

An experimental constraint on the oxygen isotope fractionation ($^{18}\text{O}/^{16}\text{O}$) between water and aqueous hydroxide ion

DAVID BAJNAI AND DANIEL HERWARTZ

University of Cologne

Presenting Author: david.bajnai@uni-koeln.de

The stable oxygen isotope fractionation factor between water and aqueous hydroxide ion (OH^-) ($10^3\ln\alpha_{\text{H}_2\text{O}-\text{OH}^-}$) is a widely used geochemical parameter, also integral to biomineralisation models. In any reaction involving water, the educt oxygen is either derived from H_2O or OH^- . Studies from the 1960s experimentally determined the $10^3\ln\alpha_{\text{H}_2\text{O}-\text{OH}^-}$ value at 15 °C to be 44(\pm 4)‰ and calculated its equilibrium temperature dependence based on partition function ratios [1]. A recent study challenged these findings on the basis that the aqueous hydroxide ion is encased in water clusters, which was neglected in previous gas-phase calculations. New quantum chemical computations yield lower $10^3\ln\alpha_{\text{H}_2\text{O}-\text{OH}^-}$ values (i.e., 19.35–23.89‰ at 15 °C) and a shallower temperature dependence than previously suggested [2].

To solve this controversy, we performed quantitative BaCO_3 precipitation experiments using tank CO_2 gas and hyperalkaline $\text{Ba}(\text{OH})_2$ solutions with known oxygen and carbon isotopic compositions. Minor differences ($< 0.2\%$) between the $\delta^{13}\text{C}$ values of the BaCO_3 and the tank CO_2 attest to quantitative precipitation. Since the precipitate directly inherited 1/3 of its oxygen from OH^- and 2/3 from the tank CO_2 , the $\delta^{18}\text{O}$ value of the OH^- can be calculated via mass balance, and subsequently, the $10^3\ln\alpha_{\text{H}_2\text{O}-\text{OH}^-}$ can be derived.

Our $10^3\ln\alpha_{\text{H}_2\text{O}-\text{OH}^-}$ values show a similar temperature dependence as the recent theoretical study [2], but our fractionation factor at 15 °C is much closer to the experimental value reported in the 1960s [1]. Possible explanations for the discrepancy between the theoretical model and experimental results include so-far-unidentified kinetic isotope effects in our precipitation experiments (e.g., at the crystal/solution interface) or that the self-ionisation of water cannot be described as a classic equilibrium. The disintegration of H_2O may produce isotopically light OH^- due to the preferential breaking of bonds between light isotopes. The back reaction, however, is controlled by diffusion of the H^+ ion and may be less isotope specific with respect to oxygen.

[1] Green, M., Taube, H. (1963) Isotopic fractionation in the OH^- - H_2O exchange reaction. *J. Phys. Chem.* 67, 7, 1565-1566.

[2] Zeebe, R. E. (2020) Oxygen isotope fractionation between water and the aqueous hydroxide ion. *Geochim. Cosmochim. Acta* 289, 182-195.