

Supplementary Information for

The emission of low pH water from Gulf of Mexico seeps as revealed by $\delta^{13}\text{C}\text{-CO}_2$ and methane oxidation data

Sydney I. Loudon^a, John D. Kessler^a

^aDepartment of Earth and Environmental Science, University of Rochester, Rochester, NY USA

Corresponding author: Sydney Loudon (slouden2@ur.rochester.edu)

Calculating the pH-dependent isotopic offset between δ_{DIC} and δ_{CO_2}

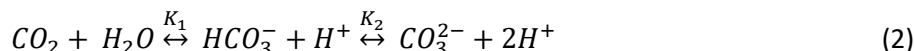
To produce our model and compare it to the measured data, we needed to be able to convert between values of δ_{DIC} and δ_{CO_2} . We achieved this using the concentration and isotopic relationships between DIC and CO_2 .

Concentration Equations

Dissolved inorganic carbon (DIC) describes the total amount of carbon dioxide (CO_2), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) in seawater (Eq. 1). (We note that CO_2 represents the sum of dissolved CO_2 and H_2CO_3 .)

$$[DIC] = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1)$$

The carbonate species comprising DIC are related through a series of equilibrium reactions (Eq. 2).



K_1 and K_2 are equilibrium constants and can be defined in terms of concentration (Eq. 3&4).

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (3)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (4)$$

Equations for K_1 and K_2 have been empirically determined as a function of temperature (T Kelvin) and salinity (S in psu) (Eq. 5&6).^{20,21*}

$$-\log K_1 = -62.008 + \frac{367.07}{T} + 9.7944 \ln(T) - 0.0118S + 0.000116S^2 \quad (5)^{20,21}$$

$$-\log K_2 = 4.777 + \frac{1394.7}{T} - 0.0184S + 0.000118S^2 \quad (6)^{20,21}$$

* The references in the supplementary information are all cited in the main text and use the same numbering as in the main text.

At the temperature and salinity of the incubation experiment (7°C and 35 ppt), $K_1 = 9.558 \times 10^{-7} \text{ mol/kg}$ and $K_2 = 5.521 \times 10^{-10} \text{ mol/kg}$.

For the purposes of this investigation, we need to solve for the carbonate species in terms of $[DIC]$, $[H^+]$, and the equilibrium constants. This can be achieved using the concentration definitions of the equilibrium constants. First, Equation 3 can be rearranged to solve for $[HCO_3^-]$ (Eq. 7).

$$[HCO_3^-] = \frac{[CO_2]K_1}{[H^+]} \quad (7)$$

Similarly, Equation 4 can be rearranged to solve for $[CO_3^{2-}]$, with Equation 7 substituted for $[HCO_3^-]$ to produce Equation 8.

$$[CO_3^{2-}] = \frac{[CO_2]K_1K_2}{[H^+]^2} \quad (8)$$

Substituting Equations 7 and 8 into Equation 1 and solving for $[CO_2]$ produces an equation for $[CO_2]$ in terms of $[DIC]$, $[H^+]$, K_1 and K_2 (Eq. 9).

$$[CO_2] = \frac{[DIC]}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}} \quad (9)$$

Equation 9 can now be substituted for $[CO_2]$ in Equation 7 to produce an equation for $[HCO_3^-]$ in terms of $[DIC]$, $[H^+]$, K_1 and K_2 (Eq. 10).

$$[HCO_3^-] = \frac{K_1[DIC]}{[H^+] + K_1 + \frac{K_1K_2}{[H^+]}} \quad (10)$$

Similarly, Equation 9 can be substituted for $[CO_2]$ in Equation 8 to produce an equation for $[CO_3^{2-}]$ in terms of $[DIC]$, $[H^+]$, K_1 and K_2 (Eq. 11).

$$[CO_3^{2-}] = \frac{K_1K_2[DIC]}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad (11)$$

Equations 9-11 are now all in terms of $[DIC]$, the equilibrium constants, and $[H^+]$, highlighting how the concentration of each carbonate species is dependent on the pH of the seawater.

