Oxygen isotope fractionation in the CaCO3-DIC-H2O system

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Abstract
The oxygen isotope ratio (δ 18 O) of inorganic and biogenic carbonates is widely used to reconstruct past environments. However, the oxygen isotope exchange between CaCO3 and H2O rarely reaches equilibrium and kinetic isotope effects (KIE) commonly complicate paleoclimate reconstructions. We present a comprehensive model of kinetic and equilibrium oxygen isotope fractionation between CaCO3 and water (αc/w) that accounts for fractionation between both (a) CaCO3 and the CO3²− pool (αc/CO3²−), and (b) CO3²− and water (αCO3²−/w), as a function of temperature, pH, salinity, calcite saturation state (Ω), the residence time of the dissolved inorganic carbon (DIC) in solution, and the activity of the enzyme carbonic anhydrase. The model results suggest that: (1) The equilibrium αc/w is only approached in solutions with low Ω (i.e. close to 1) and low ionic strength such as in the cave system of Devils Hole, Nevada. (2) The sensitivity of a c/w to the solution pH and/or the mineral growth rate depends on the level of isotopic equilibration between the CO3 2− pool and water. When the CO3 2− pool approaches isotopic equilibrium with water, small negative pH and/or growth rate effects on a c/w of about 1-2‰ occur where these parameters covary with Ω. In contrast, isotopic disequilibrium between CO3 2− and water leads to strong (> 2‰) positive or negative pH and growth rate effects on a CO3 2−/w (and a c/w) due to the isotopic imprint of oxygen atoms derived from HCO3 − , CO2 , H2O and/or OH − . (3) The temperature sensitivity of a c/w originates from the negative effect of temperature on a CO3 2−/w and is expected to deviate from the commonly accepted value (−0.22 ± 0.02‰/°C between 0 and 30 °C; Kim and O’Neil, 1997) when the CO3 2− pool is not in isotopic equilibrium with water. (4) The model suggests that the δ 18 O of planktic and benthic foraminifers reflects a quantitative precipitation of DIC in isotopic equilibrium with a high-pH calcifying fluid, leading to a relatively constant foraminifer calcite δ 18 O-temperature relationship (−0.21 ± 0.01‰/°C). The lower average coral δ 18 O data relative to foraminifers and other calcifiers is best explained by the precipitation of internal DIC derived from hydrated CO2 in a high-pH calcifying fluid and minimal subsequent DIC-H2O isotopic equilibration. This leads to a reduced and variable coral aragonite δ 18 O-temperature relationship (−0.11 to −0.22‰/°C). Together, the model presented here reconciles observations of oxygen isotope fractionation over a range of CaCO3-DIC-H2O systems.

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Oxygen isotope fractionation in the CaCO$_3$-DIC-H$_2$O system

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Abstract

The oxygen isotope ratio ($\delta^{18}O$) of inorganic or biogenic carbonates is widely used to reconstruct past environments. However, the oxygen isotope exchange between CaCO$_3$ and H$_2$O rarely reaches equilibrium and kinetic isotope effects (KIE) commonly complicate paleoclimate reconstructions. This study presents a comprehensive model of kinetic and equilibrium oxygen isotope fractionation between CaCO$_3$ and water ($\alpha_{c/w}$) that accounts for fractionation between both (a) CaCO$_3$ and the CO$_3^{2-}$ pool ($\alpha_{c/CO_3^{2-}}$), and (b) CO$_3^{2-}$ and water ($\alpha_{CO_3^{2-}/w}$), as a function of temperature, pH, salinity, calcite saturation state ($\Omega$), the residence time of the dissolved inorganic carbon (DIC) in solution, and the activity of the enzyme carbonic anhydrase. The model results suggest that: (1) in solutions with low ionic strength ($I < 0.05$) and low CO$_3^{2-}$/Ca$^{2+}$ activity ratio, $\alpha_{c/CO_3^{2-}}$ decreases from $\sim$1.005 to $\sim$1.0030 ($\sim$2.4‰ decrease in $^{18}$O/$^{16}$O) where the solution $\Omega$ increases from below $\sim$1.6 to $\sim$12. These results indicate that the equilibrium $\alpha_{c/CO_3^{2-}}$ is approached in solutions with low $\Omega$ and low ionic strength such as in the cave system of Devil's Hole, Nevada; (2) the sensitivity of $\alpha_{c/w}$ to the solution pH and/or the mineral growth rate depends on the level of isotopic equilibration between the CO$_3^{2-}$ pool and water. Where the CO$_3^{2-}$ pool approaches isotopic equilibrium with water, small negative pH and/or growth rate effects on $\alpha_{c/w}$ in the order of 1-2‰ occur where these parameters covary with $\Omega$. In contrast, isotopic disequilibrium between CO$_3^{2-}$ and water leads to strong (commonly > 2‰) positive or negative pH and growth rate effects on $\alpha_{c/CO_3^{2-}}$ and $\alpha_{c/w}$ due to the isotopic imprint of oxygen atoms derived from HCO$_3^-$, CO$_2$, H$_2$O and/or OH$^-$; (3) the temperature sensitivity of $\alpha_{c/w}$ originates from the negative effect of temperature on $\alpha_{c/CO_3^{2-}}$ and is expected to deviate from the commonly accepted value ($-0.22 \pm 0.02‰/°C$; Kim and O’Neil, 1997) when the CO$_3^{2-}$ pool is not at isotopic equilibrium with water; (4) The model suggests that the $\delta^{18}O$ of planktic and benthic foraminifers reflects the DIC of a high-pH calcifying fluid that is in isotopic equilibrium prior to calcite precipitation, leading to a relatively constant foraminifer calcite $\delta^{18}O$-temperature relationship ($-0.21 \pm 0.01‰/°C$). The lower average coral $\delta^{18}O$ data relative to foraminifers and other calcifiers is best explained by the precipitation of internal DIC derived from hydrated CO$_2$ in a high-pH calcifying fluid and minimal subsequent DIC-H$_2$O isotopic equilibration. This leads to a reduced and variable coral aragonite $\delta^{18}O$-temperature relationship ($-0.11$ to $-0.22‰/°C$). Together, the model presented here reconciles observations of oxygen isotope fractionation in a range inorganic and biogenic carbonate systems.
1. Introduction

The equilibrium fractionation of stable oxygen isotopes between carbonate minerals and their host aqueous solution is strongly temperature-dependent (Urey 1947; McCrea, 1950) making oxygen isotope ratios in marine and terrestrial carbonates the most widely used geochemical proxy for paleoenvironment reconstructions (e.g. Emiliani, 1966; Shackleton, 1967; Hays et al., 1976; Winograd et al., 1992; Wang et al., 2001; Tudhope et al., 2001; Siddall et al., 2003). The temperature-dependence of equilibrium isotope partitioning is due to the temperature-dependent bonding properties of the different isotopes (Urey, 1947), and hence equilibrium isotope fractionations are independent of chemical reaction pathways.

In many cases, the isotopic exchange between chemical phases does not reach equilibrium, and mass-dependent transport and reaction rates contribute to the isotopic fractionations. For oxygen isotopes ($^{18}O/^{16}O$) in carbonates, these so-called kinetic isotope effects (KIE) manifest in a variety of ways, including a dependence of oxygen isotopic fractionation on the CaCO$_3$ precipitation rate, the chemical speciation of the dissolved inorganic carbon (DIC; $\text{DIC} = \text{CO}_2^{aq} + \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$) and the solution pH (McCrea, 1950; Kim and O'Neil, 1997; Kim et al., 2006; Dietzel et al., 2009; Gabitov et al., 2012; Watkins et al., 2013, 2014). Many natural carbonates grow at rates that likely place them in a non-equilibrium regime and are subject to KIE. To improve interpretations of $\delta^{18}O$ data from modern and fossil carbonates, there is a need to better understand:

1) Which DIC species contribute to CaCO$_3$ growth?

2) What controls the isotopic fractionations between the precipitating DIC species and CaCO$_3$?

3) How does the isotopic composition of DIC species vary prior to and during CaCO$_3$ precipitation?

A recent advance in understanding the controls on oxygen isotope fractionation between precipitating DIC species and CaCO$_3$ (question (2) above) has come from isolating KIE arising from the mineral growth reaction in the presence of the enzyme carbonic anhydrase (CA; Watkins et al., 2013; 2014).

CA catalyses the hydration and dehydration of CO$_2$, thereby increasing the rate of oxygen isotope exchange between the DIC species and H$_2$O and promoting DIC-H$_2$O isotopic equilibrium (cf. Uchikawa and Zeebe, 2012). A key result is that in the presence of CA, calcite-water oxygen isotope fractionation is less dependent on the calcite growth rate and solution pH than in calcite growth experiments where the DIC pool is not equilibrated (e.g. Dietzel et al., 2009; Gabitov et al., 2012). This understanding of the KIE between CaCO$_3$ and the precipitating DIC species improves our knowledge of non-equilibrium calcite-water oxygen isotope fractionation but it does not fully explain > 2‰ temperature-independent variations in carbonate-water fractionation observed for laboratory grown inorganic CaCO$_3$ (e.g. Kim and O’Neil, 1997; Dietzel et al., 2009; Gabitov et al., 2012) or the
cause of oxygen isotope offsets between inorganic and biogenic carbonates (e.g. McConnaughey, 1989a; Spero et al., 1997; Xia et al., 1997; Zeebe, 1999; Adkins et al., 2003; Rollion-Bard et al., 2003; Allison et al., 2010; Ziveri et al., 2012; Hermoso et al., 2016).

In this study, we present a model of oxygen isotope fractionation in the CaCO$_3$-DIC-H$_2$O system that incorporates the new information on KIE between CaCO$_3$ and DIC (Watkins et al., 2013; 2014), and accounts for the kinetic isotopic fractionations between the DIC and H$_2$O. In the model, CO$_3^{2-}$ is the only DIC species contributing to carbonate nucleation and growth while other DIC species affect the $^{18}$O/$^{16}$O of CaCO$_3$ by conversion to CO$_3^{2-}$ shortly before or during CaCO$_3$ precipitation. The isotopic fractionation between CaCO$_3$ and CO$_3^{2-}$ is calculated as a function of the solution calcite saturation state and ionic strength based on the kinetic expressions of Zhong and Mucci (1993) for calcite precipitation and dissolution. New kinetic isotope fractionations factors (KIFF) associated with the conversions of DIC species are derived based on published experimental data and theoretical calculations. These KIFF are used with published equilibrium isotopic fractionation factors (EIFF, Beck et al., 2005) to calculate the time-dependent isotopic composition of CO$_3^{2-}$ and HCO$_3$ as the system relaxes back to an equilibrium state. The model is verified against data from inorganic calcite precipitated from isotopically equilibrated and non-equilibrated DIC pools, and explains the varying effects of calcite growth rate and pH on the calcite-water oxygen isotope fractionation observed in previous studies. Model simulations are also compared to the $^{18}$O/$^{16}$O of foraminifers and corals to test current hypotheses of oxygen isotope vital effects in biogenic CaCO$_3$.

2. Notation

The $^{18}$O/$^{16}$O of a water or carbonate sample ($^{18}R_s$) is measured as the deviation from the $^{18}$O/$^{16}$O of a standard ($^{18}R_{std}$) and is expressed using the $\delta^{18}$O notation:

$$\delta^{18}O_s = \frac{^{18}R_s - ^{18}R_{std}}{^{18}R_{std}} \times 10^3$$

(1)

where std refers to the standard ‘Vienna Pee Dee Belemnite’ (VPDB) for carbonate samples or ‘Vienna Standard Mean Ocean Water’ (VSMOW) for water samples. A carbonate $\delta^{18}$O on the VPDB scale is converted to a $\delta^{18}$O on the VSMOW scale using the equation provided by Coplen et al. (1983):

$$\delta^{18}O_{VSMOW} = 1.03091 \delta^{18}O_{VPDB} + 30.91$$

(2)

The oxygen isotope fractionation factor between any two phases A and B ($\alpha_{A/B}$) is expressed as:
\[
\alpha_{A/B} = \frac{^{18}R_A}{^{18}R_B} = \frac{1000 + \delta^{18}O_A}{1000 + \delta^{18}O_B}
\]

where \(\delta^{18}O_A\) and \(\delta^{18}O_B\) are expressed on the same scale. It is convenient to express the oxygen isotope fractionation factor in ‰ with the term \(\varepsilon\):

\[
\varepsilon_{A/B} = (\alpha_{A/B} - 1) \times 10^3 \approx \delta^{18}O_B - \delta^{18}O_A
\]

For example, an \(\alpha_{A/B}\) value of 1.0295 corresponds to a \(\varepsilon_{A/B}\) value of 29.50‰. Hereafter, for phases A or B the following shorthand notation are used: c = CaCO\(_3\) and w = H\(_2\)O.

### 3. Model background

#### 3.1. Contribution of DIC species to CaCO\(_3\) growth

For any carbonate oxygen isotope fractionation model, quantifying the relative contribution of DIC species to CaCO\(_3\) nucleation and growth is critical because these ions have distinct oxygen isotope ratios (Beck et al., 2005). In this section, we review current ideas on the relative contribution of CO\(_3^{2-}\) and HCO\(_3^-\) to CaCO\(_3\) nucleation and surface growth.

Several lines of evidence suggest that CO\(_3^{2-}\), rather than HCO\(_3^-\), is the dominant DIC species during CaCO\(_3\) nucleation. For example, negligible HCO\(_3^-\) concentrations were reported in amorphous calcium carbonate (ACC), the precursor to calcite or aragonite precipitation, suggesting that HCO\(_3^-\) ions do not contribute to CaCO\(_3\) nucleation (Nebel et al., 2008). Similarly, numerical simulations of calcite (pre-)nucleation, showed that HCO\(_3^-\) have a destabilizing effect on the formation of pre-nucleation ACC clusters in solution (Demichelis et al., 2011; Bots et al., 2012). Another clue to the relative contribution of HCO\(_3^-\) and CO\(_3^{2-}\) ions during carbonate mineral nucleation was inferred from the oxygen isotope ratio of minerals formed quasi-instantaneously following the addition of NaOH in solution (Kim et al., 2006). During these experiments, the rapid precipitation (i.e. negligible back reaction) of a small portion of a DIC pool composed of CO\(_3^{2-}\) and HCO\(_3^-\) resulted in witherite with \(\delta^{18}O\) values reflecting the \(^{18}O/^{16}O\) of isotopically equilibrated CO\(_3^{2-}\) ions. These results support minimal direct HCO\(_3^-\) contribution to carbonate mineral nucleation.

The relative contribution of DIC species to the carbonate mineral during crystal growth following nucleation is less clear. Although there is no direct evidence for HCO\(_3^-\) contribution to calcite or aragonite surface growth, the Zuddas and Mucci (1994) kinetic model of calcite growth in seawater and the Wolthers et al. (2012) ion-by-ion model of calcite growth in dilute solution both involve the
contribution of HCO$_3^-$ to explain observed mineral growth rate in low pH solutions. However, the importance of HCO$_3^-$ contribution to calcite growth greatly differs between the two models. The Zuddas and Mucci (1994) model suggests that the contribution of HCO$_3^-$ to calcite growth becomes greater than 1% when CO$_3^{2-}$ ions represent less than ~ 1.5% of the DIC concentration. In contrast, the model of Wolthers et al. (2012) predicts that HCO$_3^-$ adsorption to the growing mineral surface outpaces CO$_3^{2-}$ adsorption for solutions with pH lower than 8.6 (or [CO$_3^{2-}$]/[DIC] < 2 %), representing a contribution of HCO$_3^-$ ions to calcite growth one to two order(s) of magnitude higher than estimates from Zuddas and Mucci (1994). Of note is that Zuddas and Mucci (1994) studied calcite growth kinetics in seawater while Wolters and co-workers derived their model using data from dilute solutions. A solution’s ionic strength is known to affect the calcite growth mechanism (Zuddas and Mucci, 1998) and could potentially explain the contrasting modelling results described above. Finally, a significant contribution of HCO$_3^-$ ions to aragonite growth is not supported by oxygen isotopic studies since the $\delta^{18}$O of aragonite rapidly precipitated from isotopically equilibrated DIC shows no or very little sensitivity to the HCO$_3$/CO$_3^{2-}$ concentration ratio in solution (Kim et al., 2006).

Although future work should clarify the role of HCO$_3^-$ ions during calcite growth, the bulk of evidence suggests no or little contribution of HCO$_3^-$ to calcite nucleation and growth. The model presented in this study therefore assumes that calcite precipitates from CO$_3^{2-}$ ions exclusively and that the $\delta^{18}$O of calcite reflects the $^{18}$O/$^{16}$O of the carbonate ions consumed during mineral precipitation.

### 3.2. Models of kinetic isotopic fractionation between CaCO$_3$ and CO$_3^{2-}$ (and HCO$_3^-$)

Several models have been proposed to explain kinetic oxygen isotope fractionation between CaCO$_3$ and CO$_3^{2-}$ (and HCO$_3^-$). Watson (2004) and Gabitov et al. (2012) suggested that a competition between calcite surface growth rate and diffusion in the outer monolayers of the crystal determines the net oxygen isotope fractionation between CaCO$_3$ and CO$_3^{2-}$. This model assumes that the isotopic composition of the mineral surface reflects that of the CO$_3^{2-}$ ions, which are depleted in $^{18}$O relative to slowly precipitated CaCO$_3$ (Beck et al., 2005; Kim et al., 2006). The Watson (2004) model relies upon isotopic rearrangement in the ionic bonding environment below the mineral surface, driven by differences in the thermodynamic properties of the mineral surface relative to the bulk lattice. Although the model can reproduce some of the experimental data, it de-emphasizes processes operating on the aqueous side of the solid-fluid interface, such as mass-dependent ion desolvation kinetics, which are likely important (cf. Hofmann et al., 2012; Watkins et al., 2017). Furthermore, the diffusive transport properties of oxygen atoms in calcite at low temperature have not been quantified.

Alternatively, DePaolo (2011) proposed a model that does not require the mineral surface to be in equilibrium with the bulk solution. Instead calcite exchanges oxygen isotopes with the entire DIC pool (i.e. mainly CO$_3^{2-}$ and HCO$_3^-$ because calcite does not grow at low pH) and the fractionation
from DIC is controlled by the CaCO$_3$ dissolution/precipitation ratio $r_c/r_{rc}$ ($R_d/R_f$ in DePaolo, 2011).

