Potassium isotope systematics of oceanic basalts

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Abstract

High-temperature isotope fractionation during partial melting and other igneous differentiation processes has been observed in many non-traditional isotope systems. The potassium (K) isotope system has not been extensively investigated historically due to the lack of high-precision analysis methods; however, the recent development of the Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) now allows for high-precision potassium isotope analysis. In this study, we utilized this new method to analyze 51 geologically, geographically, and geochemically diverse oceanic basalt samples including 32 mid-ocean ridge basalts (MORB), 3 back-arc basin basalts (BABB), and 16 oceanic island basalts (OIB). We observed a limited variation of $^{41}\text{K}/^{39}\text{K}$ ratios across our spread of samples. This variation in mantle-derived rocks is restricted compared to the large K isotopic fractionation observed in low-temperature systems. The averages of MORBs, BABBs, and OIBs are $^{41}\text{K}/^{39}\text{K} = 0.44 \pm 0.17$‰ (2sd), $^{41}\text{K}/^{39}\text{K} = 0.44 \pm 0.08$‰, and $^{41}\text{K}/^{39}\text{K} = 0.41 \pm 0.16$‰, respectively, and there is no geographical variation (e.g., Indian vs. Pacific MORBs) in terms of K isotopes. Among all samples, there are two outliers, in which we have observed evidence of secondary mineral formation (i.e., palagonite) due to interaction with seawater. These two outliers have a K isotopic composition significantly heavier than other unaltered samples, close to the K isotopic composition of seawater. The grand average of all pristine samples is $^{41}\text{K}/^{39}\text{K} = 0.43 \pm 0.17$‰ (2sd) which agrees well with the Bulk Silicate Earth (BSE) value previously defined. This new study indicates the homogeneity of K isotopes in the mantle and suggests that, since K will not resolvably fractionate during partial melting, any observable fractionation of K isotopes in primitive basalts is likely due to low-temperature, post-eruptive alteration processes. This conclusion is critical for understanding the initial bulk composition of the Earth and it is essential for any interplanetary comparison.

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1. INTRODUCTION

The implications of understanding potassium (K) geochemistry are numerous. K is an incompatible lithophile, fluid-mobile alkali metal, and is the eighth most abundant element in the Earth’s crust and the fifteenth most abundant element in the bulk Earth (McDonough and Sun, 1995; Rudnick and Gao, 2003). It has only two stable isotopes, $^{39}\text{K}$ (abundance 93.26%) and $^{41}\text{K}$ (6.73%), and one long-lived radioactive isotope, $^{40}\text{K}$ (abundance 0.01%, $t_{1/2} \approx 1.25$ Gyr), which decays to $^{40}\text{Ar}$ and $^{40}\text{Ca}$ (de Laeter et al., 2003). Due to its incompatibility during melt-
ing and mobility in fluid. K preferentially enters melts/flu-
ids, allowing it to potentially be used as a tracer during sub-
duction, crust-mantle interaction, surface silicate
weathering, and seafloor reverse weathering processes
(Teng et al., 2017; Santiago Ramos et al., 2018).

The K isotope system was first extensively investigated
by Humayun and Clayton in 1995, who found no signifi-
cant K isotope fractionation among any terrestrial samples.
However, in the last two years, this conclusion has been
revised due to the improved precision of analytical tech-
niques using Multi-Collector Inductively Coupled Plasma
Mass Spectrometry (MC-ICP-MS) (Li et al., 2016; Wang
and Jacobsen, 2016; Morgan et al., 2018; Hu et al., 2018).
So far, few samples have been analyzed for their K isotope
compositions using these new high-precision techniques,
and we are still faced with two unknowns: the K iso-
topic composition of the mantle, and whether or not the mantle
is homogeneous for K isotopes.

