Oxygen isotope fractionation between water and the aqueous hydroxide ion

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Abstract

The stable oxygen isotope fractionation factor between water and the aqueous hydroxide ion is a fundamental geochemical parameter widely used in the Earth Sciences and other fields. Studies from the 1960s reported \( \frac{\Delta^{17} \text{O}}{\Delta^{18} \text{O}} \), the fractionation factor between liquid \( \text{H}_2\text{O} \) and aqueous \( \text{OH}^-/C_{0\text{aq}} \), theoretically as 1.046 and \( \frac{\Delta^{17} \text{O}}{\Delta^{18} \text{O}} \) (46‰ and 48‰ at 15 °C and 25 °C) and experimentally as 1.045 (45‰) at 15 °C. These, or similar values have been used in the literature for almost 60 years. Here I present quantum-chemical (QC) calculations, showing that the above theoretical values are fundamentally wrong as they pertain to free \( \text{OH}^- \) (incorrectly assumed equivalent to aqueous \( \text{OH}^-/C_{0\text{aq}} \)) and ignore intermolecular vibrational modes in solution. As a result, the theoretical values from the 1960s are off by a factor of 2 (when expressed in ‰), suggesting that the experimental value is also wrong. QC computations of \( \text{OH}^-/C_{0\text{aq}} \)-water clusters with up to \( n = 22 \) water molecules demonstrate that hydrogen bonding in solution significantly affects the fundamental vibrational modes associated with \( \text{OH}^- \) and substantially reduces the oxygen isotope fractionation between water and \( \text{OH}^-/C_{0\text{aq}} \), compared to the fractionation between water and free \( \text{OH}^- \). The most accurate QC methods tested here yield values for the fractionation factor between \( \text{H}_2\text{O} \) and \( \text{OH}^-/C_{0\text{aq}} \) in water clusters with \( n = 7 \) to 22 water molecules of \( \Delta^{17} \text{O} \) from 1.019 to 1.024 (19 to 24‰) at 25 °C based on the harmonic approximation. Estimated effects due to anharmonicity (from numerically demanding computations) could add uncertainties of up to 3‰ to these values.

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1. INTRODUCTION

The stable oxygen isotope fractionation factor between liquid water and the aqueous hydroxide ion, \( \frac{\Delta^{17} \text{O}}{\Delta^{18} \text{O}} \), is a fundamental physicochemical parameter widely used in geochemistry, physical chemistry, biochemistry, and other fields. For instance, \( \frac{\Delta^{17} \text{O}}{\Delta^{18} \text{O}} \) is listed in various compilations (e.g., Friedman et al., 1977; Rishavy and Cleland, 1999) and is critical to understanding oxygen isotope partitioning in natural waters (e.g., Clark et al., 1992; Clark and Fritz, 1997; Thorstenson and Parkhurst, 2002), dissolved phosphate (von Sperber et al., 2014), minerals (Devriendt et al., 2017; Böttcher et al., 2018), the aqueous CO\(_2\) system (Usdowski et al., 1991; Beck et al., 2005; Sade and Halevy, 2017), corals (Rollion-Bard et al., 2010), speleothems (Dreybrodt et al., 2016), travertines (Falk et al., 2016), microbial carbonates (Thaler et al., 2020), as well as mechanisms of triple oxygen isotope fractionation (Guo and Zhou, 2019), solvent nucleophile isotope effects (Cassano et al., 2004), and more. Despite the broad application of \( \frac{\Delta^{17} \text{O}}{\Delta^{18} \text{O}} \), the values currently in use appear to be based on just three studies published around 1960 (Hunt and Taube, 1959;
Thorton, 1962; Green and Taube, 1963), which, as shown below, are very likely in error. Note that the results of Thorton (1962) and Green and Taube (1963) have been questioned before based on indirect evidence (Böttcher et al., 2018) (see Appendix E).

The majority of geochemical applications is primarily concerned with the oxygen isotope fractionation between liquid water and the aqueous hydroxide ion. However, for theoretical and computational reasons, water vapor and the isolated (free) OH⁻ ion in the gas phase will also be discussed below (for observational/spectroscopic studies of the free OH⁻ ion, see e.g., Owartsy et al. (1985) and Lutz (1995)). In general, the ¹⁸O/¹⁶O isotopic exchange reaction between water and the hydroxide ion in different phases may be written as:

\[
H_2^{18}O(p) + ^{16}OH^- (q) = H_2^{18}O(p) + ^{16}OH^- (q)
\]

where \( p = v, l \) (vapor or liquid) and \( q = g, aq \) (gas-phase or aqueous). The equilibrium constant (\( K \)), or fractionation factor (\( \alpha \)), for reaction (1) is given by (single atom exchange):

\[
K_{p-q} = \frac{x_{(H_2O)(p)-OH^-}(q)}{x_{p-q}} = \frac{[H_2^{18}O_p]/[H_2^{16}O_p]}{[^{16}OH^-_q]/[^{18}OH^-_q]}.
\]

As detailed in Section 2, it appears that so far only three studies from the late 1950s and early 1960s have reported theoretical estimates for \( x_{p-q} \) and one experimental value for \( x_{aq} \) at 15 °C (Hunt and Taube, 1959; Thorton, 1962; Green and Taube, 1963). From the brief description of the experimental methods in Green and Taube (1963) it is not obvious how exactly \( x_{aq} \) was determined (see Appendix A). Yet, the authors state good agreement with the theoretical results, which actually pertain to \( x_{aq} \), i.e., to the free, not aqueous, OH⁻ ion (see Section 2, note that it is not suggested here the experimental results pertain to \( x_{aq} \)). Nevertheless, the results of Thorton (1962) and Green and Taube (1963) have subsequently been used in numerous studies for \( x_{aq} \) cited in various reviews, and included in several compilations (e.g., Friedman et al., 1977; Clark and Fritz, 1997; Rishavy and Cleland, 1999; Thorstenson and Parkhurst, 2002; Devriendt et al., 2017; Sade and Halevy, 2017). Using quantum-chemical (QC) calculations, I show here that the theoretical value from Green and Taube (1963) is fundamentally problematic in aqueous solution (and off by a factor of ~2 when expressed in ‰), suggesting that the experimental value is also incorrect (see Appendix A).

2. ANALYTICAL GAS-PHASE CALCULATION

The theoretical calculations from the late 1950s and early 1960s (Hunt and Taube, 1959; Thorton, 1962; Green and Taube, 1963) on the oxygen fractionation between H₂O and OH⁻ are briefly reviewed here for two reasons. First, the details of the method and calculations were not provided in the original papers. Hence being able to reproduce the results will confirm the method that was applied then. Second, the calculations illustrate the fundamental difference to the QC computations employed in this study. Taube, Thorton and co-workers apparently treated the aqueous hydroxide ion as an isolated diatomic molecule in the “gas phase”. In the harmonic oscillator approximation, the harmonic frequency is then given by:

\[
f = \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu}}
\]

where \( \kappa \) is a force constant and \( \mu = m_1m_2/(m_1 + m_2) \) is the reduced mass. Frequencies are commonly reported in wavenumbers (unit cm⁻¹), \( \omega = f/c \), where \( c \) is the speed of light. To a good approximation, \( \kappa \) is the same in the isotopically substituted molecule (primed quantities) and hence the frequency ratio is simply:

\[
\frac{\omega'}{\omega} = \sqrt{\frac{\mu'}{\mu}}.
\]

Inserting masses for \(^{16}OH^-\), \(^{18}OH^-\), and \( \omega = 3615 \text{ cm}^{-1} \) for \(^{18}OH^-\) (Thorton, 1962), gives \( \omega' = 3603.05 \text{ cm}^{-1} \), which is identical to the value given in Table II of Thorton (1962).

