**Detailed description of the ExClump38 model**

1. **Overview**

For this study, we developed a MATLAB-based numerical model for *Ex*change and *Clump*ing of 1*3*C and 1*8*O in the dissolved carbonate system (“ExClump38” model) by extending the framework of Chen et al. (2018). It simulates chemical and isotopic evolution of the (closed) dissolved carbonate system, which depends on the following chemical and isotope exchange reactions:

 (Eq. A1)

 (Eq. A2)

 (Eq. A3)

 (Eq. A4)

 (Eq. A5)

 (Eq. A6)

 (Eq. A7)

 (Eq. A8)

 (Eq. A9)

 (Eq. A10)

 (Eq. A11)

 (Eq. A12)

Here, CO2 refers to aqueous CO2 (CO2(aq)). The numbers 2, 3, 6 and 8 in these expressions indicate the 12C, 13C, 16O and 18O isotopes, respectively. The prime symbols are used specifically for the oxygen isotopes in association with OH−. In the model, we assume [266] ≈ [CO2], [H2666−] ≈ [HCO3−], [6′H−] ≈ [OH−], and [H26] ≈ [H2O] (and, by definition, [H2O] = 1 and can be ignored if necessary). Hence, we also assume that CO2 hydration and hydroxylation involving isotopically unsubstituted species (*i.e*., 12C and 16O only) can be approximated by Eq. A1 and Eq. A2, such that their rate constants are equal to *k*±1 and/or *k*±4. The 2/3 and 1/3 factors applied to the reverse rate constants in Eq. A5 to Eq. A12 follow Christensen et al. (2021). The argument for these factors is that, of one unit of HCO3− undergoing dehydration or dehydroxylation, 2/3 of oxygen go to CO2 and 1/3 go to H2O or OH− (Christensen et al., 2021). With these assumptions and following Mills and Urey (1940) (also see Chen et al., 2018, UZ12, and Christensen et al. 2021), Eq. A1 to Eq. A12 lead to a set of eight differential equations describing the changes in concentration and isotopic state of CO2(aq) and HCO3− over time:

 (Eq. A13)

 (Eq. A14)

 (Eq. A15)

 (Eq. A16)

 (Eq. A17)

 (Eq. A18)

 (Eq. A19)

 (Eq. A20)

Note that in Eq. A1 to Eq. A12, HCO3− can further dissociate to CO32− (hereafter, written as CO3= or 2666= and so on). However, instead of treating these species individually, we bundle them as DCP (as is the case for “EIC” in Chen et al., 2018 and Christensen et al., 2021) in the differential equations, where DCP stands for “dissolved carbonate pool”:

 (Eq. A21)

This should impose no biases to the model, as the chemical and isotopic equilibrium between HCO3− and CO3= can be assumed instantaneous. This is because the timescale of protonation and/or deprotonation between HCO3− and CO3= are orders of magnitude faster than CO2 hydration/dehydration (Eq. A1) and hydroxylation/dehydroxylation (Eq. A2) (UZ12; Zeebe and Wolf-Gladrow, 2001). The terms 13DCP, 18DCP and 47DCP denote 13C-substitued DCP (= [H3666−] + [3666=]), 18O-substituted DCP (= [H2866−] + [2866=]) and doubly-substituted (“clumped”) DCP (= [H3866−] + [3866=]). The terms *x*1, 13*x*1, 18*x*1 and 47*x*1 indicate [HCO3−]/[DCP], [H3666−]/[13DCP], [H2866−]/[18DCP] and [H3866−]/[47DCP] ratio, respectively.

 We reiterate that the ExClump38 model is fundamentally rooted in the earlier δ13C and δ18O equilibration model by Chen et al. (2018), yet the approach used in a similar model by Christensen et al. (2021) in regards to the oxygen isotope mass balance (*i.e*., the aforementioned 2/3 and 1/3 factors) is also adopted here. It is important to note that, though the formulations are set up differently, the two stable isotope models by Chen et al. (2018) and Christensen et al. (2021) come to mathematically equivalent results. This is explained in detail at the end of this supplementary material.

In the following, we show that all of the terms appearing in the differential equations solved in the ExClump38 model (Eq. A13 to Eq. A20) can be derived from thermodynamic principles combined with a series of well-established (equilibrium and kinetic) constants and isotope fractionation factors that can be compiled from the literature.

1. **Chemical equilibrium, reaction kinetics and isotope fractionations.**

This segment briefly goes over some fundamental aspects of chemical equilibrium and reaction kinetics, which will be followed by the notations and definitions of isotope fractionations. For further reading, Zeebe and Wolf-Gladrow (2001) is recommended.

