apatite with 1000 ppm Cl, this yields another ppm of Cl. Adding all three chlorine carriers, 23.1 + 3.1 + 1 = 27.2 ppm Cl.

Fluorine-rich apatite is the predominant carrier of fluorine in 15382,17. Using our modal apatite estimate, and an average F content of 3.5 wt.% in 15382,17 apatite, yields 35,000+0.0089+312 = 35,032 ppm F.

We follow a recent calculation of the fluorine and chlorine content of KREEP (Treiman et al., 2014), and use phosphorus as a proxy for the amount of KREEP. If KREEP has 8850 ppm P (Jolliff, 1998), 15382 has 0.55% P₂O₅ (Dowty et al., 1976), which translates to ~27% KREEP component in 15382.

F in KREEP: 312.9 ppm/27 = 1159 ppm;
Cl in KREEP: 27.2 ppm/27 = 101 ppm.

This may be an overestimate of the fluorine and chlorine in the KREEP component of 15382, as KREEP basalts still represent partial melting of the lunar mantle, and presumably the mare source(s). If we use the modal amount of apatite in 12039 as a proxy for apatite content of mare basalts (0.27 vol.%), and use 3.49 wt.% fluorine and 0.02 wt.% chlorine for a typical mare basalt apatite (McCubbin et al., 2011), we obtain 94.2 ppm F and 0.5 ppm Cl for a typical mare basalt. If 15382 has 73% mare component and 27% KREEP component, then this would lead to 124 ppm F and 0.7 ppm Cl in the mare component, which would suggest a small correction to the above estimates, that we do not employ.

For comparison, Treiman et al. (2014) made an independent analysis of the fluorine and chlorine content of KREEP, and they found 660 ppm F and 150 ppm Cl. Our chlorine contents could be low for several reasons. We used 300 ppm Cl, which is on the low end of our analyses, and thus conservative. As the Cl-rich apatite grains are normally several microns in size, and we may be underestimating this component. We find 2x higher fluorine for KREEP than Treiman et al. (2014). It is difficult to imagine 1/2 less fluorine than we calculate, as it would require an unusually low apatite/merrillite or that apatite has significantly less fluorine than we measure. Several of our apatite analyses in 15382,17 are stoichiometric, thus it would seem that KREEP likely has higher fluorine than estimated by Treiman et al. (2014).

DISCUSSION
Volatile elements can be fractionated from each other during magmatic processes, such as melting, crystallization, and degassing. Fluorine is inherently less volatile than chlorine, and on Earth, fluorine only becomes volatile at the top of magma columns (Aiuppa et al., 2009).
The lower gravity of the Moon will cause magmas to degas at greater depths (Wilson and Head, 1983; Ustunisik et al., 2015); thus, fluorine should enter the volatile phase as most lunar magmas reach the surface, if it is in sufficient concentration to reach saturation. The use of incompatible element ratios with similar partition coefficients has proven a powerful tool for understanding the chemistry of the Earth’s mantle and its product magmas (Hofmann et al., 1986). By using volatile/refractory element ratios, we can assess if fluorine has been fractionated from chlorine during lunar magmatic processes, such as degassing or crystallization. Figure 5 shows the Cl/Nb vs. F/Nd of KREEP basalt 15382 compared to the most water-rich sample from the Moon, the olivine-hosted melt inclusions of 74220 high-titanium orange glass (Hauri et al., 2011; Chen et al., 2015). Also plotted are bulk fluorine and non-leachable chlorine analyses of high-titanium and low-titanium mare basalts (Reed et al., 1972; Reed and Jovanovic, 1973). When compared to the Earth and CI chondrites, the lunar samples define their own distinct region, corresponding to ~10× depletion in F/Nd and ~100× depletion in Cl/Nb relative to Earth. Surprisingly, all lunar samples have similar Cl/Nb and F/Nd, regardless of eruption style. This would seem to provide important constraints for lunar volatile chemistry, as well as lunar evolution. The similarity in F/Nd and Cl/Nb of the lunar samples suggests either: 1) the depletion in fluorine and chlorine of the lunar samples is a global signature, that has not been overprinted by later melting, crystallization, or degassing, or 2) the Moon has elevated volatile contents, similar to Earth, and the lunar field in Cl/Nb vs. F/Nd is a result of lunar magmas reaching saturation in fluorine and chlorine and degassing upon decompression. The extensive evidence for chlorine condensates on lunar picritic glasses (e.g., McCubbin et al., 2015; Hauri et al., 2015) argues for chlorine as a volatile species in lunar magmas. The higher solubility of fluoride in magmas (Aiuppa et al., 2009) would explain the
only 10x depletion of F/Nd in lunar samples relative to the higher depletion of chlorine as a result of degassing. If lunar magmas did not reach saturation in fluorine and/or chlorine upon decompression due to overall low volatile contents, and thus did not undergo significant degassing of these elements then other constraints can be reached from the present dataset. For example, the similarity of F/Nd and CI/Nb of KREEP 15382 and the olivine hosted melt inclusions of 74220 would argue against the idea that 74220 samples a deep region of the primitive Moon that was below the lunar magma ocean (Hauri et al., 2011; Saal et al., 2013), unless all lunar magmas underwent similar amounts of degassing, regardless of eruption style. If the lunar samples did not undergo extensive loss of F and Cl during volcanism this would imply that the Moon is inherently less volatile-rich than the Earth. Interestingly, the F/Nd and CI/Nb of lunar samples are only one to two orders of magnitude more depleted than the Earth, respectively. This is consistent with the factor of three depletion in K for the Moon relative to Earth (Warren and Taylor, 2014), as well as a depletion of lunar fluorine (Albarède et al., 2015). This is in sharp contrast to the dominant paradigm of a dry Moon that emerged in the 1970’s, as well as the orders of magnitude depletion in volatiles predicted from chlorine isotopes of lunar materials (Sharp et al., 2010).

