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Tracking the formation of magma oceans in the Solar System using stable magnesium isotopes

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Abstract

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The processes associated with magma ocean formation and solidification can control the earliest compositional differentiation and volatile inventory of planetary bodies. Thus, elucidating the scale and extent to which magma oceans existed in the Solar System is critical for a full understanding of planet formation. Here we show that the magnesium isotope compositions of the co-magmatic diogenite and eucrite meteorites originating from the protoplanet Vesta are distinct and this is a predictable consequence of extensive crystallisation in a shallow magma ocean. The enrichment in the heavy magnesium isotopes observed in eucrites relative to diogenites is consistent with the isotopic differences measured between minerals and whole-rock basalts on Earth and other asteroids. This isotope effect is not readily observed on Earth due to the lower primary melt magnesium contents produced at smaller degrees of melting and less extensive amounts of mafic mineral crystallisation. However, it is discernible on other planetary bodies where magma oceans formed and crystallised and, thus, Mg isotopes provide a tracer of their previous existence.

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Introduction

22

Magma oceans are widely considered to have existed on planetary bodies in the early Solar System, given the monominerallic nature of much of the lunar crust (Wood *et al.*, 1970) and extremely ancient ages obtained for lunar, martian and asteroidal igneous rock (*e.g.*, Debaille *et al.*, 2007; Nemchin *et al.*, 2009; Schiller *et al.*, 2011). These may have been produced by planetary scale melting induced by heating of short-lived ²⁶Al in the case of early-formed protoplanets such as



Vesta (Greenwood *et al.*, 2005), or giant impacts such as the Moon-forming event in the case of the Earth and Moon (Tonks and Melosh, 1993). As such, finding robust geochemical fingerprints of these ancient magma oceans is important for understanding the earliest stages of planetary evolution.

A range of newly developed stable isotope systems are yielding novel insights into planetary accretion, differentiation and evolution (*e.g.*, Greenwood *et al.*, 2005; Georg *et al.*, 2007). However, many of these systems are multiply affected by a range of processes, potentially including core formation and crystallisation of accessory minerals, which makes interpretation of such data challenging. The lithophile, major element magnesium (Mg) is almost unique in this regard, as stable isotope fractionation in magmatic systems will be almost entirely controlled by crystallisation of high-Mg, mafic minerals, assuming isotopic fractionations exist between such minerals and magma.

The large degree of planetary melting required to generate a magma ocean would produce highly magnesian magmas, which would then subsequently crystallise large amounts of mafic, Mg-rich minerals such as olivine. Small Mg stable isotope fractionations exist between co-existing terrestrial mantle olivine, orthopyroxene and clinopyroxene, with olivine being the isotopically lightest phase (Handler *et al.*, 2009; Young *et al.*, 2009; Pogge von Strandmann *et al.*, 2011; Xiao *et al.*, 2013). Consequently, it should also be possible to detect progressive Mg isotope changes in the products of a crystallising magma ocean.

Vesta is the second largest asteroid in the Solar System and comprises a metal core, silicate mantle and crust (Russell *et al.*, 2012). Based on spectral observations and the Dawn Mission, the howardite–eucrite–diogenite (HED) meteorite suite is inferred to come from Vesta (McCord *et al.*, 1970; Binzel and Xu, 1993; Russell *et al.*, 2012). Most HED meteorites also share common nucleosynthetic isotope signatures for some elements that demonstrate their genetic affinity (Greenwood *et al.*, 2005). These lithologically diverse meteorites provide a unique archive of the timing and processes of protoplanet formation and differentiation. Diogenites are mostly orthopyroxenites, and are conventionally viewed as cumulate igneous rocks formed in a magma ocean or bodies on Vesta, whereas eucrites are basaltic and gabbroic rocks predominantly composed of pigeonite and plagioclase (Mittlefehldt, 2014).

