



The influence of pH on the oxygen isotope equilibrium fractionation between sulfite and water

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Currently, the value for the oxygen isotope equilibrium fractionation between water and sulfite in solution is poorly constrained. Sulfite is an important intermediate in the oxidative/reductive sulfur cycle and oxygen isotope exchange between sulfite and water is expected to leave an imprint on the isotope composition of sulfate affected by sulfur cycling. One reason for the lack of accurate information about isotope fractionation between sulfite and water are technical difficulties in extraction of sulfite from solution for oxygen isotope analysis. The pH dependent presence of multiple S(IV) species in solution, i.e. sulfur dioxide (SO₂), bisulfite (HSO₃⁻), pyrosulfite (S₂O₅²⁻) and sulfite (SO₃²⁻) complicates data interpretation. For example, the oxygen isotope equilibrium fractionation between water and SO₃²⁻ may be different than that between water and any of the other sulfite species in solution. We exposed sodium sulfite (Na₂SO₃) solutions to different pH conditions and monitored oxygen isotope exchange between sulfite and water, until isotope equilibrium was reached. The equilibrium value is determined by using two isotopically different sodium sulfite starting materials, one with a starting value lighter than the equilibrium value and one with a starting composition heavier than the equilibrium value. In this manner oxygen isotope equilibrium is approached from two directions. Sulfite from solution was precipitated as BaSO₃ with a set of Ba(OH)₂ solutions containing different oxygen isotope compositions. This procedure allows us to disentangle the oxygen isotope contribution from water incorporated during the precipitation from the oxygen isotope composition of sulfite in solution. We present the first results from this experimental approach and discuss the applicability of determining isotope equilibrium fractionations between water and distinct S(IV) species.