The water content of apatite in 15382,17 is very low (300 ppm OH), which could be suggestive of water-poor magmas, though apatite OH contents are not direct reflections of water content of magmas (Boyce et al., 2014). The high $\Delta D$ and low water content of apatite in 15382,17 could be explained as an extrapolation of the degassing model for apatite in KREEP basalt 15386 of Tartése et al. (2014). Arguing against this degassing scenario for the high D/H is that the D/H of this apatite ($\Delta D = +1364 \pm 96 (2\sigma)$) is extremely difficult to attain via degassing of $H_2(g)$ from magmas that begin with chondritic D/H (Sharp et al., 2013). Degassing of lunar magmas with cometary D/H (Greenwood et al., 2011) would be possible. Another point against the water content and D/H of this apatite representing that of the $\sim$99% crystallization/degassing residuum, is that we analyzed the F-rich core region of this apatite grain, and not the end-product of this grains crystallization history, as there is a CI-rich area that clearly crystallized after the F-rich core region that we analyzed (Boyce et al., 2014). Also, there are numerous, small CI-rich apatite grains in mesostasis glasses (e.g., Fig. 4.), which clearly crystallized after the large F-rich apatite grain we analyzed, providing further evidence of apatite compositions becoming more CI-rich late in the crystallization sequence of KREEP basalts 15382 and 15386.

The $H_2O/Ce$ has been used to estimate water contents of terrestrial magmas, due to similar geochemical behavior during terrestrial MORB petrogenesis (Michael, 1995), and now has been used for lunar magmas (Hauri et al., 2015; Chen et al., 2015). The Earth’s mantle is believed to have an $H_2O/Ce = 300$ (Dixon et al., 2002) or $H_2O/Ce = 168$ (Saal et al., 2002). If we assume an order of magnitude depletion in $H_2O$, as seen in the F/Nd, then we can estimate an $H_2O/Ce = 17–30$ for the Moon from our data. For comparison, the most volatile rich glass from the Moon, 74220 olivine-hosted melt inclusions, have $H_2O/Ce = 77$ (Hauri et al., 2015) or $H_2O/Ce = 64$ (Chen et al., 2015), both within a factor of 5 of our estimates for $H_2O/Ce$ of 17–30 for KREEP. The Ce content of 15386 is 213.1 ppm (Neal and Kramer, 2003); for an $H_2O/Ce = 17–30$, $H_2O = 3580–6393$ ppm for KREEP basalt. Using similar procedure as above to estimate urKREEP, we obtain ~1.3 to 2.4 wt.% $H_2O$ in urKREEP, the last residuum of the magma ocean.

