Oxygen isotope (^{18}O/^{16}O) fractionation between water and hydroxide ion

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In any reaction involving water, the educt oxygen is either derived from H_2O or OH^- (i.e., the hydroxide ion). For example, during carbonate precipitation the relative proportion of (de)hydration ($CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$) and (de)hydroxylation ($CO_2 + OH^- \rightleftharpoons HCO_3^-$) reactions is pH-dependent. When modelling this system, the oxygen isotopic composition of water can be measured directly, but the oxygen isotopic composition of hydroxide must be calculated from the respective fractionation factor ($1000\ln\alpha_{H2O-OH^-}$). Experimental studies from the 1960s determined $1000\ln\alpha_{H2O-OH^-}$ to be 39.22(±2.88)‰ at 25 °C and estimated its temperature dependence at $\sim$0.5‰ °C^{-1} (1-3). These empirical observations were recently questioned by a theoretical study that implied a much lower fractionation factor of 23.18–18.91‰ at 25 °C as well as a lower temperature dependence of $\sim$0.05‰ °C^{-1} (4).

To provide new experimental data to solve this controversy, we performed quantitative witherite ($BaCO_3$) precipitation experiments. Tank CO_2 gas of known oxygen and carbon isotopic composition was injected into saturated $Ba(OH)_2$ solution of known oxygen isotopic composition. Following the hydroxylation of the CO_2, $BaCO_3$ instantly precipitated from the high pH (>12) solution. Since the precipitate directly inherited 1/3 of its oxygen from the hydroxide ion and 2/3 from the tank CO_2, the $\delta^{18}O$ value of the OH^- can be calculated via mass balance. Subsequently, the $1000\ln\alpha_{H2O-OH^-}$ value can be derived. Altogether 18 experiments were performed at a range of temperatures (1–80 °C) and using solutions of different oxygen isotopic composition (range of ca. 20‰). Minor variations between the $\delta^{13}C$ values (< 1‰) of the $BaCO_3$ and the tank CO_2 attests the quantitative precipitation of the reference gas.

Our $1000\ln\alpha_{H2O-OH^-}$ values show a similar temperature dependence as the recent theoretical study of Zeebe (4), but our fractionation factor at 25 °C is much closer to the values reported in the 1960s. Reasons for the discrepancies between our study and previous publications in terms of $1000\ln\alpha_{H2O-OH^-}$ and its temperature dependency will be discussed. One of our hypotheses is that the $H_2O \rightarrow OH^- + H^+$ reaction introduces a large kinetic effect as isotopically light H_2O is pyrolysed more frequently. In contrast, the back reaction proceeds rapidly without an isotopic preference. Hence, the self-ionisation of water cannot be described as a classic equilibrium. Alternative explanations such as unidentified kinetic isotope effects in our precipitation experiments (i.e., on the crystal surface) cannot be ruled out.

(1) H. R. Hunt, H. Taube, The relative acidity of H_2O^{18} and H_2O^{16} coördinated to a tripositive ion. J. Phys. Chem. 63, 124-125 (1959).

(2) E. R. Thornton, Solvent isotope effects in H_2O^{16} and H_2O^{18}. J. Am. Chem. Soc. 84, 2474-2475 (1962).

(3) M. Green, H. Taube, Isotopic fractionation in the OH^-–H_2O exchange reaction. J. Phys. Chem. 67, 1565-1566 (1963).

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