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Water in the Moon's interior: Truth and consequences

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ABSTRACT

Geochemical data for H₂O and other volatiles, as well as major and trace elements, are reported for 377 samples of lunar volcanic glass from three chemical groups (A15 green, A15 yellow, A17 orange 74220). These data demonstrate that degassing is a pervasive process that has affected all extrusive lunar rocks. The data are combined with published data to estimate the total composition of the bulk silicate Moon (BSM). The estimated BSM composition for highly volatile elements, constrained by H₂O/Ce ratios and S contents in melt inclusions from orange glass sample 74220, are only moderately depleted compared with the bulk silicate Earth (avg. 0.25X BSE) and essentially overlap the composition of the terrestrial depleted MORB source. In a single giant impact origin for the Moon, the Moon-forming material experiences three stages of evolution characterized by very different timescales. Impact mass ejection and proto-lunar disk evolution both permit system loss of H₂O and other volatiles on timescales ranging from days to centuries; the early Moon is likely to have accreted from a thin magma disk of limited volume embedded in, but largely displaced from, the extended distribution of vapor around the Earth. Only the protracted evolution of the lunar magma ocean (LMO) presents a time window sufficiently long (10–200 Ma) for the Moon to gain water during the tail end of accretion. This “hot start” to lunar formation is however not the only model that matches the lunar volatile abundances; a “cold start” in which the proto-lunar disk is largely composed of solid material could result in efficient delivery of terrestrial water to the Moon, while a “warm start” producing a disk of 25% volatile-retentive solids and 75% volatile-depleted magma/vapor is also consistent with the data. At the same time, there exists little evidence that the Moon formed in a singular event, as all detailed planetary accretion models predict several giant impacts in the terrestrial planet region in which the Earth forms. It is thus conceivable that the Moon, like the Earth, experienced a history of heterogeneous accretion.

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1. Introduction

The detection of magmatic water in lunar volcanic glasses, and the high pre-eruptive abundance of water in melt inclusions from one of these samples, has provided the first definitive evidence for the accretion and retention in the Moon's interior of one of the most volatile compounds in the solar system (Saal et al., 2008, 2013; Hauri et al., 2011; Füri et al., 2014). Measurement of water in lunar apatite, at levels similar to terrestrial apatite, has added weight to this discovery (Boyce et al., 2010, 2014; McCubbin et al., 2010; Greenwood et al., 2011; Tartèse and Anand, 2013; Anand et al., 2014; Barnes et al., 2013, 2014; Tartèse et al., 2013, 2014). These surprising results, the culmination of over four decades of intensive geochemical dowsing, provide a severe con-

straint on high-temperature models that seek to explain the formation and evolution of the Moon. With increasing consideration of the orbital dynamics of the Earth–Moon–Sun system, there now exists a very wide parameter space for planetary collision models to explain the origin of the Moon by a giant impact, with the Moon formed from a circum-terrestrial disk of molten debris ejected by the collision. This class of models can explain the Earth–Moon angular momentum and early thermal history of the Moon (Cameron and Benz, 1991; Canup and Asphaug, 2001; Canup, 2012; Cuk and Stewart, 2012). However, all of these models predict wholesale melting and partial vaporization of the silicate material that enters proto-lunar orbit in the vacuum of space, and thus all of these models, as currently formulated, are unable to account for the presence of water in the Moon's interior.

Water in the lunar interior is at odds not only with existing formation models, it is also counter to one of the longest-standing observations in lunar geochemistry, namely the volatile-depleted

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nature of the Moon compared with the Earth (Krähenbühl et al., 1973a, 1973b; Tera and Wasserburg, 1976; Ringwood and Kesson, 1977; McDonough et al., 1992). There exists a large body of evidence that the abundances of highly- and moderately-volatile elements in lunar basalts are depleted to levels that are as much as 1000× lower than their abundances in terrestrial mid-ocean ridge and ocean-island basalts. The detection and abundance of magmatic water in lunar glasses and minerals, as well as other volatiles like fluorine and chlorine, is an apparently contradictory result in the context of prior laboratory studies of lunar samples. This contradiction has led to the suggestion that perhaps the water-bearing samples are a lunar anomaly, and do not say anything particularly fundamental about the formation and evolution of the Moon (Albarede et al., 2013, 2014).

Here we will demonstrate that most of these apparent contradictions – the geochemical ones at least – have arisen due to the previously unappreciated importance of a single widespread process, magmatic degassing. Degassing occurs in all eruptions of magma, with consequent release of volatile elements into an exsolved vapor phase. The degree to which different elements are highly, moderately, or barely-volatile depends on the pressure of eruption, the eruption temperature, and the evaporation temperature of the elements in question. Before the Moon's extent of volatile depletion can be confidently attributed to processes associated with large impacts and their aftermath, the degassing processes experienced by most lunar samples must be examined and critically evaluated. In this paper, we will examine the data for volatile elements in lunar samples and describe the consequences of these data for the origin of the Moon in the context of formation and evolution models.

2. Volcanic glasses, mare basalts and plutonic rocks

2.1. Overview

To estimate the water content of the bulk Moon, the ideal samples would be samples of the lunar mantle from which the H₂O content could be measured directly, as has been done with terrestrial mantle peridotites. The absence of identified mantle samples in existing lunar collections means that we must turn to mantle-derived magmatic samples for study. The new generation of data on the water content of lunar samples have come from three sample types; broadly defined, they are volcanic glasses of pyroclastic origin (Saal et al., 2008, 2013; Hauri et al., 2011; Füre et al., 2014), basaltic lava flows from the lunar maria (Boyce et al., 2010; McCubbin et al., 2010; Greenwood et al., 2011; Barnes et al., 2013; Tartèse and Anand, 2013; Tartèse et al., 2013, 2014), and various types of plutonic rocks (Greenwood et al., 2011; McCubbin et al., 2010; Hui et al., 2013; Barnes et al., 2014). All of these studies have utilized microbeam methods for determination of water contents, either SIMS or FTIR, with the goal of obtaining water contents in the interior of mineral and glass samples (thus avoiding surfaces), and to obtain this data within the petrologic context of the rocks' mineral assemblages. Both methods achieve micron-scale spatial resolution with low detection limits. In analyses of lunar volcanic glasses and melt inclusions, the analyzed glass represents a quenched sample of a discrete magmatic liquid whose composition is given simply by the composition of the glass, and thus the determination of H₂O in the glass translates into a direct measure of the water content of the melt. Analysis of H₂O in minerals requires knowledge of the mineral-melt partition coefficient in order to estimate the H₂O content of the melt.

2.2. Lunar apatite

Analyses of lunar basaltic lavas and plutonic rocks have largely concentrated on the mineral apatite, which contains hydroxyl (OH)

as a structural component; the water content of co-existing melt must be estimated using apatite-melt partition coefficients for H₂O which are complex functions of apatite and melt composition (McCubbin et al., 2010; Boyce et al., 2014). The overlap of H₂O abundances of lunar apatites with their terrestrial counterparts (Boyce et al., 2010) continues to be an irrefutable feature of the emerging apatite data. However, the measured abundances are on average 50% lower than apatite expected to crystallize from a fractionated melt that starts with MORB-like H₂O content, and this is likely due to degassing of H₂O from parental magmas prior to apatite formation (see Supplementary Material Fig. S1). Magmatic degassing is a process experienced by most terrestrial magmas, and it would be erroneous to assume that lunar magmas have somehow escaped this process. The magmas that produce apatite, both on the Earth and on the Moon, have surely experienced a protracted and irreversible history of cooling, crystallization and degassing that makes estimation of the primitive magma H₂O content nearly impossible.

