

Introduction

Understanding the volatile budget of the Moon is important because it can have profound effects on melt viscosity (Dingwell *et al.*, 1985; Baker and Vaillancourt, 1995), chemical diffusion (Harrison and Watson, 1983), and solidus temperatures (Johannes and Holtz, 1996). These properties control physiochemical processes of magmas, including degassing, which have significant effects on planetary differentiation. The lack of hydrous silicate phases and hydrothermal alteration in lunar samples returned by the Apollo missions are observations commonly used to suggest that the Moon is depleted in hydrogen (plus other volatile elements) when compared to Earth, and thus water is generally not considered important in the chemical and physical differentiation of the Moon. The relative depletion in volatile elements in the Moon is thought to have occurred during a giant impact between a proto-Earth and a Mars-sized object (Hartman and Davis, 1975; Canup and Asphaug, 2001) resulting in volatile depletion and a lunar magma ocean, although Earth may have received additional input of volatiles by impacts after Moon formation (Owen and Bar-Nun, 1995). For these reasons, the recent conflicting evidence for significant lunar water requires further investigation.

On Earth, water and halogen contents of igneous rocks generally correlate with other incompatible elements like K, Rb, Th, and U (*e.g.*, Stolper and Newman, 1994). Recent spectroscopic data from the Moon (Klima *et al.*, 2013) support this trend, with a positive correlation between water and Th. Modelling of lunar magma ocean crystallisation (Elkins-Tanton and Grove, 2011) predicts a similar chemical differentiation to that seen in magma systems on Earth, with the highest levels of hydrogen in the evolved melt residuum of the magma ocean (*i.e.* urKREEP). However, sample-based estimates of water content of KREEP-rich magmas from measurements of OH⁻, F, and Cl in lunar apatites suggest a low water concentration in the KREEP component with 2 to 140 ppm magmatic water (McCubbin *et al.*, 2010). Using these data Elkins-Tanton and Grove (2011) predict that the bulk water content of the magma ocean would have been <10 ppm. In contrast, Hui *et al.* (2013) estimate water contents of 320 ppm for the bulk Moon and 1.4 wt. % for urKREEP from water measured in lunar anorthosite.

In order to address these discrepant estimates for the water content in KREEP and ultimately the bulk water content of the Moon, we measured water in nominally anhydrous minerals in the KREEP-rich sample 15405,78. We present data for water from alkali feldspar and a silica polymorph from granitoid clasts. The measurements of water in lunar alkali feldspar are the first of their kind. Alkali feldspar and apatite are the two most important mineralogical carriers of the KREEP component; as alkali feldspar is the main K phase and apatite (± whitlockite) are the main REE and P phases on the Moon. These data in conjunction with OH⁻, F, and Cl data from apatites in rocks with varying amounts of alkali feldspar are used to determine the water distribution in the KREEP reservoir and whether water estimates from KREEP-rich rocks suggest a dry or wet bulk Moon.

Water in alkali feldspar: The effect of rhyolite generation on the lunar hydrogen budget

