Understanding chemical reaction rates and isotope fractionation at chemical equilibrium is crucial in Earth sciences, yet data in these areas are limited. Recent advances in multiple collector inductively coupled plasma mass spectrometry have enabled scientists to study these isotopic reactions with small sample volumes.

We carried out multiple isotope exchange experiments at 22, 50, and 80°C and 1 bar, and concentrations of Ba\(^{2+}\) and SO\(_4^{2−}\) at solubility equilibrium with barite. The experimental solutions were spiked with isotopes of barium, sulfur, and oxygen that differed from the natural barite crystal. The differences in isotopic compositions showed continuous fluxes of Ba\(^{2+}\) and SO\(_4^{2−}\) ions to and from the surfaces of the barite crystal at chemical equilibrium, a phenomenon that would have been otherwise imperceptible without isotope doping [1].

The experiments revealed several key findings: (1) the rates of isotope exchange between the aqueous solutions and the barite surfaces are identical, and at solubility equilibrium, they are orders of magnitude slower than the far-from-equilibrium dissolution rates; (2) Ba and S isotope equilibrium fractionation factors were obtained from the three isotope method (Table 1) as well as the apparent activation energy at barite solubility equilibrium; and (3) multiple reaction stages occurred after the contact of barite surfaces with aqueous solutions, indicating different types of reaction mechanisms.


### Table 1. Equilibrium fractionations for Ba and S

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temp (°C)</th>
<th>$\Delta_{\text{eq, barite-fluid}}$ (%), $^{137/134}\text{Ba}$</th>
<th>$\Delta_{\text{eq, barite-fluid}}$ (%), $^{34/32}\text{S}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSS22</td>
<td>22</td>
<td>-0.1098</td>
<td>0.005</td>
</tr>
<tr>
<td>SS50</td>
<td>50</td>
<td>-0.0988</td>
<td>0.0076</td>
</tr>
<tr>
<td>SS80</td>
<td>80</td>
<td>-0.1028</td>
<td>0.0087</td>
</tr>
</tbody>
</table>

**Keywords:**
equilibrium, isotope exchange and kinetics

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**Preferred Presentation Style:**
Oral

**Conference Attendance:**
In person

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