



An expression for the overall oxygen isotope fractionation between the sum of dissolved inorganic carbon and water

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[1] Stable oxygen isotope fractionation factors (α 's) between individual dissolved carbonate species ($\text{CO}_2(\text{aq.})$, H_2CO_3 , HCO_3^- , CO_3^{2-}) and water, and their sum ($S = [\text{CO}_2(\text{aq.})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$) and water are fundamental geochemical parameters. While values of $\alpha_{(\text{CO}_2(\text{aq.})-\text{H}_2\text{O})}$, $\alpha_{(\text{HCO}_3^--\text{H}_2\text{O})}$, and $\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})}$ have recently been examined, an overall mass balance for stable oxygen isotopes in the carbonate system still needs to be derived. The theoretical treatment of this mass balance is not trivial (in contrast to, e.g., stable carbon isotopes) because (1) oxygen is exchanged with H_2O and (2) complications arise from the nature of the oxygen mole fractions. I use the recently reported individual α 's to derive an expression for the overall oxygen isotope fractionation between S and water. This allows the calculation of $\alpha_{(S-\text{H}_2\text{O})}$ at any given $p\text{H}$ of the solution. The result differs from a relationship published earlier, and implications for previous studies are discussed. Numerical routines in MATLAB and Excel for the present calculation have been developed and are available as auxiliary material (Software S1). Applications of the expression include, for example, examination of biomineralization mechanisms and corrections to isotopic paleotemperature equations. The latter application can significantly alter reconstructions of Phanerozoic climate change.

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1. Introduction

[2] One of the cornerstones of stable isotope geochemistry is the knowledge of isotope fractionation factors (α 's) between different chemical compounds [Urey, 1947]. For geochemical isotope studies dealing with the carbonic acid system in aqueous solutions, isotope fractionation factors between the dissolved carbonate species ($\text{CO}_2(\text{aq.})$, H_2CO_3 , HCO_3^- , CO_3^{2-}) and water are fundamental. Oxygen

isotope fractionation factors for this system (see equation (1) for definition) have recently been examined [Beck *et al.*, 2005, and references therein]. In fresh water at 25°C , the reported fractionation factors between $\text{CO}_2(\text{aq.})$, HCO_3^- , CO_3^{2-} and water are $\alpha_{(\text{CO}_2(\text{aq.})-\text{H}_2\text{O})} = 1.0413$, $\alpha_{(\text{HCO}_3^--\text{H}_2\text{O})} = 1.0315$, and $\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})} = 1.0245$. The fractionation factor between gaseous CO_2 and water at 25°C was established earlier; $\alpha_{(\text{CO}_2(\text{g})-\text{H}_2\text{O})} = 1.0412$ [Brenninkmeijer *et al.*, 1983].

