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Chemical and isotopic kinship of iron in the Earth and Moon deduced from the lunar Mg-Suite

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ABSTRACT

The Moon and the Earth's mantle share many chemical and isotopic traits, leading to the prevailing theory that they were formed from similar material. Iron is one element that shows apparent differences between the two bodies, with models for the composition of the Moon having ≈ 1.5 times more FeO (12–14 wt.%), relative to the Earth's mantle (8 wt.%). This difference is mirrored in their isotope compositions, where lunar mare basalts have $\delta^{57}\text{Fe}$ (per mille deviation of the $^{57}\text{Fe}/^{54}\text{Fe}$ ratio from the IRMM-014 standard) 0.1–0.2‰ higher than peridotitic rocks representative of Earth's mantle, a feature initially attributed to loss of isotopically light Fe following a giant impact. However, whether basaltic rocks are suitable analogues for the Moon's composition is debatable in the light of their distinct source regions that reflect the extensive lithological stratification of the lunar mantle. Here, we evaluate the iron isotope composition of the bulk Moon through the study of igneous cumulate rocks of the lunar highlands Magnesium Suite (Mg Suite). The $\delta^{57}\text{Fe}$ of Mg Suite rocks spans a limited range, from 0.05‰ to 0.10‰, with an average $(+0.07 \pm 0.02\text{‰})$ that overlaps with Earth's mantle $(+0.05 \pm 0.01\text{‰})$, similarities that extend to their Mg#, where both reach 0.9. Numerical modelling of iron isotope fractionation during lunar magma ocean crystallisation shows that the Mg Suite should accurately reflect the composition of the bulk Moon, which is therefore $+0.07 \pm 0.02\text{‰}$, indistinguishable from Earth's mantle but heavier than chondrites $(-0.01 \pm 0.01\text{‰})$. Iron thus behaves coherently with other elements that condense at temperatures higher than Li in showing no isotopic difference between the Earth and Moon, suggesting element depletion on the Moon affected only the more volatile elements. Therefore, there is no cosmochemical basis for iron enrichment or depletion in the bulk Moon relative to the Earth's mantle, whose composition is an analogue for that of the Moon.

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1. Introduction

Comparison of the stable isotope composition of differentiated planetary bodies with their potential building blocks (chondrites) provides important information on planetary formation and evolution (e.g., Day and Moynier, 2014; Poitrasson et al., 2004; Sedaghatpour et al., 2013; Sossi et al., 2016a; Weyer et al., 2005). However, assessment of the stable isotope compositions of terrestrial bodies is hampered by two factors. Firstly, stable isotopes, even of heavy elements, fractionate as a result of magmatic differentiation, be it at shallow, crustal levels (e.g., Foden et al., 2015) or during core–mantle segregation (Shahar et al., 2015), rendering comparison with chondrites troublesome. Secondly, direct samples of planetary mantles are sparse, save for that of the Earth,

meaning basaltic rocks are oft-used as proxies for mantle composition (e.g., Poitrasson et al., 2004; Savage et al., 2015). Inner solar system basalts are either chondritic, or systematically enriched in the heavier isotopes of iron (Poitrasson et al., 2004; Weyer et al., 2005), a feature attributed to both core formation (Elardo and Shahar, 2017; Shahar et al., 2015) and volatile depletion (Poitrasson et al., 2004; Sossi et al., 2016a).

Early dynamical models showed that a giant impact of a Mars-sized body with the proto-Earth could form the Moon, where most lunar material was derived from the impactor (e.g., Canup, 2004). However, the observed chemical and isotopic kinship between the Earth and the Moon, except in volatile elements and water (e.g., Day and Moynier, 2014), led to the hypotheses that the Moon is made of material primarily derived from the proto-Earth's mantle (O'Neill, 1991; Ringwood, 1977), that efficient homogenisation occurred in an Earth–Moon disk (Pahlevan and Stevenson, 2007) or that the impactor was Earth-like (Dauphas et al., 2014a). A non-volatile element that appears to show significant differences be-

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tween the two bodies is iron, whose concentration in mare basalts, 15–25 wt.%, greatly exceeds that of their terrestrial counterparts (10–15 wt.%).

