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Exploring the pH dependency of volcanic sulfate $\Delta'^{17}O$ signals: Insights from sulfite oxidation experiments at varying pH

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The Proterozoic Era was a period of significant transitions including the oxygenation of atmosphere, and the emergence of eukaryotes. These transformations are linked to the oxygen cycle, which is hypothesized to be recorded in the isotopic compositions of sulfates. Sulfate triple-oxygen isotopes ($\delta^{18}O$ and $\Delta'^{17}O$) offer a window into past Earth surface redox conditions. Specifically, negative $\Delta'^{17}O$ anomalies in Proterozoic sulfates are considered indicators of atmospheric O_2 signals, providing insights into atmospheric pO_2/pCO_2 levels. However, the process that transfers atmospheric oxygen's negative $\Delta'^{17}O$ signal to sulfates remains debated. The prevailing hypothesis suggests atmospheric oxygen incorporation through oxidative weathering of pyrite, but this mechanism has recently been questioned. We propose an alternative pathway: the transfer could occur within volcanic clouds through the oxidation of SO_2 to sulfate by H_2O_2. Under expected Proterozoic pO_2/pCO_2 conditions, this process would carry a negative $\Delta'^{17}O$ signal, unlike today. However, this mechanism's pH dependency has not been fully explored, as previous experiments were conducted under acidic conditions only.

To fill this research gap, we synthesized barite at varying pH. The oxidation of sulfite to barite by H_2O_2 in the laboratory mirrors the final stage of sulfur oxidation to sulfate by H_2O_2 in volcanic clouds. We first synthesized barites from water with different $\delta^{18}O$ values using isotopically uniform H_2O_2 as oxidant, then from isotopically uniform water using H_2O_2 with different $\delta^{18}O$ values. We conducted oxygen isotope analysis on the barites, starting H_2O_2, and parent waters. Our preliminary results suggest that at high pH nearly all oxygen is derived from water and none from H_2O_2, whereas earlier experiments concluded that at low pH this ratio is 50:50.

Our results suggest that H_2O_2 oxygen incorporation to sulfate is pH dependent, and this process should be interpreted differently in alkaline and acidic environments. Volcanic cloud pH is thus an important factor to consider when interpreting volcanic $\Delta'^{17}O$ signals and exploring the validity of our alternative hypothesis of Proterozoic negative $\Delta'^{17}O$ anomalies. Our findings indicate that the transfer of ^{17}O-anomalous oxygen from O_2 to sulfate may differ significantly from previous assumptions, calling for the reinterpretation of sulfate $\Delta'^{17}O$-derived pO_2/pCO_2 reconstructions.