Equilibrium constant for CO2 hydration (Eq. A1) is defined as:

 (Eq. A22)

The equilibrium constant *K*1 and the kinetic rate constants for Eq. A1 (*k*+1 and *k*−1) are related, such that:

 (Eq. A23)

For dissociation of HCO3− to CO3= and H+:

 (Eq. A24)

we have *K*2:

 (Eq. A25)

Analogously, for CO2 hydroxylation (Eq. A2):

 (Eq. A26)

For dissociation of H2O:

 (Eq. A27)

we have:

 (Eq. A28)

For these expressions, [H+] and [OH−] can be obtained from the experimental pH as:

 (Eq. A29)

and

 (Eq. A30)

Then, the abundance of HCO3− and CO3= in DCP (*x*1 and *x*2, respectively) can be calculated as:

 (Eq. A31)

and

 (Eq. A32)

 We can write similar expressions for isotope exchange reactions as well. Here, we use carbon isotope exchange during CO2 hydration as an example. Although Eq. A1 is used as an approximation, the explicit expression for 12C exchange between CO2(aq) and HCO3− via CO2 hydration is:

 (Eq. A33)

We can define equilibrium constant for this reaction as 12*K*1 (also note our approximation):

 (Eq. A34)

For CO2 hydration involving 13C substituted species (Eq. A3), we can write:

 (Eq. A35)

With 12*K*1 and 13*K*1, equilibrium carbon isotope fractionation factor between CO2 and HCO3− is given by:

 (Eq. A36)

From this, can be viewed as the equilibrium constant for the isotope exchange reaction:

 (Eq. A37)

However, note also that, more operationally, can be obtained from δ13C values of CO2 and HCO3−:

 (Eq. A38)

where 13*R* is the 13C/12C ratio for CO2 and/or HCO3− and the definition of the conventional δ notation for a chemical compound/phase A is given by δ13CA = (13*R*A/13*R*Standard – 1)∙103 (for oxygen isotopes, δ18OA = (18*R*A/18*R*Standard – 1)∙103 with 18*R* = 18O/16O).

A difference between 12*k*+1 and 13*k*+1 (Eq. A3 and Eq. A33) leads to a kinetic isotope fractionation during CO2 hydration, for which we write:

 (Eq. A39)

Likewise, for the reverse reaction (dehydration of HCO3−), we have:

 (Eq. A40)

Moreover, and the rate constants 12*k*+1 and 13*k*+1 are related, such that:

 (Eq. A41)

and thus:

 (Eq. A42)

Although the same principles hold for oxygen isotope systems, the expressions become more complicated because of H2O and OH− contributions for oxygen isotopes (*e.g*., Zeebe, 2014).

 Provided with , andfrom the literature (*e.g*., Zhang et al. 1995), we can derive the following equilibrium fractionation factors:

 (Eq. A43)

 (Eq. A44)

 (Eq. A45)

 (Eq. A46)

 (Eq. A47)

Moreover, fractionation between DCP and CO2 is given by:

 (Eq. A48)

where

 (Eq. A49)

 Similarly, after compiling well-established equilibrium oxygen isotope fractionation factors , and from the literature (*e.g*., Beck et al., 2005; Uchikawa and Zeebe, 2013), we can derive:

 (Eq. A50)

 (Eq. A51)

 (Eq. A52)

and

 (Eq. A53)

We rely on the recent theoretical constraint by Zeebe (2020) for the fractionation factor .

The clumped isotope systems deal with the internal equilibrium of 13C-18O bonding in a single phase. For instance, in case of CO2:

 (Eq. A54)

for which equilibrium constant can be expressed as:

 (Eq. A55)

The abundance of doubly-substituted CO2 (*i.e*., 13C-18O clumps) is measured as:

 (Eq. A56)

where 47*R* is the ratio of doubly-substituted species to unsubstituted CO2:

 (Eq. A57)

The asterisk in Eq. A56 indicates the expected 47*R* ratio for stochastic (random) isotope distribution. If in full thermodynamic equilibrium, we can expect (Watkins and Hunt, 2015):

 (Eq. A58)

Similarly, for equilibrium of 13C-18O clumping in HCO3− and CO3=, we can write:

 (Eq. A59)

and

 (Eq. A60)

For these equations, respective equilibrium constants can be expressed as:

 (Eq. A61)

and

 (Eq. A62)