Traditionally, mantle xenoliths have been used to infer
the composition of the lithospheric mantle (Pearson et al.,
2003). However, the K abundance of mantle xenoliths is
extremely low (avg = 0.05% K2O by weight, McDonough,
2003). However, the K abundance of mantle xenoliths is
the composition of the lithospheric mantle (Pearson et al.,
is homogeneous for K isotopes.
composition of the mantle, and whether or not the mantle
and Jacobsen, 2016; Morgan et al., 2018; Hu et al., 2018).
mass located at various ridge sections; of our 32 total
MORB samples, 14 are from the Mid-Atlantic Ridge, 10
are from the East Pacific Rise, 3 are from the Red Sea,
1 is from the Galapagos Spreading Center, and 4 are from
the Gulf of Aden (Fig. 1). Samples vary in chemical com-
position, with Mg, K, and Ti abundances ranging from 6.7
to 9.2 wt.% MgO, 0.04 to 0.38 wt.% K2O, and 0.76 to 2.11
wt.% TiO2 (Fig. 2) with K2O/TiO2 ratios ranging from
0.02-0.25.

The 3 BABBs are from the North Fiji Basin and are
not resolvable by subduction processes and
thus their major and trace element geochemistry are
effectively indistinguishable from that of MORBs. Samples
vary in Mg, K, and Ti composition from 7.31 to
7.46 wt.% MgO, 0.12 to 0.24 wt.% K2O, and 1.59 to
1.60 wt.% TiO2, with K2O/TiO2 ratios ranging from
0.07-0.15 (Marty and Zimmermann, 1999; Teng et al.,
2013).

Oceanic basalts (OIBs) are often sourced from the
deep mantle (relative to MORBs) and typically are iso-
topically and chemically more variable than MORBs
(Hofmann, 1997). This heterogeneity can be accounted
for by the involvement of at least five mantle end mem-
biers (see Appendix A).

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(Hofmann, 1997). This heterogeneity can be accounted
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2. MATERIALS

We selected a set of 51 basalt samples comprising 32
MORB glasses, 3 BABBs, and 16 OIBs from a wide range
of geographic locations and geochemical character. Major-
and trace-element abundances have been reported else-
where (Fisk et al., 1982; Schilling et al., 1983; Marty and
Zimmermann, 1999; le Roux et al., 2002; Kelley et al.,
2013; Teng et al., 2013). A complete list of samples and a
map giving sample source locations are presented in Table
1 and Fig. 1, respectively.

MORBs can be divided into five main types: D
depleted), N (normal), T (transitional), E (enriched),
and P (plume-influenced). Since rare earth element
(REE) analyses (e.g., La/Sr) were not available for all
samples, MORB type determination in this study was lim-
ited to the three classes (N, E, and T) that can be deter-
mined using K2O/TiO2 (see Table 1 footnotes) according
to Marty and Zimmerman (1999). The MORB samples
in this study include pristine N-MORB, T-MORB, and
E-MORB samples sourced from quenched submarine mag-
mas located at various ridge sections; of our 32 total
MORB samples, 14 are from the Mid-Atlantic Ridge, 10
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for by the involvement of at least five mantle end mem-
biers (see Appendix A).
Table 1
Potassium isotopic compositions of oceanic basalts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Location</th>
<th>Amount dissolved (mg)</th>
<th>K₂O%</th>
<th>δ⁴¹K</th>
<th>95% c.i.</th>
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* Type: N = Normal, K₂O/TiO₂ < 0.08; T = Transitional, 0.08 < K₂O/TiO₂ < 0.13; E = Enriched, K₂O/TiO₂ > 0.13; (Marty and Zimmerman, 1999). TiO₂ data from Fisk et al., 1982; Kelley et al., 2013; le Roux et al., 2002; Marty and Zimmermann, 1999; Schilling et al., 1983; Teng et al., 2013.

95% c.i. = 95% Confidence Interval.

n = number of runs.