Fractionation varies between an equilibrium limit at $r_c/r_{rc} = 1$ and a kinetic limit at $r_c/r_{rc} = 0$. The ratio is obtained from calcite dissolution rate estimates and the measured net calcite precipitation rate $r_c$ ($r_c = r_{rc} - r_c$). The $r_c/r_{rc}$ ratio is also invoked in the model of Watkins et al. (2014). However, in the Watkins (2014) model, the contribution of CO$_3^{2-}$ and HCO$_3^-$ to calcite growth is based on an ion-by-ion model of calcite growth (Wolthers et al., 2012) and the $r_c/r_{rc}$ ratio is calculated directly from the solution calcite saturation state rather than from the net growth rate as in the DePaolo (2011) model.

The model presented here follows the same principles as the DePaolo (2011) and Watkins et al. (2014) models in that oxygen isotope fractionation during mineral growth is governed by the CaCO$_3$ dissolution/precipitation ratio. In contrast to the DePaolo (2011) and Watkins et al. (2014) models however, HCO$_3^-$ is not directly involved in calcite growth (Section 3.1). Moreover, a new expression for deriving the CaCO$_3$ dissolution/precipitation ratio is formulated from the Zhong and Mucci (1993) classical crystal growth rate expression (Section 4.2).

### 3.3. Kinetic isotope fractionations between DIC and H$_2$O

Understanding DIC-H$_2$O KIE is critical for interpreting the $\delta^{18}$O of biogenic CaCO$_3$ (e.g. McConnaughey, 1989b, Rollion-Bard et al., 2003, Allison et al., 2010, Ziveri et al., 2012, Saenger et al., 2012, Hermoso et al., 2016) and of inorganic CaCO$_3$ precipitating from rapidly dissolving gaseous CO$_2$ (e.g. Macleod et al., 1991; Clark et al., 1992; Dietzel et al., 1992; Krishnamurthy et al., 2003; Kosednar-Legenstein et al., 2008; Falk et al., 2016) or following CO$_2$ degassing (e.g. Hendy, 1971; Clark and Lauriol, 1992; Wong and Breecker, 2015).

This study specifically investigates KIE related to CO$_2$ dissolution. Experiments where calcite was rapidly precipitated in CO$_2$-fed solutions reported anomalously low calcite-water fractionation factor ($\alpha_{c/w}$) relative to that of slowly precipitated inorganic calcite at the same temperature (e.g. Usdowski and Hoefs, 1990; Clark et al., 1992; Dietzel et al., 1992, 2009; Watkins et al., 2013). Under such conditions, $\alpha_{c/w}$ is sensitive to the $^{18}$O/$^{16}$O of the CO$_2$ source and strongly decreases with the solution pH (Dietzel et al., 2009). High pH conditions result in strong KIE due to a quasi-unidirectional dissolution and conversion of CO$_2$ into HCO$_3^-$ and CO$_3^{2-}$ (limited CO$_2$ degassing), a slow rate of oxygen isotope exchange between DIC species and H$_2$O (Usdowski et al., 1991), and a fast CaCO$_3$ precipitation rate. Light oxygen isotope enrichment of calcite of ~14‰ or more in high pH solutions has been reported in several studies (Clark et al., 1992; Dietzel et al., 2009; Watkins et al., 2013, 2014) and are thought to be caused by (1) the preferential reaction of isotopically light CO$_2$ molecules with H$_2$O (hydration) and OH$^-$ (hydroxylation) during CO$_2$ dissolution (McConnaughey, 1989b) and
(2) the isotopic imprint of oxygen atoms from H_{2}O and OH\textsuperscript{-} into newly formed HCO\textsubscript{3}\textsuperscript{-} and CO\textsubscript{3}\textsuperscript{2-} (Clark et al., 1992). To better understand and accurately predict KIE related to CO\textsubscript{2} dissolution, it is critical to differentiate and quantify (1) and (2). This has not been achieved with experimental data thus far due to uncertainties regarding the level of isotopic re-equilibration between the DIC pool and H_{2}O prior to calcite precipitation and because KIE between DIC and H_{2}O could not be isolated from the overall CaCO\textsubscript{3}-H_{2}O fractionation factor.

The model presented in this study is used to distinguish and quantify CaCO\textsubscript{3}-CO\textsubscript{3}\textsuperscript{2-} and CO\textsubscript{3}\textsuperscript{2-}-H\textsubscript{2}O KIE by estimating the level of CO\textsubscript{3}\textsuperscript{2-}-H\textsubscript{2}O isotopic equilibrium based on solution parameters (Section 4.3). In turn, this permits quantifying the different factors contributing to the observed KIE between DIC and H_{2}O.

4. Model derivations

4.1. Model overview

A Microsoft Excel version of the model presented here (macro ‘\textsuperscript{18}OCD’) can be downloaded from www.LSDeviendt.com. The model integrates oxygen isotopic fractionations arising from the mineral growth reaction and isotopic exchanges between the DIC species and H\textsubscript{2}O (Fig. 1). The CaCO\textsubscript{3}-H\textsubscript{2}O fractionation factor \( \alpha_{c/w} \) is expressed as:

\[
\alpha_{c/w} = \frac{\text{\textsuperscript{18}R}_{c}}{\text{\textsuperscript{18}R}_{w}}
\]  

(5)

Since CO\textsubscript{3}\textsuperscript{2-} is assumed to be the only precipitating DIC species, the numerator and denominator of equation (5) are divided by \( \text{\textsuperscript{18}R}_{\text{CO}_3\textsuperscript{2-}} \) (the \( ^{18}\text{O}/^{16}\text{O} \) of CO\textsubscript{3}\textsuperscript{2-}) to express \( \alpha_{c/w} \) as the product of the CaCO\textsubscript{3}-CO\textsubscript{3}\textsuperscript{2-} (\( \alpha_{c/\text{CO}_3\textsuperscript{2-}} \)) and CO\textsubscript{3}\textsuperscript{2-}-H\textsubscript{2}O (\( \alpha_{\text{CO}_3\textsuperscript{2-}/w} \)) fractionation factors:

\[
\alpha_{c/w} = \frac{\text{\textsuperscript{18}R}_{c}}{\text{\textsuperscript{18}R}_{\text{CO}_3\textsuperscript{2-}}} = \alpha_{c/\text{CO}_3\textsuperscript{2-}} \cdot \alpha_{\text{CO}_3\textsuperscript{2-}/w}
\]  

(6)

In the model (Fig. 1), the \( ^{18}\text{O} \) of a calcium carbonate mineral (\( \delta^{18}\text{O}_{c} \)) is calculated from \( \text{\textsuperscript{18}R}_{\text{CO}_3\textsuperscript{2-}} \) and the fractionation factor \( \alpha_{c/\text{CO}_3\textsuperscript{2-}} \), the latter depending on the degree of isotopic equilibrium between the mineral and the carbonate ion pool (\( E_{c} \)). The fractionation factor \( \alpha_{c/\text{CO}_3\textsuperscript{2-}} \) reaches an equilibrium limit where \( E_{c} = 1 \) while a kinetic (disequilibrium) limit is attained where \( E_{c} = 0 \). Here, \( E_{c} \) depends on
the CaCO$_3$ precipitation to dissolution reaction rate ratio (DePaolo, 2011), which we infer from the calcite saturation state ($\Omega$) and the solution ionic strength through the partial reaction order for the carbonate ions ($n_3$).

The $^{18}R_{\text{CO}_3^{2-}}$ value (on which $\delta^{18}O_e$ depends) is dependent on the $\delta^{18}O$ of water ($\delta^{18}O_w$) and the fractionation factor $\alpha_{\text{CO}_3^{2-}/w}$. The value of $\alpha_{\text{CO}_3^{2-}/w}$ also varies between a kinetic and an equilibrium limit. At isotopic equilibrium, $\alpha_{\text{CO}_3^{2-}/w}$ only depends on temperature (Beck et al., 2005). Under non-equilibrium conditions, $\alpha_{\text{CO}_3^{2-}/w}$ also depends on the $^{18}O/^{16}O$ of the DIC source(s) (e.g. gaseous CO$_2$), the chemical pathways for the exchange of oxygen isotopes in the DIC-H$_2$O system and the degree of isotopic equilibrium between the DIC pool and water ($E_{\text{DIC}}$). In turn, $E_{\text{DIC}}$ varies between 0 and 1 and is a function of the DIC residence time in solution (calculated from the calcification rate $r_s$, solution volume $V$ and the DIC concentration [DIC]) and the rate of oxygen isotope exchange between DIC and water (calculated from the solution pH, DIC speciation, temperature and carbonic anhydrase activity CA; Usdowski et al., 1991, Uchikawa and Zeebe, 2012). For example, where calcite forms in a CO$_2$-fed solution (e.g. Dietzel et al., 2009, Watkins et al., 2013, 2014), the entire DIC pool is derived from hydrated (h$_s$) and hydroxylated (h$_a$) CO$_2$. These reactions initially produce HCO$_3^-$ and CO$_3^{2-}$ ions with distinct $^{18}O/^{16}O$ ratios relative to isotopic equilibrium conditions (McConnaughey, 1989b; Clark et al., 1992; Zeebe, 2014). Over a period of time however, oxygen isotope exchange between the DIC species and water brings $\alpha_{\text{CO}_3^{2-}/w}$ towards equilibrium values.

The rates of reactions in the CaCO$_3$-DIC-H$_2$O system are such that the carbonate ion pool can approach isotopic equilibrium with H$_2$O ($E_{\text{DIC}} \sim 1$) but not with CaCO$_3$ ($E_e < 1$). The opposite scenario of DIC-H$_2$O isotopic disequilibrium and H$_2$O-CaCO$_3$ equilibrium is unlikely. With respect to oxygen isotopes, the CaCO$_3$-DIC-H$_2$O system can therefore be in full disequilibrium (CaCO$_3$-CO$_3^{2-}$ and CO$_3^{2-}$-H$_2$O disequilibrated), partial equilibrium or disequilibrium (CaCO$_3$-CO$_3^{2-}$ disequilibrated, CO$_3^{2-}$-H$_2$O equilibrated) or in full equilibrium (CaCO$_3$-CO$_3^{2-}$ and CO$_3^{2-}$-H$_2$O equilibrated). When either part of the system is in disequilibrium then the overall CaCO$_3$-H$_2$O fractionation should be referred as a disequilibrium fractionation. In Section 4.2, equations for calculating the level of isotopic equilibration between calcite and CO$_3^{2-}$ ($E_e$) are derived, and then the $\alpha_{c/\text{CO}_3^{2-}}$ kinetic (disequilibrium) and equilibrium limits are quantified. Section 4.3 presents equations for calculating the level of isotopic equilibration between CO$_3^{2-}$ and H$_2$O ($E_{\text{DIC}}$), followed by the quantification of the $\alpha_{\text{CO}_3^{2-}/w}$ kinetic and equilibrium limits. Symbols, acronyms and the chemical reactions considered in this study are compiled in Appendix A1 and A2 respectively.
4.2. Isotopic fractionation between CaCO$_3$ and CO$_3^{2-}$ ($\alpha_{c/CO_3^{2-}}$)

4.2.1. Kinetic vs equilibrium isotope fractionation

As discussed in section 3.1, it is assumed that calcite forms via the following reaction pathway:

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3$$  \hspace{1cm} (7)

where $k_c$ and $k_{+c}$ are the backward and forward reaction rate constants, respectively. The isotopic fractionation between a growing mineral and the participating ions in solution was formulated by DePaolo (2011) as a function of the backward/forward reaction rate ratio and is written accordingly for $\alpha_{c/CO_3^{2-}}$:

$$\alpha_{c/CO_3^{2-}} = \frac{\alpha_{c/CO_3^{2-}}^{+c}}{1 + E_c \left(\frac{\alpha_{c/CO_3^{2-}}^{eq}}{\alpha_{c/CO_3^{2-}}^{+c}} - 1\right)}$$  \hspace{1cm} (8)

where $\alpha_{c/CO_3^{2-}}^{+c}$ and $\alpha_{c/CO_3^{2-}}^{eq}$ are the kinetic and equilibrium limits of $\alpha_{c/CO_3^{2-}}$, and $E_c$ is the degree of isotopic equilibrium between CaCO$_3$ and CO$_3^{2-}$. Where $E_c \approx 0$, $\alpha_{c/CO_3^{2-}}$ approaches $\alpha_{c/CO_3^{2-}}^{+c}$ and where $E_c \approx 1$, $\alpha_{c/CO_3^{2-}}$ approaches $\alpha_{c/CO_3^{2-}}^{eq}$. Following DePaolo (2011) approach, $E_c$ is obtained from the ratio between the backward and forward rate during CaCO$_3$ precipitation:

$$E_c = \frac{r_{-c}}{r_{+c}}$$  \hspace{1cm} (9)

where $r_{-c}$ is the backward (dissolution) rate and $r_{+c}$ is the forward (precipitation) rate. Here we derive a new expression for $r_{-c}/r_{+c}$, based on the Zhong and Mucci (1993) kinetic model of classic calcite growth. According to the reaction pathway (7), the net reaction rate $r_c$ is expressed as the difference between $r_{+c}$ and $r_{-c}$ (Lasaga, 1981):

$$r_c = r_{+c} - r_{-c} = k_{+c}(\text{Ca}^{2+})^{n_1}(\text{CO}_3^{2-})^{n_2} - k_{-c}(\text{CaCO}_3)^{n_3}$$  \hspace{1cm} (10)

where {} denotes ionic or solid activity in the bulk solution and the $n_i$ are the partial reaction rate orders. The activity of solid CaCO$_3$ may be approximated as unity, and if {Ca$^{2+}$} is constant, equation (10) can be simplified to (Zhong and Mucci, 1993):
\[ r_c = K_{+c}[CO_3^{2-}]^{n_2} - k_{-c} \]  
(11)

with

\[ K_{+c} = k_{+c}(Ca^{2+})^{n_1}Y_{CO_3^{2-}} \]  
(12)

where \([\ ]\) denotes concentration (moles/kg), and \(Y_{CO_3^{2-}}\) is the activity coefficient of the carbonate ions in solution. At chemical equilibrium, \(r_c = 0\), and \(k_{-c}\) is expressed as (Zhong and Mucci, 1993):

\[ k_{-c} = K_{+c}[CO_3^{2-}]^{n_2}_{(eq)} \]  
(13)

where \([CO_3^{2-}]_{(eq)}\) is the concentration of the carbonate ions at chemical equilibrium. Assuming that the backward reaction rate \(k_{-c}\) is constant for a given temperature and solute content (i.e., it is independent of \(\Omega\), which is akin to ‘Model 1’ in DePaolo, 2011), the backward and forward reaction rate ratio are expressed as follows:

\[ \frac{r_{-c}}{r_{+c}} = \frac{K_{+c}[CO_3^{2-}]^{n_2}_{(eq)}}{K_{+c}[CO_3^{2-}]^{n_2}} \]  
(14)

Simplifying equation (14) and multiplying the numerator and denominator by \(\left(\frac{[Ca^{2+}]}{K_{sp}^*}\right)^{n_2}\), where \(K_{sp}^*\) is the stoichiometric solubility product of a CaCO_3 mineral (Mucci, 1983, Appendix A2), yields the following relationship:

\[ \frac{r_{-c}}{r_{+c}} = \left(\frac{[CO_3^{2-}]_{(eq)}[Ca^{2+}]}{K_{sp}^*}\right)^{n_2} \]  
(15)

Since \([CO_3^{2-}]_{(eq)}\) is the \(CO_3^{2-}\) concentration at chemical equilibrium for a given solution (i.e. \([CO_3^{2-}]_{(eq)}\) varies with the solution \([Ca^{2+}]\), temperature and ionic strength), the numerator of equation (15) equals 1 regardless of the \([Ca^{2+}]\) value and equation (15) simplifies to:

\[ \frac{r_{-c}}{r_{+c}} = \Omega^{-n_2} \]  
(16)

with
\[ \Omega = \left[ \frac{[CO_3^{2-}][Ca^{2+}]}{K_{sp}} \right] \]  

(17)

Equation (16) is a convenient expression for relating \( r_c/r_+c \) to the saturation state of a carbonate mineral (\( \Omega \)) and the partial reaction order \( n_2 \). The level of isotopic equilibration between CaCO\(_3\) and CO\(_3^{2-}\) is therefore expected to decrease with increasing solution \( \Omega \) and \( n_2 \). We note, however, that if the mineral reactive surface density (i.e. the kink site density) increases with \( \Omega \) as expected by some ion-by-ion models of calcite growth (e.g. Nielsen et al., 2012; Wolthers et al., 2012), then the backward rate \( r_-c \) would also increase with \( \Omega \) and the level of isotopic equilibration between CaCO\(_3\) and CO\(_3^{2-}\) would be underestimated at high \( \Omega \) values.

4.2.2. The partial reaction order \( n_2 \)

The value of the partial reaction order \( n_2 \) is determined by the logarithmic expression of equation (11) (Zhong and Mucci, 1993):

\[ \log(r_c + k_-c) = n_2\log([CO_3^{2-}]) + \log(K_+c) \]  

(18)

When crystal growth is far from chemical equilibrium \( (r_c \gg k_-c) \), equation (18) can be approximated by:

\[ \log(r_c) = n_2\log([CO_3^{2-}]) + \log(K_+c) \]  

(19)

The partial reaction order \( n_2 \) is therefore the slope of \( \log(r_c) \) vs \( \log([CO_3^{2-}]) \) for values of \([CO_3^{2-}]\) far from chemical equilibrium. Experimentally determined \( n_2 \) values vary systematically with temperature and ionic strength (Fig. 2A and 2B, Zuddas and Mucci, 1998, Lopez et al., 2009).