Tripati et al. (2015) experimentally demonstrated that there is a measurable Δ47 difference between HCO3− and CO3= at equilibrium (= 0.713‰ and = 0.650‰). Equilibrium clumped isotope fractionation between CO3= and HCO3− can be written as:

 (Eq. A63)

We additionally need to consider Δ47 of DCP, for which we write a generalized expression without making a clear distinction between HCO3− and CO3= on this occasion:

 (Eq. A64)

By following Eq. A61 and Eq. A62, equilibrium constant for Eq. A64 as:

 (Eq. A65)

where

 (Eq. A66)

1. **Derivation of [13DCP], [18DCP] and [47DCP]**

These terms represent the abundance of 13C, 18O isotopes and 13C-18O clumps in DCP. As mentioned above, δ13C of DCP measured on the VPDB scale is given by δ13CDCP = (13*R*DCP/13*R*VPDB – 1) × 103. Thus, by assuming [12DCP] ≈ [DCP], we have:

 (Eq. A67)

Note that NaHCO3 was the only DIC source for our quantitative BaCO3 precipitation experiments. It follows that [DCP] and δ13CDCP are given by the concentration and δ13C of NaHCO3 used in our quantitative BaCO3 precipitation experiments.

 Since there are three oxygen atoms in each HCO3− and CO32− that make up DCP, the 18O/16O ratio of DCP should be defined as:

 (Eq. A68)

Therefore, [18DCP] is given by:

 (Eq. A69)

 To derive [47DCP], we first define the ratio of clumped carbonate group (3866) to isotopically unsubstituted carbonate group (2666) as:

 (Eq. A70)

This expression is for DCP in general (*e.g*., Eq. A64 to Eq. A66). Then, by assuming [44DCP] ≈ [DCP], we can write:

 (Eq. A71)

1. **Derivation of *x*1, 13*x*1, 18*x*1 and 47*x*1**

As stated in Section 1, we define *x*1, 13*x*1, 18*x*1 and 47*x*1 as the [HCO3−]/[DCP], [H3666−]/[13DCP], [H2866−]/[18DCP] and [H3866−]/[47DCP] ratio, respectively. Among these, *x*1 is already derived in Eq. A31. To derive 13*x*1, we first define 13*K*2, which is the second dissociation constant for carbonic acid, but specific to 13C-substituted HCO3− and CO3=:

 (Eq. A72)

for which 13*K*2 is:

 (Eq. A73)

Then we can derive 13*x*1 by following Eq. A31:

 (Eq. A74)

We can derive 18*x*1 by following the same approach:

 (Eq. A75)

where 18*K*2 is:

 (Eq. A76)

for

 (Eq. A77)

Analogously, we can obtain 47*x*1 as:

 (Eq. A78)

where 47*K*2 is: (Eq. A79)

for

 (Eq. A80)

Note that 47*K*2 can be described by the terms that are already defined or derived up to this point. From Eq. A61 and Eq. A62, (Eq. A63) can be written as:

By noting Eq. A47 and Eq. A52 (also see Eq. A38 for the definition of isotope fractionation factor), we can rearrange this to:

From the definition of 47*K*2 (Eq. A78) and *K*2 (Eq. A25), this simplifies to:

and therefore:

 (Eq. A81)

1. **Rate constants**

This section goes over how the forward and backward rate constants for CO2 hydration and hydroxylation involving 13C-substituted (denoted by 13*k*± in Eq. A3 and Eq. A4), 18O-substituted (*a*± and *b*± in Eq. A5 to Eq. A8) and doubly-substituted or “clumped” species (*p*± and *s*± in Eq. A9 to Eq. A12) are parameterized in the ExClump38 model. We reiterate that we assume the rate constants for the same reactions but involving isotopically unsubstituted species can be approximated by the conventional kinetic rate constants. For example, we assume Eq. A33 is essentially the same as Eq. A1, such that 12*k*+1 ≈ *k*+1 and 12*k*−1 ≈ *k*−1.

