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Investigation of magnesium isotope fractionation during basalt differentiation: Implications for a chondritic composition of the terrestrial mantle

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Abstract

To investigate whether magnesium isotopes are fractionated during basalt differentiation, we have performed high-precision Mg isotopic analyses by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) on a set of well-characterized samples from Kilauea Iki lava lake, Hawaii, USA. Samples from the Kilauea Iki lava lake, produced by closed-system crystal-melt fractionation, range from olivine-rich cumulates to highly differentiated basalts with MgO content ranging from 2.37 to 26.87 wt.%. Our results demonstrate that although these basalts have diverse chemical compositions, mineralogies, crystallization temperatures and degrees of differentiation, their Mg isotopic compositions display no measurable variation within the limits of our external precision (average $\delta^{26}\text{Mg}=-0.36\pm0.10$ and $\delta^{25}\text{Mg}=-0.20\pm0.07$; uncertainties are 2SD). This indicates that Mg isotopic fractionation during crystal-melt fractionation at temperatures of ≥ 1055 °C is undetectable at the level of precision of the current investigation. Calculations based on our data suggest that at near-magmatic temperatures the maximum fractionation in the $^{26}\text{Mg}/^{24}\text{Mg}$ ratio between olivine and melt is 0.07‰. Two additional oceanic basalts, two continental basalts (BCR-1 and BCR-2), and two primitive carbonaceous chondrites (Allende and Murchison) analyzed in this study have Mg isotopic compositions similar to the Kilauea Iki lava lake samples. In contrast to a recent report [U. Wiechert, A.N. Halliday, Non-chondritic magnesium and the origins of the inner terrestrial planets, Earth and Planetary Science Letters 256 (2007) 360–371], the results presented here suggest that the Bulk Silicate Earth has a chondritic Mg isotopic composition.

Keywords: magnesium isotopes; Kilauea Iki; magma differentiation; isotope fractionation

1. Introduction

Magnesium is a fluid-mobile major element having three isotopes, ^{24}Mg, ^{25}Mg and ^{26}Mg, with natural abundances of 78.99%, 10.00% and 11.01%, respectively (Rosman and Taylor, 1998). The relative mass difference between ^{26}Mg and ^{24}Mg is >8%, which is the second largest among the non-traditional stable isotopes (Johnson et al., 2004). This characteristic can potentially

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produce large Mg isotopic fractionations during low-temperature fluid–rock interactions and makes Mg isotopes an excellent tracer for crustal recycling. However, due to limitations in the mass spectrometry, many previous Mg isotopic studies have concentrated on either non-mass-dependent isotope anomalies to look for the radiogenic ^{26}Mg produced by the decay of short-lived ^{26}Al (Lee, 1974; Gray and Compston, 1974) or large kinetic mass-dependent isotope fractionation during evaporation (Davis et al., 1990; Goswami et al., 1994; Russell et al., 1998; Richter et al., 2002). The recent advent of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has made it possible to measure Mg isotopes with unprecedented high-precision (Galy et al., 2001; Young et al., 2002).

Thus far, there have been few investigations of the Mg isotopic compositions of silicate rocks. These studies have provided conflicting information about the Mg isotopic composition of the Bulk Silicate Earth (BSE) and other planetary reservoirs. Using laser-ablation MC-ICP-MS, Pearson et al. (2006) found significant heterogeneity (>2‰ amu^{-1}) in Mg isotopic compositions of olivines in mantle-derived peridotite xenoliths and megacrystals, which has been interpreted as resulting largely from mantle metasomatism. In contrast, Norman et al. (2006) studied olivines from different planetary bodies (Earth, Mars, Moon and pallasite parent body), with the terrestrial olivines having a range of origins, tectonic settings and mantle source compositions, and found only small variations in the Mg isotopic compositions of these samples, slightly beyond their analytical uncertainty (typically ±0.2‰ amu^{-1}, 2SD). In addition to these in-situ isotopic analyses, Wiechert and Halliday (2007) measured olivine, clinopyroxene and orthopyroxene from terrestrial peridotites with higher-precision (typically ± 0.05‰ amu^{-1}, 2SD) by using solution MC-ICP-MS and reported that the Mg isotopic composition of the Earth, as represented by mantle minerals, is relatively homogeneous and is on average ~0.1 to 0.2‰ amu^{-1} heavier than most chondrites. They suggested that the non-chondritic Mg isotopic composition of the BSE, as well as of silicate reservoirs on other differentiated planets and planetesimals, resulted from sorting of solid materials (specifically, chondrules and calcium–aluminum-rich inclusions) in the proto-planetary disk.