2.3. Lunar volcanic glasses

Volcanic glasses, by comparison, have perhaps the most simple petrogenetic history of any recovered lunar rock – they were expelled from the lunar crust as liquid droplets in pyroclastic eruptions (Delano, 1986), whereupon the magma quenched to a glass before coming to rest on the lunar surface. The remainder of this paper will focus on the volatile content of the volcanic glasses as they not only have an exceedingly simple petrologic history, they are also primitive (with high MgO contents) and they provide information on the abundance of other volatile elements in addition to water, by direct analysis of the melt quenched as glass.

The study of H₂O in lunar volcanic glasses stands largely upon the shoulders of the work of John Delano and colleagues. Delano (1986) describes the major element composition of 25 distinct types of lunar volcanic glass, classified largely based on TiO₂ and FeO contents, and provides a list of petrologic criteria to distinguish volcanic glasses from impact glasses. The lunar volcanic glasses are the most primitive magmatic samples obtained from the Moon to date; in other words, they represent magmas derived from the lunar mantle that have undergone the smallest extent of post-eruptive modification (degassing and crystallization), and thus have the closest petrologic connection to the lunar mantle. Lunar volcanic glasses are uniformly more primitive than mare basalts with similar TiO₂ contents, i.e. they have higher MgO contents and higher Mg/Al ratios indicating they have experienced less fractional crystallization than nearly all mare basalts (Delano, 1986).

At the global scale, the significance of the lunar volcanic glasses depends to some degree on their petrogenetic connection with mare basalts. Many suites of volcanic glasses have been dated, and the distribution of their eruption ages corresponds very closely with the formation ages of Apollo mare basalts and basaltic lunar meteorites (Delano and Livi, 1981; Nyquist and Shih, 1992; Spangler and Delano, 1984; Spangler et al., 1984). Fig. 1 shows MgO and TiO₂ compositions of lunar mare basalts and volcanic glasses, from the database compiled by Neal (2008) (Mare Basalt Database – U. Notre Dame) including nearly 2000 analyses of mare basalt flows and clasts sampled from lunar soils and regolith breccias. In Fig. 1 and similar major element projections (see Supplementary Material Fig. S2), the compositions of all mare basalts can be explained by fractional crystallization of olivine, spinel and pyroxene from high-MgO parent magmas that lie along tie lines between low-Ti and high-Ti lunar volcanic glass compositions. This observation serves to emphasize an important point – that lunar volcanic glasses are not a mere anomaly produced by pyroclastic eruption of exotic lunar magma sources that happened to be particularly volatile-rich. Rather, they are the most primitive magmas produced by melting and melt migration processes in the lunar

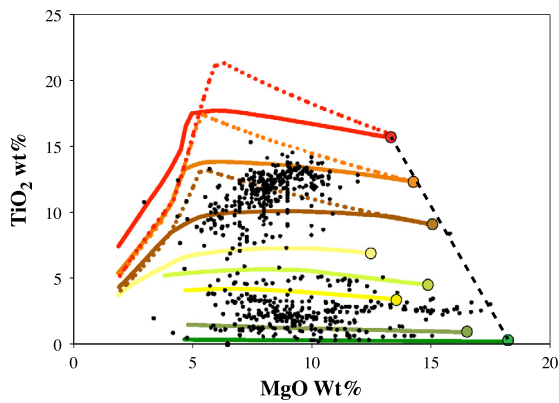


Fig. 1. MgO–TiO₂ compositions of mare basalts from the database compiled by Neal (2008). Thick colored lines are liquid lines of descent, calculated using AlphaMelts (Antoshechkina et al., 2010; Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995; Smith and Asimow, 2005) for fractional crystallization of several lunar volcanic glass compositions; low-Ti green glasses (green lines), medium-Ti yellow glasses (yellow lines), and high-Ti red glasses (red lines). Solid LLDs represent crystallization of olivine + pyroxene + oxide where the oxide phase varies continuously from Cr–Al–Mg spinel at high MgO to Fe–Ti oxide at low MgO. Dashed LLDs are calculated for a crystallizing assemblage of olivine + pyroxene + Fe–Ti oxide, with spinel crystallization suppressed, in order to compare more directly with the calculations of Longhi (1987). Dashed black line represents a mixing line between the lowest- and highest-TiO₂ volcanic glass compositions (A15 green C and A12 red). The LLDs and picritic glass parent magmas (and the array defined by mixing of these magmas) define boundaries within which all Apollo mare basalts lie. Mare basalts can thus be produced by fractional crystallization of parent magmas that lie on mixing lines connecting the compositions of lunar picritic glasses.

mantle, and they appear to be parental to the entire compositional spectrum of pristine lunar mare basalt compositions. As such they provide the most direct information about the volatile content of the lunar interior in the time period after solidification of the lunar magma ocean.

3. Volatiles and trace elements in lunar volcanic glasses and melt inclusions

3.1. SIMS data for glasses and melt inclusions

Table S1 (Supplementary Material) gives the compiled major, refractory trace and volatile element abundances for the centers of lunar volcanic glasses analyzed by our group since 2007, including trace element data for the two largest melt inclusions in olivines from sample 74220 (A2 and N8) studied in Hauri et al. (2011), and previously unpublished data on yellow glasses from Apollo 15 soil sample 15427, size-sorted green glasses from Apollo 15 sample 15426, and size-sorted orange glasses from Apollo 17 soil sample 74220. These data describe the bead-by-bead abundances of major elements, trace elements and volatiles for 371 volcanic glass beads and 6 melt inclusions, and for the first time the co-variation of these elements in lunar melt inclusions.

As with volatile studies on terrestrial volcanic glasses, we can examine the systematics of volatile elements by comparison with a non-volatile but similarly incompatible trace element measured in the same samples. Ratios of volatile to non-volatile elements, for example H₂O/Ce, have been in use for decades to infer the extent of degassing in submarine volcanic systems (Cartigny et al., 2008; Dixon and Clague, 2001) and to identify regions of the Earth's interior where volatile abundances may be variable (Cooper et al., 2012; Michael, 1995). Saal et al. (2002) and Le Roux et al. (2006) in studies of mid-ocean ridge basalts chose the ratios H₂O/Ce, F/Zr, F/Nd, S/Dy, Cl/Nb and Cl/Ba in order to study variations in degassing and terrestrial mantle heterogeneity along the East Pacific Rise. Diffusion modeling conducted in Saal et al. (2008), utilizing all the measured volatiles on a core-rim profile from a single

green glass bead, indicated a best-fit pre-diffusion H₂O content of 745 ppm, and a minimum of 265 ppm at the 95% confidence limit for the A15 very-low-Ti (VLT) magma. This modeling indicated that during the degassing stage of degassing following magma fragmentation, A15 VLT green glasses lost ~98% of their initial H₂O and ~57% of their initial Cl, but only ~45% of initial F and ~19% of initial S.

Ultimately, we wish to know the pre-eruptive magmatic volatile content in order to circumvent the confounding effects of degassing. The pre-diffusion estimate of 745 ppm H₂O from diffusion modeling of the A15 VLT glass bead (Saal et al., 2008) could possibly serve as an estimate for the pre-eruptive water content of this magma, but only if we make the assumption that this bead retained something close to a pre-eruptive water content at the time of magma fragmentation. By comparing the pre-diffusion volatile estimates of Saal et al. (2008) to the incompatible trace element content of A15 VLT glass, we obtain H₂O/Ce = 169, F/Zr = 0.4, F/Nd = 3.67, S/Dy = 129, Cl/Nb = 0.23 and Cl/Ba = 0.021. H₂O/Ce is firmly within the terrestrial mantle range, S/Dy is low by a factor of two, while F/Zr, F/Nd, Cl/Nb and Cl/Ba are low by factors of 5–20 compared with Earth's upper mantle. The anomalous depletion of the Earth in chlorine, compared with its 50% condensation temperature, has been noted previously (Sharp and Draper, 2013) and this is reflected in a high F/Cl ratio for the Earth (0.99) compared with carbonaceous chondrites (0.088, McDonough and Sun, 1995). The implied F/Cl for the Moon (30) is even higher and may suggest a preferential loss mechanism for Cl during planet formation (Sharp and Draper, 2013).

