

K isotopes as a tracer of seafloor hydrothermal alteration

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At ocean spreading ridges, circulation of seawater through rock at elevated temperatures alters the chemical and isotopic composition of oceanic crust. Samples obtained from drilling into ocean floor and from ophiolites have demonstrated that certain isotope systems, such as ¹⁸O/¹⁶O and ⁸⁷Sr/⁸⁶Sr, are systematically modified in hydrothermally altered oceanic crust. Although K is known to be mobile during hydrothermal alteration, there have not yet been any K-isotope analyses of altered oceanic crustal materials. Moreover, the ⁴¹K/³⁹K of seawater was recently found to be significantly higher than that of igneous rocks, so the addition of seawater K to oceanic crust would be expected to generate ⁴¹K/³⁹K variations in affected rocks. Here, we report high-precision ⁴¹K/³⁹K measurements for samples from the Bay of Islands ophiolite, and we document large variations in ⁴¹K/³⁹K, covarying with previous determinations of ⁸⁷Sr/⁸⁶Sr. Our data indicate that analytically resolvable ⁴¹K/³⁹K effects arise in oceanic crust as a result of hydrothermal alteration. This finding raises the possibility that ⁴¹K/³⁹K can be used as an effective tracer of oceanic crust recycled into the mantle, as a diagnostic criterion by which to identify ancient fragments of oceanic crust, and as a constraint on the flux of K between oceanic crust and seawater.

potassium isotopes | hydrothermal alteration | ocean crust | ophiolite

Hydrothermal circulation occurring at the seafloor exerts a profound influence over the distribution of elements among the earth's oceans, crust, and mantle. According to geophysical and geochemical estimates, the volume of the oceans is circulated through ridge axes on a timescale of tens of millions of years, and through ridge flanks on a timescale of tens to hundreds of thousands of years (1, 2). Heat transfer associated with hydrothermal circulation is a critical factor controlling processes of magma crystallization at midocean ridges (3) and, hence, the differentiation of oceanic crust and depleted mantle. Additionally, interaction of seawater and rock over a range of temperatures entails diverse chemical reactions, and results in significant elemental fluxes between seawater and oceanic crust.

One approach to quantifying these fluxes is to measure chemical and isotopic variations imparted to oceanic crust by hydrothermal alteration (4, 5). Such measurements of hydrothermally altered crust have been useful in constraining estimates for the hydrothermal fluxes of particular elements into or out of seawater (6–8). Characterizing the elemental and isotopic composition of altered crust also provides a means of tracking oceanic crust as it is subducted, mixed into the mantle, and incorporated into island–arc, ocean–island, and midocean-ridge volcanic products (9–11). For these purposes, ¹⁸O/¹⁶O and ⁸⁷Sr/⁸⁶Sr ratios have been used extensively, and a number of other isotope systems have been used as well.

Potassium is known to be mobile during seafloor hydrothermal alteration. Studies of hydrothermal vent fluids near ridge axes have documented that, in high-temperature environments, K is leached from oceanic crust (12, 13). However, studies of in situ oceanic crust sampled by drilling reveal that altered basalts have much higher K content than fresh midocean-ridge basalt (MORB), indicating a net flux of K into the rock (6–8, 14, 15). Measured pore-water profiles also indicate consumption of K by oceanic crust at lower temperatures (16). These observations are consistent with experimental work showing that K is leached from

basalt at temperatures greater than 150 °C, but consumed by basalt at temperatures less than 70 °C (17). Until recently it was not feasible to test how these alteration processes affected the ⁴¹K/³⁹K ratios of oceanic crust, owing to limitations in the precision of the measurement. New analytical methods have, however, made high-precision determination of ⁴¹K/³⁹K ratios possible (18, 19).

For this study, we have analyzed six samples from the Blow Me Down (BMD) massif of the Bay of Islands (BOI) ophiolite, Newfoundland, Canada, for ⁴¹K/³⁹K ratios, to test whether seafloor hydrothermal alteration has measurably shifted the ⁴¹K/³⁹K ratios of the rocks. The ⁴¹K/³⁹K ratios were determined using an Isoprobe-P multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) equipped with a collision and reaction cell that greatly reduces undesired Ar interferences. Isotope data are expressed as parts per thousand deviations from an estimate of bulk silicate earth (BSE): $\delta^{41/39}\text{K} = ((^{41}\text{K}/^{39}\text{K})_{\text{sample}} / (^{41}\text{K}/^{39}\text{K})_{\text{BSE}} - 1) \times 10^3$. In addition, elemental concentrations were measured for all samples using a Thermo Scientific Quadrupole ICPMS. Electron microprobe analyses were performed on the pillow basalt to investigate alteration textures. Details of our analytical procedures are given in *Methods*. Elemental data are provided in Table S1 and Figs. S1–S3, and back-scattered electron images in Figs. S4–S6.

