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The Moon re-examined

Stuart Ross Taylor

Research School of Earth Sciences, Australian National University, Canberra, Australia

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Abstract

Recent geochemical and geophysical data from the Moon enable a revision of earlier interpretations regarding lunar origin, structure and bulk composition. Earth and Moon show many similarities among their isotopic compositions, but they have evolved in totally dissimilar ways, probably related to the deficiency of water in the Moon as well as the vast differences in size and internal pressure. Although some global geochemical trends such as volatile depletion based on K/U ratios have been established, current lunar samples come from differentiated regions, making the establishment of a bulk composition more reliant on bulk geophysical properties or isotopic similarities although it remains unclear how the latter relate to whole Moon composition. The lack of fractionation effects among the refractory and super-refractory elements indicates that the proto-lunar material seems unlikely to have been vaporized while the depletion of volatile elements may place lower limits on proto-lunar temperatures. The apparent lack of geochemical evidence of an impacting body enables other possible impactors, such as comets, to be considered.

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Contents

1. INTRODUCTION

The Moon remains an enigma with currently little consensus on lunar composition or the origin of our satellite. Most planetary scientists have long accepted that the Moon formed as a result of the low-angle collision between the

E-mail address: Ross.Taylor@anu.edu.au

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Earth and a Mars-size impacting body. Such a scenario solved many problems but predicted that the Moon should contain a significant amount of material from the impactor, and have a bulk composition that is distinct from that of Earth. Although the close similarity of oxygen isotopic composition between Earth and Moon has been received wisdom for over a decade (although recent data by [Herwartz et al., 2014](#page-5-0), may cause a revision of this position), it has been generally held, based mostly on meteorite evidence that potential Moon-forming impactors would likely possess isotopic ratios that differ from those of Earth. Accordingly it has been surprising that recent geochemical analysis of lunar samples has revealed little trace of material other than that resembling the Earth, and geophysical data has narrowed the range of possible differences between the bulk compositions of Earth and Moon. Accordingly it seems appropriate to review some current lunar problems and open questions. This paper is not intended as a comprehensive survey of the literature, but is intended as a discussion of some key geochemical issues relating to the current state of lunar science. It begins with some observations on the composition of the Moon, which have undergone significant changes compared to earlier views, notably as a result of the GRAIL mission. This is followed by comments on the curious lack of fractionation among the refractory lithophile elements. Then follows a discussion on the confusing situation about the content and role of water in the Moon. This section is followed by observations on the origin of the Moon as these views have also changed dramatically in recent years.

2. COMPOSITION OF THE MOON

Using a set of geophysical data on crustal thickness and heat flow, [Taylor \(1982\)](#page-6-0) concluded that the Moon had a thick (52–60 km) crust and therefore a higher alumina content (6 wt% vs. 3.6 wt%) and U abundance (30 ppm vs. 18 ppm) than the Earth (see also [Taylor et al., 2006\)](#page-6-0). The data from the GRAIL Mission [\(Wieczorek et al., 2013](#page-6-0)) showed that this interpretation was erroneous and that the Moon likely has an aluminous crust 30–40 km thick, and therefore a refractory lithophile element composition broadly similar to that of the Earth. However, several open questions remain, including: the distribution of $A₁O₃$ within the lunar crust and mantle, the global distribution of heat-producing elements, and whether the crust becomes more mafic with depth, as in the case of the continental crust on the Earth.

Importantly, can the bulk composition of the Moon be obtained by geochemical procedures based on mass balance of end-member reservoirs? The Moon is a highly differentiated body that melted at or soon after it formed [\(Taylor,](#page-6-0) [1973; Pritchard and Stevenson, 2000](#page-6-0)). Early melting and large-scale differentiation of the Moon are indicated by the old differentiation ages of the lunar crust and mantle (about 4460 M.Y; but the timing and duration of crustal origin seems more complex, see [Borg et al., 2011;](#page-4-0) [Demidova et al., 2014; Gaffney and Borg, 2014\)](#page-4-0). Complementary trace element patterns in the lunar crust, mantle and KREEP reflect the relative compatibilities of these elements into the major minerals of the mantle (olivine, pyroxene, ilmenite) and crust (plagioclase), but, the extreme compositions of lunar mare basalts (up to 14 wt\% TiO₂), the presence of large concentrations of incompatible elements (Rb, Ba, REE, Zr, Hf) in the nearside Procellarum-KREEP Terrane, and the uncertain relative volumes of these highly differentiated reservoirs complicates attempts to reconstruct the lunar bulk composition by mass balance and require explanation.