Besides peridotites, another way to access the composition of the mantle is through the study of oceanic basalts, which are products of partial melting of the mantle. Indeed it is through isotopic studies of oceanic basalts that mantle heterogeneity produced by crustal recycling has been characterized and different mantle end-members have been defined (Zindler and Hart, 1986; Hofmann, 1997). Before using the isotopic composition of basalt to infer that of the upper mantle, one critical assumption is that isotope fractionation during mantle melting and basalt differentiation is insignificant and that a basalt still preserves its source's chemical and isotopic composition, and thus may be used to identify the signatures of recycled crust materials in the mantle. Theoretical studies suggest that equilibrium isotope fractionation decreases as the temperature increases (Chacko et al., 2001) and is likely to be negligible during high-temperature processes such as magmatic differentiation and some studies of natural rocks support this. For example, Tomascak et al. (1999) showed that there was no measurable Li isotopic fractionation during basaltic differentiation at temperatures greater than 1050 °C. However, as shown by the recent debate relating to Fe isotopes (Beard and Johnson, 2007; Poitrasson, 2007; Weyer et al., 2007; Weyer and Ionov, 2007), the question of stable Fe isotope fractionation during high-temperature processes as recorded in natural samples is still open. In the case of Mg isotopes, recent work indicates that they may be fractionated during high-T magmatic differentiation. Specifically, Wiechert and Halliday (2007) found that various types of lunar basalts record a significant range (of ~0.3‰ amu^{-1}) in Mg isotopes and terrestrial basalts are isotopically lighter than mantle peridotite minerals, and attributed these effects to equilibrium isotope fractionation during magmatic differentiation. Nevertheless, the petrogenetic relationships between these suites of samples are not clear, thus other factors that may have affected Mg isotopic compositions (e.g., source heterogeneities) cannot be ruled out.

Here, we present high-precision Mg isotopic compositions for a set of well-characterized samples from Kilauea Iki lava lake, Hawaii, USA. The Kilauea Iki lava lake has a relatively simple geological setting and experienced extensive internal differentiation that makes it an ideal field laboratory for studying the effect of basaltic differentiation on isotopic fractionation. As such, the primary goal of this work was to determine if there is any Mg isotope fractionation associated with igneous differentiation processes. Furthermore, the results of our study have implications for the Mg isotope composition of the BSE.

2. Geological background and samples

The Kilauea volcano is located on the southeastern side of the island of Hawaii. Kilauea Iki lava lake lies near the summit of Kilauea volcano, east of its main caldera, and was formed during the 1959 summit eruption of Kilauea volcano (Richter et al., 1970), noted for being a mixed-magma eruption (Wright, 1973). The single eruption filled a previously existing crater to a depth of approximately 135 m. A stable crust formed within a few weeks of the end of the eruption, and the lake has cooled and crystallized thereafter as a small, self-roofed, closed magma chamber, with a melt-rich interior, surrounded on all sides by partially molten regions, extending outward to fully solidified rock (Helz et al., 1989).

The original 1959 Kilauea Iki lava consists of picritic tholeiite and is composed of glass + olivine and chromite crystals, with an average MgO content of 15.43 wt.% (Wright, 1973). Glass compositions in eruption samples range from 6.5 to 10.0 wt.% MgO (Helz, 1987). The olivine phenocrysts include several distinct subpopulations, derived from different levels of Kilauea's plumbing (Helz, 1987). Internal differentiation of the magma chamber has produced a variety of rock types from olivine-rich cumulates, through olivine tholeiites, to ferrodiabase and more silicic veins, and large chemical variations with MgO content ranging from 2.37 to 26.87 wt.% (Helz, 1987). Rocks with MgO contents >7.0 wt.% contain olivine phenocrysts ($Fo_{86\pm1}$) and have been affected predominantly by settling of olivine crystals while highly differentiated rocks with MgO contents <7.0 wt.% have been produced by segregation of liquid from within coherent, crystal-rich mushes (Helz, 1987; Helz et al., 1989). The quenching temperature or minimum crystallization temperature of these samples, as estimated by the MgO content of glass (Helz and Thornber, 1987) or from thermocouple data, ranges from greater than 1216 °C down to 1055 °C (Helz and Thornber, 1987).