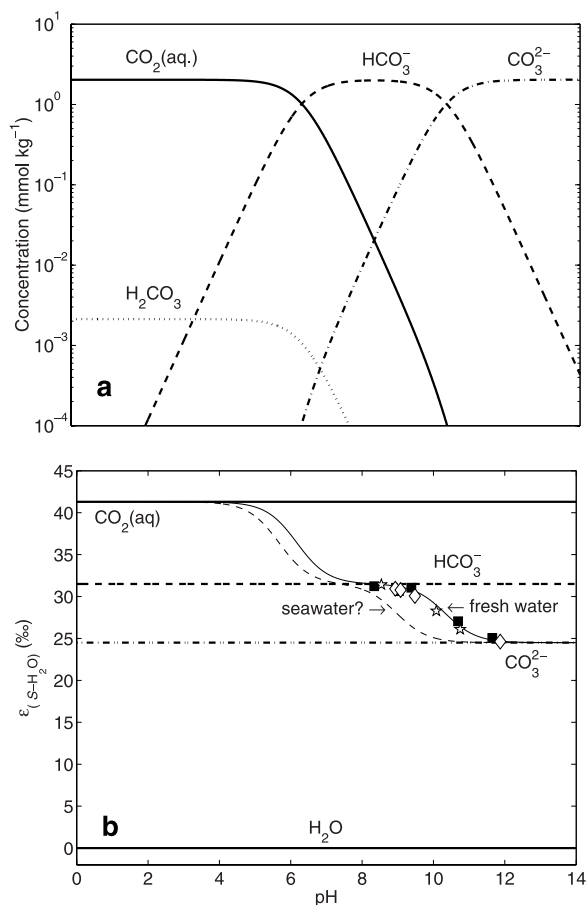


Figure 1. (a) Concentrations of the dissolved carbonate species as a function of pH : $CO_2(aq.)$ (solid line), H_2CO_3 (dotted line), HCO_3^- (dashed line), and CO_3^{2-} (dot-dashed line). The values shown correspond to fresh water conditions ($T = 25^\circ C$, $TCO_2 = 2 \text{ mmol kg}^{-1}$). (b) Corresponding overall oxygen isotope fractionation between the sum of the dissolved inorganic carbon species and water ($\alpha_{(S-H_2O)}$, solid thin line) as a function of pH according to equation (13). Note that $\varepsilon = (\alpha - 1) \times 1,000$. Experimental data are from *McCrea* [1950] (squares), *Beck et al.* [2005] (diamonds), and *Kim et al.* [2006] (stars) from precipitation experiments at $pH > 8$ (see text). *Kim et al.*'s data at three pH values have been averaged and 0.38‰ has been added; see discussion by *Kim et al.* [2006]. The seawater curve (dashed line) is based on seawater carbonate chemistry constants [*Zeebe and Wolf-Gladrow*, 2001] and fresh-water α 's. Note that the seawater curve is not necessarily appropriate for understanding carbonate precipitation and ^{18}O -fractionation in marine organisms (see text).

[3] Figure 1a shows the concentrations of the dissolved carbonate species as a function of pH . Their sum is denoted here as $S = [CO_2(aq.)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$. S is mainly in the

form of $CO_2(aq.)$, HCO_3^- , and CO_3^{2-} at low, intermediate, and high pH , respectively. Given the fractionation factors summarized above, it follows that the isotope fractionation between S and water ($\alpha_{(S-H_2O)}$) decreases with pH , dropping from 1.0413 at low pH ($CO_2(aq.)$ is the dominant species) to 1.0245 at high pH (CO_3^{2-} is the dominant species). Using the reported individual α 's [*Beck et al.*, 2005], I will calculate the functional relationship between $\alpha_{(S-H_2O)}$ and pH . As shown below, the calculation is not trivial. The reason is that oxygen is exchanged with a large reservoir of H_2O . In addition, the nature of the oxygen mole fractions preclude a simple analysis. These features of the oxygen isotope system are fundamentally different from, for example, the stable carbon isotope system.

[4] Knowledge of $\alpha_{(S-H_2O)}$ as a function of pH is essential for a variety of applications. For example, it is critical for understanding mechanisms of biomineralization in calcifying organisms [e.g., *McConnaughey*, 1989; *Zeebe*, 1999; *Adkins et al.*, 2003; *Ziveri et al.*, 2003]. The pH -dependent oxygen fractionation examined here also plays a central role in a recent debate on the primary driver of Phanerozoic climate change [*Shaviv and Veizer*, 2003; *Royer et al.*, 2004; *Rahmstorf et al.*, 2004]. Paleotemperature reconstructions based on stable oxygen isotope ratios in carbonates may be subject to corrections, if seawater pH was different in the past [*Spero et al.*, 1997; *Zeebe*, 1999, 2001]. Application of such corrections to Phanerozoic climate archives can significantly change interpretations of climate change over this time scale [*Royer et al.*, 2004]. Approaches of the types mentioned above require evaluation of $\alpha_{(S-H_2O)}$ as a function of pH . An expression that allows this evaluation is derived in the present paper. Numerical routines in MATLAB and Excel for the calculation have been developed and are available as auxiliary material¹ (Software S1).

