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Magnesium stable isotope composition of Earth's upper mantle

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ABSTRACT

The mantle is Earth's largest reservoir of Mg containing >99% of Earth's Mg inventory. However, no consensus exists on the stable Mg isotope composition of the Earth's mantle or how variable it is and, in particular, whether the mantle has the same stable Mg isotope composition as chondrite meteorites. We have determined the Mg isotope composition of olivine from 22 mantle peridotites from eastern Australia, west Antarctica, Jordan, Yemen and southwest Greenland by pseudo-high-resolution MC-ICP-MS on Mg purified to >99%. The samples include fertile lherzolites, depleted harzburgites and dunites, cryptically metasomatised ('dry') peridotites and modally metasomatised apatite ± amphibole-bearing harzburgites and wehrlites. Olivine from these samples of early Archaean through to Permian lithospheric mantle have $\delta^{25}\mathrm{Mg}_{\mathrm{DSM\text{-}3}} = -0.22$ to -0.08‰. These data indicate the bulk upper mantle as represented by peridotite olivine is homogeneous within current analytical uncertainties (external reproducibility $\leq \pm 0.07$‰ [2 sd]). We find no systematic δ^{25}Mg variations with location, lithospheric age, peridotite fertility, or degree or nature of mantle metasomatism. Although pyroxene may have slightly heavier δ^{25}Mg than coexisting olivine, any fractionation between mantle pyroxene and olivine is also within current analytical uncertainties with a mean $\Delta^{25}\mathrm{Mg}_{\mathrm{pyr\text{-}ol}} = +0.06 \pm 0.10$‰ (2 sd; $n = 5$). Our average mantle olivine $\delta^{25}\mathrm{Mg}_{\mathrm{DSM\text{-}3}} = -0.14 \pm 0.07$‰ and $\delta^{26}\mathrm{Mg}_{\mathrm{DSM\text{-}3}} = -0.27 \pm 0.14$‰ (2 sd) are indistinguishable from the average of data previously reported for terrestrial basalts, confirming that basalts have stable Mg isotope compositions representative of the mantle. Olivine from five pallasite meteorites have $\delta^{25}\mathrm{Mg}_{\mathrm{DSM\text{-}3}} = -0.16$ to -0.11‰ that are identical to terrestrial olivine and indistinguishable from the average δ^{25}Mg previously reported for chondrites. These data provide no evidence for measurable heterogeneity in the stable Mg isotope composition of the source material in the proto-planetary disc from which Earth and chondrite and pallasite parent bodies accreted.

1. Introduction

Magnesium is the third-most abundant lithophile element in the Earth and has three isotopes (24, 25, 26) with relatively large mass differences (4–8%). Magnesium stable isotopes have the potential to be significantly fractionated by physical, chemical and biological processes at low temperatures (e.g. Galy et al., 2002; Young and Galy, 2004; Tipper et al., 2006) and, possibly, during higher temperature processes within the upper mantle (Pearson et al., 2006). Magnesium stable isotope variations may thus be useful for tracing (bio) geochemical cycling of Mg in the oceans over time which will depend on the nature of stable Mg isotope fractionations and temporal changes in fluxes that characterize sources and sinks of Mg to the oceans e.g. the riverine input of Mg derived by continental weathering, the hydrothermal inputs of Mg at mid-ocean ridges and the removal of Mg from the ocean by deposition of carbonate sediments (e.g. Tipper et al., 2006). Moreover, stable Mg isotope fractionations also occur at high temperatures, for example, during the condensation and evaporation processes around the young Sun that produced the Solar System's oldest solids — calcium–aluminium-rich inclusions and chondrules (Galy et al., 2000). Experimental studies further suggest local fractionation may occur via thermal diffusion in magmatic systems where strong thermal gradients exist (Richter et al., 2008; Huang et al., 2009). Recently, one study identified large stable Mg isotope fractionations in rocks from Earth's upper mantle (Pearson et al., 2006), apparently demonstrating that large fractionations in stable Mg isotopes can be produced at high temperatures within the Earth. However, a study of basaltic rocks from Hawaii showed that magmatic differentiation at high temperatures did not generate significant stable Mg isotope variations (Teng et al., 2007).