Thirteen well-studied samples covering the whole compositional and mineralogical spectrum of the Kilauea Iki lava, including two original eruption samples (Iki-22 and Iki-58), a picrite from a depth of 6.8 m in the upper crust of the lava lake (KI-67-3-6.8) and 10 drilled core samples from the interior of the lake, were analyzed to ascertain whether there are any Mg isotopic variations during basaltic differentiation. To assess the accuracy and long-term external precision of our analyses, several well-studied samples were also measured, including the international basaltic standards BCR-1 and BCR-2, the carbonaceous chondrites Allende (CV3) and Murchison (CM2) and an aliquot of a solution of San Carlos olivine (SC olivine, provided by C. Lundstrom). In addition, a fresh olivine grain from a peridotite xenolith from the Kilbourne Hole, New Mexico (KH olivine, provided by P. Janney), a sample of mid-ocean ridge basalt (SUNY MORB, provided by F. Richter), a basalt sample from Loihi, Hawaii (T402#1, provided by N. Dauphas) and a shale composite sample from East China (D119, provided by S. Gao) have also been measured during this study.

3. Analytical methods

Magnesium isotopic analyses were performed at the Isotope Geochemistry Laboratory of the Field Museum of Natural History. The following provides a description of our analytical protocol relevant to the samples studied here as well as the tests we performed for assessing the accuracy and precision of our analyses.

3.1. Sample preparation and chromatography

All chemical procedures were carried out in a clean laboratory environment. Approximately 20 mg of rock powder was dissolved in Savillex screw-top beakers in a mixture of concentrated HF–HNO_3 (~3:1). The capped beakers were heated overnight at a temperature of 70–80 °C on a hot plate in a laminar flow exhaust hood. The solutions were evaporated to dryness the following day, with each sample beaker covered by a small Teflon enclosure to avoid any cross-contamination. In order to achieve 100% dissolution, the dried samples were refluxed with concentrated HNO_3 until completely dissolved, and then again evaporated to dryness. This dried residue was finally dissolved in 1 N HNO_3, in preparation for chromatographic separation.

Separation of Mg was achieved by cation exchange chromatography. The column was loaded with 1 ml of Bio-Rad 200–400 mesh AG50W-X8 pre-cleaned resin (rinsed with >20 times column volume of 4 N HCl and 18.2 MΩ cm Milli-Q®water). This resin was further cleaned with >5 times column volume of 1 N HNO_3 and Milli-Q® water. Magnesium was eluted through this column with 1 N HNO_3. Since Mg isotopes can be significantly fractionated during ion exchange reactions (Fig. 1, also see Chang et al. (2003)), it is essential to obtain close to ~100% Mg yield from the column chemistry. To assure close to 100% Mg yield, the position of the Mg cut was determined using both pure Mg standard solutions and dissolved rocks with different compositions (basalt and granite). Magnesium elution curves were not shifted for different matrix compositions and Mg was eluted completely through columns with 5.5 ml of 1 N HNO_3 (Fig. 1). This column procedure was repeated 2–3 times for each sample to obtain a pure Mg solution (i.e., ratio of the concentration of any cation to that of Mg was <0.05) for mass spectrometry.

3.2. Mass spectrometry

Prior to Mg isotopic analyses, the ratios of the abundances of Na, Al, Ca, Ti and Fe to Mg in each purified Mg sample solution were measured, as a cation/Mg ratio

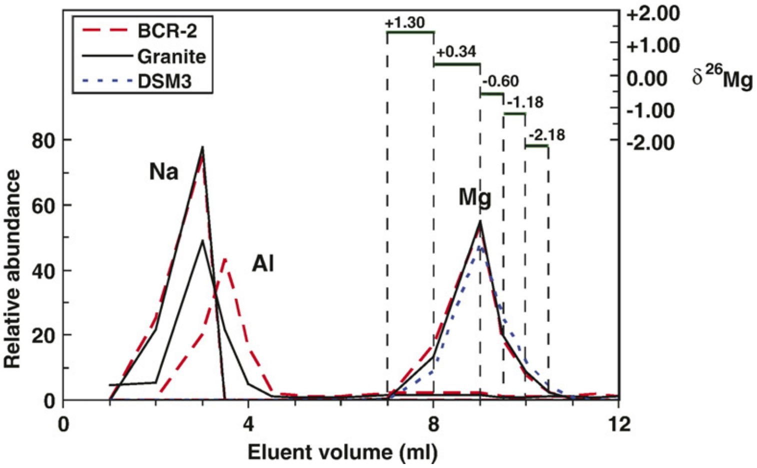

Fig. 1. Elution curves of Na, Al and Mg for a granite, a basalt (BCR-2) and DSM3. Ca, Ti and Fe are not detectable over this elution interval (0–12 ml 1 N HNO_3). The Mg isotopic compositions of 0.5–1 ml fractions of the Mg cut for DSM3 are also plotted.

greater than 0.05 for these elements can cause analytical artifacts (Galy et al., 2001). In all samples, the cation/Mg ratios in the purified Mg solutions were <0.05 after ≤3 passes through the cation exchange column.

