Potassium isotope fractionation during continental weathering and implications for global K isotopic balance

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Potassium isotope fractionation during continental weathering and implications for global K isotopic balance

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Abstract

Potassium isotopic compositions of profiles through saprolites developed on a diabase in South Carolina, U.S.A., and on a granite in Guangdong, China, allow characterization of the behavior of K isotopes during continental weathering. Saprolites from the diabase profile are heavily weathered with chemical index of alteration (CIA) values up to 95; however, their K isotopic variation is limited, with \( \delta^{41}\text{K} \) ranging from \(-0.475 \pm 0.028\%\) in the unweathered diabase to \(-0.407 \pm 0.021\%\) for the saprolites. The lack of significant K isotope fractionation mainly reflects the conservative behavior of K in the diabase weathering profile, with >50% of the original K remaining in the saprolites. By contrast, K isotopes are fractionated during granite weathering and correlate with sample depth, CIA, and kaolinite abundance, with \( \delta^{41}\text{K} \) decreasing from \(-0.493 \pm 0.030\%\) in the unweathered granites at the bottom to \(-0.628 \pm 0.021\%\) in the most weathered saprolite close to the surface. These observations suggest the preference of light K isotopes in saprolites relative to fluids, which is further supported by the overall isotopically heavy nearby stream water samples (\( \delta^{41}\text{K} = -0.709 \pm 0.017 \) to \(-0.339 \pm 0.018\%\)). These results demonstrate that continental weathering plays an important role in the global K isotopic budget through the formation of isotopically heterogeneous rivers and weathered regolith. Recycling of K-rich crustal materials with distinct K isotopic signatures may produce distinct mantle K isotopic end members.

Keywords: Potassium isotopes; Continental weathering; Granite; Diabase; Global potassium cycle

1. INTRODUCTION

Continental weathering is the first and one of the key steps in global elemental cycling (Goldich, 1938). It releases elements from the continental crust into air, plants, and rivers for a trip to the oceans. Weathering drives the chemical evolution of the atmosphere, biosphere, hydrosphere, and continents over geologic time-scales (Brantley et al., 2011; Berner and Berner, 2012).

Continental weathering exerts a primary control on global isotopic budgets; it commonly produces large isolate fractionations that ultimately leads to the formation of distinct isotopic reservoirs (Valley and Cole, 2001; Teng et al., 2017). For example, chemical weathering shifts the isotopic composition of the hydrosphere and continents away from that of the mantle (e.g., Li and Mg isotopes, Penniston-Dorland et al., 2017; Teng, 2017), which lays the foundation for using stable isotopes as tracers of crustal cycling (Teng et al., 2019).

Recent development of K isotope geochemistry has documented large K isotopic variations (up to 2\%\) that greatly exceed analytical precision (\( \pm 0.06\%\), 2\( \sigma \)) in terrestrial rocks (Wang and Jacobsen, 2016a, 2016b; Li et al., 2016, 2018; Teng et al., 2017).
To avoid samples that are significantly influenced by biological activity, the top 1.5 m of the soil was discarded and the underlying weathering profile was drilled 40 m downwards until relatively unweathered parental rock was reached (Fig. 1). The bottom section of the profile from 39.8 to 31.6 m is the relatively unweathered granite, containing significant amounts of biotite (7.7%) and chlorite (7.2%) in addition to quartz (25.6%), K-feldspar (30.7%), and plagioclase (30.9%) (Wang et al., 2018). Towards the surface, weathering intensity gradually increases. Biotite and chlorite break down first and completely disappear at 30 m depth, followed by plagioclase that is completely decomposed at 25 m depth. Due to the dissolution of these minerals, the relative abundance of K-feldspar roughly increases until 10 m depth, and subsequently decreases upwards within the top 10 m of the profile. Secondary minerals (e.g., kaolinite and illite) start forming at about 25 m depth and continue upwards through the whole profile (Fig. 1). Among primary and secondary minerals, kaolinite is the most suitable mineral index for weathering intensity as it is the dominant secondary mineral; its abundance increases systematically upwards as the intensity of weathering increases (Fig. 1).