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Abstract

Recent detection of indigenous hydrogen in a diversity of lunar materials, including volcanic glass (Saal *et al.*, 2008), melt inclusions (Hauri *et al.*, 2011), apatite (Boyce *et al.*, 2010; McCubbin *et al.*, 2010), and plagioclase (Hui *et al.*, 2013) suggests water played a role in the chemical differentiation of the Moon. Water contents measured in plagioclase feldspar, a dominant mineral in the ancient crustal lunar highlands have been used to predict that 320 ppm water initially existed in the lunar magma ocean (Hui *et al.*, 2013) whereas measurements in apatite, found as a minor mineral in lunar rocks, representing younger potassium-enriched melt predict a bulk Moon with <100 ppm water. Here we show that water in alkali feldspar, a common mineral in potassium-enriched rocks, can have ~20 ppm water, which implies magmatic water contents of ~1 wt. % in chemically evolved rhyolitic magmas. The source for these wet, potassium-rich magmas probably contained ~1000 ppm H₂O. Thus, lunar granites with ages from 4.3–3.9 Ga (Meyer *et al.*, 1996) likely crystallised from relatively wet melts that degassed upon crystallisation. Geochemical surveys by the Lunar Prospector (Jolliff *et al.*, 2011) and Diviner Lunar Radiometer Experiment (Glotch *et al.*, 2010; Jolliff *et al.*, 2011) indicating the global significance of evolved igneous rocks suggest that the formation of these granites removed water from some mantle source regions, helping to explain the existence of mare basalts with <10 ppm water, but must have left regions of the interior relatively wet as seen by the water content in volcanic glass and melt inclusions. Although these early-formed evolved melts were water-rich, their petrogenesis supports the conclusion that the Moon's mantle had <100 ppm water for most of its history.

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Results and Discussion

NanoSIMS ion microprobe measurements of water in alkali feldspar and a silica polymorph from sample 15405,78 were employed following the approach of Hauri *et al.* (2006; see Supplementary Information). In Apollo sample 15405,78 granitoid clast xenoliths are found in the groundmass (Ryder, 1976) and generally consist of intergrowths of alkali feldspar and a silica polymorph (Fig. 1). In the studied sample plagioclase is largely absent, only occurring as small patches in a few clasts. The water concentration in the alkali feldspar is uniform with values of ~20 ppm H₂O (Table 1). Reconnaissance scanning electron microscope and electron microprobe mineral compositional analysis show that the alkali feldspar is two-phase, with some high Ba zones (Fig. 1), but there is no observed variation in water content between the high- and low-Ba feldspar (although the vast majority of the analyses were made on the low-Ba feldspar). The silica polymorph OH⁻ measurements are equivalent to measurements from the anhydrous Suprasil glass standard.

Table 1 NanoSIMS data for alkali feldspar and SiO₂ phases from 2 clasts found in Apollo sample 15405,78. For alkali feldspar, data from 4 regions of interest (ROI) are presented, taken from 2 different clasts. Raw – Suprasil values are the calculated concentration data for the alkali feldspar minus the baseline calculated from the Suprasil anhydrous glass. Raw – average SiO₂ are the calculated concentration data for the alkali feldspar minus the average from the SiO₂ phase from the clasts.

| | Alkali feldspar (ppm) | | | | | |
|--------------------------------|------------------------------|-------|-------|---------|---------|--------|
| | ROI 1 | ROI 2 | ROI 3 | ROI 4 | Average | 2 S.E. |
| Raw | 22.8 | 22.3 | 20 | 21.3 | 21.6 | 1.25 |
| Raw – Suprasil | 20.7 | 20.2 | 17.9 | 19.2 | 19.5 | 1.25 |
| Raw – average SiO ₂ | 20.1 | 19.6 | 17.3 | 18.6 | 18.9 | 1.25 |
| | SiO ₂ phase (ppm) | | | | | |
| | ROI 1 | ROI 2 | ROI 3 | Average | 2 S.E. | |
| Raw | 2.89 | 2.39 | 2.78 | 2.68 | 0.304 | |

Hydrogen contained in nominally anhydrous minerals is normally in the form H₂O or OH⁻ (Johnson and Rossman, 2004) and water contents in alkali feldspars from Earth vary from 10s to 1000s of ppm (Johnson and Rossman, 2004). In alkali feldspar in plutonic rocks on Earth the hydrogen is mostly found as H₂O and in volcanic rocks it is generally OH⁻ (Johnson and Rossman, 2004). Johnson and Rossman (2004) hypothesise that the speciation of hydrogen in the feldspar is a function of the species in the liquid in equilibrium with the crystal. Thus, the H₂O in plutonic rocks on Earth might be due to late stage hydrous-fluid/rock interactions in the crust. Due to the lack of evidence of post crystallisation hydrous-fluid/mineral interactions in sample 15405,78, we suggest

