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Short Communication

Homogeneous and heavy potassium isotopic composition of global oceans

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The oceans are an important interface for chemical exchange between the continents, the seafloor, and the atmosphere. Chemical weathering of continental silicate rocks removes atmospheric CO_2 and releases rock-forming cations to the oceans through surface runoff. Secular changes in seawater chemistry thus serve as archives of long-term climate variation.

Potassium (K) is the fourth most abundant cation in the oceans (after Na, Mg, and Ca) and is hosted primarily by silicate minerals. Potassium has two stable isotopes (^{39}K, 93.358% and ^{41}K, 6.730%) that differ by 5% in mass, making K isotopes useful tracers of silicate weathering. Although K isotopes have historically been difficult to measure with high precision, recent analytical advances now permit measurements of K isotopes at the scale of sub-permil precision [1–5]. The K isotopic composition of modern seawater is an important reference point to consider when using K isotopes to trace silicate weathering records in deep time; however, it is not yet well-constrained.

The K isotopic composition of seawater also plays a pivotal role in understanding the global K budget, where seawater constitutes the isotopically heaviest terrestrial K reservoir at ~0.6‰ higher than common igneous rocks [1–8]. This significant isotopic difference between seawater and silicate rocks requires either input of isotopically heavy K from rivers [9] and oceanic ridge hydrothermal fluids, or preferential removal of isotopically-light K to altered oceanic crust and marine sediments [10], or a combination of both. Alternatively, this difference may suggest that K isotopic distribution in global oceans is not in steady state. Published data on seawater are still scarce and differ by 0.14‰ [1–4,6]. A more systematic study on global seawater samples is thus needed to assess the homogeneity of K isotope distribution in the oceans, which will also advance understanding of the fluxes and processes related to the oceanic K budget and global K cycling.

The establishment of K isotopic homogeneity of global seawater is also critical to its potential application as an inter-laboratory reference material. Seawater is readily accessible, globally available and easily processed in column chemistry. Therefore, it is a convenient natural reference material for assessing sample preparation processes such as ion exchange chromatography, during which significant K isotope fractionation occurs and thus incorporates the greatest potential for the introduction of analytical artifacts [4–6]. Previous studies by Morgan et al. [4] and Santiago Ramos et al. [10] internally corrected their data using a measured average seawater δ^{41}K value of zero. However, seawater samples measured by three other laboratories are variably higher within 2SD, with δ^{41}K at 0.06‰ by Li et al. [1], 0.10‰ by Wang and Jacobsen [2], and 0.14‰ by Hu et al. [3] and Xu et al. [6]. As precision improves with time, inconsistent seawater values will develop into a more severe problem when interlaboratory comparisons are made. A tighter constraint on this value is urgently needed.

Here, we analyze K isotopic compositions of 20 seawater samples from the Gulf of Mexico and greater Atlantic, Pacific, and Indian Oceans that are representative of a wide range of salinities, temperatures, and water depths (Fig. 1). The analytical work was carried out at the Isotope Laboratory at the University of Washington, Seattle, following the procedure outlined by Hu et al. [3] and Xu et al. [6]. Potassium isotopic compositions presented are an average of the N analyses, reported in standard delta (δ) notation:

$$\delta^{41}\mathrm{K}(‰) = \left[\frac{(^{41}\mathrm{K}/^{39}\mathrm{K})_{\mathrm{sample}}}{(^{41}\mathrm{K}/^{39}\mathrm{K})_{\mathrm{standard}}} - 1\right] \times 1000,$$

where the standard is NIST SRM 3141a and the long-term external reproducibility is better than 0.06‰ at 95% c.i. (see the Supplementary materials for details).

