



Precipitation of smithsonite under controlled pCO₂ between 25 and 60 °C - Fractionation of oxygen isotopes

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Owing to the large fractionation (i.e. $\Delta^{18}\text{O}_{\text{solid-diss.}} \sim 30\%$) between carbonate minerals and aqueous fluids with respect to their $^{18}\text{O}/^{16}\text{O}$ composition, the oxygen isotope composition of carbonates has been a fundamental tool for the estimation of mineral formation temperature by the geoscience community. Indeed the last 6 decades, a wide number of experimental studies investigated the temperature relation of $\Delta^{18}\text{O}_{\text{solid-diss.}}$ between divalent metal carbonates and aqueous fluids. To date however no experimental data exist for the temperature dependence of $\Delta^{18}\text{O}_{\text{solid-diss.}}$ between smithsonite (ZnCO_3) and fluid. This lack of data likely stems from a kinetic barrier effect, that of the dehydration of aqueous Zn^{2+} and the formation of hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$). Smithsonite is a secondary zinc mineral that is one of the components of zinc ore bodies. It is formed through oxidation of primary zinc ores by the reaction with a carbonate source or by precipitation of zinc salt solutions with a CO_2 -saturated and bicarbonate-rich solution. In this study we hydrothermally synthesized smithsonite at the temperature range between 25 and 60 °C and report the temperature dependence of oxygen isotope distribution between smithsonite and aqueous fluid. In order to avoid the formation of hydrozincite our experiments were conducted in titanium batch reactors using Teflon-inlets where the CO_2 pressure was adjusted to 10 bars. The low pH conditions provoked by the elevated pCO₂ applied, lead to the dissolution of hydrozincite, which is initially formed by mixing of Na_2HCO_3 (0.1 M) and $\text{Zn}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ (0.02 M) solutions, to yield - under the prevailing conditions - the thermodynamically stable mineral smithsonite.