Hauri et al. (2011) reported the first measurements of volatiles from lunar melt inclusions, focusing on inclusions in olivine crystals from A17 orange sample 74220. Melt inclusions are particularly advantageous for determining the pre-eruptive volatile content of magmas, as they are micro-samples of magma trapped in crystals that grow prior to eruption. The A17 orange 74220 melt inclusions contain much more H₂O than the corresponding glasses, and when combined with trace element contents, we obtain H₂O/Ce = 67–77, F/Zr = 0.44–0.46, F/Nd = 4.23–4.46, S/Dy = 90–94, Cl/Nb = 0.19–0.20 and Cl/Ba = 0.035–0.041 (Table S1). It is significant that the F/Zr, F/Nd, S/Dy, Cl/Nb and Cl/Ba ratios are somewhat similar to the reconstructed ratios in the A15 VLT glass, lending support to the modeled pre-eruptive volatile contents of the A15 VLT magma. The pre-eruptive H₂O/Ce ratio for 74220 magma is 40–48% lower than that estimated for the A15 VLT magma (Table 1), however it should be noted that there would be close agreement if one used the lower-bound H₂O content of 265 ppm for the A15 VLT magma (Saal et al., 2008).

3.2. Degassing during lunar volcanic eruptions

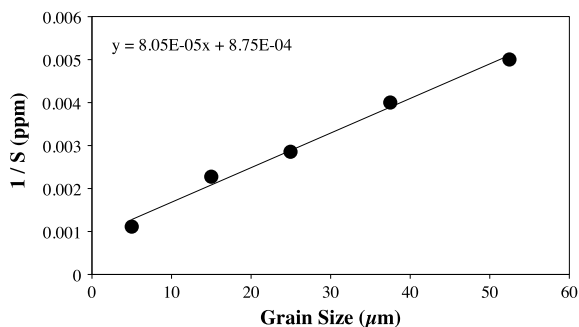
Saal et al. (2008) showed that the volatile abundances of the lunar volcanic glass beads have been affected by magmatic degassing. This degassing likely took place in two stages; release of volatiles as a separate phase during magma ascent and fragmentation, followed by diffusion of volatiles out of molten droplets after magma fragmentation. As a result of volcanic degassing, ratios of H₂O/Ce, F/Zr, F/Nd, S/Dy, Cl/Nb and Cl/Ba are orders of magnitude lower in the lunar volcanic glass beads compared with melt inclusions (Table S1).

The significance of degassing as an important process during lunar eruptions is not a particularly new idea, being first suggested in 1972 (O'Hara, 1972). Surface coatings exist on many categories of volcanic glass beads; indeed, whenever they have been searched for, they have been found to exist (Delano, 1986). These surface coatings have been found to contain high abundances of many volatile elements, including B, F, Na, S, Cl, Cu, Zn, Cd, Pb and many

Table 1

Volatile/non-volatile ratios for A15 green VLT glass, A17 orange 74220 glass, and depleted mid-ocean ridge basalt (MORB).

	H ₂ O/Ce	F/Zr	F/Nd	S/Dy	Cl/Nb	Cl/Ba
A15 green VLT ^a	169	0.40	3.67	129	0.231	0.021
A17 orange 74220 ^b	77	0.46	4.46	94.5	0.200	0.041
Depleted MORB ^c	168 ± 95	2.2 ± 0.5	40 ± 25	225 ± 50	3.0 ± 0.8	0.42 ± 0.13

^a Estimated from diffusion modeling, Saal et al. (2008).^b Highest ratios measured in 74220 melt inclusions (this study).^c Depleted MORB averages from Saal et al. (2002).**Fig. 2.** 1/S (ppm) vs bead size for 74220 glass beads, from the study of Thode and Rees (1976). Y-intercept represents the composition at infinite ratio of surface area to volume, i.e. the composition of the sulfur-rich coatings on the surfaces of the glass beads.

others (Chou et al., 1975; Cirlin et al., 1978; Krähenbühl, 1980; Thode and Rees, 1976; Wasson et al., 1976). The presence of surface coatings has been widely attributed to their deposition onto bead exteriors during cooling of clouds of volcanic gas that enveloped the glass beads and modified their cooling rates (Arndt et al., 1984; Arndt and Von Engelhardt, 1987). Though we may not necessarily expect that the surface coatings represent directly the precise composition of the volcanic gas itself, it is nevertheless instructive to examine the composition of this surface coating and see what we can infer about the degassing of other volatile elements during eruption.

Among the many studies of lunar glass surface coatings, for our purposes the most useful are those that examine the bulk composition of glass beads (including their surfaces) as a function of bead size (Chou et al., 1975; Thode and Rees, 1976; Wasson et al., 1976; Cirlin et al., 1978; Krähenbühl, 1980). In this respect, the study of S concentrations and isotopes in A17 orange glass sample 74220 by Thode and Rees (1976) provides a good example. These authors recognized that as glass bead sizes become smaller and smaller, the surface area-to-volume ratio (SA/V) becomes larger, and thus the bulk composition of the smallest bead sizes are more heavily influenced by the composition of the surface coating, and less by the degassed bead interiors. Thode and Rees (1976) demonstrated clear correlations in the abundance of S with bead size (Fig. 2); indeed, the Y-intercept of a plot such as the one in Fig. 2 can be interpreted as the bulk composition at infinitely high SA/V. In other words, the Y-intercept provides an estimate of the composition of the surface coating itself, and in the case of S we obtain an estimate of 1140 ppm S.

We can repeat this exercise using the data obtained on other volatile elements from the studies of Chou et al. (1975), Wasson et al. (1976), Cirlin et al. (1978) and Krähenbühl (1980). From these studies, we arrive at a composition for the volcanic glass surface coating given in Table 2. The high abundances of these elements, compared with their concentrations in glass bead interiors, is notable. In terrestrial subaerial settings, such elements can also act as volatile elements in volcanic systems but generally at much lower levels of volatility than has been observed in the lunar volcanic glasses.

3.3. Reconstruction of pre-eruptive lunar magma compositions

Given the composition of the surface coating, and even though it is likely to be an imperfect estimate of the actual volcanic gas, we can now try to estimate the pre-eruptive abundances of these elements in the 74220 magma by simple addition of the surface coating to the degassed composition of the 74220 glass bead interiors. The first step is to note the difference in S abundances between the 74220 glasses (avg. 323 ppm S) and the least-degassed 74220 melt inclusion (884 ppm S). We ratio the abundances of all the other trace elements in the surface coating to S, and then simply mix the surface coating composition into the glass bead interior composition until we arrive at the S content of the least-degassed 74220 melt inclusion. This gives us an estimate of the pre-eruptive abundances of the other volatile elements in the 74220 picritic magma (Table 2). Short of actually measuring these elements in melt inclusions – a daunting task by SIMS or laser ablation for these particular elements – this exercise likely provides the best estimate currently available for the pre-eruptive abundances of these elements. Among the elements listed, most were nearly completely degassed from volcanic glass beads (even Pb at ~93% degassed), with the exception of Na (42% degassed) and Ga (36% degassed).