Prior studies have established that the BOI ophiolite is an obducted fragment of ~485 Ma oceanic crust (20–22) that closely resembles typical midocean ridge crust in its elemental composition and internal structure (23). However, the ophiolite most likely formed not at a midocean ridge, but at an oceanic spreading center located above a subduction zone (22, 24). Obduction occurred by ~470 Ma, in association with the Taconic orogeny, as constrained by dating of minerals in the metamorphic aureole (25,

Significance

Elemental exchange between seawater and oceanic crust is important both in modulating the ionic composition of seawater over geologic time and in controlling the elemental and isotopic makeup of various solid-earth reservoirs. This study documents large and systematic variations in the K-isotope composition of oceanic crust that has been affected by seafloor hydrothermal alteration. These variations put constraints on the isotopic character of a fundamental flux of the marine K cycle: the hydrothermal flux. We also propose that these variations ought to be exploited in the future as an effective way of tracking oceanic crust as it is subducted into the mantle and sampled by various forms of volcanism.

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26). The subsequent history of this part of the continental margin includes events such as the Acadian and Alleghanian orogenies (27). The BMD massif of the BOI ophiolite is affected by some faults but is essentially intact (23), including in the area where our samples were obtained. The pseudostratigraphy in this area is complete, except that an estimated 400 m of the uppermost basalts may be missing (23). Neither obduction nor later tectonic events have left a discernable metamorphic overprint on the part of the ophiolite where our samples were taken (23).

The constituent rocks of the BMD massif have been variably metamorphosed in a manner consistent with hydrothermal processes. Metamorphic grade increases with depth in the stratigraphy, from prehnite–pumpellyite facies in the pillow basalts to amphibolite facies in the metagabbros (28). For a broader context, it is worth noting that, in the nearby North Arm massif, the topmost few hundred meters of the pillow basalts are preserved and are not metamorphosed to prehnite–pumpellyite grade (29). Pervasiveness of alteration—as manifest by the abundance of secondary minerals—decreases with depth (28). These features are similar to those documented in modern oceanic crust, where fluids infiltrate oceanic rocks of variable porosity in the presence of a geothermal gradient. The metamorphic textures of the BOI rocks have therefore been interpreted to be the result of hydrothermal alteration at the seafloor (23, 28).

The samples of this study were collected along a depth transect through the stratigraphy of the ophiolite, and include: a pillow basalt, two diabases from a sheeted dike complex, an oceanic plagiogranite, a hornblende gabbro, and an olivine gabbro. The samples have been described previously (30), and we supplement past observations with electron-microprobe analyses of the basalt sample. BMD-24 is a prehnite–pumpellyite facies metabasalt, with calcite veins, small crystals of plagioclase (partly replaced by albite), clinopyroxene, chlorite, and minor quartz. Potassium is concentrated in micron-sized patches, possibly of a micaceous phase, within the secondary albite (*Electron-Microprobe Analysis of Sample BMD-24*; Figs. S4–S7). BMD-10 is a greenschist facies metadiabase; it comes from a part of the sheeted dike complex where brecciation is extensive and interpreted to have resulted from the flow of supercritical seawater (28). BMD-12a is an amphibolite facies metadiabase that has been largely recrystallized. It consists predominantly of secondary amphibole and saussuritized plagioclase, with some chlorite and trace amounts of clinopyroxene. BMD-14 is an oceanic plagiogranite, located at the interface of the diabases and gabbros. BMD-8 is an amphibolite facies metagabbro with hornblende (presumably incorporating H₂O from seawater), epidote, and plagioclase. BMD-7 is a gabbro that is not significantly metamorphosed. It contains plagioclase with minor saussurization, some secondary amphibole, and olivine with minor alteration to serpentine. Jacobsen and Wasserburg (30) also reported ⁸⁷Sr/⁸⁶Sr ratios for the samples. The basalt, diabases, plagiogranite, and hornblende gabbro have high ⁸⁷Sr/⁸⁶Sr values, interpreted to reflect extensive interaction with seawater. The olivine gabbro has ⁸⁷Sr/⁸⁶Sr near what is expected for unaltered material.

