An experimental constraint on the oxygen isotope (¹⁸O/¹⁶O) fractionation between water and aqueous hydroxide ion

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Brief overview:

(1) **Main question:** What is the temperature dependence of a_{H2O-OH} ?

 $\alpha_{H_2O-OH^-} = \frac{\delta^{18}O_{H_2O} + 1000}{\delta^{18}O_{OH^-} + 1000}$

(2) Why is it interesting? The parameter α_{H2O-OH^-} is widely used in geochemical models.

③ **Is it not known already?** There is only one experimental study that determined the a_{H2O-OH} -value at 15 °C. Its temperature dependence was calculated based on statistical mechanics. A recent study pointed out several shortcomings of these earlier works and estimated different a_{H2O-OH} -values based on quantum-chemical calculations.

(4) What did we do? We did quantitative precipitation experiments at a wide range of temperatures using CO₂ gas and alkaline solutions with known δ^{13} C and δ^{18} O values. Then, we measured the δ^{18} O values of the carbonate precipitates. From these values, using a mass balance, we calculated the δ^{18} O value of OH⁻, and finally α_{H2O-OH} -.

(5) What did we find? The temperature dependence of experimentally determined α_{H2O-OH} -values agree with theoretical calculations, but the values are shifted to higher values, likely due to kinetic isotope effects on OH⁻.

(6) Our experimentally determined equation accounts for kinetic isotope effects that are $10^3 \ln \alpha_{H_2O-OH^-} = -0.037 \times T + 42.8$ superimposed on thermodynamic equilibrium $\alpha_{H_2O-OH^-}$ values in most natural systems. (*T* is in °C)

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- The first (and so far, the only) direct experimental estimate for α_{H2O-OH} is from Green & Taube (1963 \blacktriangle).
 - G&T determined the temperature dependence of a_{H2O-OH} by linear interpolation between their experimental data at 15 °C and previous theoretical data (Thornton, 1962) relevant at 25 °C (green line).
- Additional estimates for α_{H2O-OH}- can be deduced from the low-pH experiments of Beck et al. (2005 ◆) and the closed-system precipitation experiments of Clark et al. (1992 ▼).
- These earlier findings were challenged by Zeebe (2020) on the basis that the aqueous hydroxide ion is encased in water clusters, which was neglected in previous gas-phase calculations.
 - The novel quantum-chemical computations of Zeebe (2020) consider hydrogen bonds between dissolved OH⁻ and H₂O and yield much lower α_{H2O-OH^-} values and a shallower temperature dependence (**black lines**) than previously suggested.

New experimental data are needed to confirm either finding.

Theory:

- In a high pH (> 12) solution, CO₂ is transformed into bicarbonate anion via the hydroxylation reaction:
 1. CO_{2 (aq)} + OH⁻ ⇔ HCO₃⁻
- CO₂ absorption is followed by the rapid deprotonation of the bicarbonate anion and the subsequent solid carbonate precipitation:
 - 2. $HCO_3 \Leftrightarrow H^+ + CO_3^{2-}$
 - 3. $CO_3^{2-} + Ba^{2+} \Leftrightarrow BaCO_3$
- If CO_{2 (aq)} is quantitatively precipitated, the precipitate directly inherits 2/3 of its oxygen from CO₂ and 1/3 from the hydroxide ion:
 - 4. $\delta^{18}O_{BaCO3} = 2/3 \ \delta^{18}O_{CO2} + 1/3 \ \delta^{18}O_{OH}$
- By measuring the $\delta^{18}O_{BaCO3}$ value, the $\delta^{18}O_{OH}$ value can be calculated.

Practice:

- We performed quantitative BaCO₃ precipitation experiments using tank CO₂ gas and hyperalkaline Ba(OH)₂ solutions with known oxygen and carbon isotopic compositions.
- On a custom-built vacuum line, pure CO₂ gas was transferred from a gas tank into a gas syringe.
- To instantly precipitate BaCO₃, the CO₂ gas in the syringe was injected into an Exetainer vial filled with Ba(OH)₂ solution and held at the required temperature (1–80 °C).



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- If CO₂ is quantitatively precipitated, then $\delta^{13}C_{CO2} = \delta^{13}C_{BaCO3}$
- Non-quantitative precipitation of CO₂ leads to kinetic isotope effects in the dissolved inorganic carbon pool:
 - **A.** CO₂ absorption at high pH introduces a covariation between $\delta^{18}O_{BaCO3}$ vs $\delta^{13}C_{BaCO3}$ values, along a slope of ca. 0.5.
 - **B.** Consequently, $10^{3} \ln \alpha_{H2O-OH^{-}}$ values are shifted towards higher values, along a slope of -1.6.
- Two of the precipitation experiments in this study are likely affected by kinetic isotope effects in the DIC pool not 100% of the CO₂ gas in the syringe precipitated as $BaCO_3$ therefore, we excluded them from determining the temperature dependence of the a_{H2O-OH} values (X mark excluded samples).



We used two solutions with different oxygen isotope compositions, hence the bimodal distribution of the δ^{18} O values.

RESULTS: The oxygen isotope fractionation factor between water and aqueous hydroxide ion



Temperature (°C)

• The **blue line** is an error-considering linear regression fitted on the 20 data points in this study (••):

 $10^{3} \ln \alpha_{H2O-OH^{-}} = -0.037(\pm 0.004) \times T + 42.8(\pm 0.2)$

- Our data agree with previous experimental results ($\blacktriangle \diamond \lor$).
- Our data show similar temperature dependence as the quantum-chemical calculations (black lines) but are shifted to higher values by ca. 19‰.

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Kinetic isotope effects on OH-



Temperature (°C)

- Experimental α_{H2O-OH}- data are shifted to higher values compared to quantum-chemical computations. We hypothesise that this shift is likely related to kinetic isotope effects on OH⁻.
- Such kinetic isotope effects may result from the faster diffusion of the light ¹⁶OH⁻ isotopologue compared to the heavy ¹⁸OH⁻ isotopologue, resulting in the preferential reaction of the isotopically light OH⁻ during CO₂ absorption.
- Using Graham's law: the diffused OH⁻ has an up to 56‰ lower $\delta^{18}O_{OH^-}$ value.
 - The recycling of the OH⁻ pool is effectively instantaneous; thus, the preferential consumption of ¹⁶OH⁻ will not induce any Rayleigh-fractionation effects, which would isotopically enrich the residual OH⁻ pool.

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Conclusions



The experimentally determined equation in this study accounts for naturally occurring (and likely temperature independent) kinetic isotope effects on OH⁻ that are superimposed on thermodynamic equilibrium $10^{3}\ln a_{H2O-OH^{-}}$ values in most natural systems. It is recommended for future applications (*T* in °C):

 $10^{3} \ln \alpha_{H2O-OH^{-}} = -0.037(\pm 0.004) \times T + 42.8(\pm 0.2)$

Thank you for reading!

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