The largest difference in the degassing regimes of terrestrial and lunar volcanism is surface pressure. The surface pressure prevailing during eruption of lunar magmas is on the order of 10^{-10} to 10^{-15} bars (Stern, 1999), approximately one-trillionth the pressure prevailing on Earth's surface. The lunar surface is essentially under ultra-high vacuum, and at the high eruption temperatures of lunar magmas (Longhi, 1992) many elements that would normally be undegassed during terrestrial eruptions become quite volatile under the conditions of lunar eruptions. This is the most likely explanation for the large extents of degassing of the trace elements listed in Table 2.

We wish to make one final comment on lunar volcanic degassing. The evidence for degassing of volatile elements with a wide range of condensation temperatures <1100 °C is irrefutable, and can be observed as a consequence of both eruptive degassing and post-eruptive diffusive loss from fragmented magma, despite the fact that this fragmented magma quenched to glass within minutes of eruption. Mare basalts, however, very likely took days to months to solidify into lava flows, and this undoubtedly provided further opportunities for magmatic degassing. For example, it was noted that Zn is highly degassed from lunar volcanic glasses from our analysis above, and mare basalts display Zn abundances that are even lower than glasses by a factor of 10–100 (see Supplementary Material). Thus degassing is a very likely source of the isotopic fractionation observed in Zn isotopic data for lunar rocks (Paniello et al., 2012), and perhaps other solar system parent bodies that lacked atmospheres and show evidence for surface magmatism.

4. The volatile element depletion of the Moon

The composition of the bulk silicate Moon (BSM) is a critical metric for understanding its origin and evolution, as well as

Table 2

Composition of volatile elements in 74220 glass bead coatings, glass bead interiors, and reconstituted pre-eruptive composition (see text).

	S ppm	Na ppm	Zn ppm	Ga ppm	Ge ppb	Cd ppb	In ppb	Te ppb	Hg ppb	Pb ppm
A17 orange coating composition	1143	2653	466	13.8	688	304	29.9	110.3	43.1	8.13
A17 orange glass interior composition	325	2137	3.97	16.7	0.19	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.305
A17 orange glass reconstituted	884	3434	232	26.3	337	149	15	54	21	4.28
% degassed	63%	42%	97%	36%	100%	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	93%

its relationship with the Earth. Numerous authors have attempted to calculate the composition of the BSM (Wänke et al., 1975; Ringwood and Kesson, 1977; Buck and Toksoz, 1980; Warren, 1985; Rasmussen and Warren, 1985; Ringwood, 1992; Albarede et al., 2014; Taylor and Wieczorek, 2014), driven by various inputs including the analysis of returned Apollo samples, remote mapping of the lunar surface, the recognition of the highlands as being largely feldspathic, and Apollo-era analysis of seismic data suggesting the highlands crustal thickness to be in the range of 60–70 km. Based on these inputs, the major element composition of many BSM estimates have tended to be enriched in FeO, CaO, Al₂O₃ and refractory trace elements compared with the Earth.

In contrast to most major element studies, recent isotopic data on lunar rocks presents a somewhat different story, namely one in which the Earth and Moon have isotopic compositions that are so similar that they are, for nearly all measured elements, virtually identical within laboratory analytical errors (cf. Pahlevan, 2014). The list of matching isotopic compositions is long and growing; potassium (Humayun and Clayton, 1995), chromium (Lugmair and Shukolyukov, 1998), tungsten (Touboul et al., 2007), silicon (Armytage et al., 2012; Chakrabarti and Jacobsen, 2010a; Fitoussi and Bourdon, 2012), calcium (Valdes et al., 2014), titanium (Zhang et al., 2012), zirconium (Schönbächler et al., 2003), magnesium (Chakrabarti and Jacobsen, 2010b), iron (Beard and Johnson, 1999; Liu et al., 2010), and stable isotopes of strontium (Charlier et al., 2012) are all identical among lunar and terrestrial rocks. Oxygen isotopes, once thought to also be identical (Wiechert et al., 2001; Spicuzza et al., 2007; Hallis et al., 2010), may show a very small difference (Herwartz et al., 2014) that awaits confirmation. It is important to note that these isotopic similarities do not all extend to basaltic and chondritic meteorites, and by inference their parent bodies. The Moon and Earth are the only planetary pair to share such similar isotopic compositions for all of the above elements. The only isotopic exceptions to Earth–Moon identity are measured differences in the isotopes of copper and zinc (Herzog et al., 2009; Paniello et al., 2012), chlorine (Sharp et al., 2010) and hydrogen (Saal et al., 2013), all of which can be explained by isotopic fractionation during volatilization, as a consequence of the volcanic degassing discussed above. Isotopes of Yb and Er also vary in both terrestrial and lunar rocks (Albalat et al., 2012); in terrestrial rocks this is due to redox effects during melting that may be magnified in the more reduced lunar interior.

Another recent constraint on the BSM composition comes from re-analysis and reconsideration of the lunar crustal thickness; this is important due to the nearly monomineralic composition of the lunar crust. Reanalysis of lunar seismic data (Khan et al., 2000; Lognonné et al., 2003; Garcia et al., 2011; Weber et al., 2011), as well as topographic and gravity constraints from the recent GRAIL mission (Wieczorek et al., 2013; Zuber et al., 2013), now place the lunar crustal thickness at 30–40 km, roughly half the thickness of Apollo-era estimates. This greatly relaxes constraints on the CaO and Al₂O₃ contents of the BSM, to the point that there now exists no strong evidence that the major element composition of the bulk silicate Moon is any different from that of the bulk silicate Earth.

Our estimated composition for the bulk silicate Moon is given in Table 3 and detailed in the Supplementary Materials. As a result of the above isotopic arguments, we simply posit that the abundances of SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO and CaO are the same

on the Earth and Moon. This supposition is supported by the more extensive petrologic arguments of Warren (2005), Ringwood (1992) and Taylor and Wieczorek (2014) who reached the same conclusion for major elements and 27 refractory lithophile elements (FeO excepted); in our case, we assume a terrestrial FeO content, but admit that present constraints on the density of the lunar mantle and size of the lunar core would permit a slightly higher FeO and lower corresponding Mg# (Warren and Dauphas, 2014). In the same way, we also assume that the refractory lithophile elements are present at terrestrial levels in the Moon, for elements with 50% condensation temperatures >1300 K. Our BSM composition is given in Table 3 and described in detail in the Supplementary Material, and BSM/BSE ratios are shown in Fig. 3.

When compared to the composition of the bulk silicate Earth, the BSM composition is volatile depleted, but not nearly as depleted as previously thought and commonly quoted (e.g. 1% to 0.1% of BSE, Ringwood and Kesson, 1977). For H₂O our lowest estimate is within a factor of 5 of BSE; our high estimate is within a factor of 2, and as noted previously (Hauri et al., 2011) the BSM H₂O abundance overlaps completely with the Earth's depleted upper mantle. Most of the volatile elements in our compilation are within a factor of 2–10 of the corresponding abundances in the BSE; Ag, Ge, Sb, I and notably Cl do not fit this pattern, being depleted by more than a factor of 10. Without a doubt, the major difference in the volatile contents of our BSM composition compared with others is due to considering the effects of volcanic degassing, not only for the most volatile elements but also for elements not usually considered as volatile during magmatic eruptions, such as alkalis, zinc and lead. Our view is guided by the extremely large difference in the surface pressures that prevail on the Earth and Moon during volcanic eruptions. But most important to our BSM estimates are the direct measurements of lunar melt inclusions, and the re-constructed volatile composition of the 74220 picritic magma. The volatile depletion pattern for the BSM is largely flat (Fig. 3), and so does not correlate with condensation temperature at 10⁻⁴ bars nor with bond energy for likely ligands (Albarede et al., 2014). The mis-match for Ag, Ge, Sb, I and Cl may be an indication that we have not been completely successful in accounting for the effects of volcanic degassing, keeping in mind that the measured abundances of volatiles in existing lunar melt inclusions are minimum estimates for the pre-eruptive concentrations of H₂O and other volatiles. The flat volatile-element depletion pattern for the bulk Moon (avg. 0.25 × BSE) is a distinctive feature of our BSM estimate, and awaits comparison with further studies of undegassed lunar samples.