2. Derivation of $\alpha_{(S-H_2O)}$

2.1. Oxygen Isotope Mass Balance

[5] The $^{18}O/^{16}O$ fractionation factor between $S = [CO_2(aq.)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$ and H_2O , i.e., $\alpha_{(S-H_2O)}$, will be calculated over the pH range from 0 to 14. Note that all individual

¹Auxiliary materials are available in the HTML. doi:10.1029/2007GC001663.

chemical carbonate species are considered and that $\text{CO}_2(\text{aq.})$ and H_2CO_3 are not lumped together as in the definition of TCO_2 . For the individual fractionation factors the following abbreviations will be used:

$$\alpha_T = \alpha_{(\mathcal{S}-\text{H}_2\text{O})}; \quad \alpha_d = \alpha_{(\text{CO}_2(\text{aq.})-\text{H}_2\text{O})};$$

$$\alpha_a = \alpha_{(\text{H}_2\text{CO}_3-\text{H}_2\text{O})}; \quad \alpha_b = \alpha_{(\text{HCO}_3^--\text{H}_2\text{O})};$$

$$\alpha_c = \alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})}$$

where “T” stands for total, “d” stands for carbon dioxide (aq.) (occasionally “aq.” will be omitted below), “a” stands for carbonic acid, “b” stands for bicarbonate, and “c” stands for carbonate ion. By definition, α_d , for example, is given by the ratio of the total number of ^{18}O to ^{16}O atoms on $\text{CO}_2(\text{aq.})$, divided by the corresponding ratio in H_2O :

$$\begin{aligned} \alpha_d &= \alpha_{(\text{CO}_2(\text{aq.})-\text{H}_2\text{O})} \\ &= \frac{2[\text{C}^{18}\text{O}^{18}\text{O}] + [\text{C}^{18}\text{O}^{16}\text{O}]}{2[\text{C}^{16}\text{O}^{16}\text{O}] + [\text{C}^{18}\text{O}^{16}\text{O}]} \bigg/ \frac{[\text{H}_2^{18}\text{O}]}{[\text{H}_2^{16}\text{O}]} \end{aligned} \quad (1)$$

[6] Accordingly, α_T is given by

$$\begin{aligned} \alpha_T &= \frac{R_T}{R_{\text{H}_2\text{O}}} \\ &= \frac{[\text{O}^{18}\text{O}_d] + [\text{O}^{18}\text{O}_a] + [\text{O}^{18}\text{O}_b] + [\text{O}^{18}\text{O}_c]}{[\text{O}^{16}\text{O}_d] + [\text{O}^{16}\text{O}_a] + [\text{O}^{16}\text{O}_b] + [\text{O}^{16}\text{O}_c]} \frac{1}{R_{\text{H}_2\text{O}}} \end{aligned} \quad (2)$$

where R 's are $^{18}\text{O}/^{16}\text{O}$ ratios and $[\text{O}^{18}\text{O}_d]$, for example, is the total ^{18}O on $\text{CO}_2(\text{aq.})$ and $[\text{O}^{16}\text{O}_b]$ is the total ^{16}O on HCO_3^- :

$$[\text{O}^{18}\text{O}_d] = 2[\text{C}^{18}\text{O}^{18}\text{O}] + [\text{C}^{18}\text{O}^{16}\text{O}] \quad (3)$$

$$\begin{aligned} [\text{O}^{16}\text{O}_b] &= 3[\text{HC}^{16}\text{O}^{16}\text{O}^{16}\text{O}^-] + 2[\text{HC}^{18}\text{O}^{16}\text{O}^{16}\text{O}^-] \\ &\quad + [\text{HC}^{18}\text{O}^{18}\text{O}^{16}\text{O}^-] \end{aligned} \quad (4)$$

and so on. Using the notation $[\text{O}^{16}\text{O}_T] = [\text{O}^{16}\text{O}_d] + [\text{O}^{16}\text{O}_a] + [\text{O}^{16}\text{O}_b] + [\text{O}^{16}\text{O}_c]$, equation (2) can be written as

$$\alpha_T = \left(\frac{[\text{O}^{18}\text{O}_d]}{[\text{O}^{16}\text{O}_T]} + \frac{[\text{O}^{18}\text{O}_a]}{[\text{O}^{16}\text{O}_T]} + \frac{[\text{O}^{18}\text{O}_b]}{[\text{O}^{16}\text{O}_T]} + \frac{[\text{O}^{18}\text{O}_c]}{[\text{O}^{16}\text{O}_T]} \right) \times \frac{1}{R_{\text{H}_2\text{O}}} \quad (5)$$