Samples available to make estimates of the lunar bulk composition include those from the feldspathic highlands, a diverse array of mare basalts (at least 25 distinct types from a clearly heterogeneous, cumulate mantle), and KREEP-bearing lavas and impact-melt breccias. The feldspathic crust was emplaced shortly after accretion and intruded by late liquids (KREEP) While the feldspathic crust and cumulate source regions for mare basalts seem to be globally distributed ([Giguere et al., 2000; Wieczorek](#page-5-0) [et al., 2013\)](#page-5-0), the late-stage residual melts sampled as KREEP seem to have not been distributed symmetrically but instead were concentrated around the western limb of the near side of the Moon in the vicinity of the Procellarum basin ([Jolliff et al., 2000a,b; Gross et al., 2014](#page-5-0)). Although the average composition of the feldspathic crust remains somewhat uncertain, it clearly requires a large-scale fractionation that is more consistent with a lunar magma ocean than, for example, construction of the crust by serial intrusion and local differentiation of discrete batches of magmas produced by smaller degrees of melting of a primitive lunar mantle (e.g., [Solomon and Longhi, 1977; Walker, 1983](#page-6-0)), which might produce compositional differences among elements such as the REE that are surprisingly uniform in the lunar highlands crust. The feldspathic crust was also shattered and dis-aggregated by large bolide collisions that may have been concentrated around 4.1 to 3.8 b.y ([Tera](#page-6-0) [et al., 1974; Gomes et al., 2005,](#page-6-0) see [Norman, 2009](#page-5-0) for a recent review) but may have begun earlier ([Norman and](#page-5-0) [Nemchin, 2014](#page-5-0)). How much this bombardment affected the petrologic complexity of the crust (possibly via differentiated melt sheets) remains an open question.

The mare basalts are derived from a mineralogically heterogeneous interior [\(Taylor and Jakes, 1975\)](#page-6-0) and their compositions are so diverse that none could be considered as representative of the bulk lunar interior. The relative masses and distributions of their respective source regions are so poorly constrained that they provide little direct information about bulk lunar composition. Mare basalts have FeO contents (\sim 16–25 wt%) that are high relative to terrestrial basalts, and more analogous to basalts from Vesta and Mars. On this basis, the FeO content of the lunar mantle is often thought to be 13 wt% compared to 8 wt\% for the Earth (e.g., [Hood and Jones, 1987\)](#page-5-0) but if the lunar basalts were derived from FeO-rich cumulates, then they are unlikely to be representative of the bulk lunar mantle.

The deep interior of the Moon is presumably rich in Mgrich olivine or orthopyroxene, the first minerals to crystallize from the magma ocean, but these deep cumulate zones remain apparently inaccessible to direct sampling, as does a small core that is presumably rich in metallic Fe and other siderophile trace elements that are otherwise strongly depleted in the Moon relative to the Earth (e.g., [Day](#page-5-0) [et al., 2007, 2010; Rai et al., 2014\)](#page-5-0). In addition, the depth of primary differentiation of the lunar mantle associated with the magma ocean and the presence of any remaining primitive mantle is poorly constrained. Therefore estimates of the composition of the lunar interior have the status of inspired guesses. Clearly bulk geophysical properties, such as density (e.g., [Darwin, 1879; Wieczorek et al., 2006;](#page-5-0) [Garcia et al., 2011](#page-5-0)) and isotopic similarities (although it remains unclear how the latter relate to bulk composition) provide a surer guide to the bulk composition of the Moon, which appears to be broadly similar to that of the Earth's mantle, although depleted in volatile elements.