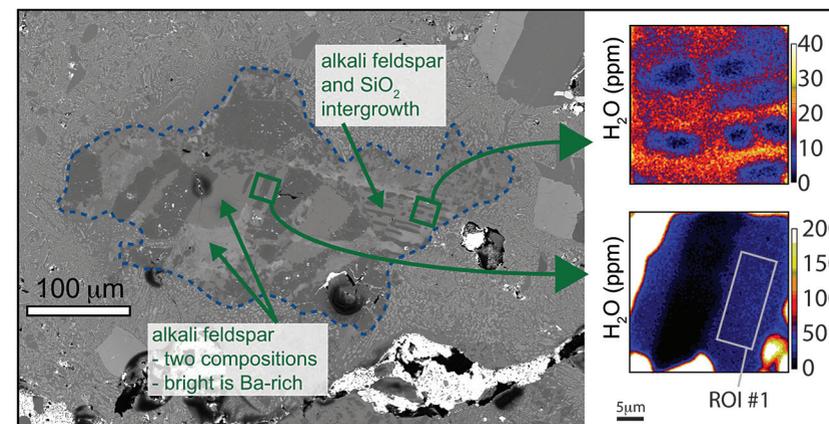


Figure 1 BSE image of granitoid clast (outlined in dashed line) from sample 15405,78, on the left. Clast consists of alkali feldspar and a silica phase. The variation in brightness of the feldspar relates to Ba (*i.e.* bright has more Ba). On the right are chemical maps obtained by NanoSIMS at DTM. Water correlates with mineralogy. The alkali feldspar consistently has ~20 ppm H₂O. The silica phase has similar water contents as the blank obtained on anhydrous glass (2–3 ppm).

water was incorporated into the feldspar during crystallisation from the silicate melt. However, future work to understand whether hydrogen in the alkali feldspar studied here is in the form OH⁻ or H₂O would help clarify the origin of the hydrogen. In addition, D/H isotopic analyses on the feldspar would help assess if there is an exogenic component.

Estimates for the water distribution coefficient (*D*) between alkali feldspar and a representative range of felsic host melts can be determined from the Bishop Tuff of California, a well-studied, compositionally zoned rhyolite. Johnson and Rossman (2004) measured 90 ppm OH⁻ in sanidines from the tuff; however, recalculation using a new molar absorption coefficient for sanidine (Mosenfelder *et al.*, 2015) produces a value of 65 ppm. Water contents from melt inclusions from the Bishop Tuff show a range from 2.3 to 6.0 wt. % (Schmitt and Simon, 2004). Thus the range of *D* for water in alkali feldspar from the Bishop Tuff is 0.001 – 0.004 using the full range in values for both the sanidine and the melt inclusions. These values are similar to a *D* obtained for plagioclase feldspar in felsic melt of 0.004 (Johnson, 2006). It should be noted that because the Moon formed under rather reducing conditions the effect of oxygen fugacity on H solubility in feldspar may be important. Experiments by Yang *et al.* (2012) show that the H solubility is higher (2–3x) at very reducing conditions, but because the oxygen fugacity during the crystallisation of the granitoids is unknown we cautiously use the range calculated from the Bishop Tuff. Using the range in *D* of 0.001 – 0.004 we obtain an estimate of 0.5 to 2 wt. % water in the felsic lunar melt (Fig. 2) at the time of alkali feldspar crystallisation for the granitoid clasts from sample



15405,78. Given that alkali feldspar and the silica polymorph make up the vast majority of these granitoid clasts, the water estimate at the time of alkali feldspar crystallisation closely approximates the magmatic value. Because the melt was initially not water saturated (Johannes and Holtz, 1996) little water should have been lost prior to crystallisation. Despite the fact that 0.5 to 2 wt. % water is the wettest magma inferred for the Moon, it still would likely not stabilise hydrous phases (Merzbacher and Eggler, 1984). Instead, the water and halogens likely left the system as a highly water-rich fluid.