[7] After multiplying the first term by $[\text{O}^{16}\text{O}_d]/[\text{O}^{16}\text{O}_d]$, the second by $[\text{O}^{16}\text{O}_a]/[\text{O}^{16}\text{O}_a]$ and so on, gives

$$\begin{aligned} \alpha_T &= \left(\frac{[\text{O}^{18}\text{O}_d]}{[\text{O}^{16}\text{O}_d]} \frac{[\text{O}^{16}\text{O}_d]}{[\text{O}^{16}\text{O}_T]} + \frac{[\text{O}^{18}\text{O}_a]}{[\text{O}^{16}\text{O}_a]} \frac{[\text{O}^{16}\text{O}_a]}{[\text{O}^{16}\text{O}_T]} \right. \\ &\quad \left. + \frac{[\text{O}^{18}\text{O}_b]}{[\text{O}^{16}\text{O}_b]} \frac{[\text{O}^{16}\text{O}_b]}{[\text{O}^{16}\text{O}_T]} + \frac{[\text{O}^{18}\text{O}_c]}{[\text{O}^{16}\text{O}_c]} \frac{[\text{O}^{16}\text{O}_c]}{[\text{O}^{16}\text{O}_T]} \right) \frac{1}{R_{\text{H}_2\text{O}}} \end{aligned}$$

and inserting the individual fractionation factors,

$$\begin{aligned} \alpha_d &= \frac{[\text{O}^{18}\text{O}_d]}{[\text{O}^{16}\text{O}_d]} \frac{1}{R_{\text{H}_2\text{O}}}; \quad \alpha_a = \frac{[\text{O}^{18}\text{O}_a]}{[\text{O}^{16}\text{O}_a]} \frac{1}{R_{\text{H}_2\text{O}}}; \\ \alpha_b &= \frac{[\text{O}^{18}\text{O}_b]}{[\text{O}^{16}\text{O}_b]} \frac{1}{R_{\text{H}_2\text{O}}}; \quad \alpha_c = \frac{[\text{O}^{18}\text{O}_c]}{[\text{O}^{16}\text{O}_c]} \frac{1}{R_{\text{H}_2\text{O}}} \end{aligned}$$

we obtain

$$\alpha_T = \alpha_d \frac{[\text{O}^{16}\text{O}_d]}{[\text{O}^{16}\text{O}_T]} + \alpha_a \frac{[\text{O}^{16}\text{O}_a]}{[\text{O}^{16}\text{O}_T]} + \alpha_b \frac{[\text{O}^{16}\text{O}_b]}{[\text{O}^{16}\text{O}_T]} + \alpha_c \frac{[\text{O}^{16}\text{O}_c]}{[\text{O}^{16}\text{O}_T]} \quad (6)$$

[8] Although equation (6) appears like a mass balance similar to that for carbon isotopes, it is not. For example, the mole fractions $[\text{O}^{16}\text{O}_d]/[\text{O}^{16}\text{O}_T] =: {}^{16}x_d$ and $[\text{O}^{16}\text{O}_a]/[\text{O}^{16}\text{O}_T] =: {}^{16}x_a$ are oxygen mole fractions and not carbon mole fractions (^{12}x), which would read $[\text{C}^{12}\text{CO}_2]/^{12}\mathcal{S}$ and $[\text{H}_2^{12}\text{CO}_3]/^{12}\mathcal{S}$. The fundamental difference is that, for example, the total ^{16}O of \mathcal{S} ($[\text{O}^{16}\text{O}_T]$) changes with $p\text{H}$ as the dominant species changes and thus the overall isotopic composition of \mathcal{S} . This is possible because oxygen is exchanged with a large volume of water. As a result, $[\text{O}^{16}\text{O}_T]$ is a non-conservative quantity among the carbonate species, whereas total ^{12}C of the carbonate species is conservative (not a function of $p\text{H}$). A priori, the ^{16}x 's can therefore not be approximated by ^{12}x 's. Note also that equation (6) cannot be directly transferred to carbon isotopes because α_T refers to the fractionation relative to oxygen in the water molecule (there is no analog of a carbon atom in a water molecule).

[9] The oxygen mole fractions ($^{16}x_i$) are not known at any given $p\text{H}$. The mass balance, equation (6), is therefore of no practical use, unless it can be rewritten in terms of known quantities.

