Comment on “The Effects of Secular Calcium and Magnesium Concentration Changes on the Thermodynamics of Seawater Acid/Base Chemistry: Implications for Eocene and Cretaceous Ocean Carbon Chemistry and Buffering” by Hain et al. (2015)

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Abstract

Hain et al. (2015, https://doi.org/10.1002/2014GB004986, hereafter H15) calculated effects of changing \([\text{Ca}^{2+}]\) and \([\text{Mg}^{2+}]\) on the equilibrium constants of the \(\text{CO}_2-\text{CaCO}_3\) system in seawater based on a Pitzer ionic interaction model (Millero & Pierrot, 1998; Pitzer, 1973). In their supporting information, H15 tabulated parameters for stoichiometric equilibrium constants (\(K^*\)’s) to be used by the community. Furthermore, H15 contended that previously published, simplified Ca-Mg corrections for \(K^*\)’s should be avoided (e.g., Tyrrell & Zeebe, 2004). The main application of such corrections were carbonate chemistry reconstructions in deep time (not sediments, not culture work, etc.), when the major ion chemistry of seawater was different from modern. Clearly, for such an approach, the complexity and accuracy of the tool employed should be in proportion to the inherent uncertainty of the target application. For example, the reconstructed changes of past temperature, salinity, \(\text{CO}_2\) system parameters, and \([\text{Ca}^{2+}]\) and \([\text{Mg}^{2+}]\) themselves have large uncertainties, which calls into question the suitability of a seemingly convoluted approach such as a Pitzer model in the first place. More importantly, however, we show here that critical results presented in H15 pertaining to the first dissociation constant of carbonic acid are fundamentally wrong. We therefore do not recommend using H15’s stoichiometric equilibrium constants to correct for past changes in major ion seawater composition.

1. Introduction

Hain et al. (2015, H15 hereafter) calculated effects of changing \([\text{Ca}^{2+}]\) and \([\text{Mg}^{2+}]\) on the equilibrium constants of the \(\text{CO}_2-\text{CaCO}_3\) system in seawater based on a Pitzer ionic interaction model (Millero & Pierrot, 1998; Pitzer, 1973). In their supporting information, H15 tabulated parameters for stoichiometric equilibrium constants (\(K^*\)’s) to be used by the community. Furthermore, H15 contended that previously published, simplified Ca-Mg corrections for \(K^*\)’s should be avoided (e.g., Tyrrell & Zeebe, 2004). The main application of such corrections were carbonate chemistry reconstructions in deep time (not sediments, not culture work, etc.), when the major ion chemistry of seawater was different from modern. Clearly, for such an approach, the complexity and accuracy of the tool employed should be in proportion to the inherent uncertainty of the target application. For example, the reconstructed changes of past temperature, salinity, \(\text{CO}_2\) system parameters, and \([\text{Ca}^{2+}]\) and \([\text{Mg}^{2+}]\) themselves have large uncertainties, which calls into question the suitability of a seemingly convoluted approach such as a Pitzer model in the first place. More importantly, however, we show here that critical results presented in H15 pertaining to the first dissociation constant of carbonic acid are fundamentally wrong. We therefore do not advise users to apply H15’s stoichiometric equilibrium constants to correct for past changes in major ion seawater composition.

According to H15, the first (stoichiometric) dissociation constant of carbonic acid, \(K_1^*\), decreases with rising \([\text{Ca}^{2+}]\) (H15, Figure 2, lower panel). This result is immediately perplexing as the following elementary reasoning shows. \(K_1^*\) is defined as (e.g., Zeebe & Wolf-Gladrow, 2001):

\[
K_1^* = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]} = K^1 \frac{\gamma_{\text{CO}_2}}{\gamma_{\text{HCO}_3^-}\gamma_{\text{H}^+}},
\]

where \(K^1\) is the thermodynamic dissociation constant (independent of solution composition) and \(\gamma\)’s values are total activity coefficients. With rising \([\text{Ca}^{2+}]\), the concentration of, for example, \(\text{CaHCO}_3^-\) ion pairs rises, reducing \(\gamma_{\text{HCO}_3^-}\). As a result, \(K_1^*\) should increase with \([\text{Ca}^{2+}]\) (see equation (1)), not decrease. Importantly, however, our primary argument regarding the correct \(K_1^*-[\text{Ca}^{2+}]\) relationship (see below) is independent of any assumptions about activity coefficients (equation (1)), or the stability of \(\text{CaHCO}_3^-\), or any other ion pairs.