With these two frequencies (and a small contribution from libration (Thorton, 1962)), the OH⁻ partition function ratio can be calculated as \( Q'/Q = 1.2279 \) (see Eqs. (5) and (6) below). Finally, the equilibrium constant, or fractionation factor, for the isotopic exchange reaction (Eq. (1)) in the gas phase at 25 °C is \( \alpha_{25} = 1.2752/1.2279 = 1.0385 \), where 1.2752 is the corresponding partition function ratio for \( H_2^{18}O(v)/H_2^{16}O(v) \).

Indeed, 1.0385 at 25 °C was given by Thorton (1962) and hence confirms the “gas phase” calculation for both OH⁻ and H₂O (cf. Section 4.1 and Table 1 below). While Thorton (1962) made no explicit distinction between gas, solution, free, and aqueous compounds in his calculations, he applied his results to isotope effects in solution. Taking into account the fractionation between liquid water and water vapor, \( x_{(H_2O)(v)-OH^-}(aq) = 1.0094 \) at 25 °C (Majoube, 1971), Thorton’s calculated fractionation factor becomes ~1.048 between liquid water and free OH⁻. Hunt and Taube (1959) and Green and Taube (1963) calculated corresponding values of 1.035 and 1.046 at 25 °C and 15 °C relative to water vapor and liquid water, respectively. These authors specifically referred to “aqueous OH⁻” and “18OH⁻aq”, whereas their calculation actually pertains to free OH⁻.

In summary, early calculations presented values for the ¹⁸O/¹⁶O fractionation between liquid water and the “aqueous” hydroxide ion upwards of 46‰ (\( T_c = 15–25 \) °C), assuming no difference between aqueous and free OH⁻. Supported by the experimental results of Green and Taube (1963), such values have been used for \( x_{(H_2O)(v)-OH^-}(aq) \) since then (see Section 1). I will show below that the gas phase treatment of the hydroxide ion in aqueous solution is fundamentally problematic because of hydrogen bonding (see Fig. 1). Hydrogen bonding significantly affects the fundamental vibrational modes associated with OH⁻ in aqueous solution and substantially reduces the oxygen isotope fractionation between water and OH⁻ (aq), compared to the fractionation between water and free OH⁻.
3. ISOTOPIC EQUILIBRIUM: THEORY

Isotopic fractionation factors in thermodynamic equilibrium are calculated from first principles based on differences in the vibrational energy of molecules. In this study, we determine harmonic frequencies and molecular forces using quantum-chemical (QC) computations (e.g. Jensen, 2004; Schauble, 2004; Zeebe, 2005; Guo et al., 2009; Zeebe and Rae, 2020). The X3LYP functional (X3LYP+) was employed for higher level optimizations and large clusters with up to \( n = 22 \) water molecules. X3LYP/6-311++G(d,p), which also adds a diffuse polarization function to hydrogen, gave nearly identical results, e.g., \( \Delta \beta = 0.2\% \) for \( \text{OH}^- \cdot (\text{H}_2\text{O})_3 \), similar for B3LYP/6-311+ +G(2d,2p), which includes 2 \( d \) and 2 \( p \) polarization functions (see Fig. 4). Computations with the most complete basis sets (representing molecular orbitals) tested here were performed with MP2/aug-cc-pVDZ (MP2DZ), which are however computationally expensive and mostly impractical for large water clusters.

We selected the methods HF, X3LYP+, and MP2DZ because they are frequently used in QC computations and similar LoT and basis sets have been applied to isotope calculations previously (e.g. Oi, 2000; Schauble, 2004; Zeebe, 2005; Liu and Tossell, 2005; Liu et al., 2010; Zeebe, 2010; Zeebe, 2014; Zeebe and Rae, 2020). The X3LYP functional was developed to improve the accuracy for hydrogen-bonded and van der Waals complexes and has been applied to large water clusters (Xu et al., 2004; Su et al., 2004). For HF frequencies, a scale factor of \( s = 0.92 \) was applied, whereas unscaled frequencies were used from X3LYP+.
and MP2DZ computations. Scale factors correct for shortcomings in theoretical treatments, including neglect of anharmonicity, incomplete electron correlation, and the use of finite basis sets. Hartree-Fock theory, for instance, tends to overestimate vibrational frequencies because of improper dissociation behavior (e.g., Scott and Radom, 1996). The scale factors applied here are close to those obtained from general low-frequency fits to >1,000 observed frequencies and are consistent with scale factors from our previous work on boron, carbon, and oxygen isotopes (Scott and Radom, 1996; Merrick et al., 2007; Zeebe, 2005; Zeebe, 2014; Zeebe and Rae, 2020). For all molecules and water clusters studied here (see Fig. 1), geometry optimizations were followed by full Hessian (force-constant matrix) runs to determine frequencies and to ensure that none of the calculated frequencies was imaginary (which would indicate unstable geometry). Frequencies of the largest clusters from X3LYP + and MP2DZ computations, including $^{18}$O and $^{17}$O substitution (of potential interest for triple oxygen isotope studies), are given in the Electronic Annex.

### 3.2. Anharmonicity

Harmonic frequencies are based on a local quadratic approximation to the potential energy surface (PES), while anharmonic frequencies are either based on the actual PES (obtained directly from observations) or an approximation closer to the actual PES. As mentioned above, Eq. (5) is based on the harmonic approximation and hence requires harmonic frequencies as input by definition (Urey, 1947; Bigeleisen and Mayer, 1947; Richet et al., 1977; Liu et al., 2010). Thus, simply inserting anharmonic frequencies into Eq. (5) to calculate $Z$ is incorrect. Yet, one still would like to know whether anharmonicity effects on the calculated $Z$’s involving the OH$^-$ ion are significant or not.