2.2. Theoretical Determination of the Oxygen Mole Fractions

[10] I will now express the oxygen mole fractions in terms of other quantities such that equation (6) yields a useful expression for α_T , starting with $[\text{O}^{16}\text{O}_d]$. $[\text{O}^{16}\text{O}_d]$ is the total ^{16}O on CO_2 which is the total O on CO_2 minus the total O-18 and O-17 on CO_2 . (After carrying out the full calculation including O-17, I found that it can be omitted

because of its very small abundance.) The total O on CO₂ is 2[CO₂]. Thus

$$[^{16}\text{O}_d] = 2[\text{CO}_2] - [^{18}\text{O}_d].$$

[11] Using $R_d = [^{18}\text{O}_d]/[^{16}\text{O}_d]$, we have

$$[^{16}\text{O}_d] = 2[\text{CO}_2] - R_d [^{16}\text{O}_d]$$

which can be solved for $[^{16}\text{O}_d]$:

$$[^{16}\text{O}_d] = \frac{2[\text{CO}_2]}{R_d + 1}. \quad (7)$$

The two steps that lead to equation (7) are critical for deriving theoretical expressions for the oxygen mole fractions. What follows below is mostly algebra. Similar equations hold for $[^{16}\text{O}_a]$, $[^{16}\text{O}_b]$, and $[^{16}\text{O}_c]$:

$$[^{16}\text{O}_a] = \frac{3[\text{H}_2\text{CO}_3]}{R_a + 1} \quad (8)$$

$$[^{16}\text{O}_b] = \frac{3[\text{HCO}_3^-]}{R_b + 1} \quad (9)$$

$$[^{16}\text{O}_c] = \frac{3[\text{CO}_3^{2-}]}{R_c + 1}. \quad (10)$$

[12] Analogously, $[^{16}\text{O}_T]$ is the total ¹⁶O on CO₂, H₂CO₃, HCO₃⁻, and CO₃²⁻ which is the total O minus the total O-18 on these species. Thus

$$[^{16}\text{O}_T] = 2[\text{CO}_2] + 3[\text{H}_2\text{CO}_3] + 3[\text{HCO}_3^-] + 3[\text{CO}_3^{2-}] - R_T [^{16}\text{O}_T]$$

which can be solved for $[^{16}\text{O}_T]$:

$$[^{16}\text{O}_T] = \frac{V}{R_T + 1} \quad (11)$$

where $V = 2[\text{CO}_2] + 3([\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}])$. Note that the introduction of the factors “2” and “3” is due to the fact that the total oxygen on the carbonate species changes from $\sim 2 \times \text{TCO}_2$ to $3 \times \text{TCO}_2$ as pH increases and the dominant species changes from CO₂ to HCO₃⁻.

2.3. An Expression for $\alpha_{(\mathcal{S}-\text{H}_2\text{O})}$

[13] Now equations (7)–(11) are inserted into a version of the mass balance equation (6) written in terms of R 's, not α 's (multiply by $R_{\text{H}_2\text{O}}$):

$$R_T = R_d \frac{[^{16}\text{O}_d]}{[^{16}\text{O}_T]} + R_a \frac{[^{16}\text{O}_a]}{[^{16}\text{O}_T]} + R_b \frac{[^{16}\text{O}_b]}{[^{16}\text{O}_T]} + R_c \frac{[^{16}\text{O}_c]}{[^{16}\text{O}_T]} \quad (12)$$

which yields

$$R_T = R_d \frac{2[\text{CO}_2]/(R_d + 1)}{V/(R_T + 1)} + R_a \frac{3[\text{H}_2\text{CO}_3]/(R_a + 1)}{V/(R_T + 1)} + R_b \frac{3[\text{HCO}_3^-]/(R_b + 1)}{V/(R_T + 1)} + R_c \frac{3[\text{CO}_3^{2-}]/(R_c + 1)}{V/(R_T + 1)}$$

and using the notation

$$z_d = \frac{2[\text{CO}_2]}{V}; z_a = \frac{3[\text{H}_2\text{CO}_3]}{V}; z_b = \frac{3[\text{HCO}_3^-]}{V}; z_c = \frac{3[\text{CO}_3^{2-}]}{V}$$

we have

$$R_T = \frac{R_d}{R_d + 1} z_d (R_T + 1) + \frac{R_a}{R_a + 1} z_a (R_T + 1) + \frac{R_b}{R_b + 1} z_b (R_T + 1) + \frac{R_c}{R_c + 1} z_c (R_T + 1).$$

