Temperature Dependence of ^{13}C-^{18}O "clumping" in Synthetic Aragonite: Calibration of a New Paleothermometer

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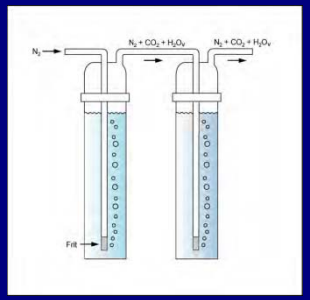
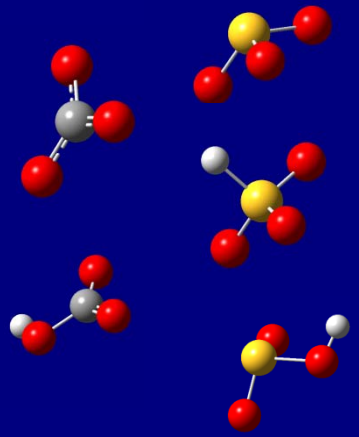
$$Ca^{13}C^{16}O^{16}O^{16}O + Ca^{12}C^{18}O^{16}O^{16}O = Ca^{13}C^{18}O^{16}O^{16}O + Ca^{12}C^{16}O^{16}O^{16}O$$





The goal of our ACS-PRF funded research is to provide scientists with a high-quality experimental calibrations of (1) an inorganic aragonite clumped isotope paleothermometer. The new clumped isotope paleothermometer based on the abundance of the doubly-substituted CO_3 isotopologue, $^{13}C^{18}O^{16}O_2$ in the aragonite mineral lattice; (2) the level of association of ^{13}C and ^{18}O of dissolved carbonate and bicarbonate; and (3) the isotope effects associated with aqueous oxidation of S(IV) (bisulfite and sulfite). This work will allow for determination of the formation temperature of the carbonate and of the pathways associated with S(IV) oxidation. The temperature constraints can then be used to constrain the isotopic composition of past ocean water which in turn can be used to place constraints on the mass of water in the oceans compared to the mass of water in ice sheets. The pathways for S(IV) oxidation can be used to constrain environmental pH conditions and redox system pathways in rainwater and gradient systems in natural waters and sediments.