By combining the relationship described in Eq. A23 and *k*+1 from the literature, we can derive the backward rate constant *k*−1 for Eq. A1 as:

 (Eq. A82)

Similarly, based on Eq. A22, Eq. A26 and Eq. A28 as well as *k*+4 from the literature, we can express *k*−4 in Eq. A2 as:

 (Eq. A83)

 Parameterization of the rate constants for CO2 hydration and hydroxylation of 13C- or 18O-substituted species in the model is based upon kinetic and equilibrium isotope fractionation factors (*i.e*., αKIF’s and αEQ’s). From Eq. A39, 13*k*+1 for Eq. A3 is:

 (Eq. A84)

And from Eq. A35 and Eq. A36 (and assuming 12*K*1 ≈ *K*1), we can express 13*k*−1 as:

 (Eq. A85)

The definition of carbon isotope kinetic isotope fractionation during CO2 hydroxylation reads:

 (Eq. A86)

Thus, for 13*k*+4, we have:

 (Eq. A87)

Following the example of Eq. A84, we can parameterize 13*k*−4 as follows:

 (Eq. A88)

 For oxygen isotope systems, we define the following for Eq. A5 to Eq. A8:

 (Eq. A89)

 (Eq. A90)

 (Eq. A91)

 (Eq. A92)

Therefore, the forward rate constants are simply given by:

 (Eq. A93)

 (Eq. A94)

 (Eq. A95)

 (Eq. A96)

Then, by combining the equilibrium constant for Eq. A5 (18*K*a1) and the relationship exemplified by Eq. A35, we can set up:

which can be rearranged for *a*−1 as:

Given that the ratios [H2866−]/[H2666−] and [H28]/[H26] simply equate to 18*R*HCO3− and 18*R*H2O (also note [H26] ≈ [H2O] = 1), this simplifies to:

And finally, from the definition of isotope fractionation factor α (Eq. A36) and *K*1 (Eq. A22), what we have for *a*−1 is:

 (Eq. A97)

Using Eq. A97 above as an example, we can derive *b*−1, *a*−4 and *b*−4:

 (Eq. A98)

 (Eq. A99)

 (Eq. A100)

 After Guo (2020), we assume that the intrinsic kinetic clumped isotope effects (47KIE) for Eq. A9 to Eq. A12 are a combination of 13αKIF, 18αKIF, and an additional KIF that is specific to doubly-substituted species (47αKIF). For instance, 47KIE for Eq. A9 is given by:

 (Eq. A101)

From this, *p*+1 is:

 (Eq. A102)

Equilibrium constant for Eq. A9 can be expressed as:

 (Eq. A103)

The right-hand side of this expression can be rearranged to:

From Eq. A22, Eq. A61 and definition of isotope fractionation factor α (Eq. A38):

 (Eq. A104)

By combining Eq. A103 and Eq. A104, we can write *p*−1 as:

 (Eq. A105)

Analogously, for Eq. A10, we have:

 (Eq. A106)

and therefore:

 (Eq. A107)

Equilibrium constant for Eq. A10 is:

 (Eq. A108)

By rearranging the right-hand side of Eq. A107, we have:

From Eq. A22, Eq. A58 and Eq. A61:

and, finally, by following the definition of α (Eq. A38):

 (Eq. A109)

By combining Eq. A108 and Eq. A109, *s*−1 can be parameterized as:

 (Eq. A110)

For Eq. A11, we have:

 (Eq. A111)

from which:

 (Eq. A112)

Equilibrium constant for Eq. A11 reads:

 (Eq. A113)

The right-hand side of Eq. A113 can be rearranged as follows:

 (Eq. A114)

From Eq. A113 and Eq. A114, *p*−4 can be written as:

 (Eq. A115)

 And lastly, for Eq. A12, we have:

 (Eq. A116)

and

 (Eq. A117)

Equilibrium constant for Eq. A12 is:

 (Eq. A118)

By rearranging the right-hand side of Eq. A118:

 (Eq. A119)

Finally, from Eq. A118 and Eq. A119, parameterization for *s*−4 is:

 (Eq. A120)

1. **Approach**

The ExClump38 model tracks the evolution of chemical and isotopic state of DCP over time by solving a set of eight differential equations (Eq. A13 to Eq. A20). And, as detailed above, all of the terms appearing in these differential equations can be parameterized by a combination of equilibrium and kinetic rate constants (*K*1, *K*2, *K*w, *k*+1 and *k*+4), equilibrium carbon and oxygen isotope fractionations factors (13αEQ and 18αEQ), kinetic carbon and oxygen isotope fractionation factors (13αKIF and 18αKIF), intrinsic clumped isotope KIEs (47KIE), and some additional constants. Of these, fairly robust constraints are available for *K*’s and *k*’s as well as αEQ’s. These are treated as fixed constants in the model, which are compiled from the literature (see Table A1 below). In contrast, kinetic fractionations for C, O and clumped isotopes during CO2 hydration and hydroxylation are less well-constrained (for details, see the main paper). These are treated as adjustable parameters to tune the model to the experimental data. The default values and equations used for these in our simulations are summarized in Table A2.