K₂O concentration for BHVO-2 from Jochum et al. (2016).
3. ANALYTICAL METHOD

The analytical method used in this study is similar to the methods reported by other groups (Li et al., 2016; Wang and Jacobsen, 2016a, 2016b; Morgan et al., 2018; Hu et al., 2018). Samples were prepared and analyzed in four steps: digestion in acid, purification for K using ion-exchange chromatography, concentration analysis using iCapQ quadrupole ICP-MS, and finally, isotope analysis using the Neptune Plus MC-ICP-MS.

3.1. Digestion

Pure glass fragments of each sample were selected and ground into a fine powder using an agate mortar and pestle. Both the mortar and pestle were cleaned thoroughly with 4N nitric acid and Milli-Q water before and after each sample. The sample literature K$_2$O concentrations (see Table 1 footnotes) show that between 40–70 mg of each sample are sufficient for our analyses. Powder was weighed out into Teflon beakers and weights were recorded for each sample (see Table 1).

The samples were then digested in two steps: first, we added 6 mL of a 3: 1 mixture of concentrated hydrofluoric acid (HF) and nitric acid (HNO$_3$) to each beaker and allowed the beaker to sit under heat lamps for a minimum of five days, at which point the beakers were opened and the solution was allowed to evaporate; second, 3 mL of 6N hydrochloric acid (HCl) was added to each beaker, and beakers were sealed for an additional day before the solution was evaporated for the final time. All samples were completely digested resulting in clear solutions.

3.2. Sample Purification

The sample purification method used here was first proposed by Strelow et al. (1970) and later widely adopted (Humayun and Clayton, 1995; Li et al., 2016; Wang and Jacobsen, 2016a, 2016b; Morgan et al., 2018; Hu et al., 2018). First, dried-down samples from the previous step were rehydrated in 0.7N HNO$_3$. The samples were then run through one cycle of “big column” followed by one cycle of “small column” ion-exchange chromatography columns. Both columns are filled with AG50-X8 100–200 mesh cation-exchange resin. Several mL (5 for big columns, 2 for small columns) are collected immediately before and after the K cut for the purpose of determining if any K is lost during this process; these are referred to as the pre- and post-cuts.

3.3. Elemental and isotopic analysis

After the K cut was collected from the final cycle of small column chemistry, we analyzed each sample with the Thermo Fisher Scientific iCapQ quadrupole ICP-MS to make sure that K was the primary element collected during the sample purification process and to acquire the concentration of K in each sample. If any other elements are present in abundance >1% relative to K, the sample must be run through another small column cycle to remove these.
elements, thereby avoiding matrix effects. Additionally, we analyze the pre- and post-cuts collected in both the big and small column cycles to determine if any K was lost outside of our cut; this serves to both double-check our column chromatography methodology, ensuring K recovery of >99%, and make sure the K concentrations are accurate.

The concentrations of each sample acquired by iCapQ were used to match our K bracketing standard (300 ppb NIST SRM3141a) within 3%. Once matched, samples were run through MC-ICP-MS. We measured each sample ~10 times using the sample-standard bracketing technique and the averages of the ~10 measurements are reported. The K isotope compositions are expressed using the per mil (‰) notation of $\delta^{41}\text{K}$ for $^{41}\text{K}/^{39}\text{K}$ ratio, where $\delta^{41}\text{K} = \left( \frac{^{41}\text{K}_{\text{sample}}}{^{41}\text{K}_{\text{NIST SRM3141a}}} - 1 \right) \times 1000$. The internal (within-run) reproducibility (95% confidence interval) of ~10 measurements is given for each sample in Table 1, and the typical reproducibility is ~0.05 ‰. The long-term (11 month) external reproducibility, evaluated with geo-standard BHVO-2, is ~0.11 ‰ (2S.D.; 2 standard deviation; Chen et al., 2019).