The development of multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has allowed high precision stable Mg isotope measurements to be made that have identified relatively large fractionations in terrestrial rocks, river water and ocean water ($\delta^{25}\mathrm{Mg}_{\mathrm{DSM\text{-}3}} = -1.3$ to $+0.1$‰; e.g. Tipper et al., 2006; Wiechert and Halliday, 2007). However, as yet, relatively few stable Mg isotope studies have been published and fundamental questions remain regarding the isotopic composition of Earth's largest Mg reservoir —

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the mantle — which is a baseline composition against which to compare stable Mg isotopic fractionation of surficial materials.

Two unresolved issues in particular stand out. Firstly, there is no consensus on the stable Mg isotope composition of Earth's mantle and the degree to which this is homogeneous. This is best epitomized by two recent laser ablation (LA)-MC-ICP-MS Mg isotope studies of mantle olivine. In one study, minimal stable Mg isotopic variations were measured in olivine, which were essentially within analytical uncertainties of ca. $\pm 0.2‰\ \mathrm{amu}^{-1}$ (Norman et al., 2006). Conversely, another study of olivine from continental lithospheric mantle suggested that an order of magnitude larger (~2‰) variations in $\delta^{25}\mathrm{Mg}_{\mathrm{DSM\text{-}3}}$ (the per mil deviation of the sample $^{25}\mathrm{Mg}/^{24}\mathrm{Mg}$ from the reference Mg standard DSM-3) existed and resulted from normal mantle processes of melt extraction and metasomatism (Pearson et al., 2006). Such variations are much greater than the reported analytical uncertainties and, if correct, suggest stable Mg isotopes may be an important tracer of mantle processes. Secondly, it is uncertain whether Earth's mantle and the basaltic magmas it produces have the same stable Mg isotope composition as chondrite and achondrite meteorites. The stable Mg isotopic composition of Earth as represented by mantle minerals and mantle-derived basalts has been compared with meteoritic Mg in two recent studies that yielded conflicting results. In one study, mantle olivine and chondrite meteorites were shown to have different stable Mg isotope compositions suggesting the Earth's mantle has non-chondritic Mg (Wiechert and Halliday, 2007), yet a second study of Hawaiian basalts did not discern any stable Mg isotopic difference as compared to chondrites suggesting the Earth's mantle has chondritic Mg (Teng et al., 2007).

To further address these apparently contradictory results, we present stable Mg isotope analyses of mantle olivine from 22 peridotites from a range of locations representing continental lithospheric mantle of early Archaean to Phanerozoic age. Data were acquired by pseudo-high-resolution MC-ICP-MS on Mg purified by a variety of chemical extraction techniques. These analyses represent the largest dataset of stable Mg isotope data yet reported for mantle olivine and constrain both the scale of stable Mg isotope homogeneity and the average Mg isotopic composition of olivine in Earth's mantle. We also report stable Mg isotope data for five olivine separates from pallasite meteorites and compare these data and the terrestrial olivine dataset with previously published chondrite and terrestrial basalt data.

2. Samples

Mineral separates were analysed from peridotite samples from five regions with lithospheric stabilisation ages ranging from >3.8 Ga to 275 Ma. While most of the analysed mineral separates are olivine, as this is the main repository of Mg in the upper mantle, we also analysed pyroxene co-existing with the olivine in three samples.

2.1. Archaean lithospheric mantle

Olivine from five spinel peridotites from the >3.8 Ga Akilia association and ultramafic enclaves within Archaean tonalites south of the Isua Supercrustal Belt (southwest Greenland) were analysed (G93/48, G01/03, G01/55, G01/56, G01/84). These are the same samples that were part of the LA-MC-ICP-MS Mg isotope study of Norman et al. (2006), and span compositions from moderately depleted lherzolite to dunite.