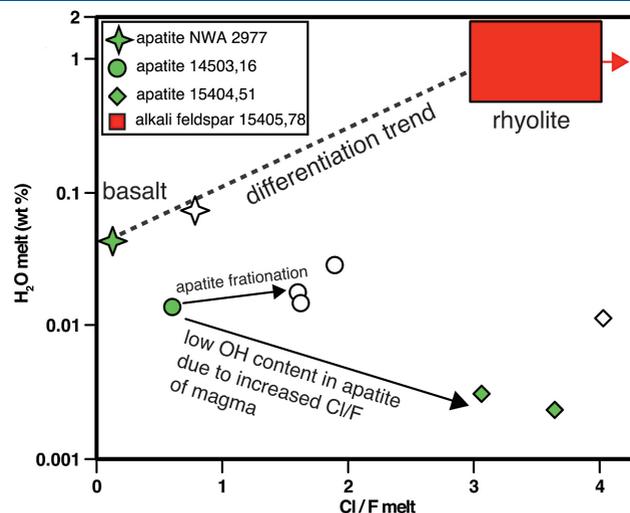


Figure 2 Plot of the estimated Cl/F ratio of magma versus estimated water content for lunar magmas (y-axis in log scale). Apatite data are from McCubbin *et al.* (2010). Water estimates from apatite assume 95 % crystallisation prior to apatite crystallisation. Cl/F melt estimates from apatite assume $D_{\text{F}}/D_{\text{Cl}}$ is 10 (Webster *et al.*, 2009). Within individual samples, boundary layer crystallisation will create apatites with higher Cl and OH⁻ contents than those initially growing from their host magma, thus the lowest water estimates from each sample (green fill) should be more representative of the initial magma composition (Boyce *et al.*, 2014). Schematic differentiation trend is shown between basalt and rhyolite. For reference, OH⁻ data from apatites from lunar granite 14321,1047 (Robinson *et al.*, 2014) predict H₂O melt compositions of 0.001 wt. %, and likely have Cl/F ratios higher than 3.

Volatile data from apatites in lunar basalts and alkali-suite clasts from McCubbin *et al.* (2010) show a conflicting trend with lower OH⁻ and higher Cl/F in rocks that have more alkali feldspar (*i.e.* more K-rich). Magmatic water estimates based on apatite measurements from an alkali-rich clast from Apollo sample 15404,51 range from as low as 0.001 to 0.014 wt. % H₂O (Fig. 2). As calculated by McCubbin *et al.* (2010) these estimates assume 95 % crystallisation of the host magma prior to formation of the apatite. Although alkali feldspar is in clasts found in sample 15404,51, it is not a major phase. To compare our magma water estimates for lunar granitoids with apatite estimates from a similar rock

type we use the published NanoSIMS OH⁻ data of apatites from evolved lunar rocks (Barnes *et al.*, 2014; Robinson *et al.*, 2014) including the largest specimen of lunar granite, 14321,1047. Following the same approach as above yields apatite water estimates for the rhyolitic magmas at <0.04 wt. % H₂O. Excluding two outlier OH⁻ measurements from Barnes *et al.* (2014) lowers the magmatic water estimate to 0.004 wt. %. Thus, magmatic water estimates from alkali feldspar and apatite in petrologically similar lunar granitoid clasts differ by approximately 2 to 3 orders of magnitude.