As in UZ12, we use freshwater *K*1, *K*2 and *K*W from Harned and Davis (1943), Harned and Scholes (1941) and Harned and Owen (1958), and *k*+1 and *k*+4 from Pinsent et al. (1956). Isotopic ratios 13*R* and 18*R* for the VPDB and VSMOW reference material are taken from Daëron et al. (2016). Equilibrium carbon isotope fractionation factors among different carbon-bearing species (, and) are all from Zhang et al. (1995). Equilibrium oxygen isotope fractionation factors and are from Zeebe (2020) and Beck et al. (2005). Beck et al. (2005) also established and as a function of temperature between 15 and 40 °C. However, instead of these fractionation factors by Beck et al. (2005), we use the values established at 25 °C by Uchikawa and Zeebe (2013) due to a better fit to our experimental data (values at 25 °C differ by only a few tenths of ‰ between these two studies). Equilibrium Δ47 signature for HCO3− and CO3= are taken from Tripati et al. (2015). These values (0.713‰ and 0.650‰, respectively) are only valid at 25 °C. To the best of our knowledge, equilibrium Δ47 signature for CO2(aq) has not been established either experimentally or theoretically. However, based on *ab initio* calculations, Hill et al. (2014) suggested Δ47 of H2CO3 to be higher than HCO3− by 0.031‰. By assuming a negligible difference in the clumped isotope signatures between H2CO3 and CO2(aq), for Δ47 of CO2(aq), we applied +0.031‰ to the Δ47 of HCO3−. We can alternatively use Δ47 for CO2(g) determined by Wang et al. (2004) based also on theoretical calculations by making a similar assumption. However, modeling results are highly insensitive to the equilibrium Δ47 value assigned for CO2(aq) due to its very low concentration at our experimental pH.

Note that these model settings are optimized for simulations at 25 °C. However, for simulations at different temperatures (see Fig. 10ef in the main paper), apparent temperature-dependence of equilibrium δ18O and Δ47 signature for HCO3− and CO32− needs to be taken into account. For the former, temperature sensitivity equations for and established between 15 and 40 °C by Beck et al. (2005) are used in the model, instead of the 25 °C constraints by Uchikawa and Zeebe (2013). For the latter, we relied on the results of *ab initio* calculations by Hill et al. (2020). As our experimental data reflect isotopic equilibration taking place in NaHCO3 solutions, we specifically used the results from their calculations in which the presence of Na+ in solutions were considered. However, at 25 °C, their theoretical constraints for Δ47 of HCO3− and CO3= are noticeably lower than the experimental data of Tripati et al. (2015) by 0.106‰ and 0.081‰, respectively. Since our experimental data are more consistent with Tripati et al. (2015), the Δ47 of HCO3− and CO3= calculated by Hill et al. (2020) were lifted by +0.106‰ and +0.081‰ (Table A3). Finally, we derived the temperature sensitivity equation for Δ47 of HCO3− and CO3= by applying a polynomial fit (Fig. A1).

**Table A1**: List of equilibrium constants and kinetic rate constants as well as equilibrium isotope fractionation factors for the CO2-H2O system used in the ExClump38 model. TK and TC in the listed equations represent temperature in Kelvin and Celsius, respectively.

|  |  |  |  |
| --- | --- | --- | --- |
| **Definition** | **Notation** | **Temp. Dependence or Single Value** | **Reference**  |
| **Equilibrium Constants** |  |  |  |
| 1st H2CO3 diss. constant | *K*1 | log10(*K*1) = −3404.71/TK + 14.8435 − 0.032786×TK | 1 |
| 2nd H2CO3 diss. constant | *K*2 | log10(*K*2) = −2902.39/TK + 6.4980 − 0.02379×TK | 2 |
| H2O diss. constant | *K*W | log10(*K*W) = −6013.79/TK + 64.7013 – [ 23.6521×log10(TK) ]  | 3 |
| **Kinetic Rate Constants** |  |  |  |
| CO2 hydration | *k*+1 | log10(*k*+1) = 329.85 – [ 110.541×log10(TK) ] − (17265.4/TK) | 4 |
| CO2 hydroxylation | *k*+4 | log10(*k*+4) = 13.635 − (2895/TK) | 4 |
| **Isotope Ratio *R* for Ref. Material** |  |  |  |
| 13*R* (=13C/12C) for VPDB | 13*R*VPDB | 0.01118 | from 5 |
| 18*R* (=18O/16O) for VSMOW | 18*R*VSMOW | 0.0020052 | from 5 |
| **Equilibrium Isotope Fractionations** |  |  |  |
| 13C fractionation, CO2(aq)-CO2(g) | 13αEQCO2(aq)-CO2(g) | 13αEQCO2(aq)-CO2(g) = 1 + [ (−0.0049×TC) − 1.31 ] × 10−3  | 6 |
| 13C fractionation, HCO3−-CO2(g) | 13αEQHCO3-CO2(g) | 13αEQHCO3-CO2(g) = 1 + [ (−0.1141×TC) + 10.78 ] × 10−3 | 6 |
| 13C fractionation, CO32−-CO2(g) | 13αEQCO3-CO2(g) | 13αEQCO3-CO2(g) = 1 + [ (−0.052×TC) + 7.22 ] × 10−3 | 6 |
| 18O fractionation, CO2(aq)-H2O | 18αEQCO2(aq)-H2O |