Our measurements show that $\delta^{41/39}\text{K}$ of the BOI samples ranges from -0.01 to $+0.67\text{‰}$ (Table 1; Fig. 1). The spread in

Table 1. Potassium concentrations and isotope compositions of BOI samples

Sample	Rock type	[K] (ppm)	$\delta^{41/39}\text{K}_{\text{BSE}}$	2SE	n
BMD-24	Pillow basalt	1,220	0.31	0.065	4
BMD-10	Diabase	5,130	0.41	0.052	4
BMD-12a	Diabase	3,830	0.40	0.035	4
BMD-14	Plagiogranite	2,970	0.67	0.029	4
BMD-8	Hornblende gabbro	2,750	0.47	0.022	4
BMD-7	Olivine gabbro	373	-0.01	0.078	2

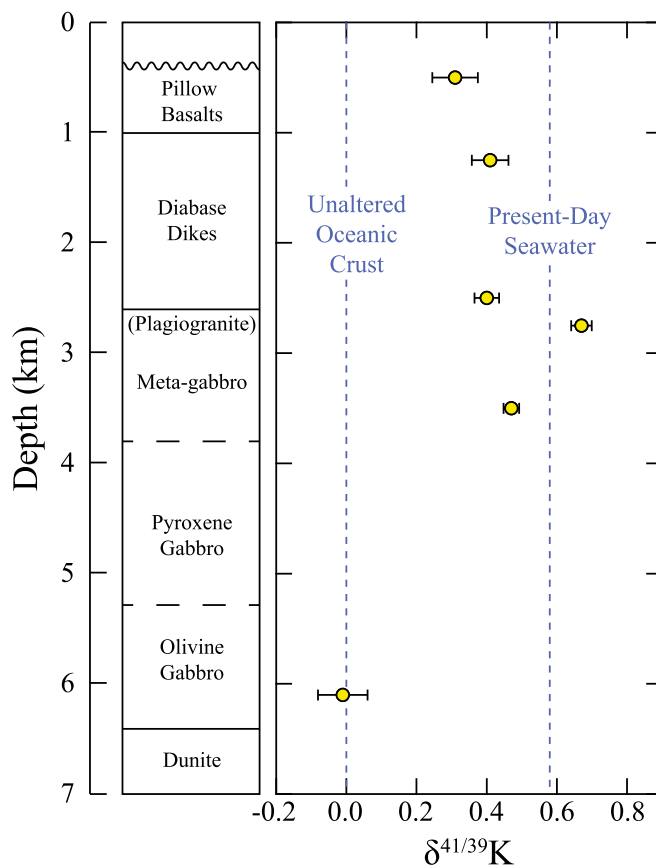


Fig. 1. The $\delta^{41/39}\text{K}$ values of the samples plotted as a function of depth within the ophiolite stratigraphy. The $\delta^{41/39}\text{K}$ estimate for BSE reported by ref. 18, which was based in part on analysis of a fresh MORB sample, is taken as the value for unaltered oceanic crust. Estimates of the $\delta^{41/39}\text{K}$ of present-day seawater are given in refs. 18 and 19.

these values is about an order of magnitude greater than analytical uncertainties. This variability in $\delta^{41/39}\text{K}$ of the ophiolite rocks is remarkable, as most terrestrial igneous rocks analyzed to date have $\delta^{41/39}\text{K}$ within $\sim 0.1\text{‰}$ of the value estimated for BSE (18, 19). Among our samples, only BMD-7 (olivine gabbro) has $\delta^{41/39}\text{K}$ within error of the estimate for BSE. All other samples have significantly elevated $\delta^{41/39}\text{K}$. The basalt and diabase samples have $\delta^{41/39}\text{K}$ between $+0.31$ and $+0.41\text{‰}$. The plagiogranite has $\delta^{41/39}\text{K}$ of $+0.67\text{‰}$. The pattern in these data, in which all samples but the olivine gabbro are isotopically enriched, resembles the trend previously documented in ⁸⁷Sr/⁸⁶Sr. Indeed, $\delta^{41/39}\text{K}$ and ⁸⁷Sr/⁸⁶Sr of the samples are correlated (Fig. 2A).