Lopez et al. (2009) derived \( n_2 \) for Mg-calcite growing in artificial seawater and NaCa-Cl\(_2\) solution of salinity 35 over the temperature range 5-70°C. A plot of the Lopez et al. (2009) \( n_2 \) values versus temperature (Fig. 2A) shows that \( n_2 \) is very similar in seawater and simple NaCa-Cl\(_2\) solutions at a given temperature and that \( n_2 \) increases linearly from 2.0 to 3.3 between 0 and 30°C (Lopez et al., 2009):

\[ n_2 = 0.045(\pm 0.002)T(°C) + 2.0(\pm 0.1) \quad (\text{for seawater}, I=0.7) \]  

(20)

This result is consistent with the findings of several other studies that reported \( n_2 \approx 3 \) for calcite precipitated in seawater at 25°C (Zhong and Mucci, 1989, 1993; Zuddas and Mucci, 1994, 1998).
value of \( n_2 \) is also strongly dependent on the solution ionic strength, increasing from 0.7 to 3.3 over the 0.1-0.9 range in ionic strength for a solution at 25°C (Fig. 2B, Zuddas and Mucci, 1998):

\[
n_2 = 3.5(\pm 0.6) I + 0.16(\pm 0.37) \quad \text{(at 25°C)}
\]

Substituting equation (20) or (21) into equation (16), the level of isotopic equilibrium between calcite and \( \text{CO}_3^{2-} \) \( (E_c = r_c/r_{ec}) \) can now be predicted as a function of the solution \( \Omega \), temperature and ionic strength. The expected values of \( E_c \) at 25°C as a function of \( \Omega \) and ionic strength are shown in Figure 3.

We note that another factor likely to affect \( n_2 \) that is not fully covered in this study is the solution \( \text{CO}_3^{2-}/\text{Ca}^{2+} \) activity ratio. At constant \( \Omega \), the net calcite growth rate is maximum where the \( \text{CO}_3^{2-}/\text{Ca}^{2+} \) activity ratio is close to 1 and minimum where it is close to 0 or very high (Wolthers et al., 2012). Hence, it can be expected that \( r_c/r_{ec} \) also varies with the solution \( \text{CO}_3^{2-}/\text{Ca}^{2+} \). However, where variations in \( \text{Ca}^{2+} \) concentration are small and \( \text{Ca}^{2+} \gg \text{CO}_3^{2-} \) (e.g. seawater and most large terrestrial water bodies), \( \Omega \) is mainly a function of \( \text{CO}_3^{2-}/\text{Ca}^{2+} \) activity and the sensitivity of \( r_c/r_{ec} \) to the solution \( \text{CO}_3^{2-}/\text{Ca}^{2+} \) should be small (Wolthers et al., 2012). Hence, we recommend the use of equations (20) and (21) within these specified conditions.

### 4.2.3. Equilibrium fractionation between \( \text{CaCO}_3 \) and \( \text{CO}_3^{2-} \)

According to equation (6), the oxygen-isotope equilibrium fractionation factor between \( \text{CaCO}_3 \) and \( \text{CO}_3^{2-} \) \( (\alpha_{c/\text{CO}_3^{2-}}^{eq}) \) is equal to the ratio of the equilibrium fractionation factor between \( \text{CaCO}_3 \) and water \( (\alpha_{c/w}^{eq}) \) and the equilibrium fractionation factor between \( \text{CO}_3^{2-} \) and water \( (\alpha_{\text{CO}_3^{2-}/w}^{eq}) \):

\[
\alpha_{c/\text{CO}_3^{2-}}^{eq} = \frac{\alpha_{c/w}^{eq}}{\alpha_{\text{CO}_3^{2-}/w}^{eq}}
\]

The true values of \( \alpha_{c/w}^{eq} \) for calcite and aragonite have been debated since the pioneering work of Urey (1947). According to equation (16), isotopic equilibrium is approached in solutions with low \( \Omega \) and low ionic strength (Fig. 3). This suggests that the best available estimates of \( \alpha_{c/w}^{eq} \) comes from the \( \alpha_{c/w} \) of inorganic calcite precipitated very slowly in the low supersaturation and low ionic strength waters of the Devils Hole cave system (see Coplen, 2007; Watkins et al., 2013; Kluge et al., 2014).

Using 1.02849 for \( \alpha_{c/w}^{eq} \) at 33.7°C (Coplen, 2007) in equation (22), and the expression of Beck et al. (2005) for \( \alpha_{\text{CO}_3^{2-}/w}^{eq} \) (Table 1), yields an \( \alpha_{c/\text{CO}_3^{2-}}^{eq} \) of 1.00542 at 33.7°C. Available data (Dietzel et al.,
2009; Baker et al., 2015, see Section 5.2) suggest that $\alpha_{c/\text{CO}_3^2-}$ is mostly independent of temperature between 5 and 40°C, and therefore $\alpha^{eq}_{c/\text{CO}_3^2-}$ is assumed to be constant. Note that an accurate determination of the temperature sensitivity of $\alpha^{eq}_{c/\text{CO}_3^2-}$ would require additional oxygen isotope data on inorganic calcite growing at low supersaturation solution (i.e. under near equilibrium conditions) and at various temperatures.

4.2.4. Kinetic fractionation between CaCO$_3$ and CO$_3^{2-}$ and between CO$_3^{2-}$ and HCO$_3^-$

Keeping in mind the framework where only CO$_3^{2-}$ participates directly in calcite growth (pathway 7), the parameters $^{16}k_{+c}$ and $^{18}k_{+c}$ are defined as rate coefficients of $^{16}$O and $^{18}$O transfer between carbonate ions and calcite. For the forward reaction, we have (DePaolo, 2011):

$$\frac{^{18}k_{+c}}{^{16}k_{+c}} = \alpha_{c/\text{CO}_3^2-}^{+c}$$ (23)

where $\alpha_{c/\text{CO}_3^2-}^{+c}$ is the kinetic limit of $\alpha_{c/\text{CO}_3^2-}$ during instantaneous calcite precipitation. Under closed system conditions, there are isotopic distillation effects that reduce the kinetic fractionation between product and reactant of a unidirectional reaction (Rayleigh, 1896). In this case, the $^{18}$O/$^{16}$O of instantaneously precipitated CaCO$_3$ formed from a finite CO$_3^{2-}$ pool is (Bigeleisen and Wolfsburg, 1958):

$$^{18}R_c = \frac{^{18}R_{c/\text{CO}_3^2-}}{^{18}R_{c/\text{CO}_3^2-}^{t_1}} \frac{1 - (1 - [\text{CO}_3^{2-}]_{+c}/[\text{CO}_3^{2-}])t_1}{[\text{CO}_3^{2-}]_{+c}/[\text{CO}_3^{2-}]_{t_1}} \alpha_{c/\text{CO}_3^2-}^{+c}$$ (24)

where $t_1$ is the time at the onset of CaCO$_3$ precipitation, $^{18}R_{c/\text{CO}_3^2-}^{t_1}$ is $^{18}R_{c/\text{CO}_3^2-}$ at $t_1$, and $[\text{CO}_3^{2-}]_{+c}/[\text{CO}_3^{2-}]_{t_1}$ is the proportion of CO$_3^{2-}$ consumed during instantaneous CaCO$_3$ precipitation.

In cases where CaCO$_3$ precipitation is triggered by a rapid increase in solution pH, all or a fraction of the HCO$_3^-$ ions in solution may be deprotonated and rapidly precipitated. This implies that $^{18}R_{c/\text{CO}_3^2-}^{t_1}$ in equation (24) can be affected by the initial $^{18}$O/$^{16}$O of the HCO$_3^-$ pool and the KIFF related to HCO$_3^-$ deprotonation (Kim et al., 2006). The interconversion of HCO$_3^-$ and CO$_3^{2-}$ occurs via the following pathway:

$$\text{CO}_3^{2-} + H^+ \overset{k_{-=5}}{\leftrightarrow} \overset{k_{+=5}}{\longrightarrow} \text{HCO}_3^-$$ (25)
where \( k_5 \) and \( k_{25} \) are the reaction rate constants of \( \text{HCO}_3^- \) deprotonation and \( \text{CO}_3^{2-} \) protonation, respectively (for the reaction rate constants, we follow the same notation as in Zeebe and Wolf-Gladrow, 2001). Similar to the treatment of the KIFF during \( \text{CO}_3^{2-} \) precipitation, \( ^{16}k_{-5} \) and \( ^{18}k_{-5} \) are defined as rate coefficients of \( ^{16}\text{O} \) and \( ^{18}\text{O} \) transfer between bicarbonate and carbonate ions during \( \text{HCO}_3^- \) deprotonation:

\[
\frac{^{18}k_{-5}}{^{16}k_{-5}} = \alpha_{\text{CO}_3^{2-}/\text{HCO}_3^-}
\]  

(26)

Taking into account distillation effects, the isotopic ratio of the newly formed \( \text{CO}_3^{2-} \) ions from deprotonated \( \text{HCO}_3^- \) is (Bigeleisen and Wolfsburg, 1958):

\[
R_{\text{CO}_3^{2-}}^{-5} = \frac{^{18}R_{\text{HCO}_3^-}^{t_0} \cdot \left( 1 - \frac{[\text{CO}_3^{2-}]_{-5}/[\text{HCO}_3^-]_{t_0}}{[\text{CO}_3^{2-}]_{-5}/[\text{HCO}_3^-]_{t_0}} \right) \alpha_{\text{CO}_3^{2-}/\text{HCO}_3^-}^{-5}}{[\text{CO}_3^{2-}]_{-5}/[\text{HCO}_3^-]_{t_0}}
\]  

(27)

where \( t_0 \) is the time at the onset of \( \text{HCO}_3^- \) deprotonation, \( ^{18}R_{\text{HCO}_3^-}^{t_0} \) is the value of \( ^{18}R_{\text{HCO}_3^-} \) at \( t_0 \), and \( [\text{CO}_3^{2-}]_{-5}/[\text{HCO}_3^-]_{t_0} \) is the proportion of deprotonated \( \text{HCO}_3^- \). Here we treat \( \text{HCO}_3^- \) deprotonation and \( \text{CaCO}_3 \) precipitation in sequence but without time-dependence (i.e. all the \( \text{HCO}_3^- \) deprotonation occurs instantaneously prior to \( \text{CaCO}_3 \) precipitation). Hence, \( [\text{CO}_3^{2-}]_{t_1} \) in equation (24) is equal to \( [\text{CO}_3^{2-}]_{t_0} + [\text{CO}_3^{2-}]_{-5} \) and the term \( ^{18}R_{\text{CO}_3^{2-}}^{t_1} \) in equation (25) can be expressed as the isotopic mass balance between an initial \( \text{CO}_3^{2-} \) pool prior to \( \text{HCO}_3^- \) deprotonation \( ([\text{CO}_3^{2-}]_{t_0}) \) and newly formed \( \text{CO}_3^{2-} \) derived from deprotonated \( \text{HCO}_3^- \) \( ([\text{CO}_3^{2-}]_{-5}) \):

\[
^{18}R_{\text{CO}_3^{2-}}^{t_1} = \left( \frac{^{18}R_{\text{CO}_3^{2-}}^{t_0} \cdot [\text{CO}_3^{2-}]_{t_0} + ^{18}R_{\text{CO}_3^{2-}}^{-5} \cdot [\text{CO}_3^{2-}]_{-5}}{^{18}R_{\text{CO}_3^{2-}}^{t_0} \cdot [\text{CO}_3^{2-}]_{t_0} + ^{18}R_{\text{CO}_3^{2-}}^{-5} \cdot [\text{CO}_3^{2-}]_{-5}} \right)^{-1} - 1
\]  

(28)

where \( ^{18}R_{\text{CO}_3^{2-}}^{t_0} \) is \( ^{18}R_{\text{CO}_3^{2-}} \) at \( t_0 \). Equation (28) can be simplified because \( ^{18}\text{O} \ll ^{16}\text{O} \) for all the isotopic ratios (Hayes, 1982):

\[
^{18}R_{\text{CO}_3^{2-}}^{t_0} \equiv \frac{^{18}R_{\text{CO}_3^{2-}}^{t_0} \cdot [\text{CO}_3^{2-}]_{t_0} + ^{18}R_{\text{CO}_3^{2-}}^{-5} \cdot [\text{CO}_3^{2-}]_{-5}}{[\text{CO}_3^{2-}]_{t_0} + [\text{CO}_3^{2-}]_{-5}}
\]  

(29)

Substituting (27) and (29) in (24) and dividing (24) by \( ^{18}R_{w} \), we obtain an expression for calculating the \( k_{c/w} \) of \( \text{CaCO}_3 \) precipitated instantaneously from a fraction of the \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \) pools:
\[ \alpha_{c/w} \cong \left( \alpha_{c,CO_3^-/w}^{t_0} \cdot [CO_3^{2-}]_{t_0} + \alpha_{HCO_3^-/w}^{t_0} \cdot [HCO_3^-]_{t_0} \cdot \varphi_{HCO_3^-} \right) \frac{\varphi_{CO_3^-}}{[CO_3^{2-}]_{t+c}} \]

(30)

with

\[ \varphi_{HCO_3^-} = 1 - (1 - [CO_3^{2-}]_{-5}/[HCO_3^-]_{t_0})^{\alpha_{c,CO_3^-/HCO_3^-}^{5}} \]

(31)

and

\[ \varphi_{CO_3^-} = 1 - [1 - [CO_3^{2-}]_{+c}/( [CO_3^{2-}]_{t_0} + [CO_3^{2-}]_{-5} )]^{\alpha_{c/CO_3^-}^{+c}} \]

(32)

The oxygen isotopic results from witherite (i.e. BaCO₃) precipitated quasi-instantaneously from an isotopically equilibrated DIC pool composed mainly of CO₃²⁻ and HCO₃⁻ (i.e. negligible CO₂aq: Kim et al., 2006) can be used to constrain \( \alpha_{c,CO_3^-/HCO_3^-}^{5} \) and \( \alpha_{c/CO_3^-}^{+c} \) in equations (31) and (32). For \( \alpha_{c/CO_3^-}^{+c} \), we assume that the \(^{18}\text{O}/^{16}\text{O} \) difference in reaction rates during calcite precipitation are similar to that of witherite precipitation. Kim et al. (2006) found that the oxygen isotope fractionation between BaCO₃ and H₂O (\( \alpha_{Ba/w} \)) increased with increasing fractions of the CO₃²⁻ pool consumed as well as with increasing fraction of deprotonated HCO₃⁻, suggesting that isotopically light CO₃²⁻ ions are preferentially incorporated into BaCO₃ and isotopically light HCO₃⁻ ions are preferentially deprotonated (Kim et al., 2006; Fig. 4A). We estimated the KFF \( \alpha_{c,CO_3^-/HCO_3^-}^{5} \) and \( \alpha_{c/CO_3^-}^{+c} \) at 25°C by fitting equation (30) to the data of Kim et al. (2006) using the following known values and relationships (Fig. 4A):

i. \( \alpha_{c,CO_3^-/w}^{t_0} \) and \( \alpha_{HCO_3^-/w}^{t_0} \) are given by the equilibrium fractionation factors \( \alpha_{c,CO_3^-/w}^{eq} \) (1.0240) and \( \alpha_{HCO_3^-/w}^{eq} \) (1.0310) at 25°C (as in Kim et al., 2006).

ii. \( [CO_3^{2-}]_{t_0} \) and \( [HCO_3^-]_{t_0} \) are obtained from the solution pH and ionic content prior to the addition of NaOH (as in Kim et al., 2006).

iii. \( [CO_3^{2-}]_{+c} \) is obtained from the molar concentration of DIC consumed (as in Kim et al., 2006).

iv. \( [CO_3^{2-}]_{-5} = 0 \) where \( [CO_3^{2-}]_{+c} < [CO_3^{2-}]_{t_0} \) and \( [CO_3^{2-}]_{-5} = [CO_3^{2-}]_{+c} - [CO_3^{2-}]_{t_0} \) where \( [CO_3^{2-}]_{+c} > [CO_3^{2-}]_{t_0} \) (these relations assumes that most of the deprotonated HCO₃⁻ precipitate as BaCO₃)

Given the constraints listed above, the best agreement between model and data is obtained with \( \alpha_{c/CO_3^-}^{+c} = 0.9995 \pm 0.0002 \) and \( \alpha_{c,CO_3^-/HCO_3^-}^{5} = 0.9950 \pm 0.0002 \) (Fig. 4A an 4B, \( r^2 = 0.98 \), p-value <
Our estimate of the CaCO$_3$-CO$_3^{2-}$ KFF ($\alpha_{c/CO_3^{2-}}^{+}$) is closer to unity than that of Watkins et al. (2014) ($\alpha_{c/CO_3^{2-}}^{+} = 0.9980$). The latter was deduced from an isotopic ion-by-ion growth model (Wolthers et al., 2012) and $\alpha_{c/w}$ versus growth rate data (Watkins et al., 2014). These authors estimated $\alpha_{c/CO_3^{2-}}^{+}$ using an $\alpha_{CO_3^{2-}/w}^{eq}$ value of 1.0268 (at 25°C), based on the equation of Wang et al. (2013). Adjusting the result of Watkins et al. (2014) for a preferred $\alpha_{CO_3^{2-}/w}^{eq}$ value within 1.0240 and 1.0245 (Beck et al., 2005; Kim et al., 2006; Kim et al., 2014), yields $\alpha_{c/CO_3^{2-}}^{+} = 1.0003$ to 1.0008, which is above unity and inconsistent with a preferential precipitation of isotopically light CO$_3^{2-}$ ions.

In short, these results suggest that the transfer of carbonate ions from the solution to the carbonate mineral induces a small oxygen isotopic fractionation of $\sim -0.5\%$ at the kinetic limit. In contrast to the small KIFF during CO$_3^{2-}$ transfer to CaCO$_3$, the KIFF during HCO$_3^-$ deprotonation ($\alpha_{CO_3^{2-}/HCO_3^-}^{5}$) results in newly formed CO$_3^{2-}$ with an $^{18}\text{O}/^{16}\text{O} \sim 5\%$ lower than the parent HCO$_3^-$.