Our results suggest an order of magnitude depletion in water for the Moon, which would predict ~1.3 to 2.4 wt.% $H_2O$ for urKREEP. This amount is similar to an estimate of 1.4 wt.% for the water content of urKREEP, calculated using analyses of OH in lunar plagioclase from ferroan anorthosite and plagioclase-melt partition coefficients (Hui et al., 2013). Our estimate for the water content of urKREEP is higher than that given by McCubbin et al. (2015), wherein they predicted 0.26–1.09 wt.% $H_2O$ for urKREEP from lunar magma ocean crystallization calculations. If KREEP basalts did not have elevated hydrogen contents that were subsequently lost via degassing, then the low water contents of apatite and glasses in KREEP 15382 suggest that water may have been decoupled from fluorine and chlorine at some point in lunar evolution. One possible mechanism for decoupling water from the other volatiles could be the reheating and remobilization of the high radiogenic element KREEP component into the upper lunar crust. A recent result of the GRAIL lunar mission was the discovery of a large circular fracture network surrounding the Procellarum region, which was interpreted as a result of remelting and migration of KREEP into this region (Andrews-Hanna et al., 2014). This reheating of KREEP could have led to the diffusion of hydrogen from the KREEP component over time, thus leading to loss of this hydrogen to the surrounding deep interior. Hydrogen is expected to dif- fuse faster than all other chemical elements in minerals (Farver, 2010). Alternatively, more extensive degassing of hydrogen (relative to chlorine and fluorine) from these KREEP basalts could have led to their depletion in water content (Tartése et al., 2014).

The high chlorine and fluorine contents of the KREEP component may have played a role in lowering the solidus of the lunar mantle during later melting events. Entrainment of KREEP during lunar mantle overturn could have re-introduced volatiles to the deep lunar mantle, or
KREEP volatiles could have played a role similar to metasomatic fluids on Earth. Germanium systematics in KREEP materials have been ascribed to complexing with chlorine, fluorine and sulfur in lunar fluids (Dickinson et al., 1989). The intimate association between mantle KREEP and the source rocks of the highland Mg-suite has previously been hypothesized to be mixing of melts of these two materials (Shervais and McGee, 1998). Here we propose lowering of the solidus of the ultramafic mantle source of the Mg-suite by KREEP volatiles as a more likely mechanism for the generation of the Mg-suite rocks.

The high chlorine contents of the KREEP glasses have important implications for lunar chlorine isotope geochemistry. Some of the most fractionated chlorine isotope values for the Moon have been found in KREEP samples (Sharp et al., 2010; Boyce et al., 2015). It has been suggested that degassing of chlorine from water-poor lunar lavas would lead to chlorine isotope fractionation (Sharp et al., 2010, 2013). Yet, the KREEP basalt glasses studied here contain an excess of chlorine, suggesting that degassing of chlorine did not go to completion in these samples, and that they should not possess fractionated chlorine isotope values. This strongly suggests that the high $^{37}\text{Cl}$ of KREEP was set in an earlier event, and is not a product of lava degassing under water-poor conditions (Sharp et al., 2010). Considering that high $^{37}\text{Cl}$ is only found in lunar samples, and possibly only in KREEP (Boyce et al., 2015), implies that elevated $^{37}\text{Cl}$ found in KREEP-rich samples was formed early in the Moon’s history, either during the giant impact or as later degassing of the mantle ocean under extremely water-poor conditions (Sharp et al., 2010). Degassing of the magma ocean would seem difficult, but could have occurred in the short time interval before the anorthosite crust sealed off the magma ocean from contact with space (Elkins-Tanton and Grove, 2011). Large impacts during late accretion have the capability to penetrate the lunar crust and expose the late-stage magma ocean volatiles to loss to space, and could have enhanced late-stage loss of volatiles from the magma ocean (Barnes et al., 2016). Alternatively, these same impacts may have delivered new water to the Moon (Greenwood et al., 2011; Botite et al., 2010).

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