Possible anharmonicity effects were therefore examined following an approach described in Zeebe (2009). Note that Zeebe’s (2009) and, e.g., Liu et al.’s (2010) methods to estimate anharmonic effects are based on similar elements (see, e.g., Nielsen, 1951; Herzberg, 1966; Richet et al., 1977) but differ. For instance, Liu et al. (2010) examined in detail a term $G_0$ in the zero-point energy (important for H/D exchange) but did not study large water clusters or applied the approach derived by Zeebe (2009) using Eqs. (11) and (12) below. Including quartic terms in the potential energy, the anharmonic zero-point energy contribution to the partition function ratio for polyatomic molecules may be written as (Richet et al., 1977):

$$
\frac{Q_v^0}{Q_v^{anh}} = \exp \left[ -\frac{\hbar^2}{kT} \sum_{i<j}(x_{ij} - x_{ij}^0)/4 \right]
$$

(9)

where $x_{ij}$ are anharmonic constants in cm$^{-1}$ (often negative for higher fundamentals) and primes refer to the isotopically substituted molecule. The ratio of the anharmonic zero-point energy contribution to the partition function ratio for two compounds A and B is denoted here as $\rho_{anh}$:

$$
\rho_{anh} = \left( \frac{Q_v^0}{Q_v^0} \right)_{anh} / \left( \frac{Q_v^0}{Q_v^0} \right)_{anh}.
$$

(10)

The contribution due to anharmonicity of excited vibrational states is usually small at room temperature and will be neglected (the same goes for other effects beyond the harmonic approximation, which are likely small for oxygen exchange, see Liu et al. (2010)). Unfortunately, the $x_{ij}$ are generally unknown for large molecules. However, if harmonic and anharmonic frequencies have been calculated numerically, Eq. (9) can be evaluated without knowing the individual $x_{ij}$. The relationship between harmonic ($\omega_0$) and anharmonic frequencies ($\omega$) may be approximated by (Herzberg, 1966):

$$
\omega_v = \omega_0 + \frac{1}{2} \sum_{i<j} x_{ij} = \omega_0 + \Delta \omega.
$$

(11)

where $x_{ij} = x_{ji}$ (note that Eq. (11) strictly only holds for non-linear triatomic molecules). The sum over all differences between $\omega_v$ and $\omega_0$ is (a corresponding expression holds for $\omega'_v$ and $\omega'_0'$):

$$
\sum_{i<j}(\omega_v - \omega_0) = \sum_{i<j} \Delta \omega_v = \sum_{i<j} x_{ij},
$$

(12)

which is just the sum required to evaluate Eq. (9). Thus given harmonic and anharmonic frequencies of a molecule and its isotopologue (e.g., obtained using quantum-chemistry computations), the anharmonic contribution to the partition function ratio and thus to $z$ may be estimated (cf. Tables 1 and 2 below). The details and issues encountered with anharmonic frequencies for H-bonded clusters from QC computations (computationally expensive) are described in Appendix B.

### 3.3. Calculated vs. observed frequencies

The calculated molecular and cluster frequencies and their shift upon isotopic substitution (harmonic $\omega_0$ and $\omega'_0$) are key to evaluate Eq. (5) and hence isotopic fractionation. Unfortunately, experimental harmonic frequencies that can be used to validate calculated $\omega'_0$’s are usually only available for selected small ions and molecules such as H$_2$O(v) (see Fig. 2). For other ions, molecules, clusters, etc. one has to rely on observed anharmonic frequencies ($\omega_v$’s). A meaningful comparison then also requires calculated anharmonic $\omega_v$’s, which, in the case of QC computations, are very expensive for larger molecules and H-bonded clusters (see Appendix B). In addition, observed $\omega_v$’s with proper mode assignment are usually only available for small clusters. Here we limit our comparison of calculated vs. observed frequencies to H$_2$O(v), free OH$^-$ and the water dimer, (H$_2$O)$_2$ (Fig. 2). All QC-computed frequencies used below obtained at X3LYP/6-311+G(d,p) and MP2/aug-cc-pVDZ level are unscaled ($\nu = 1.0$).

The agreement between observed and computed frequencies is good for H$_2^{18}$O(v) and H$_2^{17}$O(v) (harmonic), H$_2^{16}$O(v) and free OH$^-$ (anharmonic, Fig. 2a) (for QC methods to calculate anharmonic $\omega_v$’s, see Appendix B). The calculated frequency shift for $^{18}$O/$^{16}$O substitution in H$_2$O(v) also appears adequate, which is corroborated by the observed liquid water—water vapor fractionation (see Section 4.2). In contrast, calculated anharmonic frequencies
for the water dimer are somewhat problematic. For example, vibrational self-consistent field (VSCF) frequencies tend to underestimate low (intermolecular) ω’s (Fig. 2b), which is improved for second-order perturbation theory (PT2) corrected VSCF frequencies with normal mode displacements in internal coordinates. Unfortunately, PT2-VSCF (internals) tend to underestimate isotopic frequency shifts for high (intramolecular) ω’s (for details, see Section 4.3 and Appendix B).

Importantly, however, the critical quantities to evaluate isotopic fractionation are harmonic, not anharmonic, frequencies — and several arguments suggest that QC computed harmonic ω’s are adequate for the current purpose. First, the agreement between observed and computed harmonic frequencies for H$_2$O$_2$(e) is good (Fig. 2a). Second, compared to VSCF ω’s, calculated harmonic ω’s do not significantly overestimate low (intermolecular) frequencies in the water dimer (Fig. 2b). Third, compared to PT2-VSCF (internals), harmonic ω’s do not underestimate isotopic frequency shifts for high (intramolecular) frequencies in the water dimer (Appendix B, Fig. B.1). Fourth, harmonic ω’s yield stable oxygen isotope fractionation factors between H$_2$O(l)/H$_2$O(e) and CO$_2$(aq)/H$_2$O(l) consistent with observations (Section 4.2 and Zeebe (2009)).

### 4. OXYGEN ISOPTE PARTITIONING

#### 4.1. Gas phase estimates

It is instructive to consider first quantum-chemical calculations for isolated (“gas-phase”) molecules as it allows comparison to the analytical calculations from the late 1950s and early 1960s (Hunt and Taube, 1959; Thornton, 1962; Green and Taube, 1963) (see Section 2). Furthermore, the gas-phase calculations illustrate the difference in mechanisms and results for $\gamma$(H$_2$O(l)/H$_2$O(e)) vs. $\gamma$(H$_2$O(l)/OH$^-$(aq)) based on water/OH$^-$water cluster calculations described below (see Sections 4.3 and 4.4). The calculated $\gamma$(H$_2$O(l)/OH$^-$(aq)) from Thornton (1962) and the QC methods X3LYP + and MP2DZ all agree within 0.7‰ (Table 1), which suggests that for small, free molecules and ions as considered here, analytic and QC calculations yield similar results. HF/6-31G(d) predicts a slightly larger value — but as mentioned above, the method is of limited accuracy. Using $\gamma$(H$_2$O(l)/H$_2$O(e)) = 1.0094 at 25 °C (Majoube, 1971), $\gamma$(H$_2$O(l)/OH$^-$(aq)) can be calculated (Table 1). The estimated anharmonicity effect is of order 1‰, regardless of whether VSCF or PT2-VSCF frequencies, or mode coupling for

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>T62</th>
<th>HF</th>
<th>X3LYP+</th>
<th>MP2DZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O(e)</td>
<td>1.0682</td>
<td>1.0661</td>
<td>1.0662</td>
<td>1.0659</td>
</tr>
<tr>
<td>OH$^-$(g)</td>
<td>1.0286</td>
<td>1.0244</td>
<td>1.0271</td>
<td>1.0271</td>
</tr>
<tr>
<td>$\gamma$(H$_2$O(l)/OH$^-$(aq))</td>
<td>1.0385</td>
<td>1.0407</td>
<td>1.0381</td>
<td>1.0378</td>
</tr>
<tr>
<td>$\gamma$(H$_2$O(l)/OH$^-$(aq))$^b$</td>
<td>1.0483</td>
<td>1.0505</td>
<td>1.0479</td>
<td>1.0476</td>
</tr>
</tbody>
</table>

Anharmonicity effect (%)

$^a$ T62 = Thornton (1962), HF = HF/6-31G(d), X3LYP+ = X3LYP/6-311+G(d,p), MP2DZ = MP2/aug-cc-pVDZ with scale factors s = 0.92 1.00 1.00.