Before we leave this discussion of the Moon's depletion in volatile elements, it is instructive to consider the inferences to be gained by considering two radiogenic isotope systems based on volatile elements – the Rb/Sr system and the U/Pb system. For these two systems, volatile depletion works in opposite directions, resulting in low ⁸⁷Sr/⁸⁶Sr ratios like those observed in lunar anorthosites (Carlson and Lugmair, 1988), while volatile depletion works to increase the U/Pb ratio of mantle sources and results in high ratios of ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb as observed in the interiors of volcanic glass beads (Tera and Wasserburg, 1976). The point to be made here is that recent high-precision studies on well-dated lunar rocks, where multiple isotope systems give concordant ages, has revealed the isotopic evolution of initial Sr and

Table 3

Estimated major and trace element composition of the bulk silicate Moon (BSM).

Major elements wt%							
SiO ₂	45.00	Cl ^c	0.205	Nb	0.658	Tb	0.103
TiO ₂	0.20	Cl ^d	0.142	Mo	0.0021	Dy	0.705
Al ₂ O ₃	4.45	K	56.8	Ru	0.00010	Ho	0.151
FeO*	8.05	Sc	15.0	Rh	0.000026	Er	0.456
MnO	0.135	Ti	1205	Pd	0.00010	Tm	0.071
MgO	37.80	V	82	Ag	0.00018	Yb	0.463
CaO	3.55	Cr	1916	Cd	0.0117	Lu	0.070
Na ₂ O	0.12	Mn	1046	In	0.0016	Hf	0.283
K ₂ O	0.00684	Co	105	Sn	0.039	Ta	0.037
P ₂ O ₅	0.0206	Ni	588	Sb	0.000078	W	0.0107
		Cu	7.22	Te	0.00408	Re	0.00001
Trace elements ppm							
H ₂ O low	133	Zn	7.7	I	0.0003	Os	0.0001
H ₂ O hi	292	Ga	2.34	Cs	0.0067	Ir	0.0001
Li	1.20	Ge	0.015	Ba	6.60	Pt	0.0002
Be	0.0680	As	0.012	La	0.675	Au	0.00024
B	0.0743	Se	0.024	Ce	1.728	Hg	0.00093
F ^a	5.40	Br	0.026	Pr	0.262	Tl	0.0015
F ^b	4.52	Rb	0.1470	Nd	1.327	Pb	0.028
P	56.8	Sr	19.9	Sm	0.425	Bi	0.00022
S	78.9	Y	3.81	Eu	0.164	Th	0.0795
		Zr	10.5	Gd	0.572	U	0.0203

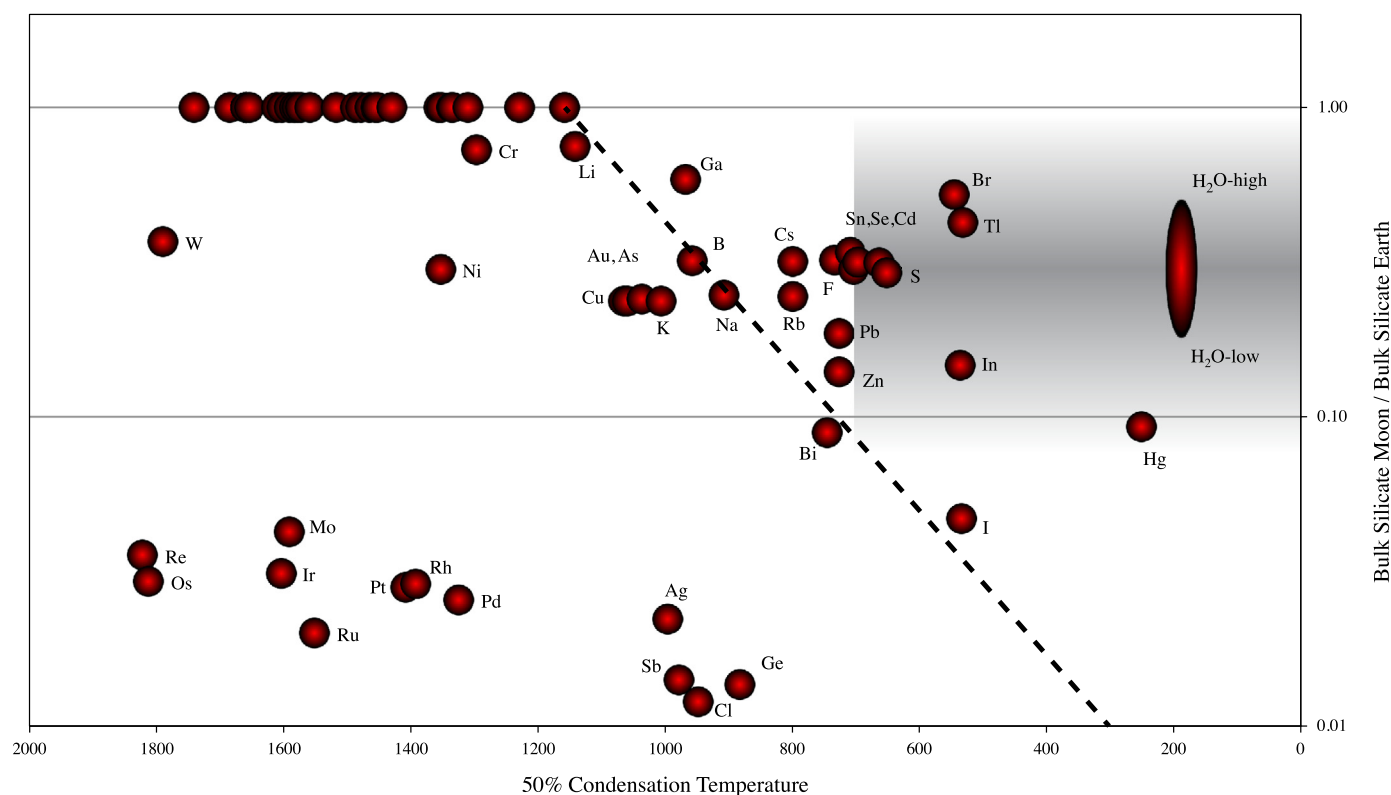
^a From F/Nd ratio.^b From F/Zr ratio.^c From Cl/Ba ratio.^d From Cl/Nb ratio.

Fig. 3. Composition of the bulk silicate Moon (BSM) relative to the composition of the bulk silicate Earth (BSE) as a function of 50% condensation temperature at 10^{-4} bars (Lodders, 2003). Dashed line represents schematically the lunar volatile depletion trend suggested by Albarede et al. (2014). Gray region illustrates the abundances of highly volatile elements ($<700^{\circ}\text{C}$) expected by addition of 0.1% to 0.4% of the lunar mass as carbonaceous chondrite (see text and Supplementary Material for details).