The fact that \(K_1^*\) increases with \([\text{Ca}^{2+}]\) has been demonstrated by experimental studies that actually measured the effect of \([\text{Ca}^{2+}]\) on \(K_1^*\) in NaCl solutions and artificial seawater, ASW (Figure 1). Pytkowicz and Hawley (1974)
Figure 1. Measured (symbols) and predicted changes (lines) in $K^*_1([\text{Ca}^{2+}])$, normalized to $K^*_1([\text{Ca}^{2+}]=0)$ for each approach (see text). Tyrrell and Zeebe (2004) applied Ben-Yaakov and Goldhaber (1973)'s sensitivity (dark green, dashed) over the range $[\text{Ca}^{2+}] \approx 10–22 \text{ mmol/kg}$ (light green, solid). Hain et al. (2015) (NaCl, red dashed line) was calculated using exactly PH74's solution compositions, including NaCl changes ($I = \text{const}$).

used NaCl + CaCl$_2$ + NaHCO$_3$ solutions (Nos. 2, 6, and 7) at 25 °C and constant ionic strength $I = 0.72$ (close to seawater) in which $K^*_1$ increased with $[\text{Ca}^{2+}]$ (Figure 1). Rushdi and Chen (1995) determined carbonic acid dissociation constants in ASW at 25 °C and $I = 0.718$ as a function of $[\text{Ca}^{2+}]$ (solution Nos. 1 and 2). Again, $K^*_1$ increased with $[\text{Ca}^{2+}]$ (Figure 1). $K^*_1$'s measured relative increase with $[\text{Ca}^{2+}]$ in ASW is consistent with $K^*_1$'s sensitivity to $[\text{Ca}^{2+}]$ as given by Ben-Yaakov and Goldhaber (1973) and used by Tyrrell and Zeebe (2004, Figure 1).

On the contrary, $K^*_1$ predicted by H15's Pitzer model strongly decreases with $[\text{Ca}^{2+}]$, both in NaCl solutions and seawater (Figure 1), suggesting something fundamentally wrong with H15's predicted activity coefficients (see equation (1)). Unfortunately, two out of three of the very same activity coefficients (for HCO$_3^-$ and H$^+$) also enter the equation for the second dissociation constant of carbonic acid:

$$K^*_2 = \frac{[\text{CO}_2^{3-}]\left[H^+\right]}{[\text{HCO}_3^-]} = K^*_0 \frac{\gamma_{\text{HCO}_3^-}}{\gamma_{\text{CO}_2^{3-}}\gamma_{H^+}},$$

suggesting that H15's values for $K^*_2$ are also in error. Thus, we do not recommend using H15's tabulated parameters to correct stoichiometric dissociation constants for past changes in seawater chemistry.

Looking forward, note that we do not advocate the use of Ben-Yaakov and Goldhaber (1973)'s sensitivity parameters for future applications, despite their apparent utility in some cases (see above). Rather, to advance the field, future research efforts should include the experimental determination of stoichiometric equilibrium constants of the CO$_2$-CaCO$_3$-H$_2$O system for the particular major ion compositions of past oceans, as opposed to the arbitrary solutions of earlier work. Reconstructions over the last 100 Myr, for instance, should at minimum include variations of the concentrations of Ca$^{2+}$, Mg$^{2+}$, and SO$_4^{2-}$ over a wide range (e.g., Horita et al., 2002).

References


