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# Magnesium isotope systematics in Martian meteorites

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## ABSTRACT

Magnesium isotope compositions are reported for a suite of Martian meteorites that span the range of petrological and geochemical types recognized to date for Mars, including crustal breccia Northwest Africa (NWA) 7034. The $\delta^{26}$Mg values (per mil units relative to DSM-3 reference material) range from −0.32 to −0.11‰; basaltic shergottites and nakhlites lie to the heavier end of the Mg isotope range whereas olivine-phyric, olivine–orthopyroxene-phyric and lherzolitic shergottites, and chassignites have slightly lighter Mg isotope compositions, attesting to modest correlation of Mg isotopes and petrology of the samples. Slightly heavier Mg isotope compositions found for surface-related materials (NWA 7034, black glass fraction of the Tissint shergottite fall; $\delta^{26}\text{Mg} > -0.17$‰) indicate measurable Mg isotope difference between the Martian mantle and crust but the true extent of Mg isotope fractionation for Martian surface materials remains unconstrained. The range of $\delta^{26}$Mg values from −0.19 to −0.11‰ in nakhlites is most likely due to accumulation of clinopyroxene during petrogenesis rather than garnet fractionation in the source or assimilation of surface material modified at low temperatures. The rather restricted range in Mg isotope compositions between spatially and temporally distinct mantle-derived samples supports the idea of inefficient/absent major tectonic cycles on Mars, which would include plate tectonics and large-scale recycling of isotopically fractionated surface materials back into the Martian mantle. The cumulative $\delta^{26}$Mg value of Martian samples, which are not influenced by late-stage alteration processes and/or crust–mantle interactions, is $-0.271 \pm 0.040$‰ (2SD) and is considered to reflect $\delta^{26}$Mg value of the Bulk Silicate Mars. This value is robust taking into account the range of lithologies involved in this estimate. It also attests to the lack of the Mg isotope variability reported for the inner Solar System bodies at current analytical precision, also noted for several other major elements.

## 1. Introduction

Together with Si, O and Fe, Mg belongs to the most abundant elements in the rocky planets of the inner Solar System (e.g., Palme and O'Neill, 2014). Isotope studies on these elements reveal different degrees of mass-dependent fractionation that are the result of a variety of geochemical and cosmochemical processes. The Mg isotope systematics of major silicate reservoirs in the Solar System have been discussed in a number of studies that have shown the absence of detectable Mg isotope fractionation during planet formation and identical Mg isotope composition for the Moon, chondrites, and achondrites (e.g., Bourdon et al., 2010; Chakrabarti and Jacobsen, 2010; Sedaghatpour et al., 2013; Teng et al., 2010) which are all similar to the estimated $\delta^{26}\text{Mg} = -0.25 \pm 0.07$‰ for the Earth's mantle (Teng et al., 2010). This isotope homogeneity in large planetary bodies has also been observed for Ca (Magna et al., 2015b; Valdes et al., 2014) while the stable isotope compositions of some other major elements (Si, Fe) display slight variations (e.g., Dauphas et al., 2015; Pringle et al., 2014; Sossi et al., 2016), possibly as a consequence of volatile loss and/or core formation.

Magnesium isotope fractionation is limited during high-temperature processes while low-temperature processes such as alteration, weathering and/or carbonate/sulfate formation may impart sizeable Mg isotope fractionation (see Teng, 2017, and references therein). Magnesium isotope fractionation has been observed during large-scale silicate differentiation (Sedaghatpour et al., 2013; Schiller et al., 2017), but this may also be attributed to the influence of material exposed to low-temperature surface processes (Yang et al., 2016). This contrasting behavior of Mg isotopes in surface versus mantle processes allows for the reconstruction of

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processes involving chemical exchange between various reservoirs during planetary differentiation.

