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Calibrating triple oxygen isotope fractionation between dissolved sulfite species and water

YU WEI[1,2], HAO YAN[1,2], YAN FANG[1,2], YONGBO PENG[3,4] AND HUIMING BAO[4,5]

[1]International Center for Isotope Effects Research, School of Earth Sciences and Engineering, Nanjing University

[2]Frontiers Science Center for Critical Earth Material Cycling, State Key Laboratory of Critical Earth Material Cycling and Mineral Deposits, School of Earth Sciences and Engineering, Nanjing University

[3]Nanjing University

[4]Frontiers Science Center for Critical Earth Material Cycling, School of Earth Sciences and Engineering, Nanjing University, China

[5]International Center for Isotope Effect Research, Nanjing University, China

The oxygen isotope composition of sulfate is widely used to constrain its origin and the ambient conditions during its formation. In the oxidative sulfur cycle, which converts reduced sulfur compounds to sulfate, sulfite acts as a key sulfoxy intermediate. The oxygen isotope composition of the resulting sulfate is therefore influenced by that of sulfite. Due to the rapid oxygen isotope exchange between sulfite and ambient water (e.g., occurring in less than one second at neutral pH), equilibrium isotope fractionation between sulfite and water is quickly established under most natural conditions. Although both experimental and computational studies have explored oxygen isotope fractionation between water and sulfite, significant discrepancies persist across these studies. Experimental efforts often struggle with accurately measuring the oxygen isotope composition of sulfite, while computational models are highly sensitive to the choice of potential energy surface scaling factors.

In this study, we refined the sulfite extraction method from aqueous solutions and employed a recently developed high-temperature conversion-electron discharge-CO_2/O_2 exchange technique to investigate triple oxygen isotope fractionation between sulfite and water over a temperature range of 12-55°C and a pH range of 4.6-9.0. We observed temperature- and pH-dependent variations in the $^{18}\alpha$ values and $\Delta'^{17}O$ values, with the pH dependence arising from changes in the SO_3^{2-} to bisulfite ratio as a function of pH. The $\delta^{18}O$ and $\Delta'^{17}O$ values of bulk bisulfite (HSO_3^- and SO_3H^-) were 5‰ higher and 10 ppm lower, respectively, than those of sulfite under equilibrium conditions. The calibrated $^{18}\alpha_{bisulfite\text{-}H2O}$ matched the computational values within 2‰, but $^{18}\alpha_{SO3\text{-}H2O}$ was ~7‰ higher. The distinct $\delta^{18}O$ values of different sulfite species help explain the pH dependence of $\delta^{18}O_{SO42-}$ during pyrite oxidation. Our results also suggest that HSO_3^- plays a major role in biologically mediated SO_4^{2-}-H_2O oxygen isotope equilibration.