$^b$ Using $\gamma$(H$_2$O(l)/H$_2$O(e)) = 1.0094 at 25 °C (Majoube, 1971).

$^c$ $\epsilon_{\text{coh}}(N_i) = (\rho_{\text{coh}} - 1) \times 10^3$ (see Eq. (10)), $N_i$ = order of mode couplings (1 for OH$^-$, see text).
H$_2$O(v) is considered or not (free OH$^-$ only has a single mode).

### 4.2. Liquid water—water vapor fractionation

The validity and accuracy of the QC methods used here for predicting $\alpha$’s involving H$_2$O structures may be evaluated by examining the known $^{18}$O/$^{16}$O fractionation between liquid water and water vapor. For example, the $\beta$-factor for H$_2$O(l) at 25 °C may be approximated by the $\beta$-factors calculated for the largest water cluster for each QC method, i.e., $n = 17$, 17, and 8 for HF, X3LYP+, and MP2DZ (cf. Table 2 below). Dividing by the corresponding $\beta$-factors for H$_2$O(v) (Table 1), yields 1.0084, 1.0098, and 1.0087. The experimental value is 1.0094 at 25 °C (Majoube, 1971), i.e., a difference of 0.4 and 0.7‰ for the more accurate methods X3LYP+ and MP2DZ. Uncertainties of this magnitude can be considered small and adequate for the current purpose. Furthermore, the agreement between QC computations and observations illustrates the basic validity of the calculated effect of H-bonding on oxygen isotope partitioning in water clusters (as has also been demonstrated for the aqueous CO$_3^-$ ion, see Zeebe (2009)).

### 4.3. Basic effect of H-bonding on oxygen isotope partitioning

A common feature of the QC computations is an increasing partition function ratio when proceeding from a gas phase molecule, or free ion, to that associated with a water cluster (the ratio also mostly increases with cluster size $n$). Considering H$_2$O, for example, the $\beta$-factor increases from 1.0662 to 1.0753 for H$_2$O(v) vs. (H$_2$O)$_4$ (X3LYP+, cf. Tables 1 and 2 below). The fundamental reason for the increase in the partition function ratio is the existence of additional intermolecular vibrational modes in the cluster, rather than changes in the intramolecular modes (skeletal fundamentals due to forces within the individual molecule or ion). For the compounds considered here, the intramolecular modes (H$_2$O and OH$^-$ skeletal frequencies) and intermolecular modes conveniently separate into a high- and low frequency band. For example, the intramolecular water fundamentals fall above ~1500 cm$^{-1}$, while the intermolecular cluster modes of (H$_2$O)$_4$ fall below ~1500 cm$^{-1}$ (see Fig. 3). This allows easy calculation of the separate intra- and intermolecular contributions to the partition function ratio (or $\beta$-factor).

Contributions to the $\beta$-factor from individual frequencies may be illustrated by considering the difference $\omega - \omega'$ (frequency shift upon $^{18}$O/$^{16}$O substitution, Fig. 3), which is the critical quantity entering Eq. (5). On the one hand, including only intramolecular modes $> 1500$ cm$^{-1}$ for (H$_2$O)$_4$ gives $\beta = 1.0636$, which is within 2.5‰ of the H$_2$O(v) value of 1.0662. On the other hand, including only intermolecular modes <1500 cm$^{-1}$ for (H$_2$O)$_4$ gives $\beta = 1.0109$, which adds ~11‰ to the reduced partition function ratio (the product 1.0636 × 1.0109 = 1.0753 gives the full (H$_2$O)$_4$ $\beta$-factor, cf. Table 2 below). As a result, by far the largest contribution to the increase in the partition function ratio when proceeding from H$_2$O(v) to (H$_2$O)$_4$ comes from intermolecular modes.

The same is true for larger clusters, e.g., the largest contribution to the increase in the partition function ratio for H$_2$O(v)----(H$_2$O)$_{17}$ and OH$^-$ (g)----OH$^-$ · (H$_2$O)$_{12}$ is due to intermolecular modes. Thus, the fundamental effect of H-bonding on oxygen isotope partitioning as studied here is an increase in the partition function ratio in water clusters due to intermolecular forces. Ultimately, the differential $\beta$-factor increase for H$_2$O and OH$^-$ causes $\alpha$ to drop (see Eq. (8)), i.e., the rise in $\beta$ for OH$^-$ outweighs that for H$_2$O (cf. Tables 1 and 2 below). Both OH$^-$ and H$_2$O are more strongly bound in the cluster (relative to the gas phase), but the effect is larger for OH$^-$. The fact that the calculated effect of H-bonding on oxygen isotope

![Fig. 3. Intra- and intermolecular modes: Calculated harmonic frequency shifts upon $^{18}$O/$^{16}$O substitution (X3LYP/6-311+G(d,p)). (a) Intramolecular frequency shifts in H$_2$O(v). (b) Inter- and intramolecular frequency shifts in (H$_2$O)$_4$.](image-url)
partitioning is consistent with observed fractionation factors (for $\chi_{\text{H}_2\text{O}^-}\text{H}_2\text{O}(g)$ see above, for $\chi_{(\text{CO}^+^2)\text{H}_2\text{O}(g)}$ see Zeebe (2009)) has at least two important implications. First, it suggests that the QC computations employed here describe H-bonding adequately for calculating $\chi$'s in water clusters. Second, the harmonic approximation (Eq. (5)) appears justified, also for low (intermolecular) modes and hence possible corrections due to anharmonicity for oxygen isotopes must be small, given that observed $\chi$'s are controlled by the actual, anharmonic frequencies of the system. For further details on anharmonic frequencies, see Appendix B.

4.4. Water/OH$^-$water clusters

In the next step, I performed geometry optimizations and Hessian (force-constant matrix) runs for large water/OH$^-$water clusters with up to $n = 22$ water molecules using the density functional theory (DFT) method X3LYP+ (cf. Fig. 1). MP2DZ is computationally too expensive and mostly impractical for large clusters; MP2DZ computations were performed for clusters with up to $n = 12$. Frequencies of the largest clusters from MP2DZ + and MP2DZ computations, including $^{17}$O and $^{18}$O substitution (of potential interest for triple oxygen isotope studies), are given in the Electronic Annex. Regardless of the method employed, all QC computations show a dramatic drop in $\chi_{\text{H}_2\text{O}^-}\text{H}_2\text{O}(g)$ for increasing $m$ and $n$ (Tables 1, 2, and Fig. 4). As explained above, the rise in $\beta$-factor for OH$^-$ outweights that for H$_2$O as $m$ and $n$ increase, causing $\chi$ to drop (see Eq. (8)). As a result, the calculated "gas-phase" $\chi$ (Thornton, 1962; Green and Taube, 1963) is greater by a factor of $\sim 2$ (when expressed in $\%$) than that calculated for largest water/OH$^-$water clusters. Estimated effects due to anharmonicity could add uncertainties of up to $\sim 3\%e$ to $\chi_{\text{H}_2\text{O}^-}\text{H}_2\text{O}(g)$ for the clusters (Table 2, see Appendix B for details).