Purified Mg sample solutions were introduced to the Ar plasma using a Cetac Aridus® desolvating nebulizer fitted with a PFA spray chamber and 100 μl/min micronebulizer. Samples were analyzed using a GV Isoprobe MC-ICP-MS, with ^{24}Mg, ^{25}Mg, ^{26}Mg and Al ion beams measured simultaneously in both high- and low-mass Faraday cups (L3, Ax, H4 and H6). Each sample analysis was bracketed by measurements of the DSM3 standard (a solution in 3% HNO_3 made from pure Mg metal) (Galy et al., 2003) having similar solution concentration as the sample (within 90%), typically 200–300 ppb, to correct for the instrumental mass bias. At least one other Mg rock standard [e.g., BCR-2 or SUNY MORB] was routinely analyzed during the course of an analytical session. With an uptake rate of 100 μl/min, a 200 ppb solution typically produced a 3.5–4 V ^{24}Mg signal (with a 10^{11} Ω resistor for the Faraday cups).

3.3. Precision and accuracy

During this study, samples with different matrices, including the pure Mg DSM3 standard solution as well as previously well-studied mineral and rock samples, have been analyzed to assess the precision and accuracy of our Mg isotopic measurements. The in-run precision on the ^{26}Mg/^{24}Mg ratio for a single measurement run of one block of 20 ratios is <±0.02‰ (2SD). The internal precision on the measured ^{26}Mg/^{24}Mg ratio based on ≥3 repeat runs of same sample solution during a single analytical session is <±0.10‰ (2SD). The external precision on the ^{26}Mg/^{24}Mg ratio, based on repeated analyses of a sample (including multiple full procedural replicates) performed over the course of this investigation is ≤±0.10‰ (2SD). For example, six total procedural replicates of KH olivine have $\delta^{26}Mg=-0.31\pm0.09$ and $\delta^{25}Mg=-0.14\pm0.08$ (2SD; see Table 1 for the definition of δ^{26}Mg and δ^{25}Mg). Furthermore, 28 repeat runs on BCR-2 performed during analytical sessions conducted over the course of this study give average values of $\delta^{26}Mg=-0.30\pm0.08$ and of $\delta^{25}Mg=-0.16\pm0.09$ (2SD), while 39 repeat runs on SUNY MORB yield average values of $\delta^{26}Mg=-0.28\pm0.06$ and of $\delta^{25}Mg=-0.14\pm0.06$ (2SD). Most previous studies of high-precision Mg isotope compositions have reported uncertainties in terms of the standard error of the mean ($2SE=2SD/\sqrt{n}$, where n is the number of repeat measurements). The uncertainties reported here are the standard deviation based on n repeat measurements (2SD) (Tables 1–3) and are typically more conservative than the 2SE values by at least a factor of two and represent our maximum, long-term external precision for measurements of the mass-dependent fractionation of Mg isotopes.

The accuracy of our Mg isotopic measurements was assessed in several ways. Several synthetic samples were analyzed, and these included a mixture of DSM3 with matrix elements (free of Mg) of a natural mineral (San Carlos olivine) and a rock (Allende) as well as a mixture of a natural rock sample (D119) with DSM3. These synthetic samples contained ≥20 μg Mg and were processed through the same analytical procedures as the natural samples (which also contained >20 μg Mg). The results show that these mixtures are isotopically indistinguishable from DSM3 (Table 1). Finally, six replicates of the Kilbourne Hole olivine (each with >50 μg of Mg) were processed through the cation exchange column (1–3

Table 1
Mg isotopic compositions of DSM3, synthetic Mg solutions, mineral and rock samples to test accuracy and precision

Sample	n[a]	δ^{26}Mg[b]	2SD[c]	δ^{25}Mg[b]	2SD	N[d]
Synthetic samples						
DSM3 (20 μg Mg)	5	0.00	0.10	0.00	0.05	1
SC ol matrix +20 μg Mg	7	−0.10	0.10	−0.05	0.09	2
Allende matrix +20 μg Mg	5	−0.10	0.10	−0.05	0.08	2
D119 (10%) + DSM3 (90%)	6	−0.01	0.06	0	0.04	2
KH olivine (procedural replicates)						
KH ol #1 (5.5 ml eluent)	3	−0.26	0.04	−0.11	0.06	1
KH ol #2 (6.5 ml eluent)	4	−0.31	0.06	−0.13	0.06	1
KH ol #3 (7.0 ml eluent)	7	−0.32	0.05	−0.15	0.06	1
KH ol #4 (6.5 ml eluent)	4	−0.29	0.05	−0.10	0.04	2
KH ol #5 (6.5 ml eluent)	4	−0.37	0.03	−0.20	0.05	2
KH ol #6 (5.5 ml eluent)	2	−0.32	0.12	−0.17	0.01	3
Average	24	−0.31	0.09	−0.14	0.08	
Shale (procedural replicates)						
D119 #1	6	0.02	0.05	0.03	0.03	2
D119 #2	4	0.03	0.03	0.01	0.04	2
D119 #3	4	0.04	0.06	0.03	0.03	2
Average	14	0.03	0.05	0.02	0.03	

[a] n = number of repeat measurements by MC-ICP-MS.