2.2. Proterozoic lithospheric mantle

Olivine from two suites of Proterozoic lithospheric mantle were analysed. Six apatite ± amphibole-bearing harzburgite, lherzolite and wehrlite xenoliths (71000, 71001, 76993, 76994, 76997, 70972) from southeastern Australia that were analysed in the LA-MC-ICP-MS study of Norman et al. (2006) were restudied here. These samples are modally metasomatised peridotites interpreted as residual mantle that recently interacted with carbonate-rich metasomatic agents resulting in crystallization of clinopyroxene + apatite ± amphibole ± carbonate (Yaxley et al., 1991; Matsumoto et al., 1997). Re–Os isotope systematics of these xenoliths suggest they represent fragments of the convecting mantle incorporated into the lithosphere during the Mesoproterozoic (Handler et al., 1997). Two lherzolite xenoliths from Jordan (J11) and Yemen (JK3) represent Neoproterozoic examples of Arabian lithospheric mantle (Shaw et al., 2007; Baker et al., 1998) that have been overprinted by later metasomatic events. J11 is an anhydrous spinel lherzolite that has a Lu–Hf model age of 1.5 Ga and is interpreted as representing convecting upper mantle incorporated into Pan-African lithospheric mantle 600–700 Ma at which time it experienced intense cryptic metasomatism that overprinted Sr–Nd–Pb isotopic signatures and enriched the mantle in incompatible trace elements mobilized in carbonatitic fluid or melts (Shaw et al., 2007). JK3 is a modally metasomatised apatite + amphibole lherzolite interpreted as representing Pan-African age lithospheric mantle overprinted by hydrous carbonatitic fluids or melts at the periphery of the Afar mantle plume head at ca. 30 Ma (Baker et al., 1998). Olivine from sample JB281 are phenocrysts of a near-primary continental flood basalt erupted in Yemen 30 Ma that represents the product of melting the Afar mantle plume (Baker et al., 1996).

2.3. Phanerozoic lithospheric mantle

Three lherzolite xenoliths from USAS Escarpment in Marie Byrd Land (West Antarctica; MB69A, E & F) and five lherzolite xenoliths from Mt Quincan (northern Queensland, northeastern Australia; MQ1, MQ6, MQ7, MQ12, MQ16) represent young fertile ($\mathrm{Al_2O_3} = 2.7$–3.7 wt.%) examples of lithospheric mantle. These samples exhibit only cryptic metasomatic enrichment in the most highly incompatible trace elements (Handler et al., 2003, 2005). These samples are compositionally similar to the cryptically metasomatised ('dry') eastern Australian lherzolites studied by Pearson et al. (2006), which showed a large range in stable Mg isotopic compositions. Highly depleted Sr–Nd isotopic data for one of the USAS lherzolites (MB69E: $^{87}\mathrm{Sr}/^{86}\mathrm{Sr} = 0.7019$; $\varepsilon_{\mathrm{Nd}} = +23$; M. Handler, unpubl. data) suggest a lithospheric stabilisation age of ca. 500 Ma contemporaneous with the Antarctic Ross Orogen, whereas a Sm–Nd bulk rock isochron indicates a younger age for the Queensland lherzolites of ca. 275 Ma (Handler et al., 2005). A single harzburgite xenolith from Franklin Island (West Antarctica) represents cryptically-metasomatised, highly depleted, lithospheric mantle.

2.4. Pallasite meteorites

In addition to olivine from the aforementioned terrestrial samples, olivine from five pallasite meteorites were analysed (Admire, Brenham, Esquel, Molong and Springwater). All the pallasite samples are main group pallasites. Olivine from Admire, Brenham, Esquel and Molong have forsterite contents of 87–89 mol%, whereas Springwater is a main group pallasite containing olivine with an unusually low forsterite content of 82 mol% (Buseck & Goldstein, 1969; Wasson and Choi, 2003).

3. Methods

Full details of the chemical extraction method are given in a supplementary file available online and are only briefly outlined here. Approximately 2 to 12 mg of handpicked olivine or pyroxene were washed in >18.2 MΩ water and dissolved in $\mathrm{HF–HNO_3}$ acid in screw-top Savillex beakers at 120 °C. An aliquot of solution equivalent to 2 mg of digested sample was processed through column chemistry to purify Mg in the following steps: (1) Fe was removed using anion exchange resin in HCl media; (2) Ca was removed using Eichrom DGA resin in 3 M $\mathrm{HNO_3}$; (3) Mn was removed using acetone–HCl-based cation exchange chemistry and, (4) a final Mg clean up on cation