Despite many decades of petrological, geochemical and chronological study, the petrogenesis of eucrites and diogenites and the relationship between them remain enigmatic. End-member models include limited partial melting or extensive (*i.e.* magma ocean) melting of Vesta (Stolper, 1977; Mandler and Elkins-Tanton, 2013; Mittlefehldt, 2014). Nearly all models are difficult to reconcile with the large range of incompatible trace element concentrations in diogenites and eucrites. However, a recent study by Mandler and Elkins-Tanton (2013) has used both chemical and physical arguments to create a model that links HED lithologies to different stages of a differentiating global-scale magma ocean.



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24

Mg Isotope Evidence for a Vestan Magma Ocean

Insights into the degree of partial melting on Vesta can be gleaned from the major and trace element chemistry of the most primitive, oldest diogenites that have the largest deficits in radiogenic ²⁶Mg (Schiller et al., 2011) and features indicating crystallisation from melts with broadly chondritic rare earth element ratios (the full methodological approach is described in the Supplementary Information). Our modelling (Fig. 1) shows that diogenites crystallised as cumulates from >50 % partial melt of a chondritic precursor. This melt would have been part of either a global magma ocean (Mandler and Elkins-Tanton, 2013) or, given thermal modelling constraints, a more localised shallow magma ocean (Neumann *et al.*, 2014). The diogenite parental magmas produced by such large degrees of melting of the vestan, post-core, silicate mantle are highly magnesian with *ca*. 19–33 wt. % MgO (*e.g.*, Ashcroft and Wood, 2015) and would undergo *ca.* >50 %–70 % olivine and orthopyroxene crystallisation before the MgO content of the residual melt approaches that of eucrites. A stable Mg isotopic difference should exist between diogenites and eucrites if they are genetically related by large amounts of olivine and orthopyroxene crystallisation, and if there is a small isotopic fractionation between olivine-orthopyroxene and melt.



Figure 1 The minimum degree of partial melting of the vestan mantle, based on modelling the selected incompatible trace element contents of primitive diogenites. Calculations are based on trace element data for pyroxene determined by laser ablation ICP-MS (Schiller *et al.*, 2011) or digestions of leached whole rock diogenites measured by solution ICP-MS (Barrat *et al.*, 2010). Details of the partial melting model can be found in the Supplementary Information.



Letter

We present high-precision stable Mg isotope data for 22 eucrites determined by multiple-collector inductively coupled plasma mass spectrometry using well established analytical protocols (Table 1; see Supplementary Information for more details) and compare these with published (n = 23) and new (n = 2) values for 25 diogenites obtained with exactly the same analytical methods (Schiller *et al.*, 2011 and this study). The mean Mg stable isotope composition

Table 1	Mg stable isotope data for 22 eucrites, 2 diogenites and the terrestrial basa	t
standard I	HVO-2 relative to the Mg standard DSM-3.	

Sample	μ ²⁵ Mg (±2 SE; ppm)	μ ²⁶ Mg (±2 SE; ppm)
Terrestrial basalt		
BHVO-2	-133 ± 20	-252 ± 38
Polymict eucrites		
EET 83227	-105 ± 6	-180 ± 10
Mg-rich eucrites		
EET 87548	-104 ± 25	-192 ± 47
LEW 87002	-37 ± 14	-65 ± 30
Brecciated eucrites		
Camel Donga	+33 ± 21	$+111 \pm 43$
EET 92003	-41 ± 12	-52 ± 24
GRA 98006	-67 ± 10	-88 ± 18
GRA 98033	-83 ± 13	-124 ± 25
GRA 98043	-63 ± 14	-89 ± 27
GRA 98055	-70 ± 25	-89 ± 49
GRA 98114	-83 ± 18	-111 ± 36
GRO 95533	-54 ± 13	-61 ± 25
Juvinas	-106 ± 4	-174 ± 7
LAP 031062	-60 ± 12	-96 ± 24
LAR 06875	-34 ± 17	-26 ± 32
Millibillilie	-60 ± 28	-76 ± 65
PCA 91193	-66 ± 18	-109 ± 35
QUE 99005	-62 ± 11	-81 ± 21
RKPA 80204	-66 ± 9	-93 ± 17
SCO 06041	-21 ± 11	-29 ± 20
Unbrecciated eucrites		
EET 92023	-96 ± 5	-156 ± 11
LEW 85035	-65 ± 17	-91 ± 33
QUE 97014	-55 ± 14	-74 ± 28
Diogenites		
Dhofar 700	-125 ± 3	-212 ± 8
NWA 4215	-112 ± 16	-212 ± 32