[b]

$$\delta^{x}\mathrm{Mg} = \left(\frac{\left(\frac{^{x}\mathrm{Mg}}{^{24}\mathrm{Mg}} \right)_{\mathrm{sample}}}{\left(\frac{^{x}\mathrm{Mg}}{^{24}\mathrm{Mg}} \right)_{\mathrm{DSM3}}} - 1 \right) \times 1000$$

where x = 25 or 26.

[c] 2SD = 2 times the standard deviation of the population of n repeat measurements of a sample solution.

[d] N = Number of passes through the cation exchange column.

passes, and using slightly different eluent volumes for the Mg cut) as were three replicates of the D119 shale composite (2 passes through the column for each); Table 1 shows that replicates of both samples have identical Mg isotopic compositions, indicating that our chemical separation procedure for Mg does not introduce any isotopic fractionation.

In addition to the samples discussed above, five well-studied mineral and rock samples that have been analyzed in different laboratories worldwide (i.e., the Allende and Murchison chondrites, the BCR-1 and BCR-2 rock standards, and San Carlos olivine) were measured and their Mg isotopic compositions are compared with previously reported data in Table 2. The Allende and Murchison carbonaceous chondrites have Mg isotopic compositions identical to previously published values when the equivalent 2SD errors are considered. The Mg isotopic compositions reported here of the BCR-1 and BCR-2 international basaltic standards are similar to each other, and identical to the value reported by Young and Galy (2004). However, these are somewhat lighter than the compositions reported by Wiechert and Halliday (2007), Baker et al. (2005) and Bizzarro et al. (2005) although still strictly within the 2SD uncertainties. Besides these rock samples, the San Carlos olivine measured in this study also has a Mg isotopic composition similar to that reported by Pearson et al. (2006) and Lundstrom (pers. comm.; sample solution is the same as that analyzed here) but different from that of Wiechert and Halliday (2007). This could result from a sampling difference and Mg isotopic heterogeneity in the San Carlos olivines, as has also been demonstrated by Pearson et al. (2006). These tests therefore demonstrate that we are

Table 2
Magnesium isotopic compositions of the Allende and Murchison chondrites, two oceanic (Loihi T402#1 and SUNY MORB) and two continental (BCR-1 and BCR-2) basalts and San Carlos olivine

Sample	n	δ^{26}Mg	2SD	δ^{25}Mg	2SD	Reference
Carbonaceous chondrites						
Allende	4	−0.37	0.06	−0.19	0.07	This study
Allende	14	−0.25	0.26	−0.13	0.15	Wiechert and Halliday (2007)
Allende	8	−0.36		−0.18	0.08	Baker et al. (2005)
Allende		−0.30	0.07	−0.16	0.03	Young and Galy (2004)
Murchison	4	−0.41	0.05	−0.21	0.05	This study
Murchison	13	−0.26	0.25	−0.14	0.14	Wiechert and Halliday (2007)
Murchison	8	−0.28		−0.14	0.06	Baker et al. (2005)
Basalts						
Loihi T402#1	4	−0.26	0.05	−0.14	0.05	This study
SUNY MORB	39	−0.28	0.06	−0.14	0.06	This study and Richter et al. (2007)
BCR-1	4	−0.34	0.06	−0.18	0.04	This study
BCR-1		−0.37	0.11	−0.19	0.07	Young and Galy (2004)
BCR-1	6	−0.09	0.27	−0.06	0.15	Wiechert and Halliday (2007)
BCR-2	28	−0.30	0.08	−0.16	0.09	This study
BCR-2 replicate	4	−0.36	0.09	−0.18	0.01	This study
BCR-2	15	−0.19		−0.09	0.07	Baker et al. (2005)
BCR-2	7	−0.17	0.35	−0.09	0.17	Bizzarro et al. (2005)
San Carlos olivine						
SC ol	4	−0.62	0.10	−0.30	0.04	This study
SC ol replicate	4	−0.73	0.06	−0.38	0.04	This study
SC ol		−0.59	0.16			Lundstrom (pers. comm.)
SC ol	6	−0.58	0.15	−0.28	0.10	Pearson et al. (2006)
SC ol	10	−0.64	0.31	−0.38	0.20	Pearson et al. (2006)
SC ol	5	−0.06	0.07	−0.03	0.04	Wiechert and Halliday (2007)