These mineralogical changes are also reflected in the chemical variations along the weathering profile, e.g., MgO and CaO contents decrease dramatically in the initial stage of weathering, reflecting the dissolution of mafic minerals and plagioclase (Wang et al., 2018). The K$_2$O concentration increases with the abundance of K-feldspar, and to a lesser extent, illite, in the weathering profile (Fig. 2). This is consistent with the fact that mineral-bound K is partially released into solution during weathering and that K-feldspar and illite are the major mineral hosts for K during granite weathering.

Eight stream water samples were collected at the base of the hill at different times over a year. They were filtered through 0.45 µm Millipore membrane filters in the field, and acidified immediately to pH < 2 using distilled nitric acid and then stored in polyethylene plastic bottles (Wang et al., 2018).

2.2. Diabase weathering profile, South Carolina

The diabase weathering profile formed during the Paleogene in a humid, subtropical climate on a diabase dike in South Carolina, U.S.A. (33°58′09″N, 81°3′7″W) (Gardner et al., 1981). Unweathered diabase contains significant amounts of talc (20%) and chlorite (8%), in addition to plagioclase (40%), clinopyroxene (29%), and opaque minerals (3%) (Gardner et al., 1981). Sапролитic samples were collected along a 11 m vertical profile through the center of the dike (Fig. 3). As the intensity of weathering increases towards the surface, talc and chlorite were weathered first, followed by clinopyroxene and plagioclase (Gardner et al., 1981). Kaolinite, smectite, and Fe-oxides are the main weathering products (Gardner et al., 1981). At a depth of ~2 m a discontinuity is recorded in the clay mineralogy and chemical composition (Gardner and Kheoruenromne, 1980; Gardner et al., 1981). This
discontinuity was interpreted to reflect a change in redox, with the upper profile being more oxidized and lacking siderite, and the lower portion being more reduced and containing siderite.

The weathering intensity recorded by the saprolites increases upwards, as indicated by increasingly lower density, higher CIA (chemical index of alteration, see Table 1 for definition) values (up to 95) and large isotopic variations in Li, Mg, Cu, and Fe (Gardner et al., 1981; Rudnick et al., 2004; Teng et al., 2010; Liu et al., 2014). Compared to other major elements (e.g., Al, Fe, Ca, and Mg), the K$_2$O concentrations show smaller variations and are equal to or higher in saprolites than in the unweathered diabase (Fig. 3) (Gardner et al., 1981).

Nine saprolite samples from the weathering profile below the 2 m discontinuity and one unweathered diabase from 30 m depth were analyzed for K isotopes. Archived samples are not available above the discontinuity and, therefore, not analyzed here.

3. ANALYTICAL METHODS

The rock powders and stream waters investigated here are the same as those used in previous studies for characterizing their mineralogical, elemental and isotopic compositions (Gardner et al., 1981; Rudnick et al., 2004; Teng et al., 2010; Liu et al., 2014; Wang et al., 2018). Potassium isotopic analyses were performed at the Isotope Laboratory of the University of Washington, Seattle, following established procedures (Hu et al., 2018; Xu et al., 2019). In brief, samples and standards were dissolved in a mixture of concentrated HF-HNO$_3$-HCl acids. Potassium is separated from matrix elements through cation exchange chromatography with Bio-Rad AG 50 W-X8 cation exchange resin (200–400 mesh) in 0.5 N HNO$_3$ media. The procedure was repeated to obtain pure K solution for mass spectrometry. The K yield is close to 100% and the total procedure blank is <9 ng. The purified K from the sample was introduced into a “cold plasma” via a DSN-100 desolvation system with the RF forward power ranging from 750 to 850 W. The K isotopes were measured by the standard-sample bracketing method using a Nu Plasma II MC-ICPMS. The intensity of $^{40}$K was not measured due to isobaric interference of $^{40}$Ar. Only $^{39}$K and $^{41}$K were measured in pseudo high-resolution mode at the interference-free
shoulders of $^{39}\text{K}$ and $^{41}\text{K}$. The K isotopic data are reported relative to the NIST K standard SRM 3141a (Hu et al., 2018):

$$\delta^{41}\text{K}(\%) = \left\{ \frac{\text{K}_{41} \text{sample}}{\text{K}_{41} \text{SRM3141a}}} - 1 \right\} \times 1000$$

The long-term external precision, based on replicate analysis of geostandards and seawater samples, is <0.06‰ (95% confidential interval) (Hu et al., 2018). Granite and basalt standards as well as Hawaiian seawater analyzed during the course of this study are within the uncertainty of previously published results (Tables 1–3) (Chen et al., 2019b; Hille et al., 2019; Xu et al., 2019).