The δ^{41}K of seawater samples displays limited variation, ranging from 0.12‰ to 0.17‰ with an average of 0.14‰ ± 0.02‰ (2SD, $n = 20$). There is no significant variation in δ^{41}K across latitude, longitude, depth or location (Fig. 2). As K has a residence time of

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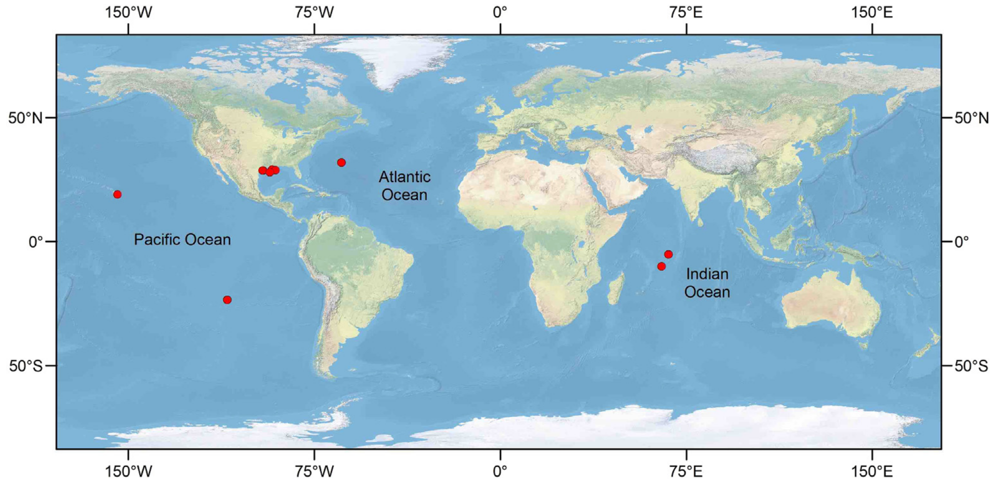

Fig. 1. (Color online) Global distribution of seawater samples. Location data are reported in Table S1 (online). Map provided by the U.S. National Park Service.

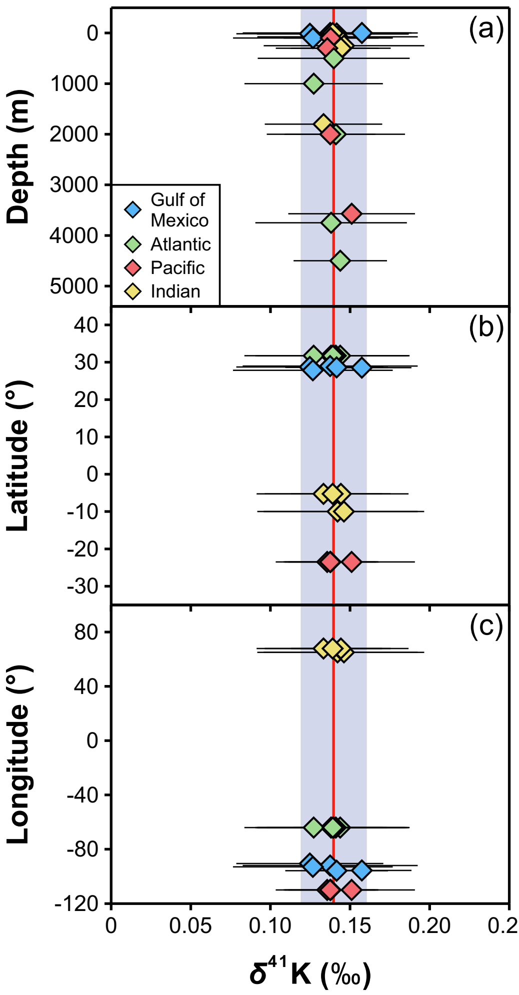

Fig. 2. (Color online) Potassium isotopic composition of seawater samples measured in this study compared across (a) depth, (b) latitude, and (c) longitude. The negative signs denote southern and western hemispheres, respectively. δ^{41}K data (‰) are plotted with 95% c.i. error. Data are reported in Table S1 (online).