Table 3
Magnesium isotopic compositions of samples from the Kilauea Iki lava lake, Hawaii

Sample	MgO[a] (wt.%)	T[b] (°C)	n	δ^{26}Mg	2SD	δ^{25}Mg	2SD
KI81-1-169.9	26.87		10	−0.34	0.05	−0.19	0.05
KI67-3-6.8	25.83		6	−0.32	0.05	−0.18	0.07
KI81-1-210	24.53	1135	4	−0.31	0.01	−0.17	0.03
IKI-22	19.52	1216	4	−0.37	0.10	−0.21	0.02
KI79-3-150.4	13.51		4	−0.41	0.03	−0.23	0.07
KI75-1-38.9	12.46		4	−0.40	0.08	−0.23	0.02
KI67-3-39	10.73		3	−0.39	0.04	−0.21	0.17
IKI-58	8.08	1144	4	−0.42	0.10	−0.25	0.06
KI67-3-81	7.73	1055	4	−0.35	0.06	−0.23	0.02
KI75-1-121.5	7.50		4	−0.40	0.08	−0.21	0.03
KI75-1-75.2	5.77		4	−0.29	0.04	−0.16	0.08
KI67-2-85.7	2.60	1060	6	−0.35	0.05	−0.19	0.06
KI81-2-88.6	2.37		7	−0.41	0.07	−0.21	0.07
Average			64	−0.36	0.10	−0.20	0.07

[a] MgO data for Kilauea Iki lavas from Helz et al. (1994) and Murata and Richter (1966).

[b] Quench temperatures estimated by the MgO geothermometry (Helz and Thornber, 1987).

able to measure accurately and precisely (i.e., within the 2SD uncertainties noted in Tables 1–3) the Mg isotopic compositions of natural samples.

4. Results and discussion

Twenty out of the twenty two samples analyzed here, including Kilbourne Hole olivine (KH olivine; Table 1), BCR-1, BCR-2, SUNY MORB, Loihi basalt, and the Murchison and Allende chondrites (Table 2), as well as the thirteen Kilauea Iki lavas (Table 3), have similar Mg isotopic compositions within the errors, with δ^{26}Mg varying from −0.42 to −0.26 and δ^{25}Mg from −0.25 to −0.11. The two exceptions are the shale sample D119 (Table 1) that has the heaviest Mg isotopic composition (δ^{26}Mg$=0.03\pm0.05$ and δ^{25}Mg$=0.02\pm0.03$; 2SD) and the San Carlos olivine (Table 2) that has the lightest Mg isotopic composition (δ^{26}Mg$=-0.67\pm0.08$ and δ^{25}Mg$=-0.34\pm0.04$, 2SD). In both cases, secondary and/or low-temperature processes (for example, metasomatism or weathering) may have resulted in the wider range of Mg isotope compositions recorded by these samples.

4.1. The absence of Mg isotope fractionation during basalt differentiation

Kilauea Iki lava lake formed during a single eruption and the wall rock is compositionally similar to the Kilauea basalt. Although the 1959 eruption was a mixed-magma eruption (Wright, 1973; Helz, 1987) and the olivine phenocryst population is heterogeneous (Helz, 1987), mixing during the eruption and subsequent settling of crystals in the small lava lake have erased any potential source heterogeneity. Therefore, any Mg isotopic variation, if present, should reflect subsequent crystallization and internal differentiation within the lava lake. The Mg isotopic compositions of thirteen samples, including original eruption picritic tholeiites, chilled picrite, and the moderately as well as the highly differentiated basalts, are identical within our external precision (Fig. 2), which indicates that no measurable isotope fractionation occurred during crystal-liquid fractionation at temperatures of ≥1055 °C. Statistical tests confirm this, and indicate that all Kilauea Iki lavas sample a uniform reservoir characterized by a mean δ^{26}Mg of -0.36 ± 0.10 (2SD, $\chi_{12}^2=0.70_{0.35}^{2}$, where the right-hand subscript and superscript refer to the range between which 95% of the expected reduced χ^2 values would be found for a sample set with 12 degrees of freedom) and a mean δ^{25}Mg of -0.20 ± 0.07 (2SD, $\chi_{12}^2=0.48_{0.35}^{2}$).