4. RESULTS

The unweathered South Carolina diabase has a $\delta^{41}\text{K}$ of $-0.475 \pm 0.028$‰. Saprolites developed on the diabase display a narrow range in $\delta^{41}\text{K}$ of $-0.462 \pm 0.028$‰ to $-0.396 \pm 0.035$‰ (Fig. 4). By contrast, $\delta^{41}\text{K}$ values in the granite weathering profile decrease systematically from $-0.493 \pm 0.030$‰ in unweathered granite samples at the bottom of the drill core to $-0.628 \pm 0.021$‰ in highly weathered saprolites approaching the surface (Fig. 5).

Stream waters collected near the granite weathering profile display a large range in $\delta^{41}\text{K}$ ($-0.709 \pm 0.017$ to $-0.339 \pm 0.018$‰), encompassing the values of relatively unweathered granites and saprolites (Fig. 6). All but one sample (LD-RW20141117) have K isotopic composition similar to or heavier than the unweathered granite. Sample LD-RW20141117 has the lightest K isotopic composition ever reported for river waters (Fig. 6).

5. DISCUSSION

Saprolites developed on the diabase from South Carolina are highly weathered, as indicated by their extremely low density and high CIA values (Fig. 3). However, the K isotopic variation within the weathering profile is limited, barely beyond the analytical uncertainty, and does not correlate with indexes of weathering such as depth and CIA values (Fig. 4). The lack of K isotope fractionation is consistent with the conservative behavior of K during chemical weathering of the diabase. Even though these samples are highly weathered, K content does not change systematically, with $\tau\text{K}_2\text{O}$ (see Table 3 for definition of $\tau\text{K}_2\text{O}$) varying from $-35$% to $36$%, indicating that some samples lost K while others gained K during weathering (Fig. 4). Therefore, large K isotope fractionation might only occur when a significantly greater amount of K is mobilized during weathering.

By contrast, K isotopes are significantly and systematically fractionated within the granite weathering profile. As inter-mineral K isotope fractionation is limited at magmatic temperatures (<0.06‰, Y.H. Li et al., 2019; Zeng et al., 2019) and K-feldspar is the dominant K-rich mineral in these granites, the observed isotopic variation is unlikely to be produced by preferential leaching of different igneous minerals. Instead, the isotopic fractionation must have been generated during chemical weathering. This is strongly supported by the negative correlations between $\delta^{41}\text{K}$ and intensity of chemical weathering, as measured by sample depth, CIA, and kaolinite abundance (Fig. 5). The heavily weathered samples at the top of the profile are enriched in light K isotopes compared to relatively unweathered granites at the bottom, suggesting that light K isotopes are preferentially retained in the weathered regolith relative to fluids. This interpretation is further supported by the variable but overall isotopically heavy K in the stream waters (Fig. 5).

Given the limited fractionation observed in the diabase weathering profile, the discussion below focuses on the factors controlling K isotope fractionation during granite weathering, followed by their implications for global K isotopic mass balance.