3. LACK OF FRACTIONATION AMONG REFRACTORY ELEMENTS

It has generally been assumed by geochemists that the refractory lithophile elements (RLE) are not fractionated in the Earth relative to their abundances in chondritic meteorites (e.g., [Palme and Jones, 2005\)](#page-5-0). Although recent high-precision determinations of some stable and shortlived isotopes have questioned that view in detail (see review by [Campbell and O'Neill, 2012\)](#page-5-0), the similarities in composition (typically within a few per mil) between the Earth and various classes of chondritic meteorites combined with independent estimates of the Earth's primitive mantle based on measured samples (e.g., [Sun, 1982](#page-6-0)) confirms the general applicability of the 'chondritic' model for RLE in the Earth.

[Lodders \(2003\)](#page-5-0) gives condensation temperatures for the rare earth elements showing that Eu and Yb (and to a lesser extent, Ce) are more volatile than the other REE. [Taylor](#page-6-0) [\(1987, 1990\)](#page-6-0) drew attention to the fact that the superrefractory elements Zr, Hf, Y and the refractory elements such as Al, Ca, Ti, REE, U, Th, Ba and Sr with condensation temperatures above 1200 K are present on the Moon in roughly chondritic proportions, despite showing fractionated behavior, based on volatility differences, in refractory inclusions (CAI, e.g., [Mason and Taylor, 1982](#page-5-0)). The super-refractory elements Zr, Hf, Sc, and Y are not fractionated in the Moon relative to the other refractory elements in contrast to their behavior in CAIs and in hibonite where they are separated from the more volatile REE. The abundance of the RLE in the Moon is generally assumed to be parallel to chondrites. Although depletions and enrichments of Eu have long been ascribed to crystalmelt partitioning, decades of study of the REE in particular show no Yb or other anomalies that would have been expected if the material now in the Moon had been exposed to high temperatures in a vaporized disk, and [Taylor \(1990\)](#page-6-0) concluded that this placed upper limits on the temperatures to which proto-lunar material had been exposed (See also [Pahlevan, 2013; Petaev et al., 2014](#page-5-0)). The depletion of the volatile elements might place some lower limits but these are difficult to quantify.

4. THE ROLE OF WATER

The presence of volatiles in the lunar mantle has been obvious since the Apollo 11 mission returned vesicular mare basalts, although thermochemical calculations suggested that the volatile phase was more likely to be predominantly C–O–S rather than water-rich (e.g., [Gibson et al.,](#page-5-0) [1975\)](#page-5-0). In addition, the abundances of S in mare basalts and S-rich coatings on picritic glasses, the low $fO₂$ of the mare basalts, and the lack of even the slightest hint of deuteric alteration along grain boundaries reinforced the view of a water-poor lunar interior.

In contrast, ppm levels of very volatile elements such as fluorine and chlorine were reported in lunar samples in the 1970s. As both elements are more volatile than water, it should not have been surprising that a minute trace of water might be incorporated within the Moon along with trace levels of many other very volatile elements during its formation. During crystallization of the lunar magma ocean, (LMO) such elements, incompatible in most common silicates, would have been concentrated in residual melts in standard geochemical models, although it is uncommon for nature to be 100% efficient, especially in geochemical processes. In this process, any incompatible element such as water would finish up in the residual melt (along with other incompatible elements such as REE), and KREEP would be the most water-rich reservoir on the Moon. Minute traces of water were likely also trapped in mineral zones in the deep interior and are now found along with fluorine and chlorine in the OH sites in minerals such as apatite, a trace mineral in the mare basalts. The crystallisation of mare basalts resembles that of the LMO in miniature in that it also creates late-stage residual melts that occur in mesostasis pockets from which trace minerals such as apatite may crystallize (see [Greenwood et al., 2011;](#page-5-0) [Boyce et al., 2014\)](#page-5-0).

The Moon is also strongly depleted in moderately volatile elements, such as potassium that are much less volatile than water, and the lunar rocks are strongly reduced. No micas, or amphiboles that contain OH, have ever been found, not even within crystalline melt inclusions that were largely protected from near-surface degassing. Ferric iron that would indicate oxidizing conditions is absent as well. Traces of water, trapped as ice in the lunar soils, were delivered from comets, or from the interaction of hydrogen from the solar wind hydrogen with surface minerals ([Ichimura](#page-5-0) [et al., 2012\)](#page-5-0). This evidence for traces of water on the surface needs to be distinguished from reports of water (present as the OH ion) in minerals derived from the interior of the Moon (e.g., [Ivanov, 2014\)](#page-5-0). Preservation of reactive materials such as glass, metal, olivine, etc. in the lunar regolith for billions of years also shows that the lunar 'hydrosphere' was especially anemic.