$\sim$10 Ma, K in the oceans is assumed to be well mixed [11]. Our study here confirms that the global oceans have a homogeneous K isotopic composition. Our data also agree with previous studies within 2SD [1–3,6] and thus provide a good reference for interlaboratory comparisons of K studies.

Our study confirms that seawater represents a high-δ^{41}K terrestrial end-member, is significantly enriched in ^{41}K and is approximately 0.6‰ heavier than the mantle (Fig. 3). Recent studies suggest that silicate weathering is an important factor in determining the δ^{41}K of seawater [7,9]; ^{41}K is preferentially released into solution during silicate weathering while ^{39}K is incorporated into secondary weathering products, thus driving the δ^{41}K value of dissolved river loads higher than BSE and contributing ^{41}K to the oceans. Nonetheless, the estimated average K isotopic composition of river waters (−0.22‰ ± 0.04‰ [10]) is still significantly lower than that of seawater, suggesting preferential removal of ^{39}K by marine K sinks. Output pathways from the oceans include K fixation and sorption with clay minerals and low-temperature alteration of oceanic crust [11]. Santiago Ramos et al. [10] postulated that light K is preferentially removed from seawater during authigenic clay formation, based on the δ^{41}K composition of deep-sea pore fluids. In contrast, low-temperature hydrothermal alteration of oceanic crust is likely not important in determining the K composition of seawater based on analyses of seawater-altered

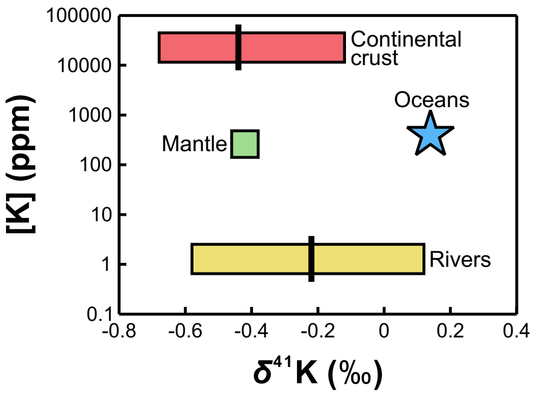

Fig. 3. (Color online) Potassium concentration [K] (ppm) plotted against the δ^{41}K (‰) of the mantle and the three primary K reservoirs: rivers, oceans and the upper continental crust. The average K concentrations in the mantle, the continental crust, rivers and oceans are from Palme and O'Neill [12], Rudnick and Gao [13], and Berner and Berner [11], respectively. The K isotopic compositions of the mantle are constrained by oceanic basalts [14], the K isotopic composition of the continental crust is from Huang et al. [7], while those of the rivers are from Li et al. [9], and that of the oceans is from this study. The black vertical bars represent the average δ^{41}K value of upper continental crust and river waters.

ophiolites [15]. The high δ^{41}K value of seawater obtained by our study suggests that K isotope fractionation during these processes needs further investigation to better constrain oceanic K-cycling.

Seawater is globally available, readily accessible in large volumes, and requires acid flux and column chemistry prior to isotopic analysis. When compared to rock reference standards, K isotopic composition of seawater is closer to the δ^{41}K values of bracketing standards used in K isotopic analyses that are typically made from seawater-derived sylvite deposits. Therefore, the well-defined seawater δ^{41}K value provided in this study will also serve as a great reference material in accuracy assessments of future high-precision K isotopic studies.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Author contributions

Fang-Zhen Teng designed the study. Madeline Hille, Yan Hu and Tian-Yi Huang carried out the laboratory work. All authors interpreted the data and wrote the paper together.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2019.09.024.

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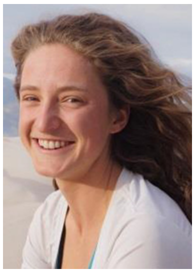

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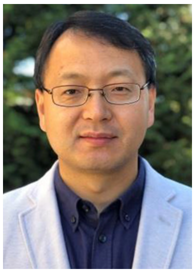

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