



The replacement of Celestine (SrSO_4) by Strontianite (SrCO_3) studied *in situ*, spatially resolved, and real-time by Raman spectroscopy

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The replacement reaction of celestine (SrSO_4) by strontianite (SrCO_3) is one of the most common ways to obtain pure strontianite that is an important industrial reagent. Thus, the replacement reaction has been studied extensively over the past decades. In this work the replacement serves as a model system to study solid-fluid reactions in particular, the behavior of oxygen isotopes during the reaction. Measurements of isotopically enriched compounds using Raman spectroscopy showed that oxo-anion groups perform localized vibrations with distinct frequencies. These vibrations reflect the oxygen-based isotopologues of the oxo-anion molecule and the relative intensities of these bands are proportional to the isotopologue fractions in the molecule species that allows the precise quantification of its isotope composition. Therefore, Raman spectroscopy provides us with a tool to monitor the behavior of oxygen isotopes at reaction interfaces and in the fluid. Combining a confocal Raman spectrometer with an in-house-made Teflon[®] fluid cell even enables spatially resolved, *in situ*, and real-time measurements.

Two different experimental setups were used to obtain general information about the replacement kinetics using isotopically natural solutions. The first experimental setup consisted of an in-house-made Teflon[®] fluid cell (with an internal heating system) filled with a 1M Na_2CO_3 solution and an equimolar amount of celestine powder. Grain sizes ranged between 63 and 125 μm and experimental temperatures were 35°C, 40°C, 45°C, and 50°C. At the start of the experiments the aqueous $\nu_1(\text{CO}_3)$ band could be observed at 1065 cm^{-1} that lost intensity over the course of the reaction. Complementary, the aqueous sulfate $\nu_1(\text{SO}_4)$ band at 981 cm^{-1} grows in intensity. From the relative changes between these bands we derived the reaction rates and the activation energy.

The second experimental setup also consisted of an in-house-made Teflon[®] fluid cell (without heating system) filled with 1M Na_2CO_3 solution and a rectangle rod of celestine (3 x 3 x 9 mm). This setup was used to measure the reaction front between mineral and fluid over the course of 10 days at room temperature ($21 \pm 1^\circ\text{C}$). First results show a fast formation of a strontianite rim, which slows down the consequential movement of the reaction front into the celestine. In the solution the intensity of $\nu_1(\text{CO}_3)_{aq}$ and $\nu_1(\text{SO}_4)_{aq}$ bands show a similar trend to the first experimental setup but near the fluid-solid interface a notable difference can be observed. The $\nu_1(\text{SO}_4)/\nu_1(\text{CO}_3)$ intensity ratio in solution decreases smoothly towards the reaction interface.

Future experiments will then be carried out with ^{18}O -labelled solution, which will allow studying the oxygen isotope exchange between aqueous carbonate, aqueous sulfate, and the solid strontianite product, while celestine is being replaced by strontianite.