Although dissolved 'water' (including OH^-) has been measured only in the picritic lunar glasses and the olivinehosted melt inclusions they contain, [McCubbin et al.](#page-5-0) [\(2011\)](#page-5-0) inferred similar water contents for much of the cumulate lunar mantle based on the compositions of latestage apatite in crystalline mare basalts. Contrary to expectations, they also concluded that the KREEP reservoir was anhydrous, and proposed a heterogeneous distribution of volatiles within the lunar interior. [Valley et al. \(2014\)](#page-6-0) also concluded that KREEP magmas were hotter and drier than evolved terrestrial magmas based on the compositions of lunar zircons. In contrast, [Hui et al. \(2013\)](#page-5-0) suggested that the KREEP reservoir may have contained up to 1.4 wt\% water, and [Barnes et al. \(2014\)](#page-4-0) concluded that parental magmas of some Mg-suite norites could have contained anywhere from 4 to 800 ppm water. [Hui et al. \(2013\)](#page-5-0) also concluded that the magmas parental to lunar anorthosites may have contained \sim 1600 ppm water but the petrologic and geochemical implications of such predictions require closer examination as plagioclase will only float in a dry magma and the formation of an anorthositic crust by flotation therefore depends on a dry Moon ([Walker and Hays,](#page-6-0) [1977](#page-6-0)).

[Elkins-Tanton and Grove \(2011\)](#page-5-0) considered the petrologic constraints on lunar magmas, and concluded that the bulk Moon contained only about 10 ppm water. They concluded that "apatites in particular may therefore reflect hydrogen rather than hydroxyl partitioning, particularly those in KREEPy rocks that coexist with iron metal". In the final stages of solidification when metal and fayalite are forming in the mesostasis as in sample 14053 where apatite exists ([Boyce et al., 2010\)](#page-4-0), there is likely to be as much or more hydrogen present than water or hydroxyl. Hydrogen partitioning between magma and apatite is unknown, but may be the critical parameter in these measurements.

Water present in apatites from the Moon has a very variable hydrogen isotope ratio (D/H) [\(Greenwood et al.,](#page-5-0) [2011](#page-5-0)), higher than that of terrestrial water (e.g., [Barnes](#page-4-0) [et al., 2014\)](#page-4-0), in contrast to the apparently identical oxygen isotope ratios in both bodies. In contrast, [Saal et al. \(2013\)](#page-5-0) found that lunar magmatic water dissolved in primitive volcanic glass and olivine-hosted melt inclusions has a hydrogen isotopic composition that is indistinguishable from that of the bulk water in carbonaceous chondrites and similar to that of terrestrial water, implying a common origin for the water contained in the interiors of Earth and the Moon. In summary of this important but currently confusing topic, my assessment is that water is expected to be present at a few ppm in the bulk Moon but its status as an incompatible element concentrated in residual melts and phases and its likely heterogeneous distribution within the lunar interior, makes it impossible to calculate a meaningful value for the bulk Moon based on direct measurements, a problem that is exacerbated by its presence in trace minerals in mare basalts, which are themselves derived from cumulate zones within the mantle. Still, it would seem unusual if the water content of the Moon were similar to that of Earth's mantle considering the strong depletions of other incompatible elements of lesser volatility (see next section). Although portions of the Moon seem a little damp, overall the Moon is much drier than the Earth ([Sharp et al., 2010; Hauri](#page-6-0) [et al., 2011; Robinson and Taylor, 2014; Valley et al.,](#page-6-0) [2014](#page-6-0)) and seems essentially devoid of water, unless one regards the presence of a few parts per million as significant.