5.1. Mechanisms for K isotope fractionation during granite weathering

K-feldspar is the major host of K in the unweathered granites; hence, the behavior of K isotopes during weathering is dominated by the incongruent weathering of K-feldspar, which breaks down to illite, then to kaolinite, accompanied by the release of soluble silica and K cations.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>K-feldspar (wt.%)</th>
<th>Illite (wt.%)</th>
<th>Kaolinite (wt.%)</th>
<th>Illite/K-feldspar</th>
<th>K₂O (wt.%)</th>
<th>τ K₂O (%)</th>
<th>CIA</th>
<th>δ¹⁸K (‰)</th>
<th>2SD (‰)</th>
<th>95% c.i. (‰)</th>
<th>N</th>
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</thead>
<tbody>
<tr>
<td>TT-1</td>
<td>1.0</td>
<td>4.2</td>
<td>42.3</td>
<td>57.0</td>
<td>0.74</td>
<td>1.65</td>
<td>-80</td>
<td>90</td>
<td>-0.649</td>
<td>0.060</td>
<td>0.048</td>
<td>4</td>
</tr>
<tr>
<td>TT-2</td>
<td>2.0</td>
<td>20.0</td>
<td>9.3</td>
<td>43.6</td>
<td>0.47</td>
<td>3.43</td>
<td>-55</td>
<td>79</td>
<td>-0.599</td>
<td>0.153</td>
<td>0.071</td>
<td>7</td>
</tr>
<tr>
<td>TT-3</td>
<td>3.0</td>
<td>18.1</td>
<td>12.1</td>
<td>40.7</td>
<td>0.67</td>
<td>3.51</td>
<td>-43</td>
<td>75</td>
<td>-0.591</td>
<td>0.051</td>
<td>0.024</td>
<td>7</td>
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<tr>
<td>TT-4</td>
<td>4.0</td>
<td>23.7</td>
<td>12.4</td>
<td>35.7</td>
<td>0.52</td>
<td>5.27</td>
<td>-18</td>
<td>63</td>
<td>-0.602</td>
<td>0.106</td>
<td>0.055</td>
<td>6</td>
</tr>
<tr>
<td>TT-5</td>
<td>5.0</td>
<td>21.7</td>
<td>12.5</td>
<td>29.6</td>
<td>0.58</td>
<td>4.71</td>
<td>-23</td>
<td>64</td>
<td>-0.597</td>
<td>0.078</td>
<td>0.048</td>
<td>5</td>
</tr>
<tr>
<td>TT-6</td>
<td>6.0</td>
<td>16.4</td>
<td>9.5</td>
<td>34.2</td>
<td>0.58</td>
<td>5.24</td>
<td>-18</td>
<td>70</td>
<td>-0.577</td>
<td>0.019</td>
<td>0.012</td>
<td>5</td>
</tr>
<tr>
<td>TT-10</td>
<td>10.0</td>
<td>39.1</td>
<td>3.5</td>
<td>25.7</td>
<td>0.09</td>
<td>6.27</td>
<td>-3</td>
<td>68</td>
<td>-0.544</td>
<td>0.088</td>
<td>0.054</td>
<td>5</td>
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<tr>
<td>TT-12-2</td>
<td>12.5</td>
<td>49.9</td>
<td>7.9</td>
<td>21</td>
<td>0.16</td>
<td>7.33</td>
<td>14</td>
<td>65</td>
<td>-0.572</td>
<td>0.072</td>
<td>0.038</td>
<td>6</td>
</tr>
<tr>
<td>TT-13-2</td>
<td>13.5</td>
<td>29.1</td>
<td>7.9</td>
<td>21</td>
<td>0.16</td>
<td>5.12</td>
<td>-15</td>
<td>70</td>
<td>-0.586</td>
<td>0.127</td>
<td>0.067</td>
<td>6</td>
</tr>
<tr>
<td>TT-14-2</td>
<td>14.5</td>
<td>53.8</td>
<td>7.3</td>
<td>20.9</td>
<td>0.13</td>
<td>6.51</td>
<td>12</td>
<td>58</td>
<td>-0.572</td>
<td>0.092</td>
<td>0.048</td>
<td>6</td>
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<tr>
<td>TT-16</td>
<td>16.0</td>
<td>55.9</td>
<td>7.3</td>
<td>20.9</td>
<td>0.13</td>
<td>7.56</td>
<td>22</td>
<td>60</td>
<td>-0.508</td>
<td>0.065</td>
<td>0.040</td>
<td>5</td>
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<tr>
<td>TT-17-3</td>
<td>17.7</td>
<td>27.5</td>
<td>12.5</td>
<td>31</td>
<td>0.45</td>
<td>5.76</td>
<td>-14</td>
<td>63</td>
<td>-0.499</td>
<td>0.064</td>
<td>0.033</td>
<td>6</td>
</tr>
<tr>
<td>TT-25-3</td>
<td>25.5</td>
<td>57.8</td>
<td>5.4</td>
<td>9.8</td>
<td>0.09</td>
<td>6.50</td>
<td>9</td>
<td>61</td>
<td>-0.525</td>
<td>0.096</td>
<td>0.077</td>
<td>4</td>
</tr>
<tr>
<td>TT-27-1</td>
<td>27.0</td>
<td>43.7</td>
<td>9.9</td>
<td>10</td>
<td>0.23</td>
<td>6.83</td>
<td>15</td>
<td>57</td>
<td>-0.548</td>
<td>0.038</td>
<td>0.023</td>
<td>5</td>
</tr>
<tr>
<td>TT-28-3</td>
<td>28.5</td>
<td>54.7</td>
<td>5.4</td>
<td>11.3</td>
<td>0.10</td>
<td>6.46</td>
<td>-1</td>
<td>61</td>
<td>-0.516</td>
<td>0.075</td>
<td>0.039</td>
<td>6</td>
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<tr>
<td>TT-29-2</td>
<td>29.3</td>
<td>38.3</td>
<td>8.4</td>
<td>7.7</td>
<td>0.22</td>
<td>5.53</td>
<td>-7</td>
<td>63</td>
<td>-0.527</td>
<td>0.033</td>
<td>0.020</td>
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<tr>
<td>TT31-4</td>
<td>31.6</td>
<td>27.6</td>
<td>4.85</td>
<td>-11</td>
<td>53</td>
<td>-0.493</td>
<td>0.057</td>
<td>0.030</td>
<td>6</td>
<td></td>
<td></td>
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<tr>
<td>TT34-4</td>
<td>34.6</td>
<td>37.9</td>
<td>6.45</td>
<td>3</td>
<td>51</td>
<td>-0.506</td>
<td>0.078</td>
<td>0.036</td>
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<tr>
<td>TT39-3</td>
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<td>23.8</td>
<td>5.77</td>
<td>-3</td>
<td>48</td>
<td>-0.496</td>
<td>0.098</td>
<td>0.041</td>
<td>8</td>
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<tr>
<td>G-2</td>
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<td></td>
<td></td>
<td>-0.496</td>
<td>0.098</td>
<td>0.041</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note 1. To evaluate the relative mobilization of K₂O during weathering, the τ K₂O was used and calculated using the following the equation: τ K₂O (%) = 100 × [(K₂O/Al₂O₃)ᵢ/(K₂O/Al₂O₃)ₚ].