Pb isotope ratios among lunar mantle sources at different ages, and these isotopic evolutions are often consistent with Rb/Sr and U/Pb ratios that begin to approach terrestrial ratios. For example, the isotopic evolution of $^{87}\text{Sr}/^{86}\text{Sr}$ in well-dated lunar anorthosite and Mg-suite rocks reveals a clearly-defined evolution of Sr isotopes with a $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of 0.035 (Carlson et al., 2014), which suggests a lunar mantle Rb abundance that is only 1/3 that of the BSE

(0.089), while Borg et al. (2009) studied a low-Ti lunar meteorite that originated from a lunar mantle source with a $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of 0.044, roughly half the BSE ratio. U/Pb isotope studies have revealed lunar mantle sources that have $^{238}\text{U}/^{204}\text{Pb}$ (μ) values of 30 (Tera and Wasserburg, 1976), 21 (Kita et al., 1995), 18 (Terada et al., 2008), and 10 (Misawa et al., 1993), compared with the BSE value of 8.5; these low source μ values reflect regions within the

Moon whose U/Pb ratio approaches that of the BSE. Part of the value of these isotopic observations are due to the fact that the evolution of the initial Sr and Pb isotope ratios are recorded in the rocks prior to the time they formed, i.e. these data represent the evolution of lunar mantle sources, and as such are not compromised by any possible Rb or Pb loss during any volcanic events the samples may have experienced. This isotopic data lends support to our estimates for the abundances of Rb ($0.245 \times$ BSE) and Pb ($0.187 \times$ BSE) in the BSM, and indeed suggests that they may be on the low side.

5. Timescales for volatile loss and gain during Moon formation

5.1. A single “hot start” giant impact

5.1.1. Overview

The Moon is widely viewed as having originated from a giant impact of some kind (Cameron and Benz, 1991; Canup and Asphaug, 2001), and with recent studies that have relaxed the constraint of conserved angular momentum in the Earth–Moon system, there now exists a large parameter space within which impact models produce an orbiting satellite that today has the present angular momentum and Moon/Earth mass ratio (Canup, 2012; Cuk and Stewart, 2012). At the same time, planetary accretion models indicate that fully formed planets are likely to have suffered multiple giant impacts (Agnor et al., 1999; Chambers, 2004; Morbidelli et al., 2012; Genda et al., 2012). In this section, we will examine critically a single giant impact origin for the Moon at face value; within this context, we will follow the evolution of the Moon-forming material from impact to solidification, and make a critical assessment of time windows within this evolution where water could have been lost or gained by the material that formed the Moon. This exercise should apply to all giant impacts with sufficient energy to form a circum-planetary disk, which make up $\sim 60\%$ of all giant impacts occurring during terrestrial planet formation (Genda et al., 2012).

Radiogenic heating by decay of ^{26}Al , and energy transfer estimates during giant impacts, conspire to predict wholesale melting of the material that forms the Moon, the so-called “hot start” (Canup, 2004). In considering the evolution of the Moon, we mark “lunar time-zero” as the moment of the giant impact, without being specific about the absolute timing of the event. From lunar time-zero, the evolution of the Moon can be broken down into three stages dominated by processes that occur over very different timescales. These three stages are (i) ejection of material into Earth orbit via the giant impact; (ii) spreading, cooling and fragmentation of the proto-lunar disk leading ultimately to coalescence of the Moon; and (iii) cooling and crystallization of the lunar magma ocean (LMO) leading ultimately to the formation of a rigid lunar lithosphere and solidification of the Moon as a one-plate body (Fig. 4).

5.1.2. Impact mass ejection

Genda and Abe (2003a) have demonstrated that giant impacts have the ability to remove the proto-Earth’s atmosphere and oceans when large global ground motions approach escape velocity, ejecting a fraction of the hydrosphere to space. For conditions in which a Mars-sized impactor collides with the proto-Earth, only 10% of the proto-Earth’s atmosphere is ejected to space, while approximately 30% of the impactor’s atmosphere is ejected; if one assumes the proto-Earth contained oceans at the time of impact, expected ground motions result in complete ejection of the atmosphere and up to 50% of the oceans (Genda and Abe, 2005). If the earliest Earth contained oceans prior to the giant impact, then it is very likely that the bulk composition of matter ejected during the collision could have a water/silicate ratio considerably higher

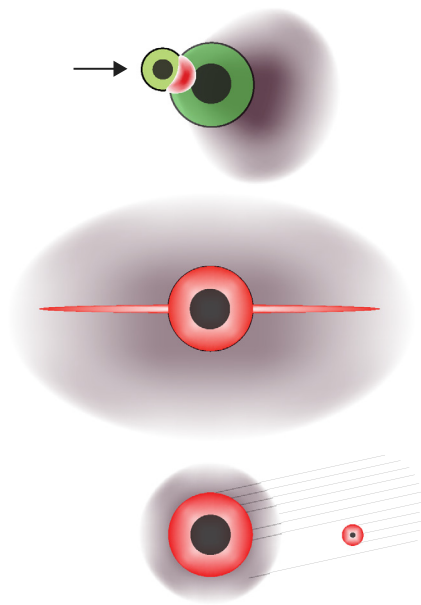


Fig. 4. Schematic illustration of three stages of evolution of material that forms the Moon, characterized by distinct timescales. Stage 1 is impact ejection of atmosphere and material that will form proto-lunar disc on a timescale of days-weeks; Stage 2 is hot Earth with proto-lunar magma disk at the midplane surrounded by disk atmosphere, that will collapse and accrete a single moon over a timescale of decades-centuries; Stage 3 is lunar (and terrestrial) convecting magma oceans bombarded by carbonaceous chondrite impactors during the tail-end of accretion (10–200 million yr timescale).

than a bulk silicate Earth composition. Furthermore, we consider it likely that any ejected atmosphere will be pushed out to large distances from the Earth, ahead of the expanding proto-lunar disk as the molten ejecta from the giant impact expands in an attempt to reach hydrostatic equilibrium (Thompson and Stevenson, 1988; Pahlevan and Stevenson, 2007; Nakajima and Stevenson, 2014a).

5.1.3. The proto-lunar disk

Fluid dynamic modeling studies of the proto-lunar disk have demonstrated that a disk of one to several Moon masses in orbit around the Earth, at the limit of its stability, has physical properties that produce midplane temperatures of 3000–7000 K (Thompson and Stevenson, 1988; Ida et al., 1997; Kokubo et al., 1998; Morishima and Watanabe, 2004; Genda and Abe, 2005; Pahlevan and Stevenson, 2007; Salmon and Canup, 2012; Desch and Taylor, 2013; Nakajima and Stevenson, 2014a, 2014b). Under such conditions, the proto-lunar disk is predicted to consist of a 2-phase mixture of silicate melt and vapor that convects turbulently in 3D and orbits the Earth on a days to weeks long timescale. Nakajima and Stevenson (2014a) have examined disk models derived from the energetics provided by SHP simulations of giant impacts, producing disks with midplane temperatures at the Roche radius of 4000–5000 K. At these temperatures, Visscher and Fegley (2013) have shown that the vapor phase in equilibrium with a magma of BSE composition is composed of approximately equal parts SiO, atomic O, O₂ and Na; hydrogen is a minor component of the vapor phase even at BSE proportions, as the silicate vapor dominates. This vapor also includes a significant fraction of alkalis both in atomic and ionized states; elements more volatile than Na (e.g. with 50% condensation temperatures <950 K) exist largely in the vapor phase. As long as the vapor phase is dominated by silicate vapor, loss of H₂O from the disk is predicted to be minimal due to collisions with heavier and more abundant gas species (Nakajima and Stevenson, 2014b).

