Equilibrium and kinetic fractionation on S-O clumping of sulfate

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Sulfur and oxygen isotopes of sulfate have been used to trace biogeochemical processes through time. Potentially, doubly-substituted isotopologues of sulfate may provide unique additional information, though the measurement of isotopic clumping has been challenging. Recently, we have developed a SO_2F_2 method to determine $\Delta^{34}S^{18}O$ value, which represents relative abundance of $^{34}S^{18}O$ species against stochastic distribution, by using high-mass-resolution mass spectrometer (Katsuta et al. in this volume). In order to understand the potential fractionation processes, we have conducted a series of experiments. First, sulfate was synthesized by oxidation of Na_2SO_3 solution at various temperature. The results show that the $\Delta^{34}S^{18}O$ value systematically decrease about 0.8‰ from 6°C to 120°C. More negative $\Delta^{34}S^{18}O$ can be observed when the sulfite was quickly oxidized and precipitated as $BaSO_4$. The results suggest that the oxygen exchange between SO_3^{2-} and H_2O is responsible for changing the abundance of ^{34}S-^{18}O bonding in the resulting sulfate, though additional kinetic effect should be accompanied during the oxidation step. Once the SO_4^{2-} ion forms, the $\Delta^{34}S^{18}O$ value seems to be quenched likely due to very slow exchange of oxygen with water. These results suggest that sulfate $\Delta^{34}S^{18}O$ may not be utilized as a geothermometer for paleo-seawater, instead may be a tracer for distinguishing several key biogeochemical processes, including oxidative weathering and microbial sulfur metabolisms.