4.5. Effect of temperature

To estimate the temperature dependence of fractionation factors, we use results from our X3LYP+ and MP2DZ calculations of water/OH$^-$water clusters with $(m, n) = (17, 22)$ and $(m, n) = (8, 12)$, respectively. From 0 to 40 $^\circ$C, the calculated $\epsilon_{\text{H}_2\text{O}^-}\text{H}_2\text{O}(g)$ is very nearly linear vs. temperature (see Fig. 5a) for which we provide a fit of the form:

$$
\varepsilon = (a - 1)10^3 = \epsilon_25 + \lambda \cdot (T_C - 25),
$$

where $T_C$ is temperature in $^\circ$C. From 0 to 300 $^\circ$C (see Fig. 5b), we use a fit of the form:

$$
\varepsilon = a + b/T + c/T^2,
$$

where $T$ is temperature in Kelvin (for fit coefficients, see Table 3). For a given QC system, the calculated slope of $\epsilon$'s temperature dependence often scales with $\chi$'s magnitude itself. For example, for the fit between 0 and 40 $^\circ$C (Eq. (13)), there is a monotonic relationship between $\lambda$ and $\epsilon_25$ for the examples shown in Fig. 5 (results for X3LYP+ at $(m, n) = (4, 12)$ included for illustration only). Simply put, the larger the fractionation factor at 25 $^\circ$C, the steeper the temperature slope in these cases.

5. DISCUSSION

The more accurate QC methods tested here (X3LYP+ and MP2DZ) yield values for $\chi_{\text{H}_2\text{O}^-}\text{H}_2\text{O}(g)$ between 1.0187 and 1.024, i.e., liquid water is enriched in $^{18}$O by about 19 to 24 $\%$. Assuming that the QC computations with large $m$ and $n$ are most representative for aqueous solutions, my best estimate for the fractionation factor between liquid H$_2$O and aqueous OH$^-$ is $\chi_{\text{H}_2\text{O}^-}\text{H}_2\text{O}(aq)$ = 1.019 to 1.024, i.e., liquid water is enriched in $^{18}$O by about 19 to 24 $\%$. The range in QC calculated values is partly due to different methods (LoT, basis sets representing molecular orbitals) and partly due to geometry effects associated with structurally different positions of the hydroxide ion in the OH$^-$water cluster for different $n$. For given $m$ and $n$, sampling a significant number of conformations might reduce the range in results for a single QC method, but not between different QC methods. For example, for $n = 3$ and 12, the $\beta$-factors differ by $\sim 2\%e$ between X3LYP+ and MP2DZ for the same conformation (Table 2). For further discussion of errors...
in QC computations, see Zeebe and Rae (2020). Moreover, estimated effects due to anharmonicity could add uncertainties of up to \( \approx 3\% \) to \( \varepsilon_{(\text{H}_2\text{O}_n^- \cdot \text{OH}^- \cdot \text{H}_2\text{O}_n)} \) (Table 2). Thus, at this point it appears unlikely that further QC computations, say, including larger clusters, various conformations, and/or higher LoT will narrow down the estimated range in \( \varepsilon_{(\text{H}_2\text{O}_l^- \cdot \text{OH}^- \cdot \text{H}_2\text{O}_l)} \).

However, the QC calculations unequivocally show that the theoretical \( \beta \)-factor hitherto used for aqueous \( \text{OH}^- \) (taken equal to that of free \( \text{OH}^- \), Thornton (1962); Green and Taube, (1963) is fundamentally wrong as it ignores intermolecular vibrational modes in solution. The resulting \( \varepsilon \) value of \( >46\% \) \( (T_C = 15 - 25 \, ^\circ\text{C}) \) involving free \( \text{OH}^- \) is off by a factor of \( \approx 2 \) compared to the present results. This suggests that the reported experimental value of 45\% at 15 \( ^\circ\text{C} \) (Green and Taube, 1963) is also wrong (see Appendix A). To settle the issue once and for all and to verify/falsify the range of 19 to 24\% calculated here, accurate and direct experimental determination of \( \varepsilon_{(\text{H}_2\text{O}_l^- \cdot \text{OH}^- \cdot \text{H}_2\text{O}_l)} \) is in order.

### Table 3

<table>
<thead>
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<th>( \varepsilon )</th>
<th>( \lambda )</th>
<th>( a )</th>
<th>( b \times 10^{-3} )</th>
<th>( c \times 10^{-6} )</th>
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</tr>
</thead>
<tbody>
<tr>
<td>23.5</td>
<td>-0.0728</td>
<td>-4.4573</td>
<td>10.3255</td>
<td>-0.5976</td>
<td>a</td>
</tr>
<tr>
<td>19.1</td>
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<td>-4.0771</td>
<td>9.8350</td>
<td>-0.8729</td>
<td>b</td>
</tr>
</tbody>
</table>

a X3LYP/6-311+G(d,p), \((m,n) = (17,22)\).

b MP2/aug-cc-pVDZ, \((m,n) = (8,12)\).

Fig. 4. Stable oxygen isotope fractionation factor (in \%) between \( (\text{H}_2\text{O})_m^- \cdot \text{OH}^- \cdot (\text{H}_2\text{O})_n \) from QC computations for water/\text{OH}^- -water clusters with up to \( n = 22 \) water molecules; \( m = 17, 17, 8, \) and 17 for HF = HF/6-31G(d), X3LYP+ = X3LYP/6-311+G(d,p), MP2DZ = MP2/aug-cc-pVDZ and B3LYP+ = B3LYP/6-311++G(2d,2p), respectively (see Table 2). All methods show a rapid drop in \( \varepsilon_{(\text{H}_2\text{O}_l^- \cdot \text{OH}^- \cdot \text{H}_2\text{O}_l)} \) due to intermolecular modes as \( n \) increases (see text).

Fig. 5. Temperature dependence of \( \varepsilon_{(\text{H}_2\text{O}_l^- \cdot \text{OH}^- \cdot \text{H}_2\text{O}_l)} \) from X3LYP/6-311+G(d,p) and MP2/aug-cc-pVDZ calculations of the largest water/\text{OH}^- -water clusters with \((m,n) = (17,22)\) and \((m,n) = (8,12)\), respectively. Results for X3LYP/6-311+G(d,p) at \((m,n) = (4,12)\) are shown for illustration only. (a) 0–40 \( ^\circ\text{C} \). (b) 0–300 \( ^\circ\text{C} \).
Note that the results of Thornton (1962) and Green and Taube (1963) have been questioned before based on indirect evidence (Böttcher et al., 2018), while other studies may appear to have confirmed them (see Section 5.1 and Appendix D and E).