As the disk orbits the Earth, the timescale for condensation and rain-out of silicate droplets is somewhat longer than the or-

bital period, on the order of a few years to tens of years depending on disk temperature (Thompson and Stevenson, 1988). Importantly, the rain-out of silicate droplets will lead to formation of a magma disk in a planar geometry around the mid-plane, while the vapor phase of the disk is predicted to expand in a nearly spherical geometry enveloping both the Earth and the disk (Genda and Abe, 2003b; Pahlevan and Stevenson, 2007; Nakajima and Stevenson, 2014a). At the edges of the disk when silicate begins to condense, the vapor phase is expected to contain roughly equal molar proportions of O₂, Na and Zn (Visscher and Fegley, 2013) and equal molar amounts of F and H₂, assuming BSE proportions of volatile elements. Because of the low pressures prevailing in the proto-lunar disk upon condensation of silicate, the solubility of H₂O in the magma disk will be low, ~1000 ppm at 1 bar (Dixon et al., 1995) and decreasing by a factor of 2 with each decade of pressure drop. As a result, the vast majority of the total hydrogen associated with the proto-lunar disk is predicted to be present in the vapor phase at the time the disk begins to condense, tens of years after emplacement (Desch and Taylor, 2013).

The gravitational forces that attract gas to the disk are exceedingly weak. Consider the full magma disk itself; consisting of 2 lunar masses, spread out to a distance of 5 Earth radii, it will have an average condensed (vapor-free) thickness of only 160 km; at high silicate vapor mass fractions associated with very energetic giant impacts, the magma disk may be only tens of kilometers thick (Nakajima and Stevenson, 2014a). Under such conditions, the atmospheric escape problem reduces to that of a gas envelope surrounding the Earth (Zahnle et al., 1988; Genda and Abe, 2003b), and at the outer regions of the disk beyond the Roche radius where proto-Moons can coalesce, the vapor pressure could be sufficiently low as to result in the condensation of very little of the gas cloud surrounding the Earth. Thus the volatile budget of proto-Moons will be set by vapor–melt exchange at the pressure and temperature conditions at which they condense (Karato, 2013), beyond the Earth's Roche radius.

We emphasize here that, in the days and weeks taken to form the proto-lunar disk from giant impact ejecta and the ~centuries over which the disk cools, fragments and forms a single Moon, the opportunity for H₂O addition from disk capture of incoming planetary embryos or other sources is miniscule. Though the extent of atmospheric escape from the Earth–Moon system is model dependent, perhaps more important is that coalescence of the Moon will occur outside the Roche radius (~3 Earth radii) from a thin magma disk, while the disk atmosphere containing the vast majority of vaporized volatiles will occupy a much larger expanded volume bound by Earth's gravity, and will likely fall back to the Earth or be lost to space as the disk cools further. Conditions are such that the Moon is likely to form with very little H₂O or other volatiles in its interior.

5.1.4. The lunar magma ocean

The final stage of lunar evolution we consider is the evolution of the lunar magma ocean (LMO) from molten state to sufficient lithospheric thickness that the Moon becomes a 1-plate body. Perhaps the most uncertain aspect of lunar evolution is the initial thermal state of the Moon; the temperature of the lunar magma ocean could be anywhere between the liquidus temperature (~1850 K) and the disk midplane temperature (3000–7000 K). Prior to the beginning of LMO crystallization, the Moon loses heat by radiation at its surface, and will not transition to conductive heat loss until the formation of a stable surface crust. The LMO could cool from 3000 K to the liquidus temperature on a timeframe of <1000 yr; once LMO crystallization begins, the thermal evolution depends strongly on the mechanism of heat loss from the surface. The model of Elkins-Tanton et al. (2011) assumes that no stable surface crust forms until plagioclase begins

to float, roughly 1000 yr after the LMO temperature reaches the liquidus. Once a stable crust forms, heat loss from the LMO slows quickly as the heat flux is limited by conduction through the surface crust. Elkins-Tanton et al. (2011) predict that the LMO, of depth 500–1000 km, becomes fully crystallized in ~10 million yr; however, if a surface crust is assumed to exist throughout LMO crystallization, the loss of heat from the LMO is reduced and the timescale for solidification can be as long as 100–200 Ma (Solomon and Longhi, 1977). This difference is an order of magnitude, thus the timescale for full Moon solidification is very sensitive to the details of heat loss through the lunar surface during LMO crystallization.

As the Moon is too small in mass to retain an atmosphere, convection of the LMO magma to the Moon's surface will release volatiles into the vacuum of space; however, the extent of degassing will be mitigated by the presence of a surface crust (Elkins-Tanton and Grove, 2011). At the same time, if there is any single time window during lunar evolution in which the Moon can gain water, it is during LMO crystallization, because it is the slowest of the three stages we have considered and it provides a mechanism (convection) for mixing impactors into the lunar interior. Assuming a suitable source of water in the form of impacting hydrous objects, the only way for the Moon to gain water and transport it to the depths of picritic magma production (250–600 km depth, Elkins-Tanton et al., 2011) is either during LMO convection, or just prior to the overturn of the lunar cumulate pile that is predicted by most models of LMO evolution (Hess and Parmentier, 1995). The main factor that limits transport of water into the deep lunar interior is the thickness of the lunar lithosphere; if there is no lithosphere, as prevails during the initial phase of rapid LMO convection, then incoming hydrous objects can be assimilated into the LMO en masse. Once the lithosphere becomes sufficiently thick, impactors cannot penetrate into the lunar mantle. The evolution of the thickness of the lunar lithosphere is thus critical to the notion that the Moon gained its water via assimilation of hydrous impactors.

5.2. The Moon's late veneer

Are these time windows sufficient to deliver the BSM's inventory of water? If the BSM contains 100–300 ppm H₂O as we have estimated, we require 7.4×10^{18} – 2.2×10^{19} kg of H₂O. We assume that carbonaceous chondrites are the delivery vehicle of choice, as appears required by the isotopic compositions of sulfur, chlorine and hydrogen in lunar volcanic glasses (Thode and Rees, 1976; Ding et al., 1983; Sharp et al., 2010; Saal et al., 2013; Tartèse et al., 2013; Füri et al., 2014). Carbonaceous chondrites contain ~7.8% H₂O on average (Robert and Epstein, 1982; Kerridge, 1985; Alexander et al., 2012, 2013), thus we require 0.95–2.8 × 10²⁰ kg to be assimilated into the lunar interior. In a 10 Ma timeframe (Elkins-Tanton et al., 2011), the resulting meteorite flux is 0.95–2.8 × 10¹³ kg/a; in a 200 Ma timeframe (Solomon and Longhi, 1977), the flux is 0.47–1.4 × 10¹² kg/a. These fluxes are on the order of 0.1% to 0.4% of the lunar mass following the giant impact, an order of magnitude higher than suggested by Albarede et al. (2014) but well within the total mass fluxes inferred for the tail-end of planetary accretion (O'Brien et al., 2014). This flux of carbonaceous chondrite is comparable to that estimated for the Earth (Morbidelli et al., 2000; Becker et al., 2006) after accounting for the difference in accretion cross section, which is 50–200× lower for the Moon (Bottke et al., 2007; Nesvorný et al., 2012; Schlichting et al., 2012). However, this scenario would require a shift in the composition of impacting objects during the last stages of accretion, as neither the Earth nor the Moon have the bulk composition of carbonaceous chondrites that are thought to have delivered water and other volatiles to both bodies (Marty, 2012;

Halliday, 2013; Saal et al., 2013; Tartèse et al., 2013; Füri et al., 2014). The fluxes are one to several orders of magnitude higher than inferred for the Late Heavy Bombardment (LHB) (Gomes et al., 2005), which in any case comes too late as the LHB impactors arrived ~500 million yr after Earth formed, at which time the Moon's lithosphere was well established and convection in the lunar mantle had long ceased.