However, the potential for basalts to represent the bulk composition of the lunar mantle is strongly compromised by its lithological stratification following lunar magma ocean (LMO) crystallisation, where Fe–Mg silicates (olivine, pyroxene) precipitated first, followed by plagioclase, and, in the later stages, ilmenite (e.g., Snyder et al., 1992). These compositionally-distinct zones were re-organised upon mantle overturn due to their inverse density distribution (i.e., ilmenite is denser than olivine). Despite cumulate overturn, discrete source regions still exist in the lunar mantle (Elkins Tanton et al., 2002). This is reflected in the disparate iron isotope compositions of lunar mare basalts, the most extensive products of lunar volcanism (BVSP, 1981), where low-Ti basalts have lighter iron isotope compositions ($\delta^{57}\text{Fe} = +0.12 \pm 0.02\text{‰}$, 2SE, $n = 19$; with n the number of samples, and 2SE the $2 \times$ standard deviation/ \sqrt{n}), than their high-Ti equivalents ($\delta^{57}\text{Fe} = +0.28 \pm 0.02\text{‰}$; 2SE, $n = 15$; Liu et al., 2010; Poitrasson et al., 2004). Although the latter are less voluminous and are shown, petrologically, to have formed from partial melting of ilmenite-rich zones (Wagner and Grove, 1997), this variation makes deduction of the Moon's iron isotope composition from basaltic rocks difficult.

Early studies considered that heavy isotope enrichment of Fe in high Ti basalts relative to terrestrial basalts, which have $\delta^{57}\text{Fe} \approx +0.10\text{‰}$, was inherited from impact-induced vaporisation (Poitrasson et al., 2004). Revision of the lunar value to reflect that of low-Ti basalts matches the $\delta^{57}\text{Fe}$ of terrestrial basalts. This, however, neglects the effect of partial melting that enriches basalts in heavy iron in the more oxidised terrestrial mantle due to the presence of Fe^{3+} , as evidenced by the lighter value of pristine mantle peridotites, $+0.05 \pm 0.01\text{‰}$, 2SE, $n = 60$ (Sossi et al., 2016b). Subsequently, based on a lunar Mg Suite dunite that yielded a markedly isotopically lighter iron isotopic composition ($\delta^{57}\text{Fe} = -0.50 \pm 0.03\text{‰}$; Wang et al., 2015), the Moon was inferred to be indistinguishable from Earth (and chondrites), near 0‰. However, in reaching this conclusion, Wang et al. (2015) had to correct for a) the diffusive fractionation of Fe isotopes and b) model lunar magma ocean differentiation with isotopic fractionation factors that were, at the time, unconstrained, and have subsequently been shown to be different (Sossi and O'Neill, 2017). As such, the iron isotopic composition of the Moon remains uncertain.

In order to more accurately assess the iron isotope composition of the Moon we study a full suite of cumulate igneous rocks from the Mg Suite, the earliest expression of lunar magmatism. They were formed from olivine-rich sources precipitating from initial crystallisation of the lunar magma ocean. Considering that olivine is the dominant mineral in the lunar mantle (Kuskov and Kronrod, 1998), the Mg Suite rocks should thus provide the best insight into its composition. Here, we present the iron isotope compositions of a set of six Mg Suite rocks that record differing stages of their magmatic evolution, from dunites to norites. These are further supplemented by 14 low Ti basalts, three high Ti basalts, and one lunar glass in order to further assess the Fe isotopic composition of lunar volcanic rocks.

2. Samples

The Mg Suite consists of cumulate rocks recording an igneous differentiation sequence of dunites, followed by trocolites, norites and finally gabbro-norites. Their defining characteristics are high Mg#s (similar to Earth's mantle, $\text{Mg\#} = 0.89$, where $\text{Mg\#} = \text{Molar MgO} / [\text{Molar MgO} + \text{Molar FeO}]$) coupled with anorthitic plagioclase and depletions in 'compatible' elements, Ni, Cr, and Co (Warren, 1986). Furthermore, Mg Suite samples collected from the

Apollo missions have enriched trace element abundances consistent with the involvement of KREEP during their genesis (Snyder et al., 1995), though whether this is a widespread feature of the Mg Suite is debated (Shearer et al., 2015). This incongruous combination of primitive major elements, coupled with evolved trace element signatures is equated with mixing of the earliest, olivine-rich magma ocean cumulates with a small KREEP component during mantle overturn (Elardo et al., 2011).