Letter

25

for 22 eucrites is $\mu^{25}Mg_{DSM-3} = -62 \pm 13$ ppm (2 SE; Fig. 2), which is heavier than the mean of diogenites [$\mu^{25}Mg_{DSM-3} = -118 \pm 11$ ppm (2 SE)]. A t-test shows that the isotopic difference between eucrites and diogenites is statistically significant (p = 5.5 × 10⁻⁸). Diogenites have stable Mg isotopes that are indistinguishable from those for Earth's mantle and chondrite meteorites, although within the heavier range for these materials. In contrast, eucrites are isotopically heavier than all these materials (Fig. 2).

Figure 2 Stable Mg isotope composition (μ^{25} Mg, where μ^{25} Mg $= [({}^{25}Mg/{}^{24}Mg)_{sample} / ({}^{25}Mg/{}^{24}Mg)$ $_{DSM-3}-1] \times 10^6$) of diogenites and eucrites (Schiller et al., 2011 and this study), phenocryst olivine and groundmass from the angrite meteorite NWA 1670 (Schiller et al., 2015), and Hawaiian basalts and olivine phenocrysts least affected by Mg-Fe inter-diffusion based on their Fe stable isotope composition (Teng et al., 2011 and references therein). The bottom of the figure shows the probability density distribution of each group and the results of t-testing. The external reproducibility reported for each respective study or the internal error, whichever was larger, was used for the calculation of the probability density distributions and t-testing. Also shown are the ranges of the Mg stable isotope compositions of Earth's mantle (Teng et al., 2010) and chondrites (Teng et al., 2010; Larsen et al., 2016), as well as the average μ^{25} Mg of olivine, orthopyroxene and clinopyroxene in Earth's mantle (Handler et al., 2009; Young et al., 2009; Pogge von Strandmann et al., 2011; Xiao et al., 2013).



26



Before attributing the stable Mg isotope difference between diogenites and eucrites to magmatic processes, it is necessary to consider other processes that might explain this. Firstly, diffusion in magmatic systems can fractionate Mg and iron (Fe) isotopes (Teng et al., 2011), which generates a negative correlation between Mg and Fe stable isotopes, with Fe isotopes being more sensitive to this process than Mg isotopes in Mg-rich olivine. This is inconsistent with the eucrite data, given that eucrites have heavy Mg compared to diogenites but indistinguishable Fe isotope compositions (Wang et al., 2012). Furthermore, diogenites have a light Mg isotope composition when compared to eucrites, which is opposite to the prediction of a heavy Mg isotope composition of olivine and pyroxene resulting from inter-diffusion with a melt (Fig. 2). Secondly, small stable Mg isotope differences exist between mafic minerals (Fig. 2) and, as such, mineralogical differences between diogenites and eucrites might explain their wholerock stable isotope offset. However, given that low-Ca pyroxene is the dominant host of Mg in both diogenites and eucrites, the isotope offset between eucrites and diogenites is too large to reflect solely mineralogical differences. Thus, we attribute the stable Mg isotope difference between diogenites and eucrites to a magmatic process, whereby extensive fractionation of mafic minerals (olivine and orthopyroxene) with light Mg from a (very) large degree melt of vestan mantle produced progressively heavier Mg isotopes in the residual (eucritic) magma.