Note 2. Chemical index of alteration (CIA) is defined as molar Al₂O₃/(Al₂O₃ + CaO* + Na₂O + K₂O), where CaO* is the amount of CaO in silicates, which has been used to measure the transformation of feldspar to clay minerals and the degree of chemical weathering (Nesbitt and Young, 1982).

Note 3. 2SD represents two standard deviation; 95% c.i. = 95% confidence interval, represents two standard error corrected by the Student’s t factor; N = number of analyses. See Hu et al. (2018) for more details.

Note 4. Replicate represents repeat sample dissolution, column chemistry, and instrumental analysis. Duplicate represents repeat analyses of the same K cut in different instrumental analytical sessions. Average represents error weighted values.

Note 5. Depth, mineral abundance and major elemental data are from Wang et al. (2018).
into solutions. These reactions can be simplified to the following two steps:

1) \(3 \text{KAlSi}_3\text{O}_8 + 2\text{H}^+ + 12 \text{H}_2\text{O} = \text{KAl}_2\text{Si}_2\text{O}_6(\text{OH})_2 + 6 \text{H}_2\text{SiO}_4 + 2 \text{K}^+\)  
\(\text{K-feldspar} \quad \text{illite (muscovite)} \quad \text{soluble silica}\)

2) \(2 \text{KAl}_3\text{Si}_3\text{O}_8(\text{OH})_2 + 2\text{H}^+ + 3 \text{H}_2\text{O} = 3 \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_3 + 2 \text{K}^+\)  
\(\text{illite} \quad \text{kaolinite}\)

Potassium isotope fractionation can potentially occur (1) between dissolved K\(^+\) and K-bearing minerals in both steps, (2) between different minerals in both steps, and (3) between adsorbed-K in kaolinite and structurally-bound K in illite in step 2. Although the last process is capable of producing large isotope fractionations in some stable isotope systems such as Mg, Cu, and Zn (see reviews of Moynier et al., 2017; Teng, 2017), it is unlikely to be the main cause for the K isotopic variation in the saprolite, as K-feldspar and illite, instead of kaolinite, dominate the K budget even in the most weathered samples. Therefore, the first two processes are likely responsible for fractionating K isotopes during weathering of the granite.