Other than the landing site of Apollo 11, rocks with geochemical and petrologic characteristics of the Mg Suite are ubiquitous in the lunar crust (Shearer et al., 2015), particularly in samples returned by Apollo 17 (samples 7xxxx), with $\approx 90\%$ of the mass and Apollo 15 (15xxx; $\approx 10\%$). The total mass is 2 kg, of which ≈ 56 g is ultramafic material, represented almost entirely by cataclastic dunite 72415. 72415 is the most magnesian end-member of the Mg Suite, with 94% angular to sub-rounded olivine ($\text{Fo}_{89.5-86}$) set in a fine-grained matrix, 4% plagioclase (An_{85-97}) and 3% of both clino- and orthopyroxene (Ryder, 1992). Magnesian olivine also typifies the coarse-grained (0.2–0.7 cm) troctolite sample, 76535, where homogeneous $\text{Fo}_{87.3}$ constitutes $\approx 35\%$ of the rock, and anorthitic plagioclase ($\text{An}_{96.2}$) and orthopyroxene ($\text{Wo}_2\text{En}_{86}\text{Fs}_{12}$) comprise the remainder. Textural and chemical evidence points to extensive down-temperature equilibration to 800–900 °C and pressures of 0.2–0.25 GPa, corresponding to 40–50 km depth (McCallum and Schwartz, 2001). These two samples, together with the shocked norite clast in 15455, have the highest degree of 'pristinity' (9; Warren, 1993) in Mg Suite rocks, describing the degree to which the sample records its primary, lunar composition. Norites are represented by 78235 and 78238, which are chips of the same boulder found in regolith at Station 8, and 15445 and 15455, which occur as clasts (Clast B and Cataclastic Anorthitic Norite 'CAN' Clast, respectively) in impact breccias in close proximity, on the rim of Spur crater. All norites show textural evidence of shock. Lithology 78235/8 consists of subequal amounts of coarse-grained (0.2–1 cm) orthopyroxene and plagioclase, both of which are very homogeneous $\text{Wo}_3\text{En}_{78}\text{Fs}_{19}$ and An_{93-95} . Both 15455 and 15445 consist roughly of 2/3 plagioclase (An_{92-95}) and 1/3 orthopyroxene (Ryder and Bower, 1977). In norites, orthopyroxene is slightly less magnesian than found in troctolites and dunites, whereas, although plagioclase composition reaches lower An contents, maximum values overlap with the more mafic lithologies.

The six Mg-suite samples are supplemented by 14 low Ti basalts, three high Ti basalts and Green Glass 15426, totalling 24 lunar samples. To date, iron isotope analyses of only three Mg Suite samples (72415 and 76535, Wang et al., 2015; and 77215, Poitrasson et al., 2004) have been reported, a number insufficient to link their isotopic composition to their petrogenesis, a deficiency we aim to remedy in this work. Although the iron isotope composition for numerous mare basalt samples studied herein have already been reported (Poitrasson et al., 2004; Liu et al., 2010), our dataset is advantageous because it permits accurate discrimination between the $\delta^{57}\text{Fe}$ of mare basalts and Mg Suite rocks.

3. Methods

Approximately 50 mg of sample was crushed using an agate mortar and pestle under acetone in a sterile, clean-lab environment. Roughly 25 mg of the powder was weighed out into 3 mL Teflon beakers, to which a concentrated $\text{HNO}_3\text{:HF:HCl}$ mixture was added (1 mL:0.5 mL:0.2 mL), and dissolved on a hot plate at 140 °C for 72 h. Upon inspection, two samples, norite 78238 and trocolite 76535 had residual chromite, and were therefore re-dissolved under-pressure in Parr bombs (78238B and 76535B). The procedure is as above, however, following table-top dissolution, the samples were evaporated and re-dissolved in 1 mL 15 M HNO_3 with a

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