[14] With

$$r_d = \frac{R_d}{R_d + 1}; r_a = \frac{R_a}{R_a + 1}; r_b = \frac{R_b}{R_b + 1}; r_c = \frac{R_c}{R_c + 1}$$

this can be simplified to

$$R_T = r_d z_d (R_T + 1) + r_a z_a (R_T + 1) + r_b z_b (R_T + 1) + r_c z_c (R_T + 1)$$

and solved for R_T , which yields

$$R_T = \frac{r_d z_d + r_a z_a + r_b z_b + r_c z_c}{1 - r_d z_d - r_a z_a - r_b z_b - r_c z_c}$$

or in terms of α_T :

$$\alpha_T = \alpha_{(\mathcal{S}-\text{H}_2\text{O})} = \frac{r_d z_d + r_a z_a + r_b z_b + r_c z_c}{1 - r_d z_d - r_a z_a - r_b z_b - r_c z_c} \times \frac{1}{R_{\text{H}_2\text{O}}} \quad (13)$$

This equation is a useful mass balance for the overall stable oxygen isotope fractionation between the sum of the dissolved inorganic carbon species and water, in which the oxygen mole fractions have been expressed by known quantities. If the individual fractionation factors, $\alpha_{(\text{CO}_2(\text{aq.})-\text{H}_2\text{O})}$, $\alpha_{(\text{H}_2\text{CO}_3-\text{H}_2\text{O})}$, $\alpha_{(\text{HCO}_3^--\text{H}_2\text{O})}$, and $\alpha_{(\text{CO}_3^{2--\text{H}_2\text{O})}$ are provided, $\alpha_{(\mathcal{S}-\text{H}_2\text{O})}$ can be calculated. It may appear that the value for $R_{\text{H}_2\text{O}}$ which occurs in equation (13) needs to be known precisely. However, this is not the case. In practice, the calculation is set up so that R 's are calculated by multiplying the given individual α 's by $R_{\text{H}_2\text{O}}$ ($R_i = \alpha_i R_{\text{H}_2\text{O}}$; see equation (12)). Finally, both sides of the equation are again divided by $R_{\text{H}_2\text{O}}$ (equation (13)), which essentially cancels out $R_{\text{H}_2\text{O}}$. The value used for $R_{\text{H}_2\text{O}}$ is therefore not important. Numerically, variation of $R_{\text{H}_2\text{O}}$ by two orders of magnitude changes the calculated value of $\alpha_{(\mathcal{S}-\text{H}_2\text{O})}$ by less

than 0.002‰ (check auxiliary material numerical routines, Software S1).

[15] Figure 1b shows $\alpha_{(S-H_2O)}$ according to equation (13) (solid thin line), and the experimental data by *McCrea* [1950] (squares), *Beck et al.* [2005] (diamonds), and *Kim et al.* [2006] (stars). Only data from precipitation experiments in the range $pH > 8$ are included in the figure. As shown by *Beck et al.* [2005], precipitation data for $pH < 8$ are not reliable due to uncertainties in the reaction mechanism, which involves hydration/hydroxylation prior to precipitation [*Zeebe and Wolf-Gladrow*, 2001]. The solid curve was calculated for 25°C in fresh water using $\alpha_{(CO_2(aq)-H_2O)} = 1.0413$, $\alpha_{(HCO_3^- - H_2O)} = 1.0315$, and $\alpha_{(CO_3^{2-} - H_2O)} = 1.0245$ [*Beck et al.*, 2005]. The value assumed for $\alpha_{(H_2CO_3 - H_2O)}$ does not affect the result. The bottom line is that equation (13) provides a theoretical means of calculating the overall stable oxygen isotope fraction between the sum of the dissolved inorganic carbon species and water in agreement with experimental data.

[16] Also shown in Figure 1b are corresponding values of $\alpha_{(S-H_2O)}$ calculated for seawater (dashed line) using seawater carbonate chemistry constants [*Zeebe and Wolf-Gladrow*, 2001], but freshwater α 's. The latter introduces uncertainties in the calculation because fractionation factors in seawater may be affected by ion pairing (e.g., between Mg^{2+} and CO_3^{2-}). Note also that the seawater curve is not necessarily appropriate for understanding carbonate precipitation and ^{18}O -fractionation in marine organisms. The solution chemistry at the site of calcification is unlikely to resemble that of natural seawater. In fact, foraminifera, for instance, appear to have strong control over the calcifying fluid's chemical composition, including its Mg^{2+} content [*Zeebe and Sanyal*, 2002].

