

ABSTRACT

Experimental Studies of Oxygen Isotope Fractionation in the Carbonic Acid System at

15°, 25°, and 40°C. (August 2004)

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In light of recent studies that show oxygen isotope fractionation in carbonate minerals to be a function of HCO_3^- and CO_3^{2-} concentrations, the oxygen isotope fractionation and exchange between water and components of the carbonic acid system (HCO_3^- , CO_3^{2-} , and $\text{CO}_{2(\text{aq})}$) were investigated at 15°, 25°, and 40°C. To investigate oxygen isotope exchange between HCO_3^- , CO_3^{2-} , and H_2O , NaHCO_3 solutions were prepared and the pH was adjusted over a range of 2 to 12 by the addition of small amounts of HCl or NaOH. After thermal, chemical, and isotopic equilibrium was attained, BaCl_2 was added to the NaHCO_3 solutions. This resulted in immediate BaCO_3 precipitation; thus, recording the isotopic composition of the dissolved inorganic carbon. Data from experiments at 15°, 25°, and 40°C (1 atm) show that the oxygen isotope fractionation between HCO_3^- and H_2O as a function of temperature is governed by the equation:

$$1000 \ln \alpha_{\text{HCO}_3^- - \text{H}_2\text{O}} = 2.66 \pm 0.05 \left(10^6 T^{-2} \right) + 1.18 \pm 0.52$$

where α is the fractionation factor and T is in kelvins. The temperature dependence of oxygen isotope fractionation between CO_3^{2-} and H_2O is

$$1000 \ln \alpha_{\text{CO}_3^{2-}\text{-H}_2\text{O}} = 2.28 \pm 0.03 (10^6 T^{-2}) - 1.50 \pm 0.29.$$

The oxygen isotope fractionation between $\text{CO}_{2(\text{aq})}$ and H_2O was investigated by acid stripping $\text{CO}_{2(\text{aq})}$ from low pH solutions; these data yield the following equation:

$$1000 \ln \alpha_{\text{CO}_{2(\text{aq})}\text{-H}_2\text{O}} = 2.52 \pm 0.03 (10^6 T^{-2}) + 12.12 \pm 0.33.$$

The kinetics of oxygen isotope exchange were also investigated. The half-times for exchange between HCO_3^- and H_2O were 3.6, 1.4, and 0.25 h at 15°, 25°, and 40°C, respectively. The half-times for exchange between CO_3^{2-} and H_2O were 1200, 170, and 41 h at 15°, 25°, and 40°C, respectively.

These results show that the $\delta^{18}\text{O}$ of the total dissolved inorganic carbon species can vary as much as 17‰ at a constant temperature. This could result in temperature independent variations in the $\delta^{18}\text{O}$ of precipitated carbonate minerals, especially in systems that are not chemically buffered.