|  |
| --- |
| 103ln18αCO2(aq)-H2O = 2.52*E*+6/TK2 + 12.12 |

 | 7 |
| 18O fractionation, COHCO3-H2O | 18αEQHCO3-H2O | 103ln18αEQHCO3-H2O = 30.58 *(only @ T = 25 °C)* | 8 |
|  |  | 103ln18αEQHCO3-H2O = 2.59*E*+6/TK2 + 1.89 *(for T ≠ 25 °C)* | 7 |
| 18O fractionation, CO2(aq)-H2O | 18αEQCO3-H2O | 103ln18αEQCO3-H2O = 24.50 *(only @ T = 25 °C)* | 8 |
|  |  | 103ln18αCO2(aq)-H2O = 2.39*E*+6/TK2 − 2.70 *(for T ≠ 25 °C)* | 7 |
| 18O fractionation, OH−-H2O | 18αEQOH-H2O | 18αEQOH-H2O = 0.9790 | 9 |

References: **1** (Harned and Davis, 1943), **2** (Harned and Scholes, 1941), **3** (Harned and Owen, 1958), **4** (Pinsent et al., 1956), **5** (Daëron et al., 2016), **6** (Zhang et al., 1995), **7** (Beck et al., 2005), **8** (Uchikawa and Zeebe, 2013), **9** (Zeebe, 2020).

**Table A1** (*continued*)

|  |  |  |  |
| --- | --- | --- | --- |
| **Definition** | **Notation** | **Temp. Dependence or Single Value** | **Reference**  |
| **Δ47 Equilibrium** |  |  |  |
| Equilibrium Δ47 of HCO3− | Δ47\_HCO3− | Δ47\_HCO3− = (9.39*E*−6 × TC) – (3.31 × TC) + 6.84*E*−1  | from 10 & 11 |
| Equilibrium Δ47 of CO32− | Δ47\_CO3= | Δ47\_CO3+ = (9.03*E*−6 × TC) – (3.13 × TC) + 6.43*E*−1 | from 10 & 11 |
| Equilibrium Δ47 of CO2(aq) | Δ47\_CO2(aq) | Δ47\_CO2(aq) = Δ47\_HCO3− + 0.031 | from 12 |

References: **10** (Tripati et al., 2015), **11** (Hill et al., 2020), **12** (Hill et al., 2014).