The most plausible explanation of these data is that $\delta^{41/39}\text{K}$ of the rocks varies as a result of chemical exchange between seawater and oceanic crust. This interpretation is consistent with the correlation between $\delta^{41/39}\text{K}$ and ⁸⁷Sr/⁸⁶Sr, with the olivine gabbro's having $\delta^{41/39}\text{K}$ and ⁸⁷Sr/⁸⁶Sr characteristic of unaltered mafic rock, and with the relatively high $\delta^{41/39}\text{K}$ and ⁸⁷Sr/⁸⁶Sr values of the other samples. The ⁸⁷Sr/⁸⁶Sr of seawater for the time of interest is well constrained by measurements of early Ordovician sediments (31). However, $\delta^{41/39}\text{K}$ is only known for present-day seawater: $\delta^{41/39}\text{K} = +0.58\text{‰}$. Although this value is likely to have fluctuated over time, it seems reasonable to assume that $\delta^{41/39}\text{K}$ of seawater has generally remained elevated relative to BSE. This assumption is supported by two analyses of evaporites from the late Permian, which have $\delta^{41/39}\text{K}$ of $+0.51$ and $+0.71\text{‰}$ (18). Thus, we use $\delta^{41/39}\text{K}$ of present-day seawater as a rough approximation for early Ordovician seawater.