5.1. Indirect reported evidence

Several experimental studies have reported data from which indirect constraints and/or values for \( \delta^{18}O \) have been inferred (e.g., Usdowski et al., 1991; Clark et al., 1992; Beck et al., 2005; Wang et al., 2013; Böttcher et al., 2018). While the experimental approaches vary (see Appendix D and E), the evidence is generally derived from the measured oxygen isotope composition (\( \delta^{18}O \)) of precipitated carbonate (e.g., BaCO₃), following the hydroxylation of CO₂:

\[
\text{CO}_2 + \text{OH}^- (aq) \rightarrow \text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+ \quad (15)
\]

\[
\text{CO}_3^{2-} + \text{Ba}^{2+} \rightarrow \text{BaCO}_3 \quad (16)
\]

where KFF is the kinetic fractionation factor associated with the kinetic isotope effect (KIE) of CO₂ hydroxylation. Reactions (15) and (16) illustrate the basic problem with the approach. The \( \delta^{18}O \) of BaCO₃ (\( \delta^{18}O_{\text{BaCO}_3} \)) depends on a variety of factors, most importantly (here) the composition of OH⁻ (aq) and the KFF, both of which result in \( \delta^{18}O \) depletion in the BaCO₃ relative to equilibrium with water. Unless these two factors can be accurately separated, no inferences about \( \delta^{18}O_{\text{H}_2\text{O} / \text{OH}^- (aq)} \) can be made. Note that while KFFs usually describe isotope depletion, they are commonly reported as absolute (positive) values.

Put differently, the measured \( \delta^{18}O_{\text{BaCO}_3} \) can be explained in two fundamentally different ways. For illustration, assume \( \delta^{18}O_{\text{BaCO}_3} = 14.6\%e \) was measured experimentally (also say, \( \delta^{18}O_{\text{H}_2\text{O}} = 0\%e \) in equilibrium with CO₂ (aq), \( \delta^{18}O_{\text{CO}_2 (aq)} \approx 41\%e \), all on the V-SMOW scale). Then the measured \( \delta^{18}O_{\text{BaCO}_3} \) can be explained by (i) a hydroxylation KFF of 26\%e relative to CO₂ (aq), or (ii) a \( \delta^{18}O_{\text{OH}^-} \) of \(-40\%e \) with the KFF being zero. For the two scenarios, \( \delta^{18}O_{\text{BaCO}_3} \) may be calculated as:

\[
(i) \ (1.026)^{-1} \times 1.041 = 1.0146 \ (14.6\%e), \quad \text{or} \quad (17)
\]

\[
(ii) \ 2/3 \times (1.041)^{-1} = 1.0145 \ (14.5\%e). \quad (18)
\]

where Eq. (17) derives from \( R_{\text{BaCO}_3} = R_{\text{KFF}} R_{\text{CO}_2 (aq)} \) (R’s are \( ^{18}O/^ {16}O \) ratios) and Eq. (18) from a mass balance for the unidirectional reaction of CO₂ and OH⁻, contributing 2 and 1 oxygen atoms to BaCO₃, respectively (see Appendix C, Eq. (C3)). Unfortunately, it appears that carbonate precipitation studies conducted so far were unable to separate the two scenarios (see Appendix D and E).

6. SUMMARY AND CONCLUSIONS

Studies from the 1960s reported the fractionation factor between liquid H₂O and aqueous OH⁻ theoretically as 1.046 and \(-1.048 \ (46\%e \ and \ 48\%e \ at \ 15^\circC \ and \ 25^\circC \) and experimentally as 1.045 (45\%e) at 15°C. These, or similar values (where the theoretical ones actually pertain to free, not aqueous, OH⁻), have been used in the literature for almost 60 years. In contrast, the present quantum-chemical calculations suggest that the above theoretical values are wrong when it comes to aqueous solutions (and off by a factor of \(-2 \) when expressed in \( %e \), suggesting that the experimental value is also wrong. Hydrogen bonding in solution significantly affects the fundamental vibrational modes associated with OH⁻ and substantially reduces the oxygen isotope fractionation between water and OH⁻ (aq), compared to the fractionation between water and free OH⁻. The most accurate QC methods tested here yield values for the fractionation factor between H₂O and OH⁻ in water clusters with \( n = 7 \) to 22 water molecules of \(-1.019 \) to \(-1.024 \ (19 \ to \ 24\%e \) at \( 25^\circC \). Accurate and direct experimental determination of \( \delta^{18}O_{\text{H}_2\text{O} / \text{OH}^- (aq)} \) is necessary to confirm or refute the theoretical predictions made here.

For the time being, I recommend that studies on oxygen isotope partitioning in, for instance, natural waters, dissolved phosphate, minerals, the aqueous CO₂ system, corals, speleothems, travertines, microbial carbonates, etc. (e.g., Thorstenson and Parkhurst, 2002; Beck et al., 2005; Rollion-Bard et al., 2010; von Sperber et al., 2014; Falk et al., 2016; Dreybrodt et al., 2016; Devriendt et al., 2017; Sade and Halevy, 2017; Böttcher et al., 2018; Guo and Zhou, 2019; Thaler et al., 2020) use the revised values for \( \delta^{18}O_{\text{H}_2\text{O} / \text{OH}^- (aq)} \) as calculated here, rather than those published earlier (Thornton, 1962; Green and Taube, 1963). Beyond systems in thermodynamic equilibrium, accurate knowledge of \( \delta^{18}O_{\text{H}_2\text{O} / \text{OH}^- (aq)} \) will also advance our understanding of kinetic oxygen isotope fractionation, including in the H₂O-CO₂-CaCO₃ system (e.g., Watkins et al., 2014; Devriendt et al., 2017; Sade and Halevy, 2017; Yumol et al., 2020).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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I am grateful to the reviewers Caroline Thaler, Jim Watkins, and one anonymous reviewer for constructive comments that improved the manuscript. I also thank Caroline Thaler for pointing out the possible mass balance approach used by Green and Taube (1963). I appreciate Zhengrong Wang’s prompt reply to clarify the approach used in Wang et al. (2013). Michael Böttcher and Jim Watkins were instrumental in encouraging me to revisit the problem.

APPENDIX A. EXPERIMENTAL METHODS OF GREEN AND TAUBE (1963)

The brief experimental section of Green and Taube (1963) (GT63 for short) reads: “The isotopic composition of a stock quantity of redistilled water was determined by equilibration with carbon dioxide. Freshly cut sodium
was held under this water to make a solution approximately 3 M in sodium hydroxide. This solution was held at approximately 15°. A measured volume of liquid was drawn off at a rate of 2–4 ml/hr. under reduced pressure as vapor which was condensed and equilibrated with carbon dioxide. The volume and molarity of the remaining solution were measured. The vapor was drawn off slowly and was therefore assumed to be in isotopic equilibrium with the solution. A value of 1.009 was taken from the graph of Dostrovsky and Raviv for x, the distillation separation factor of H₂O¹⁶ relative to H₂O¹⁸. The relative fugacities of H₂O¹⁶ and H₂O¹⁸ are unaffected by Na⁺ ions.

and use the vapor composition to determine their ½

\[ \frac{c_{\text{aq}}}{c_{\text{OH}^-}} \]