Isotope Equations

Just as $[DIC]$ is the sum of inorganic carbon species (Eq. 1), δ_{DIC} is the concentration weighted average of the isotopes of all inorganic carbon species. A mass balance relationship¹⁷ relates the isotopes and concentrations of DIC (Eq. 12).

$$\delta_{DIC}[DIC] = \delta_{CO_2}[CO_2] + \delta_{HCO_3^-}[HCO_3^-] + \delta_{CO_3^{2-}}[CO_3^{2-}] \quad (12)$$

The fractionation of isotopes between the carbonate species is an equilibrium reaction and can be described using isotope equilibrium equations.¹⁶ In an isotope equilibrium reaction, the fractionation factor, α , is equal to the ratio of the isotope ratios of two compounds, R_A and R_B . (Eq. 13)

$$\alpha_{(A \leftrightarrow B)} = \frac{R_A}{R_B} = \frac{\delta_A + 1000}{\delta_B + 1000} \quad (13)$$

The fractionation effect, ϵ , is a commonly reported form of α . The relationship between ϵ and α is shown in Equation 14.

$$\varepsilon_{(A \leftrightarrow B)} = (\alpha_{(A \leftrightarrow B)} - 1) * 1000 \quad (14)$$

The fractionation effects for the isotope equilibrium between carbonate species have been experimentally determined as a function of temperature (T in Kelvin) (Eq. 15-18).^{18,19}

$$\varepsilon_{(CO_2 \leftrightarrow HCO_3^-)} = \varepsilon_{db} = \frac{-9866}{T} + 24.12\text{‰} \quad (15)^{18}$$

$$\varepsilon_{(CO_3^{2-} \leftrightarrow CO_2(g))} = \varepsilon_{cg} = -0.052(T - 273.15) + 7.22\text{‰} \quad (16)^{19}$$

$$\varepsilon_{(HCO_3^- \leftrightarrow CO_2(g))} = \varepsilon_{bg} = -0.1141(T - 273.15) + 10.78\text{‰} \quad (17)^{19}$$

$$\varepsilon_{(CO_3^{2-} \leftrightarrow HCO_3^-)} = \varepsilon_{cb} = \frac{\varepsilon_{cg} - \varepsilon_{bg}}{1 + \varepsilon_{bg} \times 10^{-3}} \quad (18)^{19}$$

At the incubation temperature (7°C), $\varepsilon_{db} = -11.11\text{‰}$, $\varepsilon_{cg} = 6.853\text{‰}$, $\varepsilon_{bg} = 9.976\text{‰}$, and $\varepsilon_{cb} = -3.091\text{‰}$.

We now relate ε to δ by solving Equation 14 for α and equating it to Equation 13, forming Equation 19.

$$\alpha_{(A \leftrightarrow B)} = (\varepsilon_{A \leftrightarrow B} \times 10^{-3}) + 1 = \frac{\delta_A + 1000}{\delta_B + 1000} \quad (19)$$

Applying Equation 19 to the fractionation between CO_2 and HCO_3^- produces Equation 20.

$$\alpha_{(CO_2 \leftrightarrow HCO_3^-)} = \frac{\delta_{CO_2} + 1000}{\delta_{HCO_3^-} + 1000} = (\varepsilon_{db} \times 10^{-3}) + 1 \quad (20)$$

Equation 20 can be rearranged to solve for δ_{CO_2} (Eq. 21).

$$\delta_{CO_2} = \delta_{HCO_3^-} (1 + \varepsilon_{db} \times 10^{-3}) + \varepsilon_{db} \quad (21)$$

The same steps can be applied to the fractionation between CO_3^{2-} and HCO_3^- (Eq. 22).

$$\alpha_{(CO_3^{2-} \leftrightarrow HCO_3^-)} = \frac{\delta_{CO_3^{2-}} + 1000}{\delta_{HCO_3^-} + 1000} = (\varepsilon_{cb} \times 10^{-3}) + 1 \quad (22)$$

Equation 22 can then be solved for $\delta_{CO_3^{2-}}$ (Eq. 23).

$$\delta_{CO_3^{2-}} = \delta_{HCO_3^-} (1 + \varepsilon_{cb} \times 10^{-3}) + \varepsilon_{cb} \quad (23)$$

Equations 21 and 23 can now be substituted into Equation 12 (Eq. 24).

$$\begin{aligned} \delta_{DIC}[DIC] &= (\delta_{HCO_3^-} (1 + \varepsilon_{db} \times 10^{-3}) + \varepsilon_{db})[CO_2] + \delta_{HCO_3^-}[HCO_3^-] \\ &\quad + (\delta_{HCO_3^-} (1 + \varepsilon_{cb} \times 10^{-3}) + \varepsilon_{cb})[CO_3^{2-}] \end{aligned} \quad (24)$$

Equation 24 can then be rearranged to solve for $\delta_{HCO_3^-}$ (Eq. 25).