Notably, the inferred magmatic water contents based on OH⁻ in lunar apatite have recently been shown to be unreliable due to the co-dependent compatibilities of F, Cl, and OH⁻ (Boyce *et al.*, 2014). Specifically, fractionation of apatite within a single magma can remove F, leading to later forming apatites with high OH⁻ concentrations that produce inaccurate, high magmatic water estimates (Fig. 2). This likely explains the two highest OH⁻ values from Robinson *et al.* (2014) and implies that apatite with the lowest OH⁻ content in an individual sample (Fig. 2) should give the best estimate of magmatic water. More important is the fact that evolved magmas with high Cl/F can crystallise apatite that generally excludes OH⁻, regardless of the water content of the magma (McCubbin *et al.*, 2011; Boyce *et al.*, 2014). Estimated Cl/F of magmas from mare basalts, alkali suite, and KREEP-rich rocks show a progression toward higher Cl/F as magma compositions become more K-rich (Fig. 2). Associated with the increase in magma Cl/F is a decrease in OH⁻ in apatite, and thus an apparent decrease in magmatic water (Fig. 2).

Implications

Zircon ages from lunar granitic rocks (*e.g.*, Meyer *et al.*, 1996) span from 4.3 to 3.9 Ga, with an age of 4.3 Ga for 15405. Thus, granitoids analysed here either reflect the end of extensive magma ocean solidification, or the beginning of secondary crust formation through partial melting, *i.e.* very small-scale partial melts during initiation of density driven stratification (*i.e.* local mantle overturn). Regardless of whether the granitoids represent the final liquids or the first partial melts of lunar magma ocean materials, the new data imply that high water content rhyolitic magmas existed locally in the lunar crust around 4.3 Ga (Meyer *et al.*, 1996). The reduced viscosity of these rhyolitic melts appear to have allowed them to easily ascend through the crust and possibly degas. The removal of water and chlorine from the lunar interior by the generation of these magmas would likely deplete some of the source regions of later magmatic activity (*e.g.*, mare volcanism). Whether younger granites with different trace element compositions (*e.g.*, 14321,1027; Warren *et al.*, 1983) crystallised from similarly hydrous magmas is unknown.

The rhyolitic magmas are believed to represent a distilled component of the urKREEP reservoir, reflecting a 10–100x enrichment in water. If true, our data suggest urKREEP had between 50 and 2000 ppm water; consistent with a dry bulk



Moon (1–50 ppm water; Elkins-Tanton and Grove, 2011) and much less than the 1 to 2 wt. % predicted for urKREEP if the bulk Moon was as wet as suggested by Hui *et al.* (2013) from plagioclase in ferroan anorthosite. The discrepancy between the results and interpretations of Hui *et al.* (2013) and this study could be due to the hypotheses used to understand how each formed or the physical processes that affected the plagioclase from the primary crust differently than the later granitoid rocks (*e.g.*, degassing).

If the granitoid rocks on the Moon were generally produced by hydrous magmas with 0.5–2 wt. % water (~1 wt. %), then the amount of granitic material on the Moon can be used to estimate the amount of water removed from the bulk Moon by felsic magmatism. Using the K₂O concentration estimated for the silicate portion of the Moon (Longhi, 2006) there would be ~0.02 % alkali feldspar. Assuming that this alkali feldspar makes up 25–50 % of the granitic rock of the Moon, then the bulk silicate Moon would be ~0.1 % granite. Thus, the bulk Moon water content would have been decreased by ~10 ppm by felsic magmatism between 4.3 and 3.9 Ga. Globally, this early period of dehydration would have had a significant effect on the water content of the already dry bulk Moon, removing between a 1/4 to mostly all of the water. The water depletion events were likely distributed heterogeneously within the mantle, depending on the K distribution. Some regions could have retained 1000s of ppm water that contributed to later magmatism, as seen in water contents in volcanic glass and melt inclusions from mare basalts.