\( \Delta \) values of 1

\[ \Delta H \text{OH}^- \text{aq} \left( \frac{c_{\text{aq}}}{c_{\text{OH}^-}} \right) \]

where \( \delta = D^\circ \text{OH}^- \text{aq} \) is molarities, \( w = H_2O(l) \), and \( \text{OH}^- = \text{OH}^- (aq) \). Indices \( i \) and \( f \) refer to the ‘initial’ and ‘final’ H₂O(l) (before and after adding sodium, i.e., sodium addition would increase [NaOH], while decreasing [H₂O(l)]). The final \( \delta_{\text{OH}^-} \) was determined via the condensed vapor, assuming equilibrium with the remaining H₂O(l) and using \( x_i(H_2O(l) - H_2O(l)) = 1.009 \) (\( \epsilon_{\text{OH}^-} = 9\% \)). If so, the accuracy of the method is very low because \( \delta_{\text{OH}^-} \) is calculated from a relatively small change in a large quantity ([H₂O) ≈ 55.5 M vs. [OH⁻] < 5 M). Without loss of generality, let \( \delta_{i,j} = 0\% \) and use the vapor composition \( \delta_i = \delta_{i,f} - \epsilon_{i}\) then

\[ \delta_{\text{OH}^-} = -[\delta_i + \epsilon_{i}] \left( \frac{c_{\text{aq}}}{c_{\text{OH}^-}} \right) \] (A2)

Assuming values as follows gives \( \delta_{\text{OH}^-} = -4.8\% + 9\% \text{(55.5 - 4.8)/4.8} = -44\% \) (see above). However, a small uncertainty in, e.g., \( \delta_i \) leads to a large uncertainty in \( \delta_{\text{OH}^-} \). For instance, a ±1% error in \( \delta_i \) yields \( \delta_{\text{OH}^-} = -34 \) to −55%. Sources of uncertainties include Rayleigh distillation effects (how large was the water fraction drawn off as vapor?), assumed water–water vapor equilibrium, errors in the \( \delta^{18} \) determination of initial and condensed water via equilibration with CO₂, and possibly more, which is, however, difficult to infer from the brief description. In summary, GT63 did not detail their calculation of \( x_i(H_2O(l) - H_2O(l)) \) from their experimental results. While a potential mass balance approach (as suggested by one of the present reviewers) would not seem invalid in principal, its accuracy appears very low and overly sensitive to small errors in the measured quantities. The present conclusion that GT63’s experimental value is wrong is primarily based on the theoretical results obtained here, but would be compatible with problems in a mass balance approach.

**APPENDIX B. ANHARMONIC FREQUENCIES**

Anharmonic frequencies for free H₂O, OH⁻, (H₂O)ₙ, and OH⁻ · (H₂O)ₙ were obtained using the quartic force field approximation in GAMESS (Gordon and Schmidt, 2005) with and without 2-mode coupling for up to \( n = 4 \) and \( n = 13 \), respectively (see Tables 1 and 2). Note that calculations with 2-mode coupling for larger clusters are computationally very expensive. Two sets of anharmonic frequencies from the 2-mode coupling calculations for polyatomic molecules were used: (1) vibrational self-consistent field (VSCF) frequencies and (2) second-order perturbation theory (PT2) corrected VSCF frequencies (PT2-VSCF).

For small, isolated molecules, PT2-VSCF likely gives the most accurate frequencies, which were used for comparison with observed anharmonic frequencies in H₂O(O) (Fig. 2). However, in large systems with hydrogen bonds, for instance, it is well known that PT2-VSCF significantly overestimates low frequencies (< 400 cm⁻¹), particularly for normal mode displacements in Cartesian coordinates (Njugic and Gordon, 2006; Harabuchi et al., 2019).

Indeed, for the low frequencies of the H₂O- and OH⁻ -water clusters studied here, PT2-VSCF gave inconsistent and often unrealistically high values, compared to harmonic frequencies. Normal mode displacements in internal coordinates as suggested by Njugic and Gordon (2006) and Harabuchi et al. (2019) improved the low frequencies but yielded unreasonably large anharmonic corrections to the partition function ratio from high frequencies (much larger than observed \( x \)’s would permit, see Sections 4.2 and 4.3). As an example, consider the extensively studied water dimer (H₂O)₂, with a nearly linear hydrogen bond extending along the OH bond of one H₂O unit (H-bond donor) to the other H₂O unit (H-bond acceptor). Anharmonic frequencies calculated using mode displacements in internal coordinates (MP2/aug-cc-pVDZ) gave somewhat better agreement with absolute observed values than harmonic frequencies, including intramolecular modes between ~1500 and ~4000 cm⁻¹ (Harabuchi et al., 2019) (Fig. B.1). However, the computed anharmonic frequency shifts for \( ^{18} \text{O} / ^{16} \text{O} \) substitution (in both H-bond donor and acceptor, internals) are significantly smaller than the harmonic shifts and the anharmonic PT2-VSCF shifts from normal mode displacements in Cartesian coordinates. Importantly, the anharmonic PT2-VSCF shifts (internals) are also significantly smaller than observed (anharmonic) shifts (Fredin et al., 1977; Perchard, 2001; Bouletier et al., 2011) (Fig. B.1). One potential caveat regarding the observed frequency shifts is that those were obtained for water dimers trapped in solid N₂, Ar, or Ne matrices at low temperature, which could perturb the frequency shifts relative to the gas phase.

Similar to the water dimer, the computed anharmonic frequency shifts of intramolecular modes (PT2-VSCF, internals) for \( ^{18} \text{O} / ^{16} \text{O} \) substitution in various other H₂O- and OH⁻ -water clusters were also significantly smaller than the harmonic shifts. Such frequency shifts would predict unreasonably large anharmonic corrections to the partition function ratio from high (intramolecular) frequencies. As a result, for the H₂O- and OH⁻ -water clusters, the effect of anharmonicity on \( x_i(H_2O(H_2O) - H_2O(H_2O)) \) by means of Eq. (9) was evaluated using VSCF frequencies obtained using normal mode displacements in Cartesian coordinates.
APPENDIX C. 18O/16O MASS BALANCE FOR BaCO3

If a number of conditions are met (see Appendix D), a 18O/16O mass balance for reactions (15) and (16) may be written as (here OH\(^{-}\) = OH\(^{-}\)(aq), \(\text{H}_2\text{O} = \text{H}_2\text{O}(l)\)):

\[
R_{\text{BaCO}_3} = \frac{2}{3} R_{\text{CO}_2(aq)} + \frac{1}{3} R_{\text{OH}^-},
\]

where \(R\)'s are 18O/16O ratios. Dividing by \(R_{\text{H}_2\text{O}}\) yields:

\[
x_{\text{BaCO}_3,\cdot \text{H}_2\text{O}}^a = \frac{2}{3} x_{\text{CO}_2(aq),\cdot \text{H}_2\text{O}}^a + \frac{1}{3} x_{\text{H}_2\text{O},\cdot \text{OH}^-}^a,
\]

which can be solved for \(x_{\text{H}_2\text{O},\cdot \text{OH}^-}^a\):

\[
x_{\text{H}_2\text{O},\cdot \text{OH}^-}^a = \frac{3x_{\text{BaCO}_3,\cdot \text{H}_2\text{O}}^a - 2x_{\text{CO}_2(aq),\cdot \text{H}_2\text{O}}^a}{1} =: \Delta_{32}.
\]

Given measured \(\delta^{18}O_{\text{BaCO}_3}\), \(\delta^{18}O_{\text{H}_2\text{O}}\), and \(x_{\text{CO}_2(aq),\cdot \text{H}_2\text{O}}\) as, say, determined by Beck et al. (2005) via acid stripping:

\[
1000 \ln x_{\text{CO}_2(aq),\cdot \text{H}_2\text{O}} = 2.52 \times 10^6 / T^2 + 12.12,
\]

\(\Delta_{32}\) may be calculated. Ideally, \(\Delta_{32}\) would be equal to \(x_{\text{H}_2\text{O},\cdot \text{OH}^-}^a\). However, for the experiments examined here (Appendix D), the results suggest that \(\Delta_{32} \neq x_{\text{H}_2\text{O},\cdot \text{OH}^-}^a\).