Large isotope fractionation between dissolved K\(^+\) and silicate-hosted K is supported by the overall isotopically heavy stream waters relative to the saprolites (Fig. 5). The one stream sample (LD-RW20141117) with the unusually low \(\delta^{41}\text{K}\) also has the highest Na and K contents and pH (Fig. 6), which might reflect inheritance of K from the complete dissolution of isotopically light saprolites formed during a more advanced stage of weathering. The mineral dissolution process can be approximated by Rayleigh distillation, with light K isotopes preferring saprolites (e.g., K-feldspar and illite) to waters. The apparent \(\alpha = (^{41}\text{K}/^{39}\text{K})_{\text{saprolite}}/(^{41}\text{K}/^{39}\text{K})_{\text{fluid}}\) values vary from 0.99992 to 0.9996 (Fig. 7), which corresponds to a range of K isotope fractionation between saprolite and fluid from −0.08‰ to −0.4‰. This range in \(\alpha\) overlaps with the calculated K isotope fractionation between illite and water (ca. −0.2‰) (Zeng et al., 2019); however, it differs from another theoretical study, which suggests that muscovite is enriched in

### Table 2

Potassium isotopic compositions of seawater standard and stream water samples from Guangdong, China.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sampling date</th>
<th>pH</th>
<th>K (ppm)</th>
<th>Na (ppm)</th>
<th>(\delta^{41}\text{K}) (‰)</th>
<th>2SD (‰)</th>
<th>95% c.i. (‰)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD-RW20140917</td>
<td>09/17/2014</td>
<td>6.83</td>
<td>2.94</td>
<td>4.66</td>
<td>−0.494</td>
<td>0.089</td>
<td>0.040</td>
<td>6</td>
</tr>
<tr>
<td>Replicate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−0.451</td>
<td>0.032</td>
<td>0.020</td>
<td>7</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>6.85</td>
<td>3.00</td>
<td>6.11</td>
<td>−0.701</td>
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Note 1. 2SD represents two standard deviation; 95% c.i. = 95% confidence interval, represents two standard error corrected by the Student’s t factor; N = number of analyses. See Hu et al. (2018) for more details.

Note 2. Replicate represents repeat sample dissolution, column chemistry, and instrumental analysis. Duplicate represents repeat analyses of the same K cut in different instrumental analytical sessions. Average represents error weighted values.

Note 3. Sampling date, pH, K and Na contents of stream water are from Wang et al. (2018).
heavy K isotopes by ~0.5‰ compared to water, while K-feldspar is depleted by ~0.3‰ at room temperature (Y.H. Li et al., 2019).

Our saprolite data suggest that illite is enriched in light K isotopes compared to K-feldspar. This is indicated by the negative trend between δ⁴¹K and the illite/K-feldspar ratio, where more deeply weathered saprolite samples tend to have higher illite/K-feldspar ratios and lower δ⁴¹K values (Fig. 7). To account for the isotopically heavy K in stream waters, mass balance also suggests that illite in the saprolite is enriched in light isotopes relative to K-feldspar in the unweathered granite. Our conclusion is further supported by the recent theoretical calculation suggesting that illite is ~0.3‰ lighter than K-feldspar (Zeng et al., 2019). Nonetheless, the fractionation between illite and K-feldspar suggested here might reflect kinetic processes instead of equilibrium fractionation, considering the sluggishness of isotope exchange at room temperature.

### 5.2. Implications for K isotope fractionation during chemical weathering

Our study demonstrates that large K isotope fractionation occurs during chemical weathering, with fluids taking heavy K isotopes. This finding has important implications for using K isotope geochemistry to trace continental weathering, ocean chemistry, crustal cycling, and mantle heterogeneity.