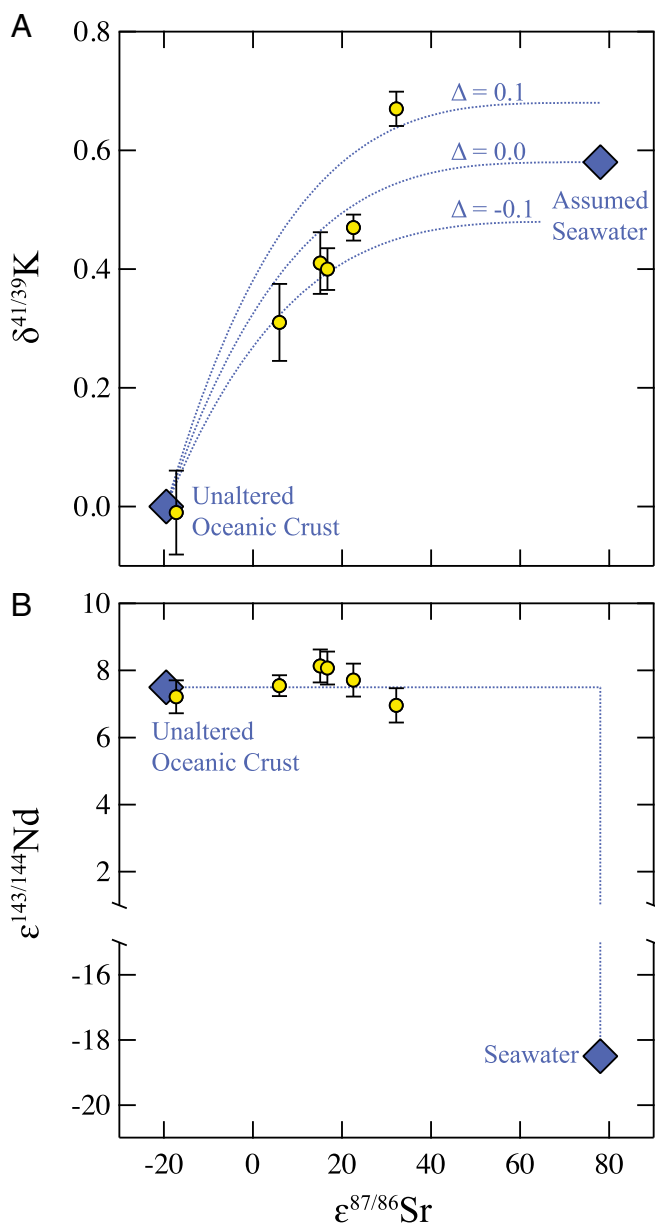


Fig. 2. The $\delta^{41/39}\text{K}$ and $\epsilon^{143/144}\text{Nd}$ vs. $\epsilon^{87/86}\text{Sr}$ for BOI samples. Error bars on $\epsilon^{87/86}\text{Sr}$ data are smaller than the symbols. Model curves show expected trends for samples affected by seafloor hydrothermal alteration (*Modeling $\delta^{41/39}\text{K}$, $\epsilon^{87/86}\text{Sr}$, and $\epsilon^{143/144}\text{Nd}$ Variations in AOC*). Data needed to estimate seawater $\epsilon^{87/86}\text{Sr}$ and $\epsilon^{143/144}\text{Nd}$ compositions are taken from refs. 31 and 40, respectively. There are no direct measurements for $\delta^{41/39}\text{K}$ of early Ordovician seawater. We use the $\delta^{41/39}\text{K}$ of present-day seawater as an approximation for the past, and note that this value is similar to values measured for two Permian sylvites (18). (A) $\delta^{41/39}\text{K}$ covaries with $\epsilon^{87/86}\text{Sr}$. Three model curves are drawn, corresponding to fractionation factors (Δ) between rock and seawater of -0.1 , 0.0 , and $+0.1$ ‰. (B) $\epsilon^{143/144}\text{Nd}$ does not covary significantly with $\epsilon^{87/86}\text{Sr}$.

Having done so, we note that the samples plot along an array in the $\delta^{41/39}\text{K}$ versus $\epsilon^{87/86}\text{Sr}$ diagram between estimates for BSE and seawater (Fig. 24).

Hydrothermal processes involving K vary in space and time. This is the case for modern oceanic crust, from which K is leached at higher temperatures (in the lower lithologies, near the ridge axis), and to which K is added at lower temperatures (in the upper lithologies, away from the ridge axis). Our pillow basalt sample (BMD-24) does not have higher K content than typical MORB.

Nonetheless, imaging reveals that K is concentrated in a secondary phase (*Electron-Microprobe Analysis of Sample BMD-24* and Figs. S4–S7), implying mobile K was acquired from a fluid phase, as would be expected during low-temperature alteration. Deeper lithologies (diabases and metagabbros) may have been affected by alteration at higher temperatures, involving K loss, and subsequently at lower temperatures, involving K gain. We consider it likely that addition of K to the rocks during relatively low-temperature alteration is primarily responsible for imparting the $\delta^{41/39}\text{K}$ effects observed here.

A limitation of this study is that it does not include samples from the uppermost ~ 400 m of the pillow basalts, as this lithology is truncated in the BMD massif. It is typically observed in oceanic drill cores that by far the greatest enrichment in K content occurs in the shallowest part of the crust (7, 32), where rock is highly porous and most affected by interaction with seawater at low temperatures. A similar enrichment in the shallowest few hundred meters has been documented in the Troodos ophiolite (33). In contrast, a study of the Macquarie Island ophiolite estimated that K had been added in large quantities to greater depths (1–1.5 km) (34). Thus, there may be significant variability among sites in how K is distributed. Regardless, future work that characterizes the $\delta^{41/39}\text{K}$ of the uppermost basalts, where much, if not most, of the total K in hydrothermally altered crust is stored, will be essential to producing a robust estimate of average $\delta^{41/39}\text{K}$ for typical altered oceanic crust (AOC).

Rocks that have been variably affected by hydrothermal fluids ought to plot in a $\delta^{41/39}\text{K}$ versus $\epsilon^{87/86}\text{Sr}$ diagram along a trend line, the curvature of which depends on the relative susceptibility of each isotope system to alteration. Trend lines were calculated, using equations for open-system exchange (refs. 35 and 36), and are depicted in Fig. 2. These curves are based on reasonable parameter choices (*Modeling $\delta^{41/39}\text{K}$, $\epsilon^{87/86}\text{Sr}$, and $\epsilon^{143/144}\text{Nd}$ Variations in AOC*). The value used for $\delta^{41/39}\text{K}$ of ancient seawater is only provisional, and the magnitude of the fractionation effects associated with partitioning of K into alteration phases is not known. If the assumed value of $\delta^{41/39}\text{K}$ for seawater is entertained, it appears that K added to oceanic crust during alteration has $\delta^{41/39}\text{K}$ similar to the seawater reservoir from which it is derived; however, it is also possible that $\delta^{41/39}\text{K}$ of early Ordovician seawater was markedly different from the present and/or that significant fractionation effects (on the order of tenths of a per mil) accompany the partitioning of K into secondary minerals. Despite uncertainties in the calculation, the agreement between the data and calculated trend lines illustrates that the $\delta^{41/39}\text{K}$ and $\epsilon^{87/86}\text{Sr}$ of the BOI samples are consistent with the interpretation that the observed isotopic variability results from seafloor hydrothermal alteration.

