A heterogeneous lunar interior for hydrogen isotopes as revealed by the lunar highlands samples

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A B S T R A C T

Knowing the amount and timing of water incorporation into the Moon has fundamental implications for our understanding of how the Earth–Moon system formed. Water has been detected in lunar samples but its abundance, distribution and origin are debated. To address these issues, we report water concentrations and hydrogen isotope ratios obtained by secondary ion mass spectrometry (SIMS) of plagioclase from ferroan anorthosites (FANs), the only available lithology thought to have crystallized directly from the lunar magma ocean (LMO). The measured water contents are consistent with previous results by Fourier transform infrared spectroscopy (FTIR). Combined with literature data, δD values of lunar igneous materials least-degassed at the time of their crystallization range from -280 to $+310$‰, the latter value being that of FAN 60015 corrected for cosmic ray exposure. We interpret these results as hydrogen isotopes being fractionated during degassing of molecular hydrogen (H_2) in the LMO, starting with the magmatic δD value of primordial water at the beginning of LMO being about -280‰, evolving to about $+310$‰ at the time of anorthite crystallization, i.e. during the formation of the primary lunar crust. The degassing of hydrogen in the LMO is consistent with those of other volatile elements. The wide range of δD values observed in lunar igneous rocks could be due to either various degrees of mixing of the different mantle end members, or from a range of mantle sources that were degassed to different degrees during magma evolution. Degassing of the LMO is a viable mechanism that resulted in a heterogeneous lunar interior for hydrogen isotopes.

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1. Introduction

The detection of indigenous water in lunar pyroclastic glass beads (Saal et al., 2008) and olivine melt inclusions (Hauri et al., 2011; Chen et al., 2015) has challenged the view held during the Apollo era that the Moon must be "dry" (Taylor et al., 2006). Since the breakthrough discovery of Saal et al. (2008), the abundance, origin and evolution of water in the lunar interior have puzzled

scientists, with scarce data and controversial interpretations. It is still debated how the lunar mantle acquired its volatiles (e.g., Barnes et al., 2016) and also how much water is actually present in the lunar interior (e.g., Boyce et al., 2014). The water contents of melt inclusions in the olivine of pyroclastic sample 74220 have been used to infer that the lunar mantle could have contained an amount of water similar to that of the terrestrial upper mantle (Hauri et al., 2011; Chen et al., 2015). The water detected in plagioclase from ferroan anorthosite (FAN) using Fourier transform infrared spectroscopy (FTIR; Hui et al., 2013) implies that water was present in an early Moon at the time of plagioclase crystallization in the LMO. However, there are uncertainties with calculations of how much might have been retained in the early stage of the

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LMO, especially as degassing was not considered in this study (Hui et al., 2013). A recent study (Mills et al., 2017) found ~20 ppm (by weight as H_2O, and hereafter) in alkali feldspar from potassium-enriched rocks, implying magmatic water contents of ~1 wt% in chemically evolved rhyolitic magmas. In contrast, Cl, Zn and K isotopes, and Zn concentrations in lunar rocks are more compatible with a volatile-depleted lunar interior (Sharp et al., 2010; Paniello et al., 2012; Albarède et al., 2015; Kato et al., 2015; Wang and Jacobsen, 2016). Finally, although some lunar apatites contain water (Greenwood et al., 2011; Barnes et al., 2014; Tartèse et al., 2014), this does not necessarily provide significant constraints on the water content of the magma that the apatite crystallized from (Boyce et al., 2014).

The interpretation of hydrogen isotope ratios of lunar materials is even more complicated. Hydrogen has two stable isotopes, H and D, and their relative abundance is expressed as δD, i.e. $\delta D = ((D/H)_{sample}/(D/H)_{standard} - 1) \times 1000$, where the standard is VSMOW. Greenwood et al. (2011) proposed that the water comes from the lunar mantle, solar wind protons, and/or comets evidenced by the large variation of hydrogen isotopic ratios ($\delta D = -202$ to $+1010\text{‰}$) in lunar apatite from mare basalts and highland rocks. Furthermore, the very low δD ($< -550\text{‰}$) of most lunar agglutinates indicate that solar wind protons are a major source of the hydrogen in lunar regolith (Liu et al., 2012). Stephant and Robert (2014) agreed that hydrogen in the lunar regolith is mostly from solar wind implantation, but argued that the D/H ratio can be increased during cosmic ray spallation. Treiman et al. (2016) suggested that the lowest δD of lunar basalts ($\delta D \leq -100\text{‰}$) could have resulted from assimilation of solar-wind-implanted lunar regolith, while their high δD (up to ~$+1100\text{‰}$) most reasonably indicates that indigenous magmatic hydrogen partially degassed molecular hydrogen (H_2). Füri et al. (2014) reported δD of $+38\text{‰}$ to $+809\text{‰}$ in lunar 74002 volcanic glasses and inferred an initial δD of the order of -100‰ and a water content of 100–300 ppm H_2O for the primary magma.