4. RESULTS

The 32 MORB samples had an average of $-0.44\%e \pm 0.17$ (2S.D.), with $\delta^{41}\text{K}$ values ranging from $-0.25\%e$ (TR154 19D) to $-0.66\%e$ (EN026 14D) (Fig. 3a). A plot of $\delta^{41}\text{K}$ values grouped by MORB type shows no measurable distinction between N-, E-, and T-type MORB (Fig. 4b). The three BABB samples had $\delta^{41}\text{K}$ values of $-0.40$, $-0.43$, and $-0.50\%e$, giving an average of $-0.44\%e \pm 0.08$ (2S.D.) for the BABB group (Fig. 3b).

The OIB had an average of $-0.41\%e \pm 0.16$ (2S.D.), overall slightly heavier than MORB and BABB; however, this discrepancy is not statistically significant (Fig. 3c). Two samples from the same seamount in the Society Islands (DTH03-02 and DTH03-03) had values ($\delta^{41}\text{K} = 0.03\%e$ and $0.01\%e$, respectively) close to seawater ($0.10 \pm 0.07\%e$; Wang and Jacobsen, 2016b). A closer examination of these two samples revealed evidence of aqueous alteration in the form of the mineral palagonite, an alteration product from the interaction of seawater. Thus, these samples cannot be classified as “pristine” and were excluded from both our OIB and overall average. Excepting the two outliers above, the OIB group had $\delta^{41}\text{K}$ values ranging from $-0.30\%e$ (TH14-03) to $-0.57\%e$ (TH14-02). The slightly greater scattering observed among MORB samples relative to BABB and OIB is likely due to the larger sample size (n = 14 for OIB versus n = 32 for MORB).

Results for each group are presented in Fig. 2 and results for each individual sample are presented in Table 1.

5. DISCUSSION

5.1. Variations in K isotopic composition in MORB, BABB, and OIB

The lack of variation between MORB, BABB, and OIB, which all come from different mantle sources (Hofmann, 2007), suggests that there are likely no measurable K isotopic differences between their mantle sources and that the mantle has a homogeneous $\delta^{41}\text{K}$ (Fig. 4). Furthermore, plots of $\delta^{41}\text{K}$ versus $[\text{K}_2\text{O}]$, $[\text{SiO}_2]$, $[\text{K}_2\text{O}]/[\text{TiO}_2]$, $[\text{MgO}]$, and $[\text{Na}_{8.0}]$ yielded no observable correlation within any sample group (Fig. 5a-f). $\text{Na}_{8.0}$ index (calculated as $[\text{Na}_2\text{O}] + 0.373 \times [\text{MgO}]) - 2.98$) reflects the degree of partial melting in the source (higher $\text{Na}_{8.0}$ indicates lower degrees of partial melting, and vice versa) and has been used in previous studies to correct for the effects of fraction-
Fig. 3. Distribution of $\delta^{41}$K values from this study for (a) MORBs, (b) BABBs, and (c) OIBs. The OIB histogram includes two outliers DTH03-02 and DTH03-03 that are excluded from our average calculations and subsequent figures.

Fig. 4. $\delta^{41}$K values for pristine samples compared by (a) basalt type, (b) MORB type, (c) MORB source location, and (d) OIB source location. The dashed line and gray shaded area represents the BSE value defined by this study ± 2 standard deviation.
The lack of a resolvable, systematic variation in any of the plots ($\delta^{41}$K versus [K$_2$O], [SiO$_2$], [K$_2$O]/[TiO$_2$], [MgO], and [Na$_8.0$]) presented in Fig. 5 suggests that all sources have the same original K isotopic composition (i.e., the mantle is homogeneous in terms of K isotope composition) and that this K isotopic composition remained unchanged throughout magmatic evolution because K isotopes are not resolvably fractionated by igneous differentiation processes as long as K behaves as a highly incompatible element. This is significant in that it indicates the K isotopic composition of a sample represents the K isotopic composition of its source.