The large chemical variations in Kilauea Iki lavas with MgO>7.0 wt.% result almost entirely from post-eruptive redistribution of olivine phenocrysts ($Fo_{86\pm1}$), with the upper part of the lake depleted and the lower part enriched in olivine (Wright, 1973; Helz, 1987). If the olivine redistribution follows the process of fractional crystallization, as an extreme end-member case, then the maximum Mg isotopic fractionation factor between olivine and melt ($^{26/24}\alpha_{ol/melt}=(^{26}Mg/^{26}Mg)olivine/(^{26}Mg/^{26}Mg)melt$) at temperatures of ≥1055 °C can be constrained. Using the 2SD external uncertainty of

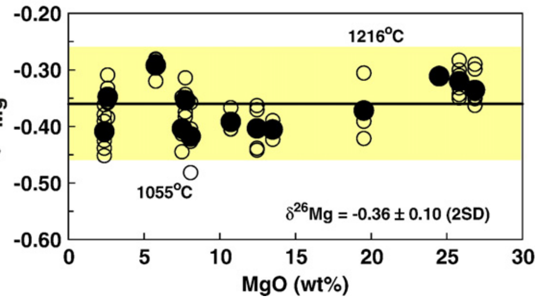

Fig. 2. δ^{26}Mg versus the degree of differentiation as represented by the MgO content for Kilauea Iki lavas. Open circles show results of individual measurements, while the solid circles show the averages for each sample. The long-term external uncertainty (2SD) of ±0.10‰ is shown as the yellow band. Solid line represents the average δ^{26}Mg value of −0.36 for all Kilauea Iki lavas. Minimum and maximum quench temperatures are also indicated. Data from Table 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

±0.10‰ as the maximum isotopic fractionation in the $^{26}Mg/^{24}Mg$ ratio and 26 wt.% olivine crystallization (Wright, 1973), the fractionation factor is calculated to be $0.99993 \leq {}^{26/24}\alpha_{ol/melt} \leq 1.00007$ (Fig. 3), i.e., there is a maximum 0.07‰ fractionation in the $^{26}Mg/^{24}Mg$ ratio between olivine and melt at $T \geq 1055$ °C.

A recent study showed that lunar basalts exhibit significant Mg isotopic variation which was attributed to isotopic fractionation during magmatic differentiation in the lunar magma ocean (Wiechert and Halliday, 2007). In contrast, the results presented here indicate that the Mg isotopic variation in lunar basalts more likely reflects other processes such as source heterogeneity or secondary alteration rather than equilibrium isotopic fractionation during high-T magmatic differentiation. On the other hand, our results also confirm that terrestrial basalts are isotopically lighter than the mantle clinopyroxene and olivine analyzed by Wiechert and Halliday (2007), which these authors interpreted as reflecting a small equilibrium fractionation between basaltic melt and mantle minerals. However, the Mg isotopic compositions of mantle minerals have been shown to be extremely heterogeneous (>2‰ amu^{-1}) as demonstrated by a more comprehensive study of mantle minerals from both Archean cratons and Phanerozoic fold belts (Pearson et al., 2006). Therefore, given the data available so far, the Mg isotopic difference between basalts and peridotite minerals cannot be inferred as equilibrium Mg isotopic fractionation during mantle melting and basaltic differentiation.

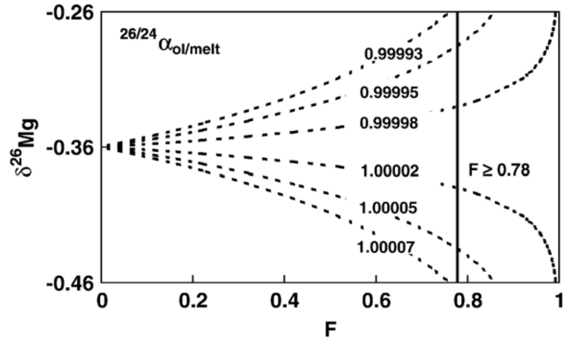

Fig. 3. Constraints on the maximum Mg isotopic fractionation factor between olivine and melt $\left({}^{26}_{24}\alpha_{olmelt} = \frac{\left(\frac{^{26}Mg}{^{24}Mg}\right)\text{olivine}}{\left(\frac{^{26}Mg}{^{24}Mg}\right)\text{melt}}\right)$ allowed by the Mg isotope compositions of the Kilauea Iki lavas. F: the mole fraction of Mg removed by olivine crystallization. The minimum F of 0.78 is calculated based on 26 wt.% olivine ($Fo_{86\pm1}$) crystallization with 15.43 wt.% of MgO in the original Kilauea Iki lava (Wright, 1973). In order to produce ≤±0.10‰ variation in $\delta^{26}Mg$ (i.e., equal to or less than the 2SD uncertainty of the $\delta^{26}Mg$ value for all Kilauea Iki lavas), the ${}^{26}_{24}\alpha_{olmelt}$ must be within the range of 0.99993 to 1.00007.

