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

R.D. Mills1#, J.I. Simon1*, C.M.O'D. Alexander2, J. Wang2, E.H. Hauri2

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 magmas probably contained ~1000 ppm H2O. Thus, lunar granites with ages from 4.3–3.9 Ga (Meyer et al., 2010) likely crystallised from relatively wet melts that degassed upon crystallisation. Geochemical surveys by the Lunar Prospector (Jolliff et al., 2008), melt inclusions (Hauri et al., 2013) whereas measurements in apatite (Boyce et al., 2010; McCubbin et al., 2010) 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.

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, 1998). 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. Melting 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.

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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 H$_2$O (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 SiO$_2$ 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 SiO$_2$ are the calculated concentration data for the alkali feldspar minus the average from the SiO$_2$ phase from the clasts.

<table>
<thead>
<tr>
<th>Alkali feldspar (ppm)</th>
<th>ROI 1</th>
<th>ROI 2</th>
<th>ROI 3</th>
<th>ROI 4</th>
<th>Average</th>
<th>S.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>22.8</td>
<td>22.3</td>
<td>20</td>
<td>21.3</td>
<td>21.6</td>
<td>1.25</td>
</tr>
<tr>
<td>Raw – Suprasil</td>
<td>20.7</td>
<td>20.2</td>
<td>17.9</td>
<td>19.2</td>
<td>19.5</td>
<td>1.25</td>
</tr>
<tr>
<td>Raw – average SiO$_2$</td>
<td>20.1</td>
<td>19.6</td>
<td>17.3</td>
<td>18.6</td>
<td>18.9</td>
<td>1.25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SiO$_2$ phase (ppm)</th>
<th>ROI 1</th>
<th>ROI 2</th>
<th>ROI 3</th>
<th>Average</th>
<th>S.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>2.89</td>
<td>2.39</td>
<td>2.78</td>
<td>2.68</td>
<td>0.304</td>
</tr>
</tbody>
</table>

Hydrogen contained in nominally anhydrous minerals is normally in the form H$_2$O 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 H$_2$O and in volcanic rocks it is generally OH$^-$. 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 H$_2$O 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 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 H$_2$O would help clarify the origin of the hydrogen. In addition, D/H isotopic analyses on the feldspar would help assess if there is an exodemic 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.

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 CI/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, CI, 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 CI/F can crystallise apatite that generally excludes OH-, regardless of the water content of the magma. Estimated CI/F of magmas from mare basalts, alkali suite, and KREEP-rich rocks show a progression toward higher CI/F as magma compositions become more K-rich (Fig. 2). Associated with the increase in magma CI/F is a decrease in OH- in apatite, and thus an apparent decrease in magmatic water (Fig. 2).

**Figure 2**  Plot of the estimated CI/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. CI/F melt estimates from apatite assume Dv/D0 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 CI/F ratios higher than 3.

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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 within 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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References