3. Discussion

[17] The expression derived here for $\alpha_{(S-H_2O)}$ (equation (13)) can be used to elucidate biomineralization mechanisms in calcifying organisms such as corals and foraminifera. If the skeletal or shell $CaCO_3$ is built from a mixture of HCO_3^- and CO_3^{2-} set by the pH of the calcifying fluid during a quantitative precipitation, then the $\delta^{18}O$ of the carbonate decreases with pH . This appears to be the case in foraminifera, as documented by culture experiments and theoretical analyses [*Spero et al.*, 1997; *Zeebe*, 1999]. The mechanism may also help to understand a phenomenon of ^{18}O -depletions in

certain skeletal parts of surface- and deep-sea corals [*McConnaughey*, 1989; *Adkins et al.*, 2003].

[18] The effect of seawater pH on oxygen isotopes in cultured foraminifera has consequences for climate reconstructions based on $\delta^{18}O$ in fossil foraminifera from the sediment record [*Spero et al.*, 1997]. If seawater pH was lower or higher in the past, then isotopic paleotemperatures tend to underestimate or overestimate actual temperatures. For example, due to lower Cretaceous surface ocean pH , actual sea surface temperatures may have been 2–3.5°C warmer than previously thought [*Zeebe*, 2001]. If a general relationship exists between seawater pH and $\delta^{18}O$ in biogenic carbonates, then corrections have to be applied to paleotemperature equations based on biogenic carbonates throughout.

3.1. Implications for Previous Work

[19] The result for $\alpha_{(S-H_2O)}$ derived in this paper differs from a relationship published earlier, which has implications for previous work. *Usdowski and Hoefs* [1993] assumed a linear relationship between oxygen isotope equilibrium and chemical equilibrium:

$$\ln \alpha_{(S-H_2O)} = a + b \ln(S'/[CO_2]) \quad (14)$$

where $S' = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$. *Beck et al.* [2005] showed that this relationship leads to incorrect fractionation factors for individual carbonate species. Figure 2 shows that the relationship is also incompatible with $\alpha_{(S-H_2O)}$ derived here (equation (13)). *Zeebe* [1999] used equation (14) to derive the overall ^{18}O fractionation as a function of pH . Thus, as a result of the present study, Figure 4 of *Zeebe* [1999] should be replaced by Figure 1b of the current paper. The mechanism suggested by *Zeebe* [1999] to explain the carbonate chemistry effect on $\delta^{18}O$ in foraminifera [*Spero et al.*, 1997] remains unchanged. The slopes of $\delta^{18}O$ - $CaCO_3$ versus $\%[CO_3^{2-}]$ in *Spero et al.*'s culture experiments and in inorganic, quantitative precipitation experiments [*McCrea*, 1950] are indistinguishable [see *Spero et al.*, 1997, Figure 4]. This result is independent of the mathematical expression for $\alpha_{(S-H_2O)}$.

3.2. Isotopic Equilibrium Between H_2O and a Single Compound Versus the Sum of Multiple Compounds

[20] The pH -dependence of the overall oxygen isotope fractionation between the sum of dissolved

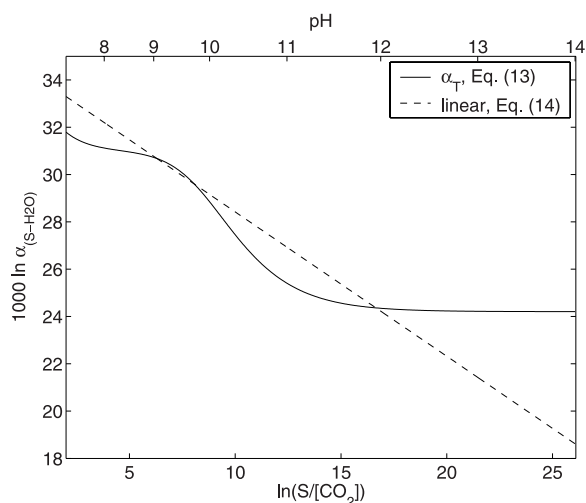


Figure 2. Comparison of the relationship between oxygen isotope equilibrium and chemical equilibrium derived in this paper (solid line, equation (13)) and the linear relationship assumed by *Usdowski and Hoefs* [1993] (dashed line, equation (14)). Calculated values are for freshwater at 25°C. Note that in the pH range shown, it is not important whether S or S' is used (see text). At pH 8.5, 11, and 14, the differences (in %) between S and S' are 0.7, 0.0004, and 5×10^{-10} , respectively.