### 4.3. Isotopic fractionation between DIC species and water ($\alpha_{CO_3^{2-}/w}$ and $\alpha_{HCO_3^-/w}$)

#### 4.3.1. Kinetic vs equilibrium fractionation

An equilibrium distribution of DIC species in solution is achieved within seconds, but oxygen isotopic equilibration takes hours or days depending on the solution pH and temperature (McConnaughey, 1989b; Usdowski et al., 1991; Zeebe and Wolf-Gladrow, 2001; Beck et al., 2005). The relatively slow isotopic exchange between DIC species and water occurs via the hydration and hydroxylation reactions (McConnaughey, 1989b; Usdowski et al., 1991):

$$CO_2 + H_2O \xrightleftharpoons{k_{+2}^*, k_{-2}^*} H_2CO_3 \Leftrightarrow HCO_3^- + H^+ \quad \text{(hydration)} \quad (33)$$

and

$$CO_2 + OH^- \xrightleftharpoons{k_{-4}^*, k_{+4}^*} HCO_3^- \quad \text{(hydroxylation)} \quad (34)$$

where $k_{+2}^*$, $k_{-2}^*$, $k_{-4}^*$, and $k_{+4}^*$ are the backward and forward reaction rate constants for CO$_2$ hydration and hydroxylation, respectively (the superscript * of $k_{+2}^*$ and $k_{+2}^*$ denote the inclusion of the effect of carbonic anhydrase on the rate of CO$_2$ (de)hydration; see Appendix A4 for calculation of rate constants). Usdowski et al. (1991) derived an expression for the oxygen isotope ratio of the DIC as a function of time:
\[
\ln \left( \frac{18R_{DIC}^t - 18R_{DIC}^{eq}}{18R_{DIC}^{t_0} - 18R_{DIC}^{eq}} \right) = -\frac{t}{\tau} \tag{35}
\]

where \( t \) is the time spent by the DIC pool in solution, \( \tau \) is the time constant and \( 18R_{DIC}^t, 18R_{DIC}^{eq} \) and \( 18R_{DIC}^{t_0} \) are the oxygen isotope ratios of DIC at time \( t, t_0 \) and at isotopic equilibrium. Equation (35) can be rewritten to express the oxygen isotope ratio of DIC at time \( t \):

\[
18R_{DIC}^t = e^{\left( -\frac{t}{\tau} \right)} \left( 18R_{DIC}^{t_0} - 18R_{DIC}^{eq} \right) + 18R_{DIC}^{eq} \tag{36}
\]

Dividing equation (36) by \( 18R_w \) provides an equation for the oxygen isotope fractionation between the DIC pool and water:

\[
\alpha_{DIC/w}^t = e^{\left( -\frac{t}{\tau} \right)} \left( \alpha_{DIC/w}^{t_0} - \alpha_{DIC/w}^{eq} \right) + \alpha_{DIC/w}^{eq} \tag{37}
\]

The rate of protonation and deprotonation among \( H_2CO_3 \), \( HCO_3^- \) and \( CO_3^{2-} \) ions is several orders of magnitude faster than the CO\(_2\) hydration and hydroxylation reactions (Zeebe and Wolf-Gladrow, 2001). Therefore, where gaseous CO\(_2\) is the dominant DIC source for CaCO\(_3\) precipitation and the system is at steady state, it can be assumed that \( H_2CO_3 \), \( HCO_3^- \) and \( CO_3^{2-} \) remain at isotopic equilibrium with each other (but not with H\(_2\)O) over the course of DIC-H\(_2\)O isotopic equilibration (this is in contrast with a unidirectional deprotonation of HCO\(_3^-\) during instantaneous carbonate precipitation; Section 4.2.4). Consequently, equation (37) can be rewritten for any of the DIC species (i):

\[
\alpha_{i/w}^t = e^{\left( -\frac{t}{\tau} \right)} \left( \alpha_{i/w}^{t_0} - \alpha_{i/w}^{eq} \right) + \alpha_{i/w}^{eq} \tag{38}
\]

Note that where \( \tau \ll t \), \( \alpha_{i/w}^t = \alpha_{i/w}^{eq} \) (i.e. the equilibrium isotopic ratio of the DIC species). The level of isotopic equilibrium between DIC species and water \( (E_{DIC}) \) can therefore be expressed as:

\[
E_{DIC} = 1 - e^{\left( -\frac{t}{\tau} \right)} \tag{39}
\]

The time constant \( \tau \) in equation (38) and (39) is a function of the hydration and hydroxylation reaction kinetics (Usdowski et al., 1991, Uchikawa and Zeebe, 2012; Appendix A5), which in turn depends on DIC speciation (Millero et al., 2006; Appendix 6), pH and temperature. Solving equation (38) requires
knowledge of the residence time of the DIC in solution ($RT_{DIC}$). Under steady state conditions, $RT_{DIC}$ is equal to the molar quantity of DIC divided by the calcite growth rate in moles/s:

$$RT_{DIC} = \frac{[DIC]V}{r_c}$$

(40)

Where $V$ is the volume of the precipitating solution. The following sections present equations for the equilibrium ($\alpha^eq_{i/w}$) and kinetic ($\alpha^{t_0}_{i/w}$) end members of equation (38).

4.3.2. Equilibrium fractionation between DIC species and water

The oxygen isotope fractionations between the DIC species and water under equilibrium conditions were determined by Beck et al. (2005) over the 15-40°C temperature range and by Kim and co-workers at 25°C and over varying ionic strength (Kim et al., 2006; Kim et al., 2014). These studies showed that the relationships determined by Beck et al. (2005) can be applied to solutions of different solute content and ionic strength (Table 1). Alternative fractionation factors were also derived by Wang et al. (2013) based on the experimental data of Beck et al. (2005) and Kim et al. (2006). Recent work by Kim et al. (2014) confirmed the initial results of Beck et al. (2005), and hence the equations from Beck et al. (2005) were used in this study (Table 1).

4.3.3. Kinetic isotope fractionation during the hydration and hydroxylation of CO$_2$

When gaseous CO$_2$ dissolves in water with a pH higher than 7, most of the CO$_2$ is rapidly converted into HCO$_3^-$ and CO$_3^{2-}$ ions via the hydration and/or hydroxylation reaction pathways (Section 4.3.1). The initial oxygen isotope ratios of ‘HCO$_3^-$ plus CO$_3^{2-}$’ ($^{18}R_{(CO_3^{2-}+HCO_3^-)}^{t_0}$) reflects the oxygen atoms from the molecules or ions involved in the CO$_2$ hydration and/or hydroxylation reactions. The parameter $\alpha_{(CO_3^{2-}+HCO_3^-)/w}^{t_0}$ is defined as the initial (kinetic) oxygen isotope fractionation between hydrated/hydroxylated CO$_2$ and water:

$$\alpha_{(CO_3^{2-}+HCO_3^-)/w}^{t_0} = \frac{^{18}R_{(CO_3^{2-}+HCO_3^-)}^{t_0}}{^{18}R_{w}}$$

(41)

In turn, $^{18}R_{(CO_3^{2-}+HCO_3^-)}^{t_0}$ is equal to the isotopic mass-balance between the initial oxygen isotopic ratios of hydrated and hydroxylated CO$_2$: 
\[ \frac{^{18}R_{(CO_2^-+HCO_3^-)}}{^{16}R_{(CO_2^-+HCO_3^-)}} \equiv \frac{^{18}R^{+2}_{(CO_2^-+HCO_3^-)} \cdot X_{+2}}{^{18}R^{+4}_{(CO_2^-+HCO_3^-)} \cdot X_{+4}} \] (42)

where \( ^{18}R^{+2}_{(CO_2^-+HCO_3^-)} \) and \( ^{18}R^{+4}_{(CO_2^-+HCO_3^-)} \) are the initial oxygen isotopic ratios of hydrated and hydroxylated CO\(_2\), respectively, and where \( X_{+2} \) and \( X_{+4} \) are the relative proportions of hydrated and hydroxylated CO\(_2\), respectively. The relative importance of CO\(_2\) hydration versus CO\(_2\) hydroxylation depends on solution pH (Johnson, 1982). According to reactions pathways (33) and (34), \( X_{+2} \) and \( X_{+4} \) are expressed as follows:

\[ X_{+2} = \frac{k^*_2}{k^*_2 + k^*_{+4}[OH^-]} \] (43)

and

\[ X_{+4} = \frac{k^*_{+4}[OH^-]}{k^*_2 + k^*_{+4}[OH^-]} \] (44)

The concentration of hydroxyl ions \([OH^-]\) in equation (43) and (44) is obtained from the stoichiometric ion product of water \( K_w^* \) (DOE, 1994; Appendix 7) and pH. Solving (42) requires knowledge of \( ^{18}R^{+2}_{(CO_2^-+HCO_3^-)} \) and \( ^{18}R^{+4}_{(CO_2^-+HCO_3^-)} \). For the hydration reaction, \( ^{18}k_{+2} \) and \( ^{16}k_{+2} \) are defined as rate coefficients of \(^{16}\)O and \(^{18}\)O transfer between the sum of the reactants ‘CO\(_2\)(aq) and H\(_2\)O’ and hydrated CO\(_2\) (i.e. mainly the sum of HCO\(_3^-\) and CO\(_3^{2-}\)). Where the reaction is strictly forward the \( ^{18}k_{+2}/^{16}k_{+2} \) ratio is related to the oxygen isotopic ratios of reactants (CO\(_2\)(aq) + H\(_2\)O) and products (HCO\(_3^-\) and CO\(_3^{2-}\)):

\[ \frac{^{18}k_{+2}}{^{16}k_{+2}} = \frac{^{18}R^{+2}_{(CO_2^-+HCO_3^-)}}{^{18}R_{(CO_2+w)}} \] (45)

where \( ^{18}R_{(CO_2+w)} \) is the oxygen isotopic ratio of ‘CO\(_2\)(aq) + H\(_2\)O’. Rearranging (45) provides an equation for \( ^{18}R^{+2}_{(CO_2^-+HCO_3^-)} \) as a function of the \( ^{18}k_{+2}/^{16}k_{+2} \) ratio:

\[ ^{18}R^{+2}_{(CO_2^-+HCO_3^-)} = ^{18}R_{(CO_2+w)} \cdot \frac{^{18}k_{+2}}{^{16}k_{+2}} \] (46)

with a contribution of two oxygen atoms from CO\(_2\)(aq) and one from H\(_2\)O, \( ^{18}R_{(CO_2+w)} \) is expressed as:
\[ {^{18}R_\text{CO}_2 + w} \approx {^{18}R_\text{CO}_2} \cdot \frac{2}{3} + {^{18}R_w} \cdot \frac{1}{3} \quad (47) \]

The value of \( ^{18}k_+^{18}k_{-2} \) in equation (45) has yet to be determined experimentally but theoretical calculations based on transition state theory and quantum chemistry suggest an overall kinetic fractionation factor between hydrated CO\(_2\) and CO\(_{2\text{(aq)}}\) (\( \alpha_{\langle\text{CO}_3^2^- + \text{HCO}_3^-\rangle/\text{CO}_2} \)) of 0.986 ± 0.001 (Zeebe, 2014). Note that Zeebe (2014) presented results for the kinetic fractionation factor between CO\(_{2\text{(aq)}}\) and hydrated CO\(_2\) (1.014 ± 0.001), and thus the fractionation factor between hydrated CO\(_2\) and CO\(_{2\text{(aq)}}\) is the inverse of 1.014. The initial oxygen isotope ratio of hydrated CO\(_2\) can therefore be expressed as a function of \( \alpha_{\langle\text{CO}_3^2^- + \text{HCO}_3^-\rangle/\text{CO}_2} \):

\[ \frac{^{18}R_{\text{CO}_3^2^- + \text{HCO}_3^-}}{^{18}R_\text{CO}_2} = \frac{^{18}R_\text{CO}_2 \cdot \alpha_{\langle\text{CO}_3^2^- + \text{HCO}_3^-\rangle/\text{CO}_2}}{2/3 + 1/3 \cdot (\alpha_{\text{CO}_2/w})^{-1}} \quad (48) \]

where \( ^{18}R_\text{CO}_2 \) is the oxygen isotope ratio of CO\(_{2\text{(aq)}}\). Substituting (48) and (47) into (46) yields an equation for \( ^{18}k_+^{18}k_{-2} \) as a function of \( \alpha_{\langle\text{CO}_3^2^- + \text{HCO}_3^-\rangle/\text{CO}_2} \):

\[ \frac{^{18}k_+^{18}k_{-2}}{^{16}k_+^{16}k_{-2}} = \frac{^{18}R_{\text{CO}_3^2^- + \text{HCO}_3^-}}{^{16}R_{\text{CO}_2 + \text{OH}^-}} \quad (49) \]

Using the equilibrium value of Beck et al. (2005) for \( \alpha_{\text{CO}_2/w} \) (Table 1) and a value of 0.986 ±0.001 for \( \alpha_{\langle\text{CO}_3^2^- + \text{HCO}_3^-\rangle/\text{CO}_2} \) (Zeebe, 2014) yields a \( ^{18}k_+^{18}k_{-2} \) ratio of 0.9994 ±0.0010 at 25°C. This calculation suggests that the mass-related KIE during CO\(_2\) hydration is on the order of 1‰ or less. The 14‰ depletion in \( ^{18}O \) between hydrated CO\(_2\) and CO\(_{2\text{(aq)}}\) (\( \alpha_{\langle\text{CO}_3^2^- + \text{HCO}_3^-\rangle/\text{CO}_2} = 0.986 ± 0.001 \), Zeebe, 2014) is therefore mainly caused by the contribution of oxygen atoms from CO\(_2\) and H\(_2\)O.

Similar to the hydration reaction above, we define \( ^{18}k_+^{18}k_{-4} \) and \( ^{16}k_+^{16}k_{-4} \) as rate coefficients of \( ^{16}O \) and \( ^{18}O \) transfer between hydroxylated CO\(_2\) (i.e. mainly the sum of HCO\(_3^-\) and CO\(_3^2^-\)) and the sum of the reactant CO\(_{2\text{(aq)}}\) and OH:

\[ \frac{^{18}k_+^{18}k_{-4}}{^{16}k_+^{16}k_{-4}} = \frac{^{18}R_{\text{CO}_3^2^- + \text{HCO}_3^-}}{^{18}R_{\text{CO}_2 + \text{OH}^-}} \quad (50) \]

where \( ^{18}R_{\text{CO}_2 + \text{OH}^-} \) is the oxygen isotopic ratio of ‘CO\(_{2\text{(aq)}}\) + OH’. Rearranging equation (50), we have:
\[ \overline{^{18}R_{(CO_2^2+HCO_3^-)}} = \overline{^{18}R_{(CO_2+OH^-)}} \cdot \frac{^{18}k_{+4}}{^{16}k_{+4}}. \] (51)

With a contribution of two oxygen atoms from CO\textsubscript{2(aq)} and one from OH\textsuperscript{−}, \( ^{18}R_{(CO_2+OH^-)} \) is expressed as:

\[ ^{18}R_{(CO_2+OH^-)} \cong ^{18}R_{CO_2} \cdot \frac{2}{3} + ^{18}R_{OH^-} \cdot \frac{1}{3}, \] (52)

where \(^{18}R_{OH^-}\) is the oxygen isotope ratio of OH\textsuperscript{−} ions. The temperature dependence of the equilibrium oxygen isotope fractionation between OH\textsuperscript{−} and H\textsubscript{2}O (\( \alpha^\text{eq}_{OH^-/H_2O} \)) was estimated by Green and Taube (1963) (Table 1). The \(^{18}k_{+4}/^{16}k_{+4}\) ratio has not been accurately measured or estimated yet, and is thus treated as a free parameter of the model.

The equations presented thus far allow for calculation of the initial oxygen isotope ratio of the sum of CO\textsubscript{3}\textsuperscript{2−} and HCO\textsubscript{3}− but not of CO\textsubscript{3}\textsuperscript{2−} or HCO\textsubscript{3}− individually. The parameter \( ^{18}R_{CO_3^2-+HCO_3^-} \) in equation (42) can be expressed as the isotopic mass balance between the initial oxygen isotope ratio of CO\textsubscript{3}\textsuperscript{2−} (\(^{18}R_{CO_3^-} \)) and HCO\textsubscript{3}− (\(^{18}R_{HCO_3^-} \)):

\[ ^{18}R_{CO_3^2-+HCO_3^-} \cong ^{18}R_{CO_3^-} \cdot X_{CO_3^2-} + ^{18}R_{HCO_3^-} \cdot X_{HCO_3^-}. \] (53)

where \( X_{CO_3^2-} \) and \( X_{HCO_3^-} \) are the relative proportions of CO\textsubscript{3}\textsuperscript{2−} and HCO\textsubscript{3}− ions, respectively, and are obtained from the first and second dissociation constants of carbonic acid (Millero et al, 2006; Appendix A5). As mentioned in Section 4.3.1, CO\textsubscript{3}\textsuperscript{2−} and HCO\textsubscript{3}− are considered to be in isotopic equilibrium with each other due to the fast rate of protonation and deprotonation between these species relative to the rate of the hydration and hydroxylation reactions. The ratio of \( ^{18}R_{CO_3^-} \) to \( ^{18}R_{HCO_3^-} \) is therefore equal to the equilibrium fractionation factor between CO\textsubscript{3}\textsuperscript{2−} and HCO\textsubscript{3}− (\( \alpha^\text{eq}_{CO_3^2-/HCO_3^-} \)):

\[ \frac{^{18}R_{CO_3^-}}{^{18}R_{HCO_3^-}} = \alpha^\text{eq}_{CO_3^2-/HCO_3^-}. \] (54)
Substituting (54) into (53) and dividing each isotopic ratio by \(^{18}R_w\), expressions for \(\alpha_{\text{CO}_3^{-}/w}^t\) and \(\alpha_{\text{HCO}_3^{-}/w}^t\) are as follows:

\[
\alpha_{\text{CO}_3^{-}/w}^t \equiv \frac{\alpha_{(\text{CO}_3^{2-}+\text{HCO}_3^{-})/w}^t}{X_{\text{CO}_3^{2-}} + X_{\text{HCO}_3^{-}} \cdot \left(\alpha_{\text{CO}_3^{2-}+\text{HCO}_3^{-}}^{eq}/\text{HCO}_3^{-}\right)^{-1}} \tag{55}
\]

and

\[
\alpha_{\text{HCO}_3^{-}/w}^t \equiv \frac{\alpha_{(\text{CO}_3^{2-}+\text{HCO}_3^{-})/w}^t}{X_{\text{CO}_3^{2-}} \cdot \alpha_{\text{CO}_3^{2-}+\text{HCO}_3^{-}}^{eq} + X_{\text{HCO}_3^{-}}} \tag{56}
\]

The value of \(\alpha_{\text{CO}_3^{2-}+\text{HCO}_3^{-}}^{eq}/\text{HCO}_3^{-}\) in equations (55) and (56) is obtained from the equilibrium isotopic fractionation factors \(\alpha_{\text{CO}_3^{2-}+\text{HCO}_3^{-}}^{eq}/\text{HCO}_3^{-}\) and \(\alpha_{\text{CO}_3^{2-}+\text{HCO}_3^{-}}^{eq}/\text{HCO}_3^{-}\) (Beck et al., 2005; Table 1):

\[
\alpha_{\text{CO}_3^{2-}+\text{HCO}_3^{-}}^{eq}/\text{HCO}_3^{-} = \frac{\alpha_{\text{CO}_3^{2-}+\text{HCO}_3^{-}}^{eq}/\text{HCO}_3^{-}}{\alpha_{\text{CO}_3^{2-}+\text{HCO}_3^{-}}^{eq}/\text{HCO}_3^{-}} \tag{57}
\]

From this set of equations it is possible to calculate, and display graphically, the kinetic limits \(\alpha_{\text{CO}_3^{2-}/w}^t\) and \(\alpha_{\text{HCO}_3^{-}/w}^t\) as a function of temperature and chemical speciation (Fig. 5). The increasing contribution of the hydroxylation reaction and increasing \(\text{CO}_3^{2-}/\text{HCO}_3^{-}\) ratio with increasing pH (Fig. 5A) make \(\alpha_{\text{CO}_3^{2-}/w}^t\) and \(\alpha_{\text{HCO}_3^{-}/w}^t\) highly sensitive to changes in solution pH (Fig. 5B). Overall, both \(\alpha_{\text{CO}_3^{2-}/w}^t\) and \(\alpha_{\text{HCO}_3^{-}/w}^t\) decrease with increasing pH, although minimum values are attained when the hydroxylation/hydration reaction rate ratio is near the maximum value but the \(\text{CO}_3^{2-}/\text{HCO}_3^{-}\) ratio is low (vertical line in Fig. 5A and 5B). For a solution at 25°C and salinity of 2.5, both \(\alpha_{\text{CO}_3^{2-}/w}^t\) and \(\alpha_{\text{HCO}_3^{-}/w}^t\) reach minimum values at pH ~ 9.6 (Fig. 5B). Since in our model \(\text{CO}_3^{2-}\) is the only precipitating DIC species, the kinetic limit of \(\alpha_{c/w}\) is always ~ 0.5‰ lower than \(\alpha_{\text{CO}_3^{2-}/w}^t\) (see Section 4.2.4). At high pH, the \(\alpha_{\text{CO}_3^{2-}/w}^t\) and \(\alpha_{\text{HCO}_3^{-}/w}^t\) values and the kinetic limit of \(\alpha_{c/w}\) depend on the \(^{18}k_{+d}/^{18}k_{+e}\) ratio, which is constrained by experimental data in Section 5.3.
5. Data-model comparison

5.1. Experimental data

We used the temperatures, pH, salinities, [DIC], [Ca$^{2+}$], calcite growth rates and carbonic anhydrase activities from the calcite growth experiments of Dietzel et al. (2009) and Baker (2015) to calculate model calcite-H$_2$O fractionation factors for comparison to measured calcite-H$_2$O fractionation factors. In both Dietzel and Baker experiments, the source of DIC was gaseous CO$_2$ and the solution pH was maintained constant while calcite was precipitated at various temperature, pH and Ω. In the experiments of Dietzel et al. (2009), CO$_2$(g) diffused passively across a membrane from an inner solution to the precipitating solution. In the experiments of Baker (2015), CO$_2$(g) was bubbled directly into the precipitating solution. The δ$^{18}$O of the incoming CO$_2$(g) ranged from 28.6 to 30.1‰ (VSMOW) for the experiments of Baker (2015) but it was not reported by Dietzel et al. (2009). However, for the experiments of Dietzel et al. (2009), we assumed that CO$_2$(aq) entered the precipitating solution at isotopic equilibrium with water since the CO$_2$(g) originated from an external solution rather than a gas tank.

Monitoring of the DIC concentration during the experiments of Baker (2015) suggests (near) steady state conditions during calcite precipitation. In the experiments of Dietzel et al. (2009), the DIC concentration was only measured at the onset of calcite precipitation. For our data-model comparison, we assumed that in each of Dietzel’s experiments, calcite precipitated under steady state conditions and the DIC concentration decreased in a similar manner as in the experiments of Baker (2015). We therefore base our calculations on an average [DIC] concentration of $2/3 \pm 1/3$ of the initial [DIC] reported by Dietzel et al. (2009) (i.e. 33 to 100% of the reported maximum [DIC]).

Calculated isotopic equilibration levels between DIC and water ($E_{DIC}$; Eq. 39, Table 3 and Fig. 6A) indicate that calcite was precipitated from an isotopically equilibrated DIC pool ($E_{DIC} > 0.99$) in all of Baker’s experiments (due to the presence of the enzyme carbonic anhydrase in solution), and in at least 15 of the 40 experiments conducted by Dietzel et al. (2009). The remaining 25 experiments of Dietzel et al. (2009) display a wide range of $E_{DIC}$ values from 0.01 to 0.99. The range of calculated $E_{DIC}$ is due to the differences in pH, [DIC] and calcite growth rate among the experiments (Table 3). A plot of $\alpha_{c/w}$ versus temperature (Fig. 6B) for the experimental data of Dietzel et al. (2009) and Baker (2015) confirms that most of the scatter in $\alpha_{c/w}$ values reported by Dietzel et al. (2009) arises from non-equilibrated DIC pool ($E_{DIC} \leq 0.99$). On the other hand, the data of Dietzel et al. (2009) and Baker (2015) are in good agreement when considering $\alpha_{c/w}$ from experiments with $E_{DIC} > 0.99$ (Fig. 6B). Importantly, the average temperature sensitivity of $\alpha_{c/w}$ between 5 and 40°C obtained using Dietzel’s and Baker’s data with $E_{DIC} > 0.99$ is equal to $-0.21 \pm 0.01$‰/°C, which is within error of the
temperature sensitivity of $\alpha_{CO_3^{2-}/w}$ ($-0.22 \pm 0.01\%/{ }^\circ C$, Beck et al., 2005) and slightly lower than the temperature sensitivity reported by Kim and O’Neil (1997) for $\alpha_{c/w}$ ($-0.25\%/{ }^\circ C$). The potential reasons for the lower temperature sensitivity of $\alpha_{c/w}$ reported here relative to that obtained from the widely used relation of Kim and O’Neil (1997) are explored in Section 7.

In the following sections, the equilibrium $\alpha_{CO_3^{2-}/w}$ values (Beck et al., 2005) and the measured $\alpha_{c/w}$ values of Dietzel and Baker for the experiments where $E_{DIC} > 0.99$ are used to infer $\alpha_{c/CO_3^{2-}}$ values for those experiments, and to fine-tune the model parameter $n_2$. The quantification of these parameters then allows us to investigate and quantify KIE between CO$_3^{2-}$ and H$_2$O for experiments where $E_{DIC} \leq 0.99$.

5.2. Calcite precipitated from isotopically equilibrated DIC

Where calcite precipitates from an isotopically equilibrated DIC pool, $\alpha_{c/w}$ is independent of the DIC source(s) because H$_2$O is by far the dominant oxygen-bearing species and the $^{18}$O/$^{16}$O of the DIC species reflect the known fractionations between DIC species and water (Table 1, Beck et al., 2005). Thus, the only model unknown is the fractionation between calcite and CO$_3^{2-}$ ($\alpha_{c/CO_3^{2-}}$), which can be inferred from a measured $\alpha_{c/w}$ value and the known $\alpha_{CO_3^{2-}/w}^{eq}$ value (see Eq. 6). Calculated $\alpha_{c/CO_3^{2-}}$ values for experimental conditions where $E_{DIC} > 0.99$ vary from 1.0028 to 1.0049 (Fig. 7A, ‘measured’ $e^{18}$O$_{c/CO_3^{2-}}$) and appear independent of temperature and experimental setup. Importantly, the $\alpha_{c/CO_3^{2-}}$ values are negatively correlated with the calcite saturation state ($r^2 = 0.34$, p-value = 0.003) and are closer to the $\alpha_{c/CO_3^{2-}}$ equilibrium limit ($\alpha_{c/CO_3^{2-}}^{eq} = 1.0054$) than the $\alpha_{c/CO_3^{2-}}$ kinetic limit ($\alpha_{c/CO_3^{2-}}^+ = 0.9995$). The lack of a significant temperature effect on $\alpha_{c/CO_3^{2-}}$ (Fig. 7A) implies that the $\alpha_{c/CO_3^{2-}}^+$ and $\alpha_{c/CO_3^{2-}}^+$ limits are also independent of temperature and can thus be considered as constants. This is an important finding as it implies that the temperature sensitivity of calcite $^{18}$O/$^{16}$O originates from the effect of temperature on the $^{18}$O/$^{16}$O of CO$_3^{2-}$. Using the known temperature sensitivity of $\alpha_{CO_3^{2-}/w}^{eq}$ and constant values for $\alpha_{c/CO_3^{2-}}^{eq}$ and $\alpha_{c/CO_3^{2-}}^+$ (Table 1 and Table 2), the $\alpha_{c/w}^{eq}$ and $\alpha_{c/w}^+$ can be expressed as a function of temperature ($T$ in Kelvin):

$$\alpha_{c/w}^{eq} = \exp(2390 T^{-2} - 0.0027) \cdot 1.00542$$

(56)
\[ \alpha_{c/w}^\pm = \exp(2390 T^{-2} - 0.0027) \cdot 0.9995 \quad \text{(for an equilibrated DIC pool only)} \]  

In the model, \( \alpha_{c/w} \) varies between \( \alpha_{c/w}^{eq} \) and \( \alpha_{c/w}^{\pm} \) as a function of \( \Omega \) and the partial reaction order \( n_2 \) (Fig. 3, Section 4.2.2). The parameter \( n_2 \) could not be derived directly from the available data but is estimated using a sensitivity analysis of model-data agreement for \( n_2 \) values varying from 0.1 to 1.0 (Fig. 7B).

Measured and modelled \( \alpha_{c/w} \) values agree best at \( n_2 = 0.22 \pm 0.02 \) (Fig. 7B and 7C, average \( |\Delta^{18}O_{\text{data-model}}| = 0.25\% \), \( r^2 = 0.96 \), p-value < 0.001) for both experimental studies and for all temperatures. The inferred \( n_2 \) value fits in the lower range of \( n_2 \) predicted by Zuddas and Mucci (1998) for a solution with an ionic strength of \( \sim 0.04 \) (Fig. 7B). The sensitivity analysis presented in Figure 7B, and the relatively narrow range in the ‘measured’ \( \alpha_{c/CO_3^2-} \) values, confirms previous suggestions that most of the variations in \( \alpha_{c/w} \) arise from the \(^{18}O/^{16}O \) of the precipitating DIC species (Wang et al., 2013, Watkins et al., 2013, 2014). Understanding how the \( \alpha_{c/w} \) is affected by KIE between DIC and water is therefore critical for interpreting the \( \delta^{18}O \) of calcite precipitated in CO\(_2\)-fed solutions such as in the calcifying fluid of biological calcifiers (McConnaughey, 1989a,b). The following section compares the measured and modelled \( \alpha_{c/w} \) for experimental conditions with various degrees of isotopic disequilibrium between the DIC pool and water.

5.3. Calcite precipitated from isotopically non-equilibrated DIC

Kinetic isotope effects related to the CO\(_2\) hydration and hydroxylation reactions produce anomalously low \( \alpha_{c/w} \) values relative to calcite precipitated from an equilibrated DIC pool (McConnaughey, 1989b, Clark et al., 1992). However, these kinetic effects have not been fully quantified or integrated in a general isotopic model of calcite growth. Our model estimates the fractionation between calcite and CO\(_3^2-\) (Section 5.2), and the only model unknown remaining to quantify DIC-H\(_2\)O kinetic effects is the kinetic isotope fractionation related to the hydroxylation of CO\(_2\) \((^{18}k_{+d} \delta^{16}k_{+d})\). One measured \( \alpha_{c/w} \) value from an experiment at pH 10.5 and 5°C (Fig. 8A, experiment D6 in Table 3; Dietzel et al., 2009) can be used to estimate \( ^{18}k_{+d} \delta^{16}k_{+d} \) directly due to negligible CO\(_2\) hydration at this pH and the very low level of isotopic equilibration between DIC and H\(_2\)O (\( E_{DIC} = 0.01 \)). Our model reproduces the \( \alpha_{c/w} \) of experiment D6 at \( ^{18}k_{+d} \delta^{16}k_{+d} = 0.9958 \) (using \( n_2 = 0.22 \), Section 5.2). A very similar result \((^{18}k_{+d} \delta^{16}k_{+d} = 0.9956 \pm 0.0002)\) is also obtained by conducting a sensitivity analysis of data-model agreement for the entire dataset of Dietzel et al. (2009) (average \( |\Delta^{18}O_{\text{data-model}}| = 0.91\% \), \( r^2 = 0.89 \)). Overall, 40 of the 48 measured \( \alpha_{c/w} \) values are within error of model outputs (Fig. 8, Table 3).
indicating that the model reasonably predicts the oxygen isotope fractionation between CaCO$_3$ and CO$_3^{2-}$ and between CO$_3^{2-}$ and H$_2$O over a wide range of temperature, pH, Ω and DIC residence times.

Despite the overall good data-model agreement, three $\alpha_{c/w}$ values measured by Dietzel et al. (2009) significantly differ from the modelled $\alpha_{c/w}$ values (D1, D38b, D39b in Table 3) and it is conceivable that these differences are not caused by uncertainties in model input parameters. Potential model limitations include the assumptions of CaCO$_3$ precipitation from an infinite DIC pool and negligible CO$_2$ escape from the precipitating solution. Both CaCO$_3$ precipitation from a finite DIC pool and CO$_2$ escape from solution would result in higher $\alpha_{c/w}$ values (Kim et al., 2006; Clark and Lauriol, 1992).

Hence, our model would underestimate $\alpha_{CO_3^{2-}/w}$ if the above assumptions are not valid. New calcite growth experiments in CO$_2$-fed solution without carbonic anhydrase and with a close monitoring of the solution pH, [DIC] and mineral growth rate would help to resolve these issues.

6. Discussion

6.1. Controls on $\alpha_{c/w}$ where DIC is isotopically equilibrated

The oxygen isotope fractionation between calcite and water ($\alpha_{c/w}$) depends on fractionations between the DIC species and water and fractionations between calcite and the DIC species involved in calcite growth (Watkins et al., 2013). In the simplest case where the DIC pool is isotopically equilibrated with water and for a given temperature, the fractionation between each DIC species and water remain constant. In this case, $\alpha_{c/w}$ only depends on surface reaction-controlled kinetics between calcite and the precipitating DIC species (DePaolo, 2011; Watkins et al., 2013, 2014). Measured $\alpha_{c/w}$ values for experimental conditions where calcite precipitated from an isotopically equilibrated pool show temperature-independent variations of more than 1.0 ‰ (Fig. 7A), suggesting that one or more parameter, other than temperature, affects fractionation at the mineral/water interface.

There are competing hypotheses to explain the variability of $\alpha_{c/w}$ under these conditions: (1) $\alpha_{c/w}$ decreases as pH increases due to a shift from HCO$_3^-$ to CO$_3^{2-}$ as the dominant adsorbed ions onto the growing calcite surface (Watkins et al., 2014), (2) $\alpha_{c/w}$ is shifted towards lower values due to a competition between calcite surface growth rate and diffusive processes in the inner crystal region (Watson, 2004), and (3) $\alpha_{c/w}$ is shifted towards lower values due to an increase in calcite precipitation rate relative to calcite dissolution rate with increasing Ω (this study). These hypotheses can be tested against the experimental data of Dietzel et al. (2009) and Baker (2015) since the solution pH, DIC speciation, Ω and the net calcite growth rate are reasonably well constrained, and because it
is possible to identify those experiments for which the DIC pool was isotopically equilibrated (Fig. 6, Table 3).

In the study of Baker (2015), $\alpha_{c/w}$ decreases by ~0.7‰ between pH 7.5 and 9.3 (Fig. 9A). This pH dependence is less pronounced than the previously reported value of ~1.6‰ between pH 7.7 and 9.3 (Watkins et al., 2014). Although the Watkins et al. (2014) model can reproduce either of these pH dependencies by ascribing the $\alpha_{c/w}$ variations to an increasing contribution of $\text{HCO}_3^-$ with decreasing pH (Fig. 9A and 9B), the model cannot reproduce the results of Dietzel et al. (2009), which exhibit $\alpha_{c/w}$ variations of 1.5‰ at the single pH value of 8.3 (Fig. 9A). Moreover, the Watkins et al. (2014) model uses the value of $\alpha_{\text{eq}_{\text{CO}_3^2-}/w}=1.0268$ (at 25°C) from Wang et al. (2013), which is significantly higher than the $\alpha_{\text{eq}_{\text{CO}_3^2-}/w}$ value of 1.0245 (at 25°C) from Beck et al. (2005). Using the latter value with the Watkins et al. (2014) model results in a significant overestimation of the pH dependence of $\alpha_{c/w}$.

It is possible that $\text{HCO}_3^-$ does not contribute as directly to the oxygen isotope budget of calcite (via attachment followed by deprotonation) as indicated by the ion-by-ion model of Watkins et al. (2014). This conclusion is supported by inorganic aragonite precipitation experiments, which show no significant pH effect on the oxygen isotope fractionation between rapidly precipitated aragonite and water (Kim et al., 2006). Based on these considerations, our current thinking is that $\text{CO}_3^{2-}$ is the main contributing DIC species to calcite and aragonite growth, even at pH values where $\text{HCO}_3^-$ is by far the dominant species in solution.

In the model of Watson (2004), the level of isotopic equilibration is determined by a competition between calcite growth rate and diffusive processes on the solid side of the solid-fluid interface. The prediction is that $\alpha_{c/w}$ should decrease systematically with increasing net calcite growth rate, yet we observe no apparent relationship for growth rates varying from 0.05 to 1.05 µmol/m²/s (Fig. 9C). The Watson (2004) model does not make predictions regarding solution ionic strength and does not account for isotopic effects arising on the aqueous side of the solid-fluid interface, such as mass-dependent ion desolvation rates, that are likely significant (Hofmann et al., 2012; Watkins et al., 2017).

In the model presented in this study, $\text{CO}_3^{2-}$ is the only precipitating DIC species and the fractionation between calcite and $\text{CO}_3^{2-}$ ($\alpha_{c/\text{CO}_3^{2-}}$) is determined by the $r_s/r_x$, ratio, which in turn is a function of the solution $\Omega$ and ionic strength through the partial reaction order $n_2$ (Section 4.2). This model therefore predicts that $\alpha_{c/w}$ should decrease with increasing $\Omega$ where calcite precipitates from an isotopically equilibrated DIC pool. Measured $\alpha_{c/w}$ values appear inversely related to $\Omega$ (Fig. 7A and 9D), although the uncertainties in $\Omega$ are relatively large. A more systematic relationship may emerge with
additional experiments in which calcite is grown in solutions near chemical equilibrium and in solutions that are highly supersaturated. Importantly, if $\text{CO}_3^{2-}$ is the only precipitating DIC species, $\alpha_{c/w}$ should be insensitive to pH when $\Omega$ is constant. The systematic pH dependence on $\alpha_{c/w}$ observed in previous studies (Watkins et al., 2014; Baker, 2015) may in fact be due to a systematic increase in $\Omega$ with increasing pH in those experiments (Table 3). Another expectation from the model is that increasing ionic strength should push the system towards the kinetic limit (Eq. 16) and lead to larger $\text{CaCO}_3$-$\text{CO}_3^{2-}$ fractionations. This hypothesis can be tested with experiments at constant $\Omega$ but variable ionic strength.

6.2. Controls on $\alpha_{c/w}$ where DIC is isotopically non-equilibrated

Measured $\alpha_{c/w}$ values for slowly and rapidly precipitated calcite in the absence of carbonic anhydrase decrease by as much 19‰ where the solution pH increases from ~8.5 to 10.0 (Fig. 8A, Dietzel et al., 2009). This decrease in $\alpha_{c/w}$ cannot be attributed to a change in the contribution of DIC species to calcite growth since DIC speciation does not significantly affect $\alpha_{c/w}$ when the DIC is isotopically equilibrated (Section 6.1). The strong pH dependence of $\alpha_{c/w}$ is therefore related to disequilibrium isotope effects between $\text{CO}_3^{2-}$ and water that are related to the hydration and hydroxylation of $\text{CO}_2$ (McConnaughey, 1989b; Usdowski and Hoefs, 1990; Clark et al., 1992; Dietzel et al., 1992). In this case, $\text{CO}_3^{2-}$ (partially) inherits the $^{18}\text{O}/^{16}\text{O}$ of $\text{CO}_2$, $\text{H}_2\text{O}$ and OH$^-$ and the fractionation between $\text{CO}_3^{2-}$ and water ($\alpha_{\text{CO}_3^{2-}/w}$) decreases with pH because (1) the rate of isotopic exchange between the DIC species and water decreases with increasing pH, and (2) the CO$_2$ hydroxylation reaction rate increases with pH, lowering the initial $^{18}\text{O}/^{16}\text{O}$ of HCO$_3^-$ and CO$_3^{2-}$ (Fig. 5) because OH$^-$ has a low $^{18}\text{O}/^{16}\text{O}$ value relative to $\text{H}_2\text{O}$ (~39‰ at 25°C, Green and Taube, 1963). In other words, strong KIE between $\text{CO}_3^{2-}$ and $\text{H}_2\text{O}$ are more likely at high pH, and the KIFF related to the conversion of CO$_2$ to HCO$_3^-$ and CO$_3^{2-}$ increases with pH (Fig. 5 and Fig. 8).

The 19‰ and 11‰ variations in measured $\alpha_{c/w}$ at 5°C and 40°C reported by Dietzel et al. (2009) are explained almost entirely by the variations in the $^{18}\text{O}/^{16}\text{O}$ of the $\text{CO}_3^{2-}$ pool (Fig. 8, grey shaded area), supporting the idea that the fractionation between calcite and $\text{CO}_3^{2-}$ is not significantly affected by the solution temperature and pH. Another notable model result supported by the experimental data is the reduction of the difference between the equilibrium and kinetic limits of $\alpha_{\text{CO}_3^{2-}/w}$ (and $\alpha_{c/w}$) with increasing temperature. This is explained by the decrease of the $\text{CO}_3^{2-}$-water equilibrium fractionation factor ($\alpha_{\text{CO}_3^{2-}/w}^{eq}$) with temperature but a limited temperature sensitivity on the initial $^{18}\text{O}/^{16}\text{O}$ of hydrated and hydroxylated CO$_2$. 


This study focuses on KIE during CO2 hydration and hydroxylation, however opposite KIE (i.e. 18O enrichment of the DIC pool) are known to occur during the reverse reactions of CO2 dehydration and dehydroxylation (Clark and Lauriol, 1992). These latter KIE are likely to affect the 18O/16O of CaCO3 where precipitation follows rapid CO2 degassing such as during the formation of cave calcite (Hendy, 1971). The degassing of CO2 elevates the solution pH, which causes the dehydration of carbonic acid and shifts the DIC speciation towards carbonate ions. Hence, we predict that in addition to the KIE related to the CO2 dehydration/dehydroxylation reactions, HCO3- deprotonation also contributes to the 18O enrichment of the CO32- pool (and CaCO3) during CO2 degassing (see Section 4.2.4).

7. Implications

7.1. The equilibrium limit of \( \alpha_{c/w} \)

For about two decades, the \( \alpha_{c/w} \) versus temperature relationship proposed by Kim and O’Neil (1997) (KO97) was widely used to assess isotopic equilibrium in biogenic calcite (e.g. Bemis et al., 1998; von Grafenstein et al., 1999; Barras et al., 2010; Candelier et al., 2013; Marchitto et al., 2014; Rollion-Bard et al., 2016 and many others). However, in the KO97 experiments calcite precipitation was triggered by CO2 degassing, which can increase the 18O/16O of DIC and CaCO3 (Section 6.2). If the rate of calcite precipitation outpaces the rate of isotopic equilibration between the DIC species and water, then the \( \alpha_{c/w} \) will reflect the isotopic disequilibrium between the DIC and water (Watkins et al., 2013). Interestingly, KO97 reported a 1 to 2‰ increase in \( \alpha_{c/w} \) with increasing Ca2+ and DIC concentration and thus with increasing \( \Omega \). This is the opposite pattern expected for calcite precipitating from an isotopically equilibrated DIC pool (cf. Section 4.2, Fig. 7A). We postulate that the positive relationship between \( \alpha_{c/w} \) and \( \Omega \) reported by KO97 is due to a negative correlation between \( \Omega \) and the DIC residence time in solution. The time available for DIC-H2O isotopic equilibration likely decreases with \( \Omega \) because the rate of calcite precipitation commonly increases with the solution \( \Omega \). As a result, KIE between DIC and H2O are likely to increase with \( \Omega \). Another supporting observation for the imprint of DIC-H2O kinetic isotope effects on \( \alpha_{c/w} \) during the KO97 experiments is the reducing effect of \( \Omega \) on \( \alpha_{c/w} \) with increasing temperature (cf. Fig. 6 in Kim et al., 1997). DIC-H2O kinetic isotope effects should decrease with increasing temperature because the isotopic exchange rate between DIC and water increases significantly with temperature. Finally, based on reported Ca2+ and HCO3- concentrations of 5 mM for the less concentrated solution of KO97 and a pH of 7.6 to 8.2, a \( \Omega \) of 7 to 40 is estimated for the precipitating solutions. It is unlikely that isotopic equilibrium between calcite and carbonate ions would have been reached at these high \( \Omega \) values (i.e. calcite precipitated in conditions far from chemical equilibrium). Hence, the \( \alpha_{c/w} \) reported by Kim
and O’Neil (1997) most likely reflects KIE between calcite and CO$_3^{2-}$ and perhaps KIE between CO$_3^{2-}$ and H$_2$O.

Based on theoretical constraints presented in Section 4.2 and Figure 3 (i.e. isotopic equilibrium is approached in solution of low Ω and low ionic strength), we support previous suggestions that the natural inorganic calcite from Devils Hole cave system formed near isotopic equilibrium conditions (Coplen, 2007; Watkins et al., 2013; Kluge et al., 2014). However, the calculated (near) equilibrium value of $\alpha_{c/w}$ at Devils Hole (1.02849 at 33.7°C, Coplen, 2007) remains poorly constrained because of uncertainties in the water temperature (±2.6°C, Kluge et al., 2014), and in the $\delta^{18}$O value at time of calcite growth approximately 4,000 years ago. Moreover, the temperature sensitivity of equilibrium $\alpha_{c/w}$ has yet to be determined accurately, since data from Devils Hole is limited to a single temperature of calcite precipitation. Hence, new experimental determinations of equilibrium $\alpha_{c/w}$, especially at lower temperature (5-20°C), would help resolve discrepancies in equilibrium $\alpha_{c/w}$ estimates. Such experiments should take advantage of the hypotheses presented herein regarding the effect of the solution Ω and ionic strength on the isotopic equilibration between CaCO$_3$ and CO$_3^{2-}$. In summary, until new experimental data become available, the Kim and O’Neil (1997) expression is a useful reference for comparison of oxygen isotope data between studies.

### 7.2. Oxygen isotope “vital effects” in biogenic CaCO$_3$

Deviations in $^{18}$O/$^{16}$O among biogenic CaCO$_3$ (e.g. corals, foraminifers, coccolithophores, ostracods, molluscs, urchins) and inorganic calcite or aragonite precipitated in the same environmental conditions are due to biologically induced modifications of the carbonate chemistry in the calcifying fluid (CF) relative to the external environment (McConnaughey, 1989a, Rollion-Bard et al., 2003, Ziveri et al., 2012, Hermoso et al., 2016). These “vital effects” in $^{18}$O/$^{16}$O ratio vary between taxonomic groups and are thought to originate from (1) kinetic isotope effects related to the contribution of metabolic CO$_2$ to the precipitating DIC pool (McConnaughey, 1989a, Rollion-Bard et al., 2003, Hermoso et al., 2016), and/or (2) a CF with an elevated pH relative to that of the surrounding water (Adkins et al., 2003, Rollion-Bard et al., 2003, Ziveri et al., 2012). Another potential factor contributing to oxygen isotope vital effects is the formation of amorphous calcium carbonate (ACC) and subsequent transformation to a CaCO$_3$ polymorph (Dietzel et al., 2015). We do not consider ACC transformation to carbonate polymorphs in this study due to the absence of published results.

The model presented in this study can be used to test hypothesis (1) and (2) for different groups of organisms, since it integrates kinetic isotope effects arising from the dissolution of CO$_2$ in water coupled with the effect of pH on isotopic fractionations in the CaCO$_3$-DIC-H$_2$O system. Here we
focus on foraminifers and corals because the calcifying fluid pH (pH$_{cf}$) of these organisms has been measured directly with microelectrodes and/or pH sensitive dyes (foraminifers: de Nooijer et al., 2009, Bentov et al., 2009; tropical corals: Al-Horani et al., 2003, Venn et al., 2011, Cai et al., 2016). These studies showed that for both foraminifers and corals, calcification takes place in a closed or semi-closed environment with an elevated pH$_{cf}$ relative to that of seawater and a DIC residence time in the CF that is very short (i.e. seconds to minutes). For foraminifers, the pH$_{cf}$ (seawater scale) is 8.8 ±0.2 (de Nooijer et al., 2009, Bentov et al., 2009) while tropical corals have pH$_{cf}$ values ranging from 8.5 to 9.5 (Al-Horani et al., 2003, Venn et al., 2011, Cai et al., 2016). An elevated pH$_{cf}$ for foraminifers and corals is also supported by δ$^{11}$B measurements of the tests/skeletons of these organisms (foraminifers: Sanyal et al., 1995, 1996, 2001, Foster, 2008, Hönisch et al., 2008, Rae et al., 2011; tropical corals: Allison et al., 2010, 2014, Rollion-Bard et al., 2011, McCulloch et al., 2012) but uncertainties regarding the mode of boron incorporation in CaCO$_3$ limit the accuracy of the δ$^{11}$B pH-proxy (Foster and Rae, 2016). Thus only direct pH$_{cf}$ measurements are considered here. With knowledge of the pH$_{cf}$ values, the remaining unknown model parameters to simulate the $^{18}$O/$^{16}$O of the DIC in the CF (DIC$_{cf}$) of foraminifers and corals are the sources of DIC$_{cf}$ (metabolic CO$_2$ vs DIC from seawater) and the activity of the enzyme carbonic anhydrase in the CF (cf. Uchikawa and Zeebe, 2012). Assuming minimal oxygen isotopic fractionation between CaCO$_3$ and the DIC$_{cf}$ due to the short DIC$_{cf}$ residence time and slow rate of DIC-H$_2$O isotopic equilibration in the high pH calcifying fluid environment (Usdowski et al., 1991, Uchikawa and Zeebe, 2012), $\alpha_{c/w}$ is simulated for CaCO$_3$ precipitating at 25°C in a seawater-like solution (i.e. salinity = 35 g/kg, [DIC] = 2 mmol/kg, [Ca$^{2+}$] = 10 mmol/kg) as a function of pH$_{cf}$ and under the following scenarios:

a) the DIC$_{cf}$ pool is at isotopic equilibrium with water prior to a rapid precipitation of DIC ($E_{DIC} \sim 1$, ‘Zeebe, 1999’ and ‘Akins et al., 2003’ scenarios),

b) the DIC$_{cf}$ pool derives exclusively from dissolved CO$_2$, and a short residence time of DIC$_{cf}$ in solution prevents DIC$_{cf}$-H$_2$O isotopic equilibration ($E_{DIC} \sim 0$, ‘McConnaughey 1989b’ scenario),

c) same as (b) but with a carbonic anhydrase activity in the calcifying fluid within the 5-100 s$^{-1}$ range (i.e. as measured in the tissues of Porites corals, Hopkinson et al., 2015).

Note that scenario (a) leads to the same model results for systems with and without carbonic anhydrase in solution since the equilibrium oxygen isotopic composition of DIC is independent of the presence/absence of carbonic anhydrase (Uchikawa and Zeebe, 2012). It is also important to realize that the small and closed calcifying fluid of foraminifers and corals is not analogous to the open system simulations presented in Section 5 where the DIC residence time in solution is in the order of hours to days (Fig. 6A) and where DIC precipitation is not quantitative. A slow precipitation of CaCO$_3$ in open system conditions leads to a significant isotopic fractionation between CaCO$_3$ and
CO$_3^{2-}$ (and DIC) while a fast and quantitative precipitation of DIC in a closed system results in no isotopic fractionation between CaCO$_3$ and DIC (cf. McCrea, 1950, Beck et al., 2005, Kim et al., 2006, 2014). The ‘closed system and quantitative DIC precipitation’ assumption for the CF of corals and foraminifers does not compromise the physical basis of our inorganic model: namely that CO$_3^{2-}$ is the dominant DIC species contributing to CaCO$_3$ growth. In fact, within a high and regulated pH environment such as in the CF of corals and foraminifers, consumed CO$_3^{2-}$ ions during CaCO$_3$ growth would be constantly replaced by deprotonated HCO$_3^-$ to maintain the chemical equilibrium imposed by the regulated pH environment. Hence, a DIC pool may be quantitatively consumed without a direct contribution of HCO$_3^-$ ions to calcite growth (Fig. 4, Eq. 30). Because DIC-H$_2$O isotopic exchanges are very slow at high pH (Usdowski et al., 1991, Beck et al., 2005, Uchikawa and Zeebe, 2012), the newly formed CO$_3^{2-}$ ions would likely retain the $^{18}$O/$^{16}$O of the HCO$_3^-$ ions and hence the resulting $\delta^{18}$O$_c$ would reflect the $^{18}$O/$^{16}$O of the DIC in solution (Kim et al., 2006, Fig. 4). In other words, HCO$_3^-$ ions contribute to the $^{18}$O/$^{16}$O of a precipitating carbonate mineral where these ions deprotonate in solution (e.g. due to an increase in solution pH) and the newly formed CO$_3^{2-}$ ions are incorporated into CaCO$_3$ before reaching isotopic equilibrium with H$_2$O. Finally, since we assume that biogenic CaCO$_3$ reflects the $^{18}$O/$^{16}$O of DIC in the calcifying fluid, modelling outputs are independent of the CaCO$_3$ mineral (e.g. calcite vs aragonite).

A comparison of model outputs with biogenic oxygen isotope data (Fig. 10A) shows that scenario (a) agrees with the $\alpha_{c/w}$ of the planktic foraminifers Orbulina universa and Globigerina bulloides ($\varepsilon_{c/w}$ = 28.7‰ at 25°C, calculated from Bemis et al., 1998) and the benthic foraminifer Cibicidoides ($\varepsilon_{c/w}$ = 28.9‰ at 25°C, calculated from Marchitto et al., 2014) at the measured pH$_{c}$ value of 8.8 ±0.2 (de Nooijer et al., 2009, Bentov et al., 2009). Note that the $\alpha_{c/w}$ of planktic and benthic foraminifers cannot be explained by a quantitative precipitation of external seawater DIC (‘Zeebe, 1999’ model or scenario (a) at pH 8.1±1) or by either scenarios (b) or (c). If the $\delta^{18}$O of foraminifers reflects the $^{18}$O/$^{16}$O of an internal DIC pool that is isotopically equilibrated (scenario (a) at pH$_{c}$ ~ 8.8), then any changes in the pH$_{c}$ should affect the foraminifer $\delta^{18}$O value. The $^{18}$O/$^{16}$O of planktic foraminifers decreases with increasing seawater pH (Spero et al., 1997), which together with our model results suggests that the internal calcifying fluid of planktic foraminifers is dependent on the external seawater pH. Another important point is that the reasonable agreement in $\alpha_{c/w}$ values between foraminiferal calcite and the inorganic calcite from the Kim and O’Neil (1997) experiments (KO97, light blue line in Fig. 10) could be coincidental since the $\alpha_{c/w}$ expected from the KO97 equation is very similar to the DIC-H$_2$O fractionation factor ($\alpha_{DIC/w}$) at pH ~ 8.8 and salinity 35.

The low $\alpha_{c/w}$ of coral aragonite ($\varepsilon_{c/w}$ = 25.4 to 27.1‰ at 25°C, for Porites, calculated from Felis et al., 2003, 2004, Suzuki et al., 2005 and Omata et al., 2008) compared to that of foraminiferal calcite
can be explained by scenario (a) at a pH of ~ 9.5, a combination of scenario (a) and (b) (i.e. partially equilibrated DIC) or by scenario (c). Since carbonic anhydrase is thought to be present in the coral calcifying fluid (Tambutte et al., 2007, Bertucci et al., 2013, Hopkinson et al, 2015), scenario (a) and (c) may be the most realistic scenarios for corals. Scenario (a) and (c) are further tested against coral data in Section 7.3.

7.3. The temperature sensitivity of $\delta^{18}O_c$

The temperature dependence of $\delta^{18}O_c$ (and $\alpha_{c/w}$) for slowly precipitated inorganic calcite and aragonite averages $-0.22 \pm 0.02‰/°C$ between 0 and 30°C (O'Neil et al., 1969; Kim and O'Neil, 1997; Kim et al., 2007; Watkins et al., 2013; this study). There are suggestions that that the temperature dependence of $\delta^{18}O_c$ is caused by the effect of temperature on the $^{18}O/^{16}O$ of $CO_3^{2-}$ and $HCO_3^{-}$, based on the similar temperature sensitivities of $\alpha_{c/w}$, $\alpha_{CO_3^{2-}/w}$ and $\alpha_{HCO_3^{-}/w}$ (Wang et al., 2013). Our investigation of the calcite-$CO_3^{2-}$ oxygen isotope fractionation ($\alpha_{c/CO_3^{2-}}$; Fig. 7) shows for the first time that $\alpha_{c/CO_3^{2-}}$ is not significantly affected by temperature, implying that the temperature dependence of $\alpha_{c/w}$ originates from the $CO_3^{2-}$-$H_2O$ fractionation step rather than the calcite-$CO_3^{2-}$ fractionation step. An important implication of our result is that the temperature dependence of $\alpha_{CO_3^{2-}/w}$ and $\alpha_{c/w}$ should deviate from $-0.21 \pm 0.02‰/°C$ when the precipitating $CO_3^{2-}$ ions are not isotopically equilibrated with water. On the other hand, isotopic disequilibrium effects between calcite and $CO_3^{2-}$ should have limited impact on the temperature sensitivity of $\alpha_{c/w}$. This explains why the $\delta^{18}O$ from many biogenic carbonates (e.g. foraminifers, ostracods, coccolithophores) display similar temperature sensitivities despite the carbonates forming in conditions far from isotopic equilibrium (e.g. Xia et al., 1997; Bemis et al. 1998; Chivas et al., 2002; Barras et al., 2010; Candelier et al., 2013; Marchitto et al., 2014).

Figure 10B shows modelled average temperature sensitivities for $\delta^{18}O_c$ between 0 and 30°C as a function of pH for calcite precipitating in seawater under the three scenarios described in Section 7.2 (scenario (a): DIC is isotopically equilibrated; scenario (b): DIC derives from CO2 and is not isotopically equilibrated; scenario (c): same as (b) but with carbonic anhydrase in solution). Under scenario (a), the temperature sensitivity of $\delta^{18}O_c$ is $-0.21 \pm 0.01‰/°C$ and is not significantly dependant on pH because the equilibrium $\epsilon_{CO_3^{2-}/w}$ and $\epsilon_{HCO_3^{-}/w}$ values are similar ($-0.20‰/°C$ and $-0.22‰/°C$ respectively, Beck et al., 2005). The good agreement between scenario (a) and foraminiferal data further support the notion that foraminifers precipitate calcite from an isotopically equilibrated DIC pool. Hence, the $\delta^{18}O$-thermometer should work well with foraminiferal calcite as
long as the carbonate chemistry of the CF remained similar between specimens from the same species.

Under scenario (b) and (c), the temperature dependences of $\delta^{18}\text{O}$ are lower than for scenario (a) due to the isotopic imprint from the contributions of oxygen atoms from $\text{H}_2\text{O}$ and $\text{OH}^-$ during the CO$_2$ hydration and hydroxylation reactions (pathway 31 and 32, Section 4.3.3). In both scenarios (b) and (c), $\delta^{18}\text{O}$ becomes less sensitive to temperature at high $\text{pH}$ values because of the increasing contribution of oxygen atoms from $\text{OH}^-$ to the initial isotopic composition of the DIC. As opposed to the $^{18}\text{O}/^{16}\text{O}$ of CO$_2$, HCO$_3^-$ and CO$_3^{2-}$, the $^{18}\text{O}/^{16}\text{O}$ of OH$^-$ ions increases with increasing temperature (Green and Taube, 1963), leading to an overall reduced temperature effect on the initial $^{18}\text{O}/^{16}\text{O}$ of DIC derived from hydroxylated CO$_2$. Interestingly, scenario (b) and (c) may explain why the temperature sensitivity of Porites $\delta^{18}\text{O}$ ($-0.11\%$/°C to $-0.22\%$/°C; Gagan et al., 2012) is lower and more variable than for foraminiferal calcite ($-0.21 \pm 0.1\%$/°C, Bemis et al., 1998; Marchitto et al., 2014). Combining the model results from Figure 10A and 10B suggests that the coral data is best explained by scenario (c). Hence, it is postulated that the hydration of metabolic CO$_2$ in the coral calcifying fluid is the dominant mechanism causing the anomalously low coral $\delta^{18}\text{O}$ values and reduced coral $\delta^{18}\text{O}$-temperature sensitivity compared to that of other marine calcifiers.

Overall, the model results suggest that inorganic processes are sufficient to explain oxygen isotope “vital effects” in foraminifers while the catalytic effect of carbonic anhydrase on CO$_2$ hydration is a likely explanation for vital effects in coral $\delta^{18}\text{O}$.

8. Conclusions

We presented a new model for the oxygen isotope fractionation between CaCO$_3$ and water ($\alpha_{c/w}$) that includes kinetic isotope fractionations between CaCO$_3$ and CO$_3^{2-}$ ions ($\alpha_{c/CO_3^{2-}}$) and between CO$_3^{2-}$ ions and water ($\alpha_{CO_3^{2-}/w}$). In the model, CO$_3^{2-}$ is the only precipitating DIC species while the other DIC species affect $\alpha_{c/w}$ via conversion to CO$_3^{2-}$ shortly before or during CaCO$_3$ precipitation. The level of isotopic equilibration between CaCO$_3$ and CO$_3^{2-}$ ions is expressed as a function of the solution $\Omega$ and ionic strength through the partial reaction order for CO$_3^{2-}$ (Zhong and Mucci, 1993), while kinetic isotope fractionations between CO$_3^{2-}$ and H$_2$O are calculated from the kinetics of CO$_2$ hydration and hydroxylation in water (Usdowski et al., 1991, Uchikawa and Zeebe, 2012). A comparison of modelled and measured $\alpha_{c/w}$ values leads to the following conclusions:

1. In solutions with low ionic strength ($I < 0.05$) and low CO$_3^{2-}$/Ca$^{2+}$ activity ratio, $\alpha_{c/CO_3^{2-}}$ decreases from $-1.0054$ to $-1.0030$ ($-2.4\%$ decrease in $^{18}\text{O}/^{16}\text{O}$) where the solution $\Omega$ increases from below...
~1.6 to ~12. These results indicate that oxygen isotope equilibration between CaCO$_3$ and the CO$_3^{2-}$ pool is enhanced in solutions with low $\Omega$ and ionic strength such as the conditions of inorganic calcite formation within the Devils Hole cave system. In contrast, calcite or aragonite secreted by marine calcifiers is likely to form in conditions far from isotopic equilibrium because of high $\Omega$ and ionic strength in the organism’s calcifying fluid.

2. The pH and mineral growth rate sensitivities of $\alpha_{c/w}$ depend on the level of isotopic equilibration between the precipitating CO$_3^{2-}$ pool and water. When the precipitating CO$_3^{2-}$ pool approaches isotopic equilibrium with water, small negative pH and/or growth effects on $\alpha_{c/w}$ occur because these parameters are positively correlated with $\Omega$. This suggests that a pH dependence of $\alpha_{c/w}$ can arise even without any contribution of HCO$_3^-$ ions to calcite growth. On the other hand, disequilibrium effects between CO$_3^{2-}$ and H$_2$O can lead to strong positive or negative pH effects on $\alpha_{c/w}$ depending on the chemical pathways antecedent to the production of CO$_3^{2-}$ (e.g. CO$_2$ (de)hydration and (de)hydroxylation, HCO$_3^-$ deprotonation).

3. Highly variable $\alpha_{c/w}$ values occur where the carbonate ion pool derives from gaseous CO$_2$ and the residence time of the DIC pool in solution is significantly shorter than the time required to reach DIC-H$_2$O isotopic equilibrium. These conditions make $\alpha_{c/w}$ sensitive to the $^{16}$O/$^{18}$O of the CO$_2$ source and favour a strong negative correlation between $\alpha_{c/w}$ and pH due to the increasing contribution of oxygen atoms from OH$^-$( $^{18}$O/$^{16}$O = ~39‰ relative to H$_2$O at 25°C) to the precipitating DIC pool with increasing pH (i.e. increasing CO$_2$ hydroxylation rate) and the negative effect of pH on the rate of DIC-H$_2$O isotopic equilibration. Where the DIC derives from dissolved CO$_2$, the combined effect of pH on CaCO$_3$-CO$_3^{2-}$ and CO$_3^{2-}$-H$_2$O fractionation leads to a maximum negative pH effect on $\alpha_{c/w}$ of ~22‰ at 25°C. The effect of pH on $\alpha_{c/w}$ also decreases with increasing temperature.

4. The temperature dependence of $\alpha_{c/w}$ appears to originate from the effect of temperature on the $^{18}$O/$^{16}$O of CO$_3^{2-}$ in solution. This implies that isotopic disequilibrium effects between CaCO$_3$ and CO$_3^{2-}$ should have little influence on the temperature dependence of $\alpha_{c/w}$. On the other hand, the temperature sensitivity of $\alpha_{c/w}$ is expected to deviate from $-0.22 \pm 0.02$‰/°C (Kim and O’Neil, 1997) when the CO$_3^{2-}$ pool does not reach isotopic equilibrium with water prior to CaCO$_3$ precipitation.

5. The $\delta^{18}$O of foraminifers and corals can be explained by rapid and quantitative precipitation of internal DIC pools hosted in high-pH fluids. For planktic and benthic foraminifers, model results suggest that the DIC of the calcifying fluid is isotopically equilibrated at pH ~ 8.8 prior to calcite precipitation. In contrast, coral $\delta^{18}$O data is best explained by the precipitation of internal DIC derived from hydrated CO$_2$ and minimal subsequent DIC-H$_2$O isotopic equilibration. These models also show
that the reduced and variable δ¹⁸O-temperature sensitivity of *Porites* coral aragonite (−0.11 to −0.22‰°C) relative to that of foraminiferal calcite (−0.21 ±0.01‰°C) can be explained by variable kinetic isotope effects associated to CO₂ hydration in the coral calcifying fluid.

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E. Baker, M. Dietzel and J. Tang are thanked for sharing and explaining their valuable datasets. We are grateful to thoughtful input from R. Zeebe and A. Suzuki on early versions of this manuscript. We thank two anonymous reviewers for their valuable comments, which improved the manuscript. LSD was supported by a *University Postgraduate Award* from the University of Wollongong. JMW was supported by University of Oregon startup funds. HVM acknowledges support from Australian Research Council *Discovery Project* grant DP1092945 and from *Future Fellowship* FT140100286.

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Figure 1. Factors controlling the δ\(^{18}\)O of inorganic CaCO\(_3\) precipitated in a CO\(_2\)-fed solution. Model input parameters (light coloured boxes) are used to calculate a set of output parameters (full coloured boxes) upon which the δ\(^{18}\)O of inorganic CaCO\(_3\) depends. The arrows indicate the cause and effect relations between the input and output parameters (e.g. Ω is controlled by [Ca\(^{2+}\)], [DIC], DIC speciation, salinity and temperature). Where two arrows cross each other, one appears in grey to aid the reading of the flow chart. The subscripts are: “c”: CaCO\(_3\); “w”: water. The symbols and capital letters are: “\(r_c\)”: CaCO\(_3\) precipitation rate (mol/s); “V”: volume of precipitating solution (L); “CA”: carbonic anhydrase activity (s\(^{-1}\)); “[DIC]”: DIC concentration (µmol/kg); “\(I\)”: ionic strength; “[Ca\(^{2+}\]”:\(\) Ca\(^{2+}\) concentration (µmol/kg); “\(h_+4/h_+2\)”: CO\(_2\) hydroxylation to hydration reaction rate ratio; “\(E_{DIC}\)”: isotopic equilibration level between DIC and water (0 to 1); “Ω”: calcite or aragonite saturation state (> 1); “\(n_2\)”: partial reaction order with respect to the solution CO\(_3\)\(^2-\) concentration; \(\{18\}R\): \(\{18\}/16\)O ratio; \(\alpha\): oxygen isotope fractionation factor; “\(T\)”: temperature (°C or K); “\(E_c\)”: level of isotopic equilibration between CaCO\(_3\) and CO\(_3\)\(^2-\) (0 to 1). Where \(E_{DIC} = 1\), \(\alpha_{\text{CO}_3^2-/w}\) only depends on temperature and \(\alpha_{c/w}\) only depends on temperaure and \(E_c\). Where \(E_{DIC} < 1\), \(\alpha_{\text{CO}_3^2-/w}\) and \(\alpha_{c/w}\) also depend on the δ\(^{18}\)O of the DIC source, \(E_{DIC}\), pH and DIC speciation.

Figure 2. The effect of temperature and ionic strength on the partial reaction order \(n_2\) for calcite precipitating in seawater and simple NaCl-CaCl\(_2\) solutions. (A) Temperature dependence of \(n_2\), data from Lopez et al. (2009) and Zuddas and Mucci (1998). (B) Ionic strength dependence of \(n_2\), data from Zuddas and Mucci (1998). An \(n_2\) value of 0.22 ±0.02 was estimated for the experimental conditions of Baker (2015) (orange diamond, ionic strength ~ 0.05) and Dietzel et al. (2009) (red diamond, ionic strength ~ 0.03). The parameter \(n_2\) is dependent on the solution temperature and ionic strength, and if these parameters are known, together with the solution Ω, the level of isotopic equilibration between calcite and CO\(_3\)\(^2-\) \(E_c\) can be calculated.

Figure 3. Modelled isotopic equilibrium level \(E_c\) between calcite and CO\(_3\)\(^2-\) \(E_c = r_c/r_{c+};\) Eq. 16) at 25°C as a function of the solution Ω and for different ionic strengths (\(I\)). The lines showing \(E_c\) as a function of \(1/Ω\) were calculated using equations (16) and (21). Dotted lines are extrapolations of equation (21) for \(I < 0.1\). The expectation is that \(E_c\) will approach 1 where calcite precipitates at low Ω and low ionic strength (e.g. Devils Hole calcite, \(I < 0.01\), \(Ω < 1.6\); Coplen, 2007) and will approach 0 where calcite precipitates at high Ω and high ionic strength (e.g. calcite secreted by marine organisms, 0.5 < \(I < 1.0\), \(Ω > 5\); Al-Horani et al., 2003; de Nooijer et al., 2009; Bentov et al., 2009; McCulloch et al., 2012; Cai et al., 2016). The oxygen isotope data of Dietzel et al. (2009) and Baker (2015) most closely match the low ionic strength end-member of the model (orange curve, \(n_2 = 0.22\), see Section 5.2 and Fig. 7). In comparison, \(E_c\) is independent of the ionic strength in the Watkins et al. (2014) model (grey line).
Figure 4. The effect of pH and partial DIC precipitation on the oxygen isotope fractionation between instantaneously precipitated BaCO$_3$ and water ($\varepsilon_{Ba/w}$) at 25°C (data from Kim et al., 2006). (A) Comparison of measured and modelled $\varepsilon_{Ba/w}$ at pH 8.3, 10.1 and 10.7, as a function of the proportion of DIC precipitated. (B) Measured versus modelled $\varepsilon_{Ba/w}$ values ($r^2 = 0.98$, p-value < 0.01). These diagrams show the best agreement between measured and modelled $\varepsilon_{Ba/w}$ obtained with a KIFF between the carbonate mineral and CO$_3^{2-}$ ($^{18}k_{r+}/k_{r}$) of 0.9995 and a CO$_3^{2-}$-HCO$_3^{-}$ KIFF ($^{18}k_{z}/^{16}k_{z}$, HCO$_3^{-}$ deprotonation) of 0.9950. The preferential precipitation of isotopically light CO$_3^{2-}$ ions and the preferential deprotonation of isotopically light HCO$_3^{-}$ make BaCO$_3$ depleted in $^{18}$O relative to the DIC pool where precipitation is instantaneous but not quantitative.

Figure 5. Kinetic isotope fractionation in the CaCO$_3$-DIC-H$_2$O system during the hydration and hydroxylation of CO$_2$. (A) DIC speciation (solid lines) and relative importance of the hydroxylation vs hydration reaction (dash line) as a function of pH for T = 25°C and $J = 0.05$. (B) Initial oxygen isotope fractionation (kinetic limit) relative to water for CO$_3^{2-}$, HCO$_3^{-}$ and CaCO$_3$ following the hydration and hydroxylation of CO$_2$ in the solution defined in (A). In (B), the CO$_3^{2-}$ (red) and HCO$_3^{-}$ (light blue) lines were constructed with an equilibrium fractionation factor between CO$_3^{2-}$ and HCO$_3^{-}$ ($\varepsilon_{CO_3^{2-}/HCO_3^{-}}$) of 0.9932 and a pH-dependent fractionation factor between hydrated/hydroxylated CO$_2$ (i.e., CO$_3^{2-}$ + HCO$_3^{-}$, dashed line) and water varying from 1.0269 to 1.0105. The mass dependent kinetic isotope fractionation during CO$_2$ hydration ($^{18}k_{4+2}/^{16}k_{4+2}$ = 0.9994) is seen in the difference between the “CO$_3^{2-}$ + HCO$_3^{-}$” and “CO$_2$(aq) + H$_2$O” lines at low pH values. For the CO$_2$ hydroxylation reaction, the mass dependent kinetic fractionation ($^{18}k_{4+4}/^{16}k_{4+4}$ = 0.9956) is seen in the difference between the “CO$_3^{2-}$ + HCO$_3^{-}$” and “CO$_2$(aq) +OH” lines at high pH values. Instantaneously precipitated CaCO$_3$ from a small fraction of the CO$_3^{2-}$ pool would be depleted by ~ 0.5 % ($^{18}k_{+e}/^{16}k_{+e}$ = 0.9995) relative to the CO$_3^{2-}$ pool (black continuous line). The fractionations relative to water for CO$_3^{2-}$, HCO$_3^{-}$ and CaCO$_3$ are lowest where the hydroxylation/hydration reaction rate ratio is high but the CO$_3^{2-}$/HCO$_3^{-}$ ratio is low (vertical line in panel A and B). For a CO$_2$-fed solution at 25°C, the kinetic limit of the oxygen isotope fractionation between CaCO$_3$ and water depends on the solution pH and varies from 19.5 to 8.5‰ (i.e. 1.0195 to 1.0085) between pH 7 and 9.6.

Figure 6. Level of isotopic equilibrium between the DIC pool and water ($E_{DIC}$) during the calcite precipitation experiments of Dietzel et al. (2009) and Baker (2015). (A) $E_{DIC}$ calculated as a function of the DIC residence time in solution ($RT_{DIC}$) and the rate of isotopic equilibration between DIC and water expressed as the time constant $\tau$. Data points represent individual precipitation experiment with $E_{DIC}$ ranging from ~ 0.01 (disequilibrium limit) to more than 0.99 (equilibrium limit). (B) Oxygen isotope fractionation ($\varepsilon_{e/w}$) vs temperature for calcite precipitated from an equilibrated ($E_{DIC}$ > 0.99)
and non-equilibrated ($E_{DIC} < 0.99$) DIC pool. For a given temperature, and where the DIC pool is isotopically equilibrated, the $\varepsilon_{c/w}$ are restricted to a narrow range of values that are similar to the $\varepsilon_{c/w}$ expected from the relation of Kim and O’Neil (1997).

**Figure 7.** Measured versus modelled oxygen isotope fractionation between calcite and water for experimental conditions where the DIC pool was isotopically equilibrated. (A) ‘Measured’ and modelled oxygen isotope fractionation between calcite and $CO_3^{2-}$ ($\varepsilon_{c/CO_3^{2-}}$) versus $1/\Omega$ for the experiments of Dietzel et al. (2009) and Baker (2015). ‘Measured’ $\varepsilon_{c/CO_3^{2-}}$ values were inferred from oxygen isotope fractionation between calcite and water and the known oxygen isotope fractionation between isotopically equilibrated $CO_3^{2-}$ and water (Beck et al., 2005). Uncertainties in the calcite saturation ($\Omega$) during each precipitation experiment (error bars) are significantly higher for the experiments of Dietzel et al. (2009) than Baker (2015). A model output using $n_2 = 0.2$ shows $\varepsilon_{c/CO_3^{2-}}$ vs $1/\Omega$ (continuous line) with its uncertainties (dashed lines). Modelled $\varepsilon_{c/CO_3^{2-}}$ values assume an equilibrium limit of $+5.5 \pm 0.2\%$ (calculated from Coplen, 2007 and Kluge, 2014) and a kinetic limit of $-0.5 \pm 0.2\%$ (calculated from Kim et al., 2006). (B) Sensitivity analysis of the model parameter $n_2$ (partial reaction order with respect to $CO_3^{2-}$) showing the best data-model agreement at $n_2 = 0.22 \pm 0.02$ for all experiments and temperatures. This result fits in the lower range of expected $n_2$ value for solutions with an ionic strength of $\sim 0.04$ (Zuddas and Mucci, 1998). (C) Modeled versus measured $\varepsilon_{c/w}$ values using $n_2 = 0.22$. Uncertainties on modelled $\varepsilon_{c/w}$ values (error bars) are primarily due to the uncertainties on the solution $\Omega$ during calcite precipitation. These figures show that where the DIC pool is isotopically equilibrated, the oxygen isotope fractionation between calcite and the $CO_3^{2-}$ pool ($\varepsilon_{c/CO_3^{2-}}$) is independent of temperature. The solution $\Omega$ seems to have a weak negative effect on $\varepsilon_{c/CO_3^{2-}}$, with $\varepsilon_{c/CO_3^{2-}}$ decreasing from $\sim +4.1\%$ to $\sim +2.9\%$ between the 3-12 range in $\Omega$ (i.e. 0.4-0.1 range in $1/\Omega$).

**Figure 8.** Measured versus modelled oxygen isotope fractionation between calcite and water ($\varepsilon_{c/w}$) for all experimental conditions at (A) 5°C, (B) 25°C and (C) 40°C. The experimental data include all the $\varepsilon_{c/w}$ values presented in Figure 7 and additional $\varepsilon_{c/w}$ values from the experiments of Dietzel et al. (2009) where calcite precipitated from non-isotopically equilibrated DIC (cf. Figure 6). Modelled $\varepsilon_{c/w}$ values depend on the oxygen isotope fractionation between $CO_3^{2-}$ and water ($\varepsilon_{CO_3^{2-}/w}$) and the oxygen isotope fractionation between calcite and $CO_3^{2-}$ ($\varepsilon_{c/CO_3^{2-}}$). All modelled $\varepsilon_{c/w}$ were calculated using a partial reaction order $n_2$ value of 0.22 (cf. Figure 7 and Section 5.2). The model assumes that the equilibrium limit of $\varepsilon_{c/w}$ (upper horizontal line) is independent of pH while the kinetic limit of $\varepsilon_{c/w}$ depends on the $CO_2$ hydroxylation to $CO_2$ hydration reaction rate ratio, which depends on pH (lower curved line). At any pH, the difference between the equilibrium and kinetic limit of $\varepsilon_{CO_3^{2-}/w}$
(grey shaded area) and $\varepsilon_{c/w}$ (straight and curves lines) decreases with temperature. (D) Compilation of measured versus modelled $\varepsilon_{c/w}$ values at 5°C, 25°C and 40°C temperatures. A linear regression between modelled and measured $\varepsilon_{c/w}$ values (pink dash line) yields an $r^2$ value of 0.89. In each plot, uncertainties on modelled $\varepsilon_{c/w}$ values (error bars) were calculated as the square root of the sum of square uncertainties from each model input parameter (cf. Appendix A8). The good data-model agreement suggests that kinetic isotope effects between DIC and H$_2$O and between calcite and CO$_3^{2-}$ are well predicted by the model.

**Figure 9.** Measured oxygen isotope fractionation between calcite and water ($\varepsilon_{c/w}$) at 25°C for experimental conditions with isotopically equilibrated DIC (data from Dietzel et al., 2009 and Baker, 2005). (A) $\varepsilon_{c/w}$ vs pH. (B) $\varepsilon_{c/w}$ vs the relative proportion of CO$_3^{2-}$ and HCO$_3^-$ in solution. (C) $\varepsilon_{c/w}$ vs the calcite growth rate (normalized to the calcite surface area). (D) $\varepsilon_{c/w}$ vs calcite saturation state (1/Ω). Also shown for comparison are model outputs form the Watkins et al. (2014) model (panel A and B; computed with $\alpha_{c/CO_3^{2-}}^e = 0.9995$ and $\alpha_{c/HCO_3^-}^e = 0.9967$) and the model presented in this study (panel D; computed with $\alpha_{c/CO_3^{2-}}^e = 0.9995$ and $n_2 = 0.22$). The Watkins et al. (2014) model agrees with measured $\varepsilon_{c/w}$ from Baker (2015) but cannot reproduce the scatter of the Dietzel et al. (2009) data. The model presented in this study potentially explains the measured $\varepsilon_{c/w}$ from both Baker (2015) and Dietzel et al. (2009).

**Figure 10.** Comparison of modelled and measured biogenic CaCO$_3$ oxygen isotope data. (A) Oxygen isotope fractionation between CaCO$_3$ and H$_2$O (expressed in ‰ as $\varepsilon_{c/w}$) at 25°C and as a function of pH$_{SWS}$ (seawater scale). (B) Average temperature sensitivity of CaCO$_3$ $\delta^{18}$O ($\delta^{18}$O$_c$) between 0 and 30°C as a function of pH$_{SWS}$. Model outputs are compared to data from planktic foraminifers *Orbulina universa* and *Globigerina bulloides* (Bemis et al., 1998), benthic foraminifer *Cibicidoides* (Marchitto et al., 2014) and *Porites* corals (panel A: calculated from Felis et al., 2003, 2004, Suzuki et al., 2005, Omata et al., 2008; panel B: Gagan et al., 2012). The calcifying fluid pH$_{SWS}$ is 8.8 ±0.2 for foraminifers (de Nooijer et al., 2009; Bentov et al., 2009) and 9.0 ±0.5 for tropical corals (Al-Horani et al., 2003; Venn et al., 2011; Cai et al., 2016). Simulations were performed assuming a quantitative precipitation of the DIC pool and for different scenarios: (a) CaCO$_3$ precipitates from an isotopically equilibrated DIC pool ($E_{DIC} = 1$), (b) CaCO$_3$ precipitates from a DIC pool that is not isotopically equilibrated ($E_{DIC} = 0$) and all the DIC derives from hydrated and hydroxylated CO$_2$, (c) same as (b) but the enzyme carbonic anhydrase increases the rate of CO$_2$ hydration by a factor of 100 to 2000, as in the tissues of *Porites* corals (Hopkinson et al., 2015). For the simulations (b) and (c), shaded areas include uncertainties in the CO$_2$ hydration/hydroxylation fractionation factors and carbonic anhydrase activity. All simulations were performed with salinity = 35, [Ca$^{2+}$] = 10 mmol/kg and [DIC] = 2 mmol/kg. The $\varepsilon_{c/w}$ and temperature sensitivity of $\delta^{18}$O$_c$ expected from the expression of Kim and
O’Neil (1997) (KO97, light blue line) are shown in panel A and B for comparison. These diagrams suggest that the calcite secreted by planktic and benthic foraminifers formed from a (near) isotopically equilibrated DIC pool, while the aragonite secreted by shallow corals is best explained by the precipitation of non- to partially isotopically equilibrated DIC deriving from hydrated CO$_2$. 
Table 1 Equilibrium fractionation factors used in this study.

<table>
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<tr>
<th>Equilibrium $\alpha$</th>
<th>Equation ($T$ in Kelvin)</th>
<th>$25^\circ$C</th>
<th>Reference</th>
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<td>$\alpha_{\text{CO}_3^{2-}/w}^{eq}$</td>
<td>$\exp(2390 \ T^2 - 0.00270)$</td>
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<td>$\exp(2590 \ T^2 + 0.00189)$</td>
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Table 2 Kinetic isotope fractionation factors used in this study.

<table>
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<td>CaCO₃ - CO₃²⁻</td>
<td>$^{18}k_{+c}/^{16}k_{+c}$</td>
<td>0.9995 ± 0.0002  calculated after Kim et al. (2006)</td>
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<td>CO₃²⁻ - HCO₃⁻</td>
<td>$^{18}k_{-5}/^{16}k_{-5}$</td>
<td>0.9950 ± 0.0002  calculated after Kim et al. (2006)</td>
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<td>HCO₃⁻ - (CO₂ + H₂O)</td>
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<td>0.9994 ± 0.0010  calculated after Zeebe (2014)</td>
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<td>HCO₃⁻ - (CO₂ + OH)</td>
<td>$^{18}k_{+4}/^{16}k_{+4}$</td>
<td>0.9958 ± 0.0003  model parameter</td>
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*For example, a $^{18}k_{+c}/^{16}k_{+c}$ of 0.9995 ± 0.0002 at 25°C indicates that the product (CaCO₃) has a lower $^{18}O/^{16}O$ than the reactant (CO₃²⁻).
Table 3. Model input and output parameters for the calcite growth experiment of Baker (2015) and Dietzel et al. (2009).

<table>
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<th>T (°C)</th>
<th>pH(^{(b)})</th>
<th>[DIC](^{(c)})</th>
<th>[Ca(^{2+})]</th>
<th>(r_c)</th>
<th>[CA]</th>
<th>(\Omega)</th>
<th>(E_{\text{DIC}})</th>
<th>(E_c)(^{(c,d)})</th>
<th>measured (\varepsilon^{18}\text{O} (%o))</th>
<th>(\sigma)</th>
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$^{(b)}$ For the experiment of Dietzel et al. (2009), [DIC] was not monitored during calcite precipitation. It is assumed that the average [DIC] during calcite precipitation was 2/3 ± 1/3 of the measured [DIC] at the onset of calcite precipitation (cf. Section 5.1).

$^{(c)}$ Model output parameters.

$^{(d)}$ Calculated using a partial reaction order $n_2$ of 0.22 (cf. Section 4.2)
### A1. Notation

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<th>Symbol</th>
<th>Definition</th>
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<td>KIE</td>
<td>Kinetic isotope effect</td>
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<td>Kinetic isotope fractionation</td>
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A2. List of chemical reaction considered in this study

\[ \text{Ca}^{2+} + \text{CO}_3^{2-} \xrightleftharpoons[k_{-c}]{k_{+c}} \text{CaCO}_3 \]
\[ \text{CO}_3^{2-} + H^+ \xrightleftharpoons{k_{-5} \ k_{+5}} HCO_3^- \]  
\( \text{(A2)} \)

\[ \text{CO}_2 + H_2O \xrightleftharpoons{k_{-2} \ k_{+2}} H_2\text{CO}_3 \Leftrightarrow HCO_3^- + H^+ \]  
\( \text{(A3)} \)

\[ \text{CO}_2 + OH^- \xrightleftharpoons{k_{-4} \ k_{+4}} HCO_3^- \]  
\( \text{(A4)} \)

**A3. Calcite and aragonite stoichiometric solubility product \( K_{sp}^* \)**

The \( K_{sp}^* \) of calcite and aragonite in seawater was determined by Mucci (1983) as a function of temperature \( (T \text{ in Kelvin}) \) and salinity \( (S \text{ in g/Kg}) \).

**Calcite:**

\[ K_{spc}^* = 10^\left(-171.9065 - 0.077993T + 2839.319/T + 71.595LOG(T) + (-0.77712 + 0.0028426T + 178.34/T)S^{1/2} - 0.07711S + 0.0041249S^{3/2}\right) \]  
\( \text{(A5)} \)

**Aragonite:**

\[ K_{spa}^* = 10^\left(-171.945 - 0.077993T + 2903.293/T + 71.595LOG(T) + (-0.068393 + 0.0017276T + 88.135/T)S^{1/2} - 0.10018S + 0.0059415S^{3/2}\right) \]  
\( \text{(A6)} \)

**A4. Reaction rate constants for CO\(_2\) hydration \( (k_{+2}) \) and hydroxylation \( (k_{+4}) \)**

The rate constant \( k_{+2} \) was determined by Johnson (1982) while \( k_{+4} \) was calculated by Zeebe and Wolf-Gladrow (2001) from the data of Johnson (1982) as a function of temperature \( (T \text{ in Kelvin}) \):  

\[ k_{+2} = \exp(1246.98 - 6.19 \cdot 10^4 T^{-1} - 183 lnT) \]  
\( \text{(A7)} \)

\[ k_{+4} = 4.7 \times 10^7 \cdot \exp(-23200/(8.314T)) \]  
\( \text{(A8)} \)
A5. The time constant $\tau$

The time constant $\tau$ represents the rate of oxygen isotope equilibration between DIC species and $H_2O$. It is a function of the hydration and hydroxylation reaction kinetics (Usdowski et al., 1991, Uchikawa and Zeebe, 2012):

$\tau^{-1} = \frac{1}{2} \cdot [k_{1+2} + k_{4}[OH^-]]$

\[ \cdot \left[ 1 + \frac{[CO_2]}{[DIC] - [CO_2]} - \sqrt{1 + 2 \cdot \frac{[CO_2]}{3[Dic] - [CO_2]} + \left( \frac{[CO_2]}{[Dic] - [CO_2]} \right)^2} \right] \]

(A9)

with

$k_{1+2}^* = k_{+2} + \frac{k_{cat}}{K_M} \cdot [CA]$  \hspace{1cm} (A10)

where $k_{1+2}^*$ and $k_{+4}$ are the forward reaction rate constants for CO$_2$ hydration and hydroxylation, respectively (the superscript * of $k_{1+2}^*$ denote the inclusion of the effect of carbonic anhydrase on the rate of CO$_2$ (de)hydration), $k_{cat}$ is the catalytic rate constant, $K_M$ is the Michaelis–Menten constant and $[CA]$ is the concentration of carbonic anhydrase in solution (Uchikawa and Zeebe, 2012).

A6. The relative abundances of DIC species

The carbonate species are related by the following forward and backward reactions:

$CO_2(g) + H_2O \rightleftharpoons CO_2(aq) + H_2O \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+$  \hspace{1cm} (A11)

The DIC speciation is determined by the solution pH and the stoichiometric dissociation constants of carbonic acid $K_1^*$ and $K_2^*$ (the notation * denote stoichiometric constants), defined as follow:

$K_1^* = \frac{[HCO_3^-][H^+]}{[CO_2(aq)]} \hspace{1cm} pK_1^* = pH + log[CO_2(aq)] - log[HCO_3^-]$  \hspace{1cm} (A12)

$K_2^* = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \hspace{1cm} pK_2^* = pH + log[HCO_3^-] - log[CO_3^{2-}]$  \hspace{1cm} (A13)
Where $pK_1^*$ and $pK_2^*$ are the negative $\log_{10}$ of the first and second dissociation constants of carbonic acid respectively.

Using equations (A12) and (