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Additional Information

Supplementary Information accompanies this letter at www.geochemicalperspectivesletters.org/article1712

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Water in alkali feldspar: The effect of rhyolite generation on the lunar hydrogen budget

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Supplementary Information

This supplementary information includes:

- Supplementary Methods
- Supplementary Information References

Supplementary Methods

H₂O abundance analyses by NanoSIMS

The abundance of H₂O was measured in nominally anhydrous minerals (feldspar and a SiO₂- phase) using the Cameca NanoSIMS 50L scanning ion microprobe at the Carnegie Institution of Washington's Department of Terrestrial Magnetism, following the techniques of Hauri *et al.* (2006; 2011). A primary ion beam of Cs was used to raster over an area of 25x25 pm, and negatively charged ions of the isotopes ¹²C, ¹⁶OH, ¹⁹F, ³⁰Si, ³²S and ³⁵Cl were measured simultaneously on six electron multipliers using ion counting. For every analysis location, we first performed a pre-sputtering step on a 30x30 pm area for 2 minutes with a 10 nA primary beam, then switched to a primary beam of 1 nA on a 25x25 pm area for data acquisition. Data were recorded as scanning ion images obtained simultaneously on each mass (¹²C, ¹⁶OH, F, Si, S and C); in this mode, acquisition of a single frame of 256x256 pixel takes 32.768 seconds, and 5 frames were acquired at

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each analysis location, resulting in a total acquisition time of ~3 minutes. We used basaltic glass ALV519-4-1 as a standard to determine relative sensitivity factors for C, OH, F, S and Cl, and we used the anhydrous Suprasil standard to monitor the detection limits of these elements, as described in Koga *et al.* (2003) and Hauri *et al.* (2006). Mass resolving power of the instrument was set to ~6000 in order to separate $^{16}\text{OH}^-$ from ^{17}O as well as other isobaric interferences; average ^{30}Si count rates were on the order of 200,000 cps. For standardisation and detection limit determinations, we obtained data in two different modes of operation: standard Dynamic SIMS, and Scanning Ion Imaging SIMS. For the measurements of lunar nominally anhydrous minerals, only Scanning Ion Imaging SIMS was used.

Data were extracted and processed from the ion images using the L'Image software package for PV Wave written by Larry Nittler (DTM-CIW). Data were corrected for system deadtime, and the five image frames of individual species were drift-corrected and summed; images were ratioed to produce scanning isotope ratio images ($^{12}\text{C}/^{30}\text{Si}$, $^{16}\text{OH}/^{30}\text{Si}$, $^{19}\text{F}/^{30}\text{Si}$, $^{32}\text{S}/^{30}\text{Si}$ and $^{35}\text{Cl}/^{30}\text{Si}$), and data were extracted from specific user-defined regions of interest (ROIs: feldspar and a SiO_2 -phase) located within the isotope ratio images. We used a synthetic silica glass (the anhydrous Suprasil glass standard) to establish the H_2O detection limit of ≤ 3 ppm, as determined by multiple separate measurements interspersed with the analyses of the lunar phases. The reported uncertainties based on these count rates follow a Poisson distribution. The reported precision of the feldspar analyses is negligibly affected by the reproducibility of the detection limit (2.7 ± 0.3 2 S.E.). The reported volatile concentrations are obtained by simply subtracting the detection limit from the measured concentrations (Table 1). For the uncertainties, we assigned a conservative 7 % (2 S.E.) for H_2O on all the measured regions of interest, which represent the uncertainty calculated by propagating the errors in the detection limit and the counting statistics obtained with the NanoSIMS.

X-ray mapping and mineral compositions by scanning electron microscope and microprobe

Mineral compositions, X-ray maps and backscattered electron (BSE) maps were obtained at NASA Johnson Space Center (JSC) following standard methods to study the petrography of the clasts, guide NanoSIMS traverses, and verify the mineralogy of the analysis spots. High-resolution BSE images and digital X-ray maps were obtained with a JEOL JSM-7600F SEM at JSC. X-ray maps were obtained with a ThermoElectron SDD X-ray detector and ThermoElectron software using a 15 kV beam and 30 nA beam current.

Supplementary Information References

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