On Earth, surface materials enter the mantle via plate tectonic processes. This can be observed in melt products derived from the mantle that bear evidence for incorporation of surface-weathered materials. In this respect, Mg isotopes may potentially be employed as a tracer of recycling (Huang et al., 2016; Ke et al., 2016). Therefore, the investigation of Mg isotope systematics of Martian magmatic rocks has the potential both to provide insights into the extent of surface–mantle interaction and to reveal the Mg isotope composition of the bulk Mars. Mars, which has about one-eighth the mass of the Earth, is a unique terrestrial planet that has undergone all planetary evolutionary stages but did not develop plate tectonics (Breuer and Spohn, 2003). Previous studies of Mg isotope composition of Martian meteorites have been inconsistent between individual laboratories (Bizzarro et al., 2011; Chakrabarti and Jacobsen, 2010; Wiechert and Halliday, 2007), which has so far prevented evaluating the Mg isotope composition of Mars. Despite these issues, Mg isotope ratios determined on materials from Mars are broadly identical to the range observed for the Earth, Moon, and chondrites, suggesting a homogeneous Mg isotope distribution within the inner Solar System.

This study presents the first comprehensive and systematic survey of Mg isotope compositions for a total of 31 Martian meteorites that span a range of Martian lithologies recognized to date, including materials compositionally similar to Martian crust. Combined with the published Mg isotope data for the Earth, Moon, chondrites and other planetary bodies of the inner Solar System (e.g., Vesta), this study provides further constraints on the Mg isotope (in)variability of mantles of the inner Solar System planetary bodies and on the interaction of surface material with mantle rocks on Mars, which contribute to our understanding of planetary evolution.

## 2. Samples and methods

Magnesium isotope compositions were obtained for 21 shergottites, six clinopyroxene-bearing nakhlites [Nakhla, Lafayette, Miller Range (MIL) 03346, Yamato (Y)-000593, Northwest Africa (NWA) 817, NWA 5790], two dunitic chassignites (Chassigny, NWA 2737), orthopyroxenite Allan Hills (ALH) 84001 and polymict crustal breccia NWA 7034 (Agee et al., 2013). Shergottites include five basaltic (Shergotty, Zagami, Los Angeles, NWA 856, NWA 4864), ten olivine-phyric [Elephant Moraine (EETA) 79001 lithology A, Larkman Nunataks (LAR) 06319, Y-980459, NWA 1068, NWA 4925, NWA 6162, Sayh al Uhaymir (SaU) 005, SaU 051, SaU 094, Tissint], two olivine–orthopyroxene-phyric [Roberts Massif (RBT) 04262, Dar al Gani (DaG) 476], three lherzolitic (ALH 77005, Y-000097, NWA 1950), and one diabasic shergottite (NWA 5990). Fusion crusts were removed from samples and only interior portions of the meteorites were processed. These samples were previously characterized for their Li and Ca isotope systematics (Magna et al. 2015a, 2015b).

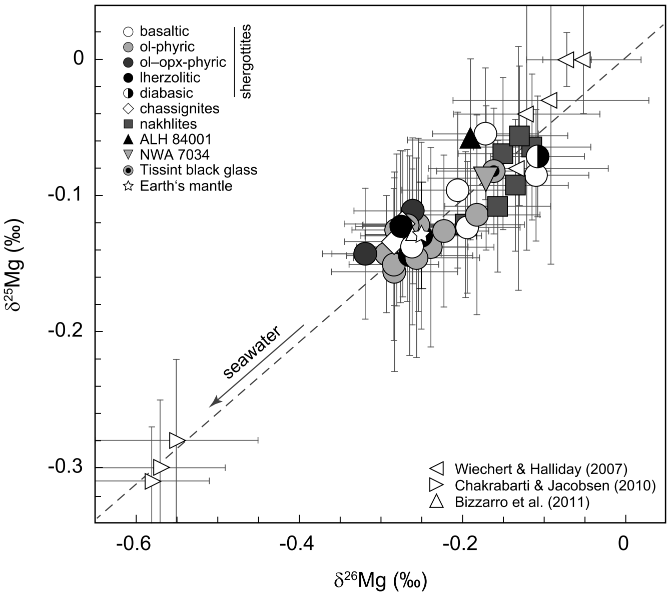

**Fig. 1.** Magnesium three-isotope plot for the Martian meteorite suite from this study. The dashed line represents the fractionation line with a slope of 0.515. The Mg isotope composition of the Earth's mantle is from Teng et al. (2010).