Accretion of carbonaceous chondrites by the Moon during the last stages of accretion accounts not only for H₂O but also other elements that are within 0.1–1× of the composition of the bulk silicate Earth (Fig. 3). This model would overestimate the abundances of HSE in the lunar mantle (Day et al., 2007), but can be reconciled via HSE sequestration into the lunar core, or possibly an upward revision in lunar mantle HSE budgets (see Supplementary Material). Among the volatile elements that we have considered here, this model is not able to reproduce the lunar abundance of Cl or other highly depleted volatiles <1/10th of the BSE composition; it is possible our volatile reconstruction in Section 3 underestimates these elements in lunar magmas.

6. Acceptable models for the formation of the Moon

The constraints provided by our BSM estimate suggest an average volatile depletion factor of ~0.25× BSE, consistent with the K/U and H₂O/Ce ratios estimated here, and similar to that estimated by Delano (1986) and Ringwood (1992). With the composition of the BSM in hand, and given the timescales and energetics of the stages of lunar accretion described in the previous section, we can make a critical evaluation of the origin of the Moon as the result of a single giant impact. If the Moon is to be made this way, proto-lunar disk evolution makes it possible, but perhaps unlikely, that the Moon inherited most of its water from the Earth. If not from the Earth, the abundance and isotopic composition of lunar water requires a heterogeneous accretion, with a flux of carbonaceous chondrites to the Moon on the order of 0.95–2.8 × 10¹³ kg/a in a time window 10–200 Ma following the giant impact, such that their assimilation into the lunar interior occurs before the formation of a rigid lunar lithosphere.

Heterogeneous accretion of the Moon is admissible from several lines of evidence. Planetary accretion models predict several giant impacts were likely suffered by the terrestrial planets (Chambers, 2004; Jacobson et al., 2014; O'Brien et al., 2014), and more than half of these impacts are predicted to generate circumplanetary disks (Genda et al., 2012) that could add material to an earlier-formed proto-Moon. At least one giant impact study has demonstrated the occasional formation of two satellites in orbit around the Earth (which eventually merge) as an outcome from a single impact (Canup et al., 1999). The formation of the Moon in multiple steps has been suggested previously (Jutzi and Asphaug, 2012), and was implicit in the shallow magma ocean modeling of Solomon and Lonhgi (1977). Indeed, the thickness of the anorthositic lunar crust can be produced from a magma ocean no deeper than ~800 km (Elkins-Tanton et al., 2011), and thus the Moon need not have formed in a fully molten state from a single giant impact. All these observations admit the possibility of a multi-stage heterogeneous accretion of the Moon. Future modeling efforts may illuminate these possibilities; such a multi-stage history will depend on the likelihood of retention versus scattering of proto-moons during multiple giant impacts.

Several alternative scenarios for Moon formation are also consistent with the limited volatile depletion that we have estimated here. Radiogenic heating by decay of ²⁶Al and energy transfer estimates during giant impacts indicate that total melting of the material that forms the Moon is likely, the so-called “hot start” (Canup, 2004) that we have examined above. If pre- or post-impact temperature effects have been overestimated, however, then a “cold

start” scenario becomes admissible, in which material in the proto-lunar disk is largely solid and has never melted. Accretion of the Moon from a proto-lunar disk of unmelted solid material would perhaps increase the likelihood of preserving isotopic differences between the Earth and Moon, as magma-vapor homogenization in the disk (Pahlevan and Stevenson, 2007) would be suppressed. Hydrogen diffusion is, however, known to be uniquely rapid even in silicate crystal lattices (cf. Demouchy and Mackwell, 2006); but if the characteristic size of ejected debris is much larger than the hydrogen diffusion lengthscale, then a “cold-start” scenario could result in efficient transfer of water from the Earth and impactor to the newly-formed Moon.

The level of volatile depletion in the Moon (avg. 0.25× BSE) also suggests an obvious middle ground; a giant impact providing a “warm start” to lunar formation, in which the Moon formed from a proto-lunar disk with a mixture of 25% material that retained volatiles, and 75% of material that was highly volatile depleted. This balance between volatile-rich and volatile-depleted material happens to be similar to the target/impactor mixing ratios predicted by Moon-forming canonical impact models (Canup, 2014); however this scenario is predicted to produce stable isotope differences between the Earth and Moon that are larger than currently measured (Pahlevan, 2014).

7. Conclusions

We have reported on the volatile, major and trace element content of lunar volcanic glasses from three of the 25 known compositional categories of picritic glass returned from the Moon. The volatile and trace element compositions of the A17 orange, A15 green and A15 yellow glasses are used together with published data to produce a comprehensive estimate of the composition of the bulk silicate Moon (BSM). This composition is volatile depleted compared with the Earth, but is considerably more volatile rich than nearly all other published estimates (save Delano, 1986 and Ringwood, 1992). This increase in the estimated volatile inventory of the Moon is constrained by the abundances of water and other volatiles in olivine-hosted melt inclusions from sample 74 220, as well as a careful consideration of the widespread, yet underappreciated process of volcanic degassing. The abundance of H₂O in the BSM is depleted by only a factor of 2 to 5 compared with the bulk silicate Earth, while most other volatiles with higher condensation temperatures have abundances in the BSM within a factor of 2–10 of the BSE.

The evolution of the material that would form the Moon can be broken down into three stages characterized by very different timescales, which offer time windows within which H₂O can be gained, retained or lost. The giant impact delivers high-temperature material into Earth orbit on the timescale of days to weeks; impact erosion ejects some fraction of the impactor's and Earth's atmospheres into space, but it is likely that a significant fraction of this gas is lost while some is emplaced with the spreading proto-lunar magma disk. The proto-lunar disk spreads, cools and begins to fragment on a timescale of ~100–1000 yr, and the Moon is expected to coalesce at the edge of the disk where partial pressures of H₂O are lowest. Finally, cooling and crystallization of the LMO occurs on the longest timescale (10 to 200 Ma) and offers a time window within which assimilation of carbonaceous chondrites can add H₂O and other volatiles to the lunar interior before the formation of a rigid lunar lithosphere. Further convection and degassing of the LMO results in a gradual shallowing and decrease in the volume of the fractionating LMO magma, leading to further opportunities for degassing and production of low H₂O/Ce ratios in the lunar interior.

A “hot start” to lunar evolution can be reconciled with the abundances of volatiles in the Moon if the tail end of accretion

delivers 0.001–0.004 lunar masses of carbonaceous chondrite to volatile-depleted Moon before the formation of a thick lunar lithosphere. Alternatively, a “cold start” giant impact could conceivably transfer water from the Earth directly to the Moon largely in the solid state. An intermediate “warm start” could also make the Moon from a 3:1 mixture of volatile-depleted material and BSE material.

The frequency of giant impacts during terrestrial planet formation suggests, however, that we should not simply settle for making the Moon in a singular event. As we have already done for the Earth, the weight of the geochemical evidence suggests we must admit (and perhaps embrace) the possibility of heterogeneous accretion of the Moon. Discovery of primitive lunar glass samples with higher H₂O/Ce than reported here could provide a test of the idea that the bulk silicate Moon had water contents approaching those of the bulk silicate Earth. Clearly there is much more work to be done before we have a clear picture of how the Moon could have formed and incorporated H₂O and other volatile elements at the levels that are observed from studies of returned lunar samples.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2014.10.053>.

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