The contribution of chemical weathering to global elemental distribution and cycling has been well documented (Berner and Berner, 2012). Our results here suggest that chemical weathering also governs global K isotopic distribution and is the major process that produces the complementary and highly heterogeneous K isotopic compositions of crustal rocks and rivers. Furthermore, our data reveal a strong negative correlation between δ⁴¹K and indexes of chemical weathering, and hence greater K isotopic variation would be expected to occur at extreme weathering conditions. The most weathered sample in the granite weathering profile still contains 1.5 wt.% K₂O after losing ~80% K₂O. As weathering intensifies, the enhanced K loss in the saprolite will lead to an even lighter K isotopic composition of stream waters studied here is complemented to the variably light weathered residues resulting from differential weathering. Furthermore, K is biologically available to plants and microorganisms.
active and is enriched in plants. Biological processes are expected to play a role in fractionating K isotopes during weathering (Li et al., 2016; Christensen et al., 2018). Thus, chemical weathering, combined with contributions from heterogeneous bedrocks and plants, might be responsible for the large K isotopic variations observed in other rivers (S.L. Li et al., 2019). Our results also provide insight into the K isotopic balance of the oceans. The average $\delta^{41}$K of stream samples in our study is lower than that of the seawater. Similar results have also been observed for rivers from other locations (S.L. Li et al., 2019). Hence, the K isotopic composition of seawater is controlled by other processes in addition to the riverine inputs, which are required to either remove light K isotopes from, or add heavy K isotopes to the oceans in order to shift the bulk oceanic $\delta^{41}$K to the current value of 0.14‰ (Hille et al., 2019). The K elemental budget of the oceans is mainly controlled by inputs from continental runoff (mainly riverine input) and high-temperature hydrothermal activity, and by outputs to low-temperature alteration of seafloor basalts and sediments (reverse weathering, diagenetic K fixation, cation exchange) (Berner and Berner, 2012). Large K isotopic variation has recently been observed in ophiolites and pore fluids (Parendo et al., 2017; Santiago Ramos et al., 2018). These studies indicate that K isotopes are not quantitatively removed from seawater to altered products, and the large K isotope fractionation associated with oceanic sinks might be responsible for balancing the seawater isotopic budget. Thus, secular variations of seawater K isotopic compositions may prove to be a powerful tracer of continental weathering, atmospheric evolution, and hydrothermal activity over geologic time.

Our study, together with recent literature (Parendo et al., 2017; Santiago Ramos et al., 2018; Huang et al., 2020), shows that large K isotope fractionation occurs during water-rock interactions, especially at low temperatures, similar to other stable isotope systems (Valley and Cole, 2001; Teng et al., 2017). These processes result in highly heterogeneous K isotopic distribution in both continental crust (Huang et al., 2020) and subducting slabs. This isotopic heterogeneity, coupled with variable but generally high K concentration in crustal materials, makes K isotopes a powerful tracer of crustal cycling in the mantle (e.g., Sun et al., 2020).
6. CONCLUSIONS

High-precision K isotopic data for saprolites developed on diabase and granite weathering profiles, as well as data from local stream waters, lead to the following conclusions:

1. Saprolites from the diabase weathering profile are heavily weathered, but display limited K isotopic variation, which mainly reflects the conservative behavior of K during diabase weathering, with >50% of the original K remaining in the saprolites.

2. Saprolites from the granite weathering profile show significant and systematic K isotope fractionation \((\delta^{41}K / \delta^{39}K)_{\text{fluid}} / (\delta^{41}K / \delta^{39}K)_{\text{saprolite}} \geq 0.2\). Nearby stream waters display a slightly larger range \((\delta^{41}K / \delta^{39}K)_{\text{fluid}} \geq 0.37\‰\).

3. The large variation in \(\delta^{41}K\) in the granitic saprolites results from isotope fractionation during chemical weathering, as indicated by the negative correlation between \(\delta^{41}K\) with various indexes of weathering (e.g., sample depth, CIA, and kaolinite abundance).

4. Light K isotopes partition into weathered residues relative to fluids, as supported by the isotopically light saprolites and overall isotopically heavy stream water samples.

5. Continental weathering fractionates K isotopes significantly and is thus one of the main processes producing highly heterogeneous rivers and crustal rocks.

6. Large K isotope fractionation produced by fluid-rock interactions at Earth's surface, coupled with variably high K contents in surface materials, makes K isotopes a potentially powerful tracer of crustal recycling into the mantle.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fig. 6. Potassium isotopic variation versus water compositions (K, Na and pH) for nearby streams measured in this study (filled squares) and rivers from the literature (open squares) (S.L. Li et al., 2019).

Fig. 7. Plots of \(\delta^{41}K\) versus illite/K-feldspar (top panel) and versus \(\tau K_2O\) (bottom panel). Dotted lines in the bottom panel depict K removal via Rayleigh distillation for different values of the fractionation factor \(\tau = \frac{\delta^{41}K_{\text{fluid}}}{\delta^{41}K_{\text{saprolite}}}\). Stars represent the average of the relatively unweathered granites.
APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gca.2020.02.029.

REFERENCES


*Associate editor:* Brian W. Stewart