inorganic carbon and water is frequently misunderstood. In thermodynamic equilibrium and at given temperature and pressure, there is only one value for the isotopic fractionation factor between two chemical compounds, say CO_2 and H_2O . However, $S = [CO_2(aq.)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$ is the sum of multiple compounds and therefore the fractionation factor $\alpha_{(S-H_2O)}$ changes with pH , depending on the concentrations of the individual species that comprise S at any given pH value (Figure 1).

[21] This is the mechanism called upon by *Zeebe* [1999] to explain carbonate chemistry effects on $\delta^{18}O$ in foraminifera [*Spero et al.*, 1997] and not the thermodynamic equilibrium fractionation between say, the $CaCO_3$ crystal and H_2O . *Kim et al.* [2006] studied equilibrium oxygen isotope fractionation between aragonite crystals and water at different pH . They state: “To test *Zeebe’s* (1999) hypothesis at low temperatures, aragonites were precipitated slowly. . .” (p. 5795). During slow precipitation, thermodynamic equilibrium is achieved between the $CaCO_3$ crystal and H_2O . Their “slow-precipitation” approach is therefore unsuitable for testing *Zeebe’s* (1999) hypothesis in regard to foraminifera. However, *Kim et al.* [2006] do con-

firm the pH -effect on $\delta^{18}O$ in carbonates in their “quantitative precipitation” experiments. In case of rapid and complete precipitation of dissolved carbonate as $BaCO_3$, the isotopic composition of $BaCO_3$ reflects that of the dissolved species. As a result, the fractionation factor reported by *Kim et al.* [2006] varied by 5.6‰ between pH 8.25 and 10.75 (see their Figure 2 and Table 2). These data have been included in Figure 1 and are well explained by the theoretical curve derived here (equation (13)). In summary, it is critical to comprehend that the equilibrium fractionation between the sum of the carbonate species and H_2O does vary with pH , whereas the equilibrium fractionation between a single compound and H_2O does not.

3.3. Broader Implications: Phanerozoic Climate Change

[22] Recently, a controversy has arisen over the primary driver of Phanerozoic climate change in which the pH -correction of isotopic paleotemperatures plays a critical role [*Shaviv and Veizer*, 2003; *Royer et al.*, 2004; *Rahmstorf et al.*, 2004; *Wallmann*, 2004]. *Shaviv and Veizer* [2003] questioned a dominant role of atmospheric CO_2 in Phanerozoic climate change, while *Royer et al.* [2004] argued in favor of CO_2 [cf. *Berner and Kothavala*, 2001] using a Phanerozoic $\delta^{18}O$ record that was corrected for pH changes (based on *Spero et al.* [1997] and *Zeebe* [1999]). One of the critical assumptions that would need to be addressed in order to settle the issue is whether or not pH -corrections can be applied to fossil brachiopod and belemnite carbonates (which are included in the record). Regardless of the controversy’s outcome, the discussion has demonstrated that application of pH -corrections to carbonate- $\delta^{18}O$ records can significantly change interpretations of climate change over geologic time scale. Climate reconstructions that apply such corrections require a functional relationship between $\alpha_{(S-H_2O)}$ and pH based on recent values of individual α ’s [*Beck et al.*, 2005]. This has been provided by the present study.

4. Summary

[23] I have derived an analytical expression for the overall oxygen isotope fractionation between the sum of the dissolved inorganic carbon species and water (equation (13)). The result differs from a relationship published earlier and implications for previous studies have been discussed. The expression can be used to calculate $\alpha_{(S-H_2O)}$ at any given

pH of the solution. In order to facilitate its practical application in, for example, biomineralization or paleoclimate research, I have developed numerical routines in MATLAB and Excel; they are available as auxiliary material (Software S1).

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