APPENDIX D. LOW-pH EQUILIBRATION

Carbon dioxide is equilibrated with water at low pH and constant temperature. Once isotopic equilibrium has been attained, the pH is rapidly raised by adding buffer/NaOH and BaCl\(_2\), upon which the dissolved inorganic carbon (DIC) is precipitated as BaCO\(_3\) (e.g., Uudowski et al., 1991; Beck et al., 2005) (U91, B05 for short). Note that Wang et al.’s (2013) analysis for low-pH equilibration is based on B05’s data. One could attempt to deduce \(x_{\text{H}_2\text{O},\cdot \text{OH}^-}^a\) from such experiments, which requires, however, multiple critical conditions to be met.

First, during equilibration, the pH must be low enough such that the CO\(_2(aq)\) fraction is essentially 1.0 ([HCO\(_3^-\)] = [CO\(_2^-\)] \(\approx 0\)). Second, the reaction mechanism must follow exactly Eqs. (15) and (16). That is, unidirectional hydroxylation to HCO\(_3^-\), no dehydroxylation, no hydration, no dehydration, no oxygen exchange between HCO\(_3^-\)/CO\(_2^+\) and water, no CO\(_2\) uptake/d egassing etc. Third, the conversion from CO\(_2(aq)\) to BaCO\(_3\) must be quantitative, i.e., the yield of DIC must be 100%. Only in this case is the kinetic isotope effect (KIE) from hydroxylation not expressed. The KIE tends to deplete the reaction product HCO\(_3^-\) in 18O and enrich the residual CO\(_2(aq)\) in 18O, respectively. This is inconsequential if upon completion, all isotopically heavy CO\(_2(aq)\) has been converted to BaCO\(_3\) (100% yield). However, if a fraction of the DIC is lost (yield < 100%), the isotopically heavy residual can escape and the KIE is expressed in the BaCO\(_3\). In that case, KIE and OH\(^{-}\)(aq) composition cannot be separated (see Section 5.1). Fourth, the 18O fractionation factor between CO\(_2(aq)\) and H\(_2\)O must be accurately known.

Only if all the above conditions are strictly met, one may attempt to calculate \(x_{\text{H}_2\text{O},\cdot \text{OH}^-}^a\) from the experimental results (see Appendix C). While U91’s equilibration pH = 3.89 appears adequate, they provided no information on the DIC yield. Note also that U91 actually attempted to determine \(x_{\text{CO}_2(aq),\cdot \text{H}_2\text{O}}\) (likely in error, see B05), not \(x_{\text{H}_2\text{O},\cdot \text{OH}^-}^a\). B05 equilibrated at pH \(\sim 2.3\) but reported yields of only 74 to 93% (their experiments No. 32, 11, 21). They commented on U91’s method: “Because of the lack of \(z_{\text{OH}^-\cdot \text{H}_2\text{O}}\) data and uncertainty in the reaction mechanism, a different method for calculating the CO\(_2(aq)\)-H\(_2\)O fractionation was needed.” The fractionation factor \(x_{\text{CO}_2(aq),\cdot \text{H}_2\text{O}}\) was determined by B05 via acid stripping (Appendix C), which we may assume to be accurate for the current purpose.
Finally, a quantity $\Delta_{\text{HCO}_3}$ may be calculated that would ideally equal $\delta_{\text{H}_2\text{O}(l)/-\text{OH}^{\text{aq}}}$ (see Appendix C). Unfortunately, U91’s and B05’s experimental data yield inconsistent results for $\Delta_{\text{HCO}_3}$, differing by $\sim 30\%$ (Fig. D.1). Also, $\Delta_{\text{HCO}_3}$ based on B05’s data shows no consistent temperature trend, contrary to the temperature dependence of many other $\delta^{18}$O’s and contrary to the results of the present study (see Fig. 5). The largest cause of error is likely loss of DIC from the system (< 100% yield), which is known to be the case for B05’s data. Also note that the calculated $\Delta_{\text{HCO}_3}$ is rather sensitive to uncertainties in $\delta^{18}\text{O}_{\text{BaCO}_3}$. For example, a $-5\%e$ shift in $\delta^{18}\text{O}_{\text{BaCO}_3}$ gives roughly a $+15\%e$ shift in $\Delta_{\text{HCO}_3}$ (Eq. (C5)). Hence if, say, BaCO$_3$ was actually depleted by 5% due to the contribution from kinetic effects, then the calculated $\Delta_{\text{HCO}_3}$ would be an overestimate by $\sim 15\%e$, compared to the true $\delta_{\text{H}_2\text{O}(l)/-\text{OH}^{\text{aq}}}$ (assuming no errors otherwise). One plausible reason for the low-$p\text{H}$ equilibrium method to be prone to uncertainties (including < 100% yield) is gas exchange. For example, at low $p\text{H}$ the high CO$_2$ concentration can cause CO$_2$ degassing, at high $p\text{H}$ (once buffer/NaOH has been added), the low CO$_2$ concentration can cause CO$_2$ uptake. In summary, given the various caveats discussed above, the low-$p\text{H}$ equilibration method does not appear to be a robust approach to determine $\delta_{\text{H}_2\text{O}(l)/-\text{OH}^{\text{aq}}}$.

**APPENDIX E. HYPERALKALINE SOLUTIONS**

Gaseous CO$_2$ is taken up into a hyperalkaline Ba$^{2+}$ solution ($p\text{H}$ usually > 11), promoting BaCO$_3$ precipitation (reactions (15) and (16)). The $\delta^{18}\text{O}_{\text{BaCO}_3}$ is subsequently analyzed by mass spectrometry (e.g., Baertschi, 1952; Clark et al., 1992; Böttcher et al., 2018). Clark et al. (1992) stated that their observed $\delta^{18}\text{O}$ depletion in BaCO$_3$ at 22 $^\circ$C can be accounted for by $\delta_{\text{H}_2\text{O}(l)/-\text{OH}^{\text{aq}}}$ = 40%e. Importantly, however, Clark et al. (1992) actually took the $\delta_{\text{H}_2\text{O}(l)/-\text{OH}^{\text{aq}}}$ value from Green and Taube (1963) (25 $^\circ$C) and assumed it to be correct, which led to their conclusion of no evidence for a significant KFF in oxygen. Per-
APPENDIX F. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.gca.2020.08.025.

REFERENCES