A study of basaltic samples from the Kileaua Iki lava lake on Hawaii (Teng *et al.*, 2007) provide a possible upper limit on the μ^{25} Mg difference between olivine and melt of 35 ppm. The analytical uncertainty of our μ^{25} Mg measurements and the larger extent of mafic mineral fractionation during magma evolution on Vesta explain why changes in μ^{25} Mg are detectable in HED meteorites. Further evidence of high-temperature stable Mg isotope fractionation between minerals and melt in different settings is shown in Figure 2. Firstly, Mg-rich olivines and surrounding quenched groundmass in the angrite meteorite NWA 1670 have a statistically significant Mg stable isotopic difference ($\mu^{25}Mg_{melt-olivine} = +42$ ppm; Fig. 2; Schiller et al., 2015). Published data for Hawaiian basalts and their olivine phenocrysts that have stable Fe isotopes least affected by diffusion (*i.e.* heavy olivine Fe isotopes) also have a statistically significant difference in μ^{25} Mg with μ^{25} Mg_{melt-olivine} = +28 ppm (Fig. 2; Teng *et al.*, 2011 and references therein). As such, we consider that extensive mafic mineral crystallisation from a large degree partial melt represents the most viable explanation for the heavy Mg isotope composition of eucrites and the μ^{25} Mg offset between diogenites and eucrites.

A simple model for the evolving MgO and μ^{25} Mg in a magma undergoing olivine and orthopyroxene crystallisation is illustrated in Figure 3. This shows that *ca.* 45 % olivine equilibrium crystallisation and 30 % orthopyroxene fractional crystallisation from a 100 % melt of the vestan silicate mantle will produce a melt residue with MgO (*ca.* 6 wt. %) and μ^{25} Mg (–64 ppm), which is comparable to that of eucrites. Although mineral–melt equilibrium isotope fractionation at high temperatures is small, only a μ^{25} Mg_{melt-olivine} = +35 ppm and μ^{25} Mg_{melt-orthopyroxene} = +20 ppm would be required to generate this isotopic fractionation (Fig. 3). Alternatively, the data can also be modelled from a parental





Figure 3 Modelled MgO and stable Mg isotope (μ^{25} Mg) evolution of a 100 % putative primary melt on Vesta (Ashcroft and Wood, 2015) of the post-core formation, vestan silicate mantle (MgO = 31.8 wt. %). Melt-olivine μ^{25} Mg fractionation of +35 ppm (μ^{25} Mg_{melt-olivine}) and melt-orthopyroxene μ^{25} Mg fractionation of +20 ppm (μ^{25} Mg_{melt-orthopyroxene}) can generate the heavy stable Mg isotopes (μ^{25} Mg = -62 ppm) and MgO contents (*ca.* 6 wt. %) of eucrites. Olivine-orthopyroxenite cumulates generated during this process have μ^{25} Mg values in the range of diogenites.

magma produced by smaller, but still very large, degrees of melting (65 %) that undergoes crystallisation (Fig. S-1b). The lighter Mg isotopic composition of olivine and orthopyroxene as compared with basaltic melt is broadly consistent with stable isotope theory (Wilding *et al.*, 2004; Henderson *et al.*, 2006), given that Mg is in six-fold and five-fold coordination in olivine–orthopyroxene crystals and silicate melts, respectively. Moreover, the high MgO contents of large degree melts of the vestan silicate mantle along with the lower pressure crystallisation on this protoplanet are predicted to result in even lower Mg coordination in vestan silicate melts than terrestrial magmas (Wilding *et al.*, 2004).

Conclusions

Although our results cannot distinguish between a global scale or a shallow magma ocean, we consider a global scale magma ocean to be inconsistent with recent thermal models (Neumann *et al.*, 2014) and other geochemical evidence (Barrat and Yamaguchi, 2014). Irrespective, we have shown that very large degrees of melting characterised at least parts of Vesta and that a co-magmatic relationship broadly exists between diogenites and eucrites. This study also shows that high-temperature, magmatic processes can fractionate stable Mg isotopes in evolving mafic magmas. With the current resolution of analytical techniques,



this isotopic difference is not readily observed in igneous rocks from Earth due to the lower primary melt Mg contents of post-Archean igneous rocks produced at smaller degrees of melting and consequently more limited amounts of olivine crystallisation (Fig. S-1b) relative to Vesta. However, stable Mg isotope fractionations should be discernible on other rocky planets, satellites and asteroids where silicate melting was extensive and magma oceans formed and crystallised.

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Additional Information

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Geochemical Perspectives Letters

Letter

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Letter

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30