5.2. Estimation of the K isotopic composition of the mantle and implications for interplanetary comparison

Together, MORB ($\delta^{41}$K = $-0.44 \pm 0.17 \permil$, 2S.D., n = 32), BABB ($\delta^{41}$K = $-0.44 \pm 0.08 \permil$, 2S.D., n = 3), and OIB ($\delta^{41}$K = $-0.41 \pm 0.16 \permil$, 2S.D., n = 14) samples from across the world are isotopically homogeneous for K isotopes within uncertainties (Fig. 4a). Our 49 pristine samples had an overall average of $-0.43 \pm 0.17 \permil$ (2sd). With uncertainty, this average agrees with the BSE value of $-0.48 \pm 0.03 \permil$ (2S.D.; Wang and Jacobsen, 2016b) defined with three samples. This overall average of global basaltic samples also agrees well with basaltic samples reported from other groups (Li et al., 2016; Morgan et al., 2018; Hu et al., 2018). The average also generally agrees with the K isotopic compositions of nearly all igneous rocks except for pegmatites (Morgan et al., 2018). It also appears, as predicted by theory, that K isotopes do not fractionate during partial melting and other high-temperature igneous differentiation processes in the absence of a significant K-bearing phase (Wang and Jacobsen, 2016a).

Thus, from the average of 49 unaltered terrestrial basalts investigated here, we define the K isotopic composition of the mantle as $-0.43 \pm 0.17 \permil$ (2S.D., n = 49) relative to NIST SRM3141a. Owing to the lack of K isotope fractionation during mantle melting and differentiation of basaltic melts, this mantle average should be representative of the Bulk Silicate Earth (BSE).

This newly defined value for the BSE can be used for interplanetary comparison. As shown in Fig. 6, this K isotope composition of the BSE is marginally higher, however statistically indistinguishable from that of the CI chondrite ($-0.53 \pm 0.10 \permil$; Wang and Jacobsen, 2016a), the most primitive and most volatile-rich material in the solar system. This conclusion still agrees with Humayun and Clayton (1995), although analytical precision has improved.
Martian meteorites (−0.36 ± 0.12 ‰; Tian et al., 2018). However, this K isotopic composition of the BSE is significantly different from that of the Moon (−0.04 ± 0.04‰; Wang and Jacobsen, 2016a). Apollo lunar samples show a significant enrichment of heavy K isotopes compared to terrestrial samples and this result has been explained as the result of a high-energy and high-angular-momentum Giant Impact origin of the Moon from evaporated terrestrial material (Lock et al., 2018); however, this conclusion is still controversial (Dauphas, 2018). Further investigation of whether K isotopes can be used to test different lunar formation models is still needed.

5.3. Potential of K isotopes as a tracer of subducted oceanic crust

The homogeneity of K isotopes among terrestrial basalts, and the suggested lack of significant K isotope fractionation during igneous differentiation and partial melting, is consistent with other isotope systematics in basalts, perhaps most notably that of lithium (Li). Although Li is more compatible than K, the isotope systematics of the two systems are quite similar in oceanic basalts: the Li isotopes in MORBs show a relatively restricted range (Chan et al., 1992; Niu et al., 1999; Regelous et al., 1999; Chan et al., 2002; Tomascak et al., 2008; Marschall et al., 2017) and most OIBs are similar to MORBs in terms of Li isotope ratios, except for some HIMU basalts (Nishio et al., 2004; Chan et al., 2009; Vlastélic et al., 2009). These differences were explained as results of either alteration by seawater, assimilation of altered basalts, or diffusion (Chan and Frey, 2003; Chan et al., 2009; genske et al., 2014).