In reality, the processes that affected the various lithologies of the ophiolite must have been more complex than the simple open-system exchange model that we use. Fluid flow is likely to have been somewhat restricted, especially in the lower parts of the stratigraphy, below the volcanic zone. As a result, the fluids interacting with rocks at these depths would not simply have the chemical makeup of seawater but, rather, would have the composition of a seawater-derived fluid that had been modified during transport through shallower regions of the oceanic crust. Moreover, the plagiogranite may have formed by processes that influenced its isotopic composition in complex ways. Oceanic plagiogranites may be generated either by extreme differentiation of a tholeiitic parental magma or by hydrous partial melting of gabbro or diabase (37). In either of these scenarios, it is possible that the felsic magma bodies, from which plagiogranites crystallize, acquire distinct $\delta^{41/39}\text{K}$ and $\epsilon^{87/86}\text{Sr}$ as a result of processes such as wall rock assimilation or incorporation of hydrothermal fluids into the melts. In addition, mass-dependent fractionation of K isotopes may occur during some of the stages of plagiogranite formation. These factors may or may not be relevant to explaining how the plagiogranite came to have a $\delta^{41/39}\text{K}$ that is

quite high. Nevertheless, the elevated $^{87}\text{Sr}/^{86}\text{Sr}$ of the plagiogranite (which does not reflect mass-dependent fractionation) points to incorporation of significant amounts of material derived from seawater, regardless of the exact process by which this occurred: water–rock exchange, assimilation of altered wall rock, or other. Studies performed with higher sampling density should be able to determine whether the processes that control $\delta^{41/39}\text{K}$ of plagiogranite are fundamentally different from those that control $\delta^{41/39}\text{K}$ of the mafic lithologies of oceanic crust.

The magnitude of variability in $\delta^{41/39}\text{K}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in the BOI samples cannot easily be attributed to other mechanisms, such as igneous fractionation effects or heterogeneity in the magma source materials. Partial melting is not expected to generate much $\delta^{41/39}\text{K}$ variability in magmatic products, because K is highly incompatible and partitions nearly quantitatively into melts. The $\delta^{41/39}\text{K}$ may be affected by fractional crystallization; however, most igneous rocks measured to date—including basalts, andesites, and granites—span a very limited range of only $\sim 0.1\%$, suggesting that fractional crystallization of basaltic magmas does not commonly produce $\delta^{41/39}\text{K}$ effects of the size we report. Most importantly, the correlation between $\delta^{41/39}\text{K}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ cannot be ascribed to an igneous fractionation mechanism, because $^{87}\text{Sr}/^{86}\text{Sr}$ values are not affected by mass-dependent fractionation processes.

We also consider it unlikely that source heterogeneity can explain the full range of variability in $\delta^{41/39}\text{K}$ and $^{87}\text{Sr}/^{86}\text{Sr}$. Like most well-known ophiolites, the BOI rocks have elemental compositions that show evidence of a subduction influence, consistent with a model in which the rocks formed at a spreading ridge situated above a subduction zone (refs. 22 and 24; *Elemental Compositions of BOI Samples*). Although incorporation of variable amounts of a subduction component into the magmas may have occurred, there are multiple reasons to doubt that this is the primary driver of the observed isotopic variability. (i) The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the BOI rocks are elevated to a greater extent than what is generally seen in suprasubduction volcanic products, such as island–arc rocks or back-arc–basin basalts. (ii) Variable incorporation of a subduction component might be expected to result in variations in $^{143}\text{Nd}/^{144}\text{Nd}$ coupled to those in $\delta^{41/39}\text{K}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, but $^{143}\text{Nd}/^{144}\text{Nd}$ is essentially constant among the samples (Fig. 2B). Also, the age-corrected $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the samples are relatively high. Lavas that erupted in settings such as island arcs may show a range in $^{87}\text{Sr}/^{86}\text{Sr}$ with only modest variation in $^{143}\text{Nd}/^{144}\text{Nd}$ as a result of a subduction influence, but these volcanic products also tend to have lower $^{143}\text{Nd}/^{144}\text{Nd}$. In this way, the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios support a common—or, at least, similar—source material for all of the rocks sampled, because $^{143}\text{Nd}/^{144}\text{Nd}$ is sensitive to mantle heterogeneity but is basically insensitive to hydrothermal alteration effects. (iii) The $\delta^{41/39}\text{K}$ values of the BOI rocks are enriched more than essentially all other common igneous rocks analyzed to date, including one arc andesite—albeit the existing $\delta^{41/39}\text{K}$ dataset is small. (iv) Mixing with a subduction component would not be expected to generate any simple relationships between $\delta^{41/39}\text{K}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values and depth, yet $\delta^{41/39}\text{K}$ values are identical to BSE at depth and different from BSE in the upper stratigraphy (Fig. 1).