Magnesium isotope compositions of Martian meteorites were measured at the University of Arkansas, with the exception of Tissint and NWA 7034, which were analyzed at the University of Washington. The analytical procedures for the chemical separation and isotope analysis of Mg followed those reported elsewhere (Teng et al. 2010, 2015). Aliquots of dissolved Martian meteorites from the previous study of Magna et al. (2015a) were used. After drying down, residues were refluxed with concentrated $HNO_3$ and then diluted to 1 M $HNO_3$ solution for cation exchange chromatography. Pure Mg solutions were obtained by two passes through quartz glass columns packed with Bio-Rad AG50W-X8 resin (200–400 mesh) in 1 M $HNO_3$. Total procedure blank (<10 ng) was considered negligible compared to Mg processed. At least two reference materials were processed together with unknown samples for each batch of column chemistry. Magnesium isotope compositions were measured using the standard–sample bracketing method on a *Nu Plasma* multiple-collector inductively-coupled-plasma mass spectrometer (MC-ICPMS), housed at the University of Arkansas, and a *Nu Plasma II* MC-ICPMS, housed at the University of Washington, respectively. The Mg isotope data are expressed relative to the DSM-3 reference material (Galy et al., 2003) and reported as $\delta^{x}\mathrm{Mg}\ (‰) = [({}^{x}\mathrm{Mg}/{}^{24}\mathrm{Mg})_{\mathrm{sample}}/({}^{x}\mathrm{Mg}/{}^{24}\mathrm{Mg})_{\mathrm{DSM\text{-}3}} - 1] \times 1000$, where ${}^{x}$Mg denotes ${}^{25}$Mg and ${}^{26}$Mg, respectively. Throughout this study, $\delta^{26}$Mg value is used considering mass-dependent fractionation within analytical uncertainties. The external reproducibility of Mg isotope measurements was better than ±0.07‰ ($2\sigma$) for $\delta^{26}$Mg and ±0.05‰ ($2\sigma$) for $\delta^{25}$Mg, verified by duplicate and replicate measurements of synthetic solutions over the four-year period (Teng et al., 2015). The Mg isotope compositions for reference materials (Kilbourne Hole olivine: $\delta^{26}\mathrm{Mg} = -0.268 \pm 0.029‰$; Hawaiian seawater: $\delta^{26}\mathrm{Mg} = -0.836 \pm 0.046‰$; Murchison chondrite: $\delta^{26}\mathrm{Mg} = -0.290 \pm 0.044‰$) agree with published values (see Teng et al., 2015, and references therein).

## 3. Results

The Mg isotope compositions of Martian meteorites are listed in Table 1. The $\delta^{25}$Mg and $\delta^{26}$Mg values range from −0.156 to −0.055‰ and −0.318 to −0.106‰, respectively, and follow the mass-dependent fractionation line (Fig. 1). The new Mg isotope data for Zagami, Nakhla, Chassigny and ALH 84001 are consistently intermediate between those reported by Wiechert and Halliday (2007) and Chakrabarti and Jacobsen (2010) but we note that their data were critically reviewed elsewhere (e.g., Bizzarro et al., 2011; Teng et al., 2015) and considered an analytical artifact. The Mg isotope composition of NWA 856 is identical within the analytical error to that reported by Bizzarro et al. (2011).

In contrast to terrestrial peridotites, OIB and MORB (Bourdon et al., 2010; Teng et al., 2010), Martian meteorites display measurable Mg isotope variations, reflecting their petrological diversity. Basaltic shergottites and nakhlites have among the highest $\delta^{26}$Mg values of the entire suite whereas olivine-phyric, olivine–

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