Altered basalts in both this study and studies of Li isotopes show clear seawater signatures (e.g., Chan et al., 2002, 1992). Both the K and Li isotopic compositions of seawater are significantly different from those of the Bulk Silicate Earth value (i.e., fresh MORB value), proposed reasons for which include high-temperature hydrothermal input, continental weathering, “reverse weathering” characterized by the preferential uptake of $^{39}$K and $^{6}$Li during the formation of aluminosilicates, and low-temperature alteration of oceanic crust (Bloch and Bischoff, 1979; Staudigel and Hart, 1983; Kronberg, 1985; Santiago Ramos et al., 2018). As shown in the two palagonite-bearing altered basalts (DTH03-02 and DTH03-03), their $\delta^{41}$K values are significantly heavier than those of pristine basalts and are indistinguishable from the seawater value. Thus, through the exchange of K (and Li) between seawater and basalts, the $\delta^{41}$K (and $\delta^{6}$Li) values of the altered basalts are elevated to values closer to those of seawater. Such low-temperature alteration processes are the major mechanisms responsible for changing the K (and Li) isotope compositions of submarine basalts. Compared to low-temperature seafloor alteration processes, igneous fractionation processes produce negligible K isotope fractionation. Thus, K isotopes, together with Li isotopes, could be indicators of subducted (altered) oceanic crust. Further study of the K isotopic composition of altered samples will be needed to probe the robustness of K as a potential tracer.

Fig. 6. Comparison showing the average K isotopic compositions ±2S.D. for the Bulk Silicate Earth estimated in this study (also indicated by the dashed line and gray bar), CI Chondrites (Wang and Jacobsen, 2016a), Mars (Tian et al., 2018), and Howardite/Eucrite/Diogenite (HED) parent body (Tian et al., 2018).

This newly defined K isotopic composition of the BSE is also indistinguishable from the K isotopic composition of
6. CONCLUSION

In this study, we measured the K isotopic composition of a wide range of MORB, BABB, and OIB from different localities. The main conclusions to be drawn from this study are:

(1) The mantle is isotopically homogenous for K, within uncertainties, and there is no statistically significant difference in $\delta^{41}$K values between MORBs, BABBs, and OIBs.

(2) Together, 32 globally sourced MORBs, 3 BABBs, and 14 OIBs define a BSE $\delta^{41}$K value of $-0.43 \pm 0.17$ (2S.D.).

(3) Post-eruptive processes such as aqueous alteration can significantly fractionate K, and further studies of altered basalts are necessary to determine to what extent K is fractionated by such processes.

(4) The K isotopic composition of pristine, unaltered basalts can likely be used to infer the K isotopic composition of their source, since K does not appear to significantly fractionate during basaltic differentiation.

Declaration of Competing Interest

None.

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APPENDIX A

Detailed descriptions of OIB sample sources

Generally, isotopic heterogeneity in the mantle can be accounted for by the mixing and partial mixing of at least five mantle end members: HIMU (high ‘μ’, or high 238U/204Pb), EM-1 and EM-2 (enriched mantle 1 and 2, respectively), DMM (depleted MORB mantle), and the hypothesized FOZO (FOcal ZOne, with Pb and Sr values respectively), DMM (e.g., White and Duncan, 2013), and trend towards the EM-2 mantle endmembers (Teng et al., 2013). Polynesian samples investigated in this study are from the Society (n = 12) and Cook-Austral (n = 2) chains. Of the Society samples, 1 is from the Rocord Seamount, 8 from the Teahitia Seamount, and 2 from an unnamed seamount termed “Seamount #2” (Marty and Dauphas, 2003). Compared to other oceanic island basalts, Society basalts have intermediate 206Pb/204Pb Pb ratios and Sr and Nd isotope ratios ranging from intermediate to extremely high and extremely low, respectively, are enriched in incompatible elements relative to the DMM (e.g., White and Duncan, 2013), and trend towards the EM-2 component on the mantle array.

Both Cook-Austral samples investigated here are from the MacDonald Seamount, an active submarine volcano located at the southeastern terminus of the Cook-Austral chain. The Cook-Austral chain is one of the two regions on Earth (the other being St. Helena in the Atlantic) where the most typical HIMU basalts occur (Kogiso et al., 1997).

APPENDIX B. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gca.2019.06.001.

REFERENCES


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