The high $\delta^{41/39}\text{K}$ of the BOI samples indicates that hydrothermally altered crust is likely to have $\delta^{41/39}\text{K}$ that is elevated in comparison with BSE (which is estimated to have $\delta^{41/39}\text{K} = 0.0\%$). However, more research is needed to determine how representative these samples are of typical altered oceanic crust. The data in this study show that the BOI ophiolite has high $\delta^{41/39}\text{K}$ at least in regions below ~ 400 m. The basalt and diabase samples have $\delta^{41/39}\text{K}$ values that range between $+0.31$ and $+0.41\%$. It remains to be tested whether these values are characteristic of the shallowest crust, where a large amount of K is stored. The plagiogranite has higher $\delta^{41/39}\text{K}$, but this lithology is a minor constituent by mass of the ophiolite. Another consideration is that oceanic crust generated

in suprasubduction zone settings appears generally to be more extensively altered than crust formed at midocean ridges (38, 39). Accordingly, the BOI ophiolite may have been altered more thoroughly or to a greater depth than typical AOC. On the other hand, the processes of alteration—and the direction of chemical and isotopic effects—appear to be broadly similar in both types of tectonic setting (38). Also, the basalt and diabase samples of this study have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are comparable to those of AOC obtained in drill cores, so these samples may in fact be reasonable proxies for AOC. Going forward, there will be value in examining $\delta^{41/39}\text{K}$ at higher resolution in ophiolitic and drill-cored oceanic crust from diverse locations. This will allow a more thorough assessment of how $\delta^{41/39}\text{K}$ effects depend upon factors such as depth below seafloor, grade of metamorphism, and tectonic setting. Based on the data from the BOI ophiolite, it appears that altered material tends to have high $\delta^{41/39}\text{K}$, but a robust estimate of the magnitude of this effect in average AOC is not yet possible.

If elevated $\delta^{41/39}\text{K}$ is a feature of AOC as this study suggests, then K isotopes will be useful as a tracer of AOC recycling. The isotopic contrast in $\delta^{41/39}\text{K}$ between AOC and the mantle ($\delta^{41/39}\text{K} \sim 0.0\%$) is potentially large. Moreover, the concentration of K in AOC is many times greater than in the mantle. As a result, addition of even small amounts of subducted AOC material to the mantle is likely to generate large $\delta^{41/39}\text{K}$ effects in the resultant mixtures. All of this implies that, in the future, $\delta^{41/39}\text{K}$ may be used to track the fate of subducted material as it is mixed into the mantle and sampled by island–arc, ocean–island, and midocean-ridge volcanism.

A distinctive $\delta^{41/39}\text{K}$ of AOC could also be useful for establishing whether certain old rocks that have undergone complex deformation or metamorphism are, in fact, ancient fragments of oceanic crust. The effectiveness of K isotopes toward this purpose would depend on multiple factors, one being whether extensive interaction between the rocks and continental-derived fluids had occurred.

Last, as the $\delta^{41/39}\text{K}$ of AOC is constrained, it will be possible to better characterize the hydrothermal flux of K between oceanic crust and seawater, which is an important flux for the marine K cycle. Determining the isotope effects associated with this and other fluxes is critical for constructing an improved mass balance for the sources and sinks of K to and from the oceans. Potassium-isotope data therefore fit into a long-term project of constraining the rates of processes such as hydrothermal alteration, weathering, and reverse weathering that are known to modulate seawater chemistry over geologic time.