5. THE ORIGIN OF THE MOON

The origin of the Moon, thought to have been settled for a generation by the Giant Impact hypothesis (e.g., [Benz](#page-4-0) [et al., 1989](#page-4-0)), is once again in a state of flux with new geochemical data and geophysical models drawing a more direct link to the Earth as the primary source of proto-lunar material, and allowing a wider range of dynamical conditions that includes both larger ([Canup, 2012\)](#page-4-0) and smaller [\(Cuk and Stewart, 2012](#page-4-0)) impactors than the canonical Mars-sized impactor, in order to account for the angular momentum constraint.

The following geochemical facts about the Moon appear reasonably well established. The Moon has an isotopic composition that is identical to the silicate mantle of the Earth within the relatively tight analytical constraints provided by modern instrumentation for O [\(Weichert et al.,](#page-6-0) [2001](#page-6-0)), Si [\(Armytage et al., 2012](#page-4-0)), Ca ([Simon et al., 2009](#page-6-0)) Mg ([Sedaghatpour et al., 2013\)](#page-5-0), Fe ([Moynier et al., 2006](#page-5-0)) Ti ([Zhang et al., 2012](#page-6-0)), Sr [\(Moynier et al., 2010a\)](#page-5-0), and Cr [\(Lugmair and Shukolyukov, 1998](#page-5-0)) but it has had a totally different geochemical development. The similarity in oxygen isotopes seems particularly significant as O^{2-} is a large anion and the packing of oxygen anions largely controls the abundance of other elements in silicates. However, it should be noted that [Herwartz et al. \(2014\)](#page-5-0) have produced new oxygen isotopic data that shows a slight difference (12 ppm) in Δ^{17} O from that of the Earth and so this might be a signature of the impacting body, although other possible explanations are given. This unconfirmed but potentially important observation, if correct, raises many issues and reminds one of the early times of trace element geochemistry when discrepant results from different laboratories were common.

The Moon is depleted in volatile elements ([Wolf and](#page-6-0) [Anders, 1980](#page-6-0)) relative to the Earth, which in turn is depleted relative to CI abundances. This is shown most clearly by K/U ratios, 2500 for the Moon relative to 10,000–12,500 for the Earth and 60,000 for CI,. Potassium isotopes show no difference between Earth, Moon and other inner solar system bodies [\(Humayun and Clayton,](#page-5-0) [1995](#page-5-0)) suggesting that a depletion of potassium in the inner solar system took place close to T_{zero} . This finding is reinforced by the primitive value of the lunar $87\text{Sr}/86\text{Sr}$ ratio (LUNI; [Nyquist, 1977](#page-5-0)), although the value for the Earth is not well established. Although Li isotopes appear to have been fractionated by the magma ocean, they do not seem greatly different between the Earth and the Moon [\(Magna](#page-5-0) [et al., 2006\)](#page-5-0). A general conclusion from these observations seems to be that the Moon appears to have apparently little trace of the impacting body (but see [Herwartz et al., 2014](#page-5-0)) although models continue to show that the impactor makes a significant contribution to the putative proto-lunar disk resulting from the collision [\(Canup, 2012\)](#page-4-0). One of the few isotopic differences between the Moon and Earth is the enrichment of the heavy isotopes of Zn in the Moon, which has been ascribed to volatile loss during the formation of the Moon ([Paniello et al., 2012](#page-5-0)).

The origin of the Moon has always been an improbable event and seems to have become more so. The Earth was assembled, in the planetesimal hypothesis, from a wide variety of bodies, which may have been differentiated into cores and mantles, with presumably differing oxygen isotope ratios. Was the Earth homogenized in isotopic composition before the Moon-forming event or by that event? What happened to the Moon-forming impacting body and its possible core? Was it larger or smaller than the Mars-sized body implied by earlier dynamical models of the giant impact (e.g., [Benz et al., 1989](#page-4-0))? Was it incorporated into the Earth and homogenized, or lost? Models have always assumed that the impactor was differentiated and that the core was incorporated into the Earth in order to account

for the low density of the Moon compared to the Earth. However if the Moon was derived from the terrestrial mantle after core formation, the proto-lunar material was low in iron in any event. Was there indeed a vapor cloud resulting from the putative impact from which the Moon may have formed ([Pahlevan and Stevenson, 2007; Pahlevan et al.,](#page-5-0) [2011\)](#page-5-0)?