$$\delta_{HCO_3^-} = \frac{\delta_{DIC}[DIC] - \varepsilon_{db}[CO_2] - \varepsilon_{cb}[CO_3^{2-}]}{[CO_2] + (\varepsilon_{db} \times 10^{-3})[CO_2] + [HCO_3^-] + (\varepsilon_{cb} \times 10^{-3})[CO_3^{2-}]} \quad (25)$$

The remaining δ value to solve for is δ_{DIC} . Here, we assume that the isotopes of all carbonate species sum to zero, $\delta_{DIC} = 0\text{‰}$.^{17,19} The goal of this analysis is to calculate the difference between

δ_{DIC} and δ_{CO_2} , and not a true value for δ_{DIC} . The isotopic difference, or offset, is used to convert an initial, background $\delta^{13}C - CO_2$ measurement to a background DIC value, $\delta_{DIC,B}$. The offset value is then used to revert modelled δ_{DIC} back to δ_{CO_2} for comparison with the measured $\delta^{13}C - CO_2$ data. As evident in Equation 12, $[DIC]$ does influence the isotope values if $\delta_{DIC} \neq 0\text{‰}$, however, assuming $\delta_{DIC} = 0\text{‰}$ causes less than a 1% error in the per mill difference between δ_{DIC} and δ_{CO_2} .

We can now write an equation for the offset, assuming $\delta_{DIC} = 0\text{‰}$ (Eq. 26).

$$\delta_{DIC} - \delta_{CO_2} = 0 - \delta_{CO_2} \quad (26)$$

Equation 21 is then substituted for δ_{CO_2} (Eq. 27).

$$\delta_{DIC} - \delta_{CO_2} = 0 - \delta_{CO_2} = -(\delta_{HCO_3^-}(1 + \varepsilon_{db} \times 10^{-3}) + \varepsilon_{db}) \quad (27)$$

Next, Equation 25 is substituted for $\delta_{HCO_3^-}$ to produce an equation for the offset as a function of the concentrations of carbonate species (Eq. 28).

$$\delta_{DIC} - \delta_{CO_2} = \frac{\varepsilon_{db}[CO_2] + \varepsilon_{cb}[CO_3^{2-}]}{[CO_2] + (\varepsilon_{db} \times 10^{-3})[CO_2] + [HCO_3^-] + [CO_3^{2-}] + (\varepsilon_{cb} \times 10^{-3})[CO_3^{2-}]} (1 + \varepsilon_{db} \times 10^{-3}) - \varepsilon_{db} \quad (28)$$

Equations 9-11 can then be substituted for the corresponding concentrations in Equation 28 to produce an equation for the offset dependent on $[DIC]$ and pH (Eq. 29).

$$\delta_{DIC} - \delta_{CO_2} = \frac{\frac{\varepsilon_{db}[DIC]}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}} + \frac{\varepsilon_{cb} K_1 K_2 [DIC]}{[H^+]^2 + K_1 [H^+] + K_1 K_2}}{\frac{(1 + \varepsilon_{db} \times 10^{-3})[DIC]}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}} + \frac{K_1 [DIC]}{[H^+] + K_1 + \frac{K_1 K_2}{[H^+]}} + \frac{(1 + \varepsilon_{cb} \times 10^{-3}) K_1 K_2 [DIC]}{[H^+]^2 + K_1 [H^+] + K_1 K_2}} (1 + \varepsilon_{db} \times 10^{-3}) - \varepsilon_{db} \quad (29)$$

$[DIC]$ cancels out of the fraction in Equation 29, resulting in an offset equation that is a function of pH (Eq. 30).

$$\delta_{DIC} - \delta_{CO_2} = \frac{\frac{\varepsilon_{db}}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}} + \frac{\varepsilon_{cb} K_1 K_2}{[H^+]^2 + K_1 [H^+] + K_1 K_2}}{\frac{1 + \varepsilon_{db} \times 10^{-3}}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}} + \frac{K_1}{[H^+] + K_1 + \frac{K_1 K_2}{[H^+]}} + \frac{(1 + \varepsilon_{cb} \times 10^{-3}) K_1 K_2}{[H^+]^2 + K_1 [H^+] + K_1 K_2}} (1 + \varepsilon_{db} \times 10^{-3}) - \varepsilon_{db} \quad (30)$$

Finally, Equation 30 is solved using the calculated values for K_1 (Eq. 5), K_2 (Eq. 6), ε_{db} (Eq. 15), and ε_{cb} (Eq. 18) and the chosen pH values.