Among lithologies analyzed for water content and hydrogen isotopes (e.g., Boyce et al., 2010; McCubbin et al., 2010; Saal et al., 2013; Tartèse et al., 2013; Anand et al., 2014; Robinson and Taylor, 2014; Barnes et al., 2016; Robinson et al., 2016; Mills et al., 2017), plutonic rocks and olivine-hosted melt inclusions are likely the least affected by degassing of hydrogen-bearing species and assimilation of regolith. Therefore, these least modified hydrogen isotope ratios may best represent those in the lunar interior. Two contrasting observations have been obtained: low hydrogen isotope ratios of highland noritic apatites ($\delta D = -281$ to -27‰; Barnes et al., 2014) and of some "undegassed" KREEP (K + REE [rare earth elements] + P) apatites ($\delta D = -130 \pm 50\text{‰}$; Tartèse et al., 2014); and high hydrogen isotope ratios and pre-eruptive water content of the least degassed olivine-hosted melt inclusion measured ($\delta D = +187\text{‰}$, 1144 ppm H_2O; Saal et al., 2013) from pyroclastic sample 74220. Saal et al. (2013) interpreted the high δD of olivine-hosted melt inclusions as representing an upper limit on the primary value of the magma in the lunar interior. The large range of δD in primitive lunar igneous rocks is so far poorly understood and the origin and evolution of water of the Moon's interior is still unconstrained.

One major complication regarding the sources of lunar water is that geologic processes (e.g., late addition and magmatic degassing) may have modified the hydrogen isotopic ratios of lunar materials. It has been proposed that some water may have been added to the lunar mantle and regolith by later impacts (Elkins-Tanton and Grove, 2011; Greenwood et al., 2011). Conversely, a decrease of water content and an increase of D/H ratio in crystallizing magma could have resulted from degassing of H_2 (Saal et al., 2013; Füri et al., 2014; Tartèse et al., 2014). Therefore, given the limited amount of data and possible late-stage pro-

cesses, it may be difficult (if not impossible) to assess the effects on hydrogen of the magmatic processes that could have occurred in the Moon and to infer the initial hydrogen concentration of the LMO. Previous hydrogen isotope studies (e.g., Greenwood et al., 2011; Liu et al., 2012; Saal et al., 2013; Barnes et al., 2014; Füri et al., 2014; Tartèse et al., 2014; Stephant and Robert, 2014; Treiman et al., 2016) were all targeting samples derived from partial melting of the lunar mantle. The latter crystallized from the LMO, thus these samples have the potential to sample hydrogen signatures from events occurring after LMO crystallization. Furthermore, lunar basalts erupted in a vacuum and have undergone extensive degassing, which fractionates hydrogen isotopes (Saal et al., 2013). In contrast, water detected in plagioclases from FAN samples, which presumably crystallized directly from the LMO, allowed us to speculate that the LMO could have contained ~320 ppm H_2O (Hui et al., 2013). Note that this concentration should be revised to ~136 ppm, taking into account new FTIR absorption coefficient for plagioclase (Mosenfelder et al., 2015) and new partition coefficient for hydrogen between plagioclase and melt (Hamada et al., 2013). The fact that water is detectable in these FANs presents the best opportunity for determining δD of the only available lunar lithology directly formed from the LMO (e.g., Shearer et al., 2006). This assumes that shock has minimal effects on hydrogen content and isotopic ratios of plagioclase, which will be discussed because ferroan anorthosites have experienced various degrees of impact on the Moon's surface. Here, we present hydrogen isotope measurements in lunar FAN lithologies and address the origin of water in the early Moon.

2. Samples studied

Lunar plagioclase grains selected for this study are from ferroan anorthosites 15415,238 and 60015,787, and Mg-suite troctolite 76535,164 and are the same grains previously analyzed for water contents using FTIR (Hui et al., 2013). A summary of the samples' characteristics (Hui et al., 2013) is presented here.

Sample 15415, which was collected on the rim of Apur Crater during the Apollo 15 mission, is a chemically pristine coarse-grained ferroan anorthosite made up of >98% anorthite ($An_{96.6–98.2}$) and accessory pyroxene (Morgan et al., 1972; Dixon and Papike, 1975; McGee, 1993). Ferroan anorthosite 60015 is covered by a rind of thick black glass and was collected near the Lunar Module during the Apollo 16 mission (Dixon and Papike, 1975). No crystallization ages using isochron dating methods have been determined for these two ferroan anorthosites, but it is generally believed that ferroan anorthosite are relics of primary feldspathic lunar crust having formed by accumulating plagioclase crystallizing from the LMO by floatation (Norman et al., 2003; Shearer et al., 2006). However, this simple LMO model may not explain the whole range of Mg# (Mg# = molar Mg/(Mg + Fe^{2+})) in mafic minerals exhibited by anorthosites from lunar feldspathic meteorites (Gross et al., 2014). An age of 4.46 ± 0.04 Ga has been determined for the crystallization age of lunar ferroan anorthosites using an $^{147}Sm–^{143}Nd$ isochron based on mafic fractions from four different ferroan anorthosites (60025, 62236, 67016c, and 67215c; Norman et al., 2003). However, younger ages have also been reported for some ferroan anorthosites (Borg et al., 2011, 2015). This suggests that the LMO may have cooled over an extended duration (Elkins-Tanton et al., 2011; Borg et al., 2015) or that these samples are comprised of clasts of different ages, not all primary products of the LMO.

Sample 76535, collected at Station 6 during the Apollo 17 mission, is an Mg-suite troctolite. This coarse-grained plutonic rock is composed of 60% olivine ($Fo_{87.3}$), 35% plagioclase ($An_{96.2}$) and 5% orthopyroxene ($En_{84.1}Wo_{0.9}$) (Dymek et al., 1975). It has been shown that troctolite 76535 is chemically pristine