**Table A2**: Kinetic isotope fractionation factors associated with CO2 hydration and hydroxylation used in the model.

|  |  |  |  |
| --- | --- | --- | --- |
| **KIF/KIE & Definition** | **Relevant Eqs.** | **Temp. Dependence or Single value** | **Reference**  |
| ***CO2 Hydration*** |  |  |  |
| 13αKIF*k*+1 = *k*+1 / 13*k*+1 | Eq. A1 & A3 | 1.0176 | 1 |
| 18αKIF*a*+1 = *k*+1 / *a*+1 | Eq. A1 & A5 | 103 ln( 18αKIF*a*+1 ) = (1.5992*E*+6 / TK2) + (2.0211*E*+3 / TK) − 16.1 | 2 |
| 18αKIF*b*+1 = *k*+1 / *b*+1 | Eq. A1 & A6 | 103 ln( 18αKIF*b*+1 ) = (7.5198*E*+6 / TK2) − (4.050*E*+3 / TK) + 0.8 | 2 |
| 47KIE*p*+1 = 13*k*+1·*a*+1 / *p*+1·*k*+1 | Eq. A1, A9 & A100 | 47KIE*p*+1 = 1 + [ (4613.8393 / TK2) − (4.0389 / TK) − 0.185 ] × 10−3 | 3 |
| 47KIE*s*+1 = 13*k*+1·*b*+1 / *s*+1·*k*+1 | Eq. A1, A10 & A105 | 47KIE*s*+1 = 1 + [ (−5705.688 / TK2) − (41.5925 / TK) − 0.015 ] × 10−3 | 3 |
| ***CO2 Hydroxylation*** |  |  |  |
| 13αKIF*k*+4 = *k*+4 / 13*k*+4 | Eq. A2 & A4 | 1.017 | 4 |
| 18αKIF*a*+4 = *k*+4 / *a*+4 | Eq. A2 & A7 | 103 ln( 18αKIF*a*+4 ) = (−7.681*E*+5 / TK2) + (3.8436*E*+4 / TK) − 124.6 | 2 |
| 18αKIF*b*+4 = *k*+4 / *b*+4 | Eq. A2 & A8 | 103 ln( 18αKIF*b*+4 ) = (7.7752*E*+5 / TK2) − (1.8330*E*+3 / TK) + 0.9 | 2 |
| 47KIE*p*+4 = 13*k*+4·*a*+4 / *p*+4·*k*+4 | Eq. A2, A11 & A110 | 47KIE*p*+4 = 1 + { (−902.7635/TK2) + (157.1718/TK) − 0.533 } × 10−3 | 3 |
| 47KIE*s*+4 = 13*k*+4·*b*+4 / *s*+4·*k*+4 | Eq. A2, A12 & A115 | 47KIE*s*+4 = 1 + { (−11771.2832/TK2) − (62.7060/TK) + 0.168 } × 10−3 | 3 |

References: **1** (Yumol et al., 2020), **2** (Guo and Zhou, 2019), **3** (Guo, 2020), **4** (Christensen et al., 2021)

**Table A3**: Temperature dependence of Δ47 of HCO3− and CO3= in solution containing Na+ based on *ab-initio* calculations by Hill et al. (2020) and comparison to the direct experimental constraints by Tripati et al. (2015), showing Δ47 discrepancy of 0.106‰ and 0.081‰ for HCO3− and CO3= at 25 °C. The theoretical Δ47 of HCO3− and CO3= as a function of temperature by Hill et al. (2020) were corrected for these offsets prior to the polynomial fit shown in Figure A1 (see above for details).

|  |  |  |  |
| --- | --- | --- | --- |
|   |  Hill et al. (2020) Original |  Tripati et al. (2015) |  Hill et al. (2020) Corrected |
| Temp. | Δ47 of HCO3− | Δ47 of CO3= | Δ47 of HCO3− | Δ47 of CO3= | Δ47 of HCO3− | Δ47 of CO3= |
| ( °C ) | ( ‰ ) | ( ‰ ) | ( ‰ ) | ( ‰ ) | ( ‰ ) | ( ‰ ) |
| 0 | 0.6855933 | 0.6438500 |   |  | 0.7919516 | 0.7245610 |
| 10 | 0.6520202 | 0.6121198 |   |  | 0.7583785 | 0.6928308 |
| 20 | 0.6211478 | 0.5829716 |   |  | 0.7275061 | 0.6636826 |
| 22 | 0.6152739 | 0.5774300 |   |  | 0.7216322 | 0.6581410 |
| 25 | 0.6066417 | 0.5692890 | 0.713 | 0.650 | 0.7130000 | 0.6500000 |
| 30 | 0.5927157 | 0.5561631 |   |  | 0.6990740 | 0.6368741 |
| 40 | 0.5664953 | 0.5314793 |   |  | 0.6728536 | 0.6121903 |
| 50 | 0.5422840 | 0.5087289 |   |  | 0.6486423 | 0.5894399 |
| 60 | 0.5199024 | 0.4877408 |   |  | 0.6262607 | 0.5684518 |
| 70 | 0.4991903 | 0.4683614 |   |  | 0.6055486 | 0.5490724 |
| 80 | 0.4800044 | 0.4504526 |   |  | 0.5863627 | 0.5311636 |
| 90 | 0.4622161 | 0.4338899 |   |  | 0.5685744 | 0.5146009 |
| 100 | 0.4457095 | 0.4185606 |   |   | 0.5520678 | 0.4992716 |



**Figure A1**: Polynomial fit applied to the results of *ab initio* calculations by Hill et al. (2020) in order to derive the temperature dependence of Δ47 of HCO3− and CO3= (solid blue and red curve). Note that, at 25 °C, the original theoretical estimate for Δ47 of HCO3− and CO3= by Hill et al. (2020) (open blue diamonds and red circles) are lower than the direct experimental constraints by Tripati et al. (2015) (yellow squares) that showed a good consistency with our own experimental data. Thus, polynomial fit was performed on the Hill et al. (2020) data corrected for the offsets (filled blue diamonds and red circles).