No impactor seems to be needed by the geochemistry at present (but see [Herwartz et al., 2014](#page-5-0)) but a highly energetic origin is still required. Impacts by planetesimals, differentiated or not, seem unable to account for the composition of the Moon coupled with the lack of much sign of the impacting body. The Moon bears a signature of the chemistry of the mantle of the Earth but it is both depleted in volatile elements and water.

Do we need new models of the impactor? The composition of the Moon looks like massive distal ejecta from the terrestrial mantle. The apparent absence of definitive evidence of the impacting body (but see [Herwartz et al.,](#page-5-0) [2014\)](#page-5-0) naturally draws attention to the possibility of a cometary impact. Perhaps only massive impacts on the terrestrial mantle by icy comets or planetesimals may be capable of providing the low iron content of the Moon, the necessary energy to melt most of the Moon, deplete the volatile elements, and leave little or any trace of the impactor. But comets, as impactors in the early inner solar system are not without their problems. In current models, they seem to come from the vicinity of Jupiter at least ([Morbidelli et al., 2012\)](#page-5-0), as rare interlopers into the dry early inner solar system. Thus they might impact at high velocities, in contrast to current models for forming the Moon that call for low velocity impacts. Indeed, if comets were involved, then the formation of the Moon becomes an even more improbable event.

Another possibility is worth considering. The lunar composition bears a curious parallel to the compositions of tektites, notably in its depletion of volatile elements (including water), heavy Zn isotopic composition, and lack of a geochemical signature of the impactor. Is this a mere coincidence or does it tell us something significant about the origin of the Moon? Tektites are mm- to cm-sized, glassy objects produced by the impact of asteroids under some specific conditions onto the crust of the Earth (e.g., [Koeberl, 1986\)](#page-5-0). Their RLE, notably REE, compositions broadly reflect those of near-surface, terrestrial materials which in turn image the composition of the Earth's crust. However, like the Moon, tektites are also depleted in volatile elements, including water, (20–200 pm; [Koeberl and](#page-5-0) [Beran, 1988\)](#page-5-0) and they show debatable or barely detectable traces of the impactor. Tektites are also have heavy Zn isotopic compositions ([Moynier et al., 2009](#page-5-0)), although the isotopically heavy Cu in tektites contrasts with the lunar composition ([Moynier et al., 2006, 2010b](#page-5-0)) and may require a different set of conditions for the volatile loss. [Taylor and](#page-6-0) [Koeberl \(2013\)](#page-6-0) drew attention to the parallels between the composition of tektites derived from terrestrial crustal rocks by relatively small meteorite impacts and that of the Moon, presumably formed by an immensely larger event involving the terrestrial mantle. These interesting comparisons imply that the Moon was derived from distal

ejecta from a massive impact on the Earth but on a scale many orders of magnitude larger scale than was involved in the production of tektites. The analogy may be worth pursuing as it results in volatile-depleted ejecta from the Earth without leaving much trace of the impactor, The implication of this conceptual model is that the Moon reflects the composition of the target (i.e., proto-Earth) rather than that of the impactor as implied by earlier dynamical models and that the impacting body leaves little trace of itself.

6. SUMMARY

Although the Earth and Moon show many similarities among their isotopic compositions, they have evolved in totally dissimilar ways, probably related to the deficiency of water in the Moon. Samples from the Moon are derived from highly differentiated zones, making estimates of bulk composition more reliant on bulk geophysical measurements or isotopic similarities. In view of the lack of fractionation effects among the refractory and superrefractory elements, the proto-lunar material seems unlikely to have been vaporized (i.e., no condensation seems to have taken place at temperatures in excess of the melting points of silicates). Is this a real constraint or does it merely illustrate the difficulties of modelling huge events? The formation of tektites points to one possible model that excavates over one percent of the terrestrial mantle (low in metallic iron), depletes the proto-lunar material in volatiles, melts much of the material and leaves apparently little or no trace of itself. An alternative could be the impact of an icy comet, raising vast new problems for modelers.

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