Methods

Sample Dissolution and Chromatographic Separation of K. Samples were powdered and dissolved in a multistep process. For each sample, aliquots of 20–100 mg of rock powder were used. First, powders were put into digestion vessels with a mix of concentrated acids (0.5 mL HF, 2 mL HNO_3 , and 1 mL HCl), with HF included to break Si–O bonds, and were heated by a CEM Microwave Accelerated Reaction System to 200 °C for 1.5 h. Second, the solutions were dried down, redissolved in a different mix of acids (0.5 HNO_3 , 1.5 HCl, 1 mL H_2O) to facilitate dissociation of CaF_2 residues, and heated in the same manner as before. Third, samples were dried down and redissolved in acids (0.5 HNO_3 , 1.5 HCl, 1 mL H_2O) without microwave heating. Finally, samples were dried down and redissolved in 1 mL of 0.5 N HNO_3 in preparation for chromatography.

The two-step procedure used for chromatography has been described in ref. 18. For the first step, we used quartz-glass columns with 1-cm inner diameter, filled with Bio-Rad AG50W-X8 (100–200 mesh) cation exchange resin. The resin volume is 13 mL, as measured when it is saturated in 4N HNO_3 . Before each use, columns were cleaned with 300 mL 4 N HCl. Some Milli-Q water was added to flush out the HCl, and then columns were conditioned with 50 mL of 0.5 N HNO_3 . Samples were loaded in 1 mL 0.5 N HNO_3 and eluted with 340 mL of 0.5 N HNO_3 , and the K-containing cut at 160–340 mL was collected. The solution was dried down. For the second step, we used quartz-glass columns with 0.4-cm inner diameter and 1.6 mL of the same resin. Columns were cleaned with 100 mL 4 N HCl, flushed with 10 mL Milli-Q water, and conditioned with 20 mL 0.5 N HNO_3 .

Samples were loaded in 0.5 mL 0.5 N HNO₃ and eluted with 47 mL 0.5 N HNO₃. The cut at 28–47 mL was collected. The solutions were dried down and redissolved in 0.32 N HNO₃.

Measurement of ⁴¹K/³⁹K by Mass Spectrometry. Our method for measuring ⁴¹K/³⁹K ratios has been described in ref. 18. Analyses were performed with a GV Instruments IsoProbe-P MC-ICPMS. The instrument is equipped with a hexapole collision and reaction cell, which greatly reduces Ar-hydride interferences (i.e., ⁴⁰Ar¹H and ³⁸Ar¹H). Analyses of sample solutions were bracketed by analyses of blank (0.32 N HNO₃) and standard, to conduct blank subtractions and to express ⁴¹K/³⁹K ratios relative to our reference material. The laboratory standard is Merck KGaA Suprapur high-purity potassium nitrate (KNO₃). An estimate of BSE relative to this standard was provided by ref. 18, which has made it possible for us to express the data of this study relative to the BSE estimate. That is, we initially generated ⁴¹K/³⁹K values relative to the laboratory standard, which we can express in delta notation as follows: $\delta^{41/39}K_{\text{relative to lab standard}} = ((^{41}K/^{39}K)_{\text{sample}} / (^{41}K/^{39}K)_{\text{lab standard}} - 1) \times 10^3$. To express our data relative to the BSE estimate of ref. 18, we used the following conversion: $\delta^{41/39}K_{\text{relative to BSE}} = 1.000479 \times \delta^{41/39}K_{\text{relative to lab standard}} + 0.479230$. Repeat

analyses of standards and samples during the course of this project demonstrated an external reproducibility of ~0.07 (2SD). A single measurement in this study consists of running a sample solution, bracketed by a standard solution, 5–6 times over the course of some hours. Replicate measurements allowed us to determine $\delta^{41/39}K$ of samples to precisions typically of ~0.035 (2SE).

Measurement of Elemental Concentrations by Mass Spectrometry. Major and trace elements were measured using a Thermo Scientific Quadrupole ICPMS. Calibration curves, relating signal intensities to elemental concentrations, were generated by analyzing United States Geological Survey standards BCR-1, BHVO-1, and AGV-1.

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