**Table A3**: Input parameters for the ExClump38 model simulations of our experimental conditions presented in Figure 9 of the main paper.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Parameter | Model Code | TS2 | TS2-mnCA | TS2-2CA | TS2-3CA |
| Temperature (°C) | Tc | 25 | 25 | 25 | 25 |
| pH (NBS) | pH | 8.886 | 8.886 | 8.886 | 8.886 |
| [DCP] (mol/L) | NaHCO3 | 0.015 | 0.015 | 0.015 | 0.015 |
| δ18OH2O (‰, VSMOW) | d18O\_w | −3.0309 | −3.077 | −3.13 | −3.1 |
| δ13CDCP (‰, VPDB) | d13C\_SB | −2.7831 | −2.7831 | −2.7831 | −2.7831 |
| δ18ODCP (‰, VPDB) | d18O\_1st | −14.482 | −14.237 | −13.641 | −12.934 |
| Δ47\_CO2(aq) (‰, ARF) | D47\_co2 | 0.6 | 0.6 | 0.6 | 0.6 |
| Δ47\_DCP (‰, ARF) | D47\_DCP | 0.606 | 0.591 | 0.58 | 0.591 |
| CA Concentration | CA | 0 | 3.7*E*−9 | 9.3*E*−9 | 1.9*E*−8 |
|  |  |   |  |  |  |
| Time Zero (sec.) | T0 | 210 | 220 | 160 | 190 |
| Time Final (sec.) | Tf | 600,000 | 600,000 | 600,000 | 600,000 |
| Time Increment (sec.) | T\_inc | 120 | 120 | 30 | 30 |
| Max Time Step |   | 100 | 100 | 40 | 40 |

**Proof of the Mathematical Equivalence of the 18O Formulations in Chen et al. (2018) and Christensen et al. (2021)**

There are notable differences in the formulations of the exchange of 18O between DIC and water in the models developed by Chen et al. (2018) and Christensen et al. (2021), which was raised during the review process of this paper. Here we demonstrate that the two formulations are mathematically equivalent and generate identical results.

In Christensen et al. (2021), Eq. A9 and Eq. A10 (see Supplementary Material A) describe the evolution of 18O-substituted CO2 and EIC (defined as [HCO3–] + [CO32–] by Chen et al., 2018, called DCP in the current study). When we only consider the isotope exchange terms in the aqueous phase, Eq. A9 and Eq. A10 simplify to:

 (Eq. B1)

 (Eq. B2)

Meanwhile, the definitions of 18O/16O ratios for CO2 and EIC listed in Table 6 of Christensen et al. (2021) are:

 (Eq. B3)

 (Eq. B4)

From Eq. (B3) and (B4), we can get the following relations:

 (Eq. B5)

 (Eq. B6)

We can plug the relations in Eq. B5 and Eq. B6 into Eq. B1 and Eq. B2 and get the following:

 (Eq. B7)

 (Eq. B8)

Now if we divide both sides by a factor of 2 in Eq. B7 and a factor of 3 in Eq. B8, we get the following:

 (Eq. B9)

 (Eq. B10)

Now if we redefine and as new variables X and Y, we get:

 (Eq. B11)

 (Eq. B12)

The formulation of Eq. B11 and Eq. B12 is the same as that of Eq.7 and Eq. 8 in the Appendix of Chen et al. (2018) when only the aqueous isotope exchange terms are considered. Therefore, the Chen et al. (2018) formulation of DIC-H2O oxygen isotope exchange can be derived from the Christensen et al. (2021) formulation, just by changing the definition of the variables being tracked in the differential equations. When correctly implemented, the two formulations generate mathematically identical results.

However, it should be pointed out that variables and in Eq. B11 and Eq. B12 were inappropriately referred to as [C18OO] and [18EIC] in Chen et al. (2018), while they were actually implemented as X and Y in Eq. B11 and Eq. B12. The stoichiometrically correct expressions should be those in Eq. B5 and Eq. B6 from Christensen et al. (2021). Therefore, despite the two formulations generating the same mathematical results, we choose to convert to the formulation by Christensen et al. (2021) and recommend it for future modeling work.