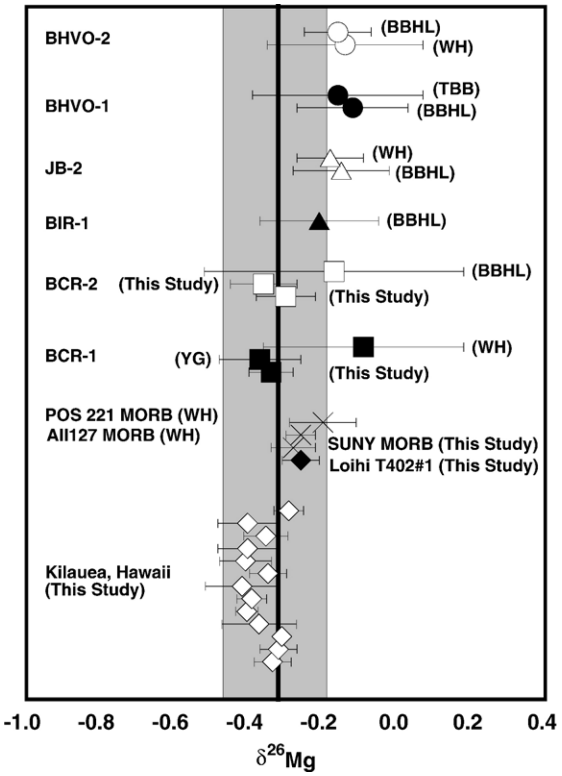

Fig. 4. Compilation of all available Mg isotopic data for terrestrial basalts. The solid line represents the weighted average $\delta^{26}Mg$ value calculated from the Mg isotopic compositions of all basalts (−0.32) and grey band represents the average Mg isotopic composition of chondrites, i.e., −0.33±0.14 (2SD), based on all available data. Data are from Tables 2 and 3 (this study), Bizzarro et al. (2005) (BBHL), Thrane et al. (2006) (TBB), Wiechert and Halliday (2007) (WH) and Young and Galy (2004) (YG) ($\delta^{26}Mg$ values for BHVO-1, BIR-1 and BCR-2 from Baker et al. (2005), for which uncertainties were not reported, are not shown here). All uncertainties are 2SD.

4.2. Implications for Mg isotope geochemistry of the mantle

Studies of olivines from peridotite xenoliths do not present a clear picture of the Mg isotope composition of the terrestrial mantle, mainly due to overprinting by mantle metasomatism (Pearson et al., 2006). In this work, we have demonstrated that Mg isotopes are not fractionated beyond the limits of our current analytical precision during magmatic differentiation. As such, the implication is that the Mg isotope composition of terrestrial basalts reflects that of the mantle. Continental basalts (BCR-1 and BCR-2) and two additional oceanic basalts analyzed in this study have Mg isotopic compositions similar to the Kilauea Iki lava lake samples and agree with previously published data for basaltic samples within the 2SD uncertainties (Fig. 4). These compositions are additionally similar to those of the Allende and Murchison carbonaceous chondrites analyzed here and the ordinary and carbonaceous chondrites (also including Allende and Murchison) measured by Wiechert and Halliday (2007) (Fig. 4). The similarity in the Mg isotope compositions of terrestrial basalts and chondrites indicates that the mantle (and thus the BSE) has a chondritic Mg isotopic composition. This obviates the need for a model such as that of Wiechert and Halliday (2007) (i.e., involving sorting of chondrules and calcium–aluminum-rich inclusions in the proto-planetary disk), which would be required to explain a non-chondritic Mg isotopic composition for the BSE.

5. Conclusions

The chemically diverse Kilauea Iki lavas exhibit no resolvable variations in their Mg isotopic compositions. As such, these samples reflect a lack of any detectable Mg isotopic fractionation during crystal-melt fractionation at temperatures of ≥1055 °C. The homogenous Mg isotopic compositions of bulk rock samples of lavas indicate that fractionation in the $^{26}Mg/^{24}Mg$ ratio between olivine and melt during olivine crystallization at $T \geq 1055$ °C is less than 0.07‰. These results are thus consistent with the view that equilibrium fractionation of Mg isotopes at high temperatures is insignificant and that the Mg isotopic composition of a basalt reflects that of its mantle source reservoir.

Compared with peridotites, which are significantly heterogeneous in Mg isotopic compositions, basalts analyzed so far have relatively homogeneous Mg isotopic compositions, which are similar to those of chondrites. This suggests that the BSE has a chondritic Mg isotopic composition. Nevertheless, the database of Mg isotopic compositions is still very limited. In order to make robust inferences regarding the Mg isotopic compositions of the Bulk Silicate Earth, more systematic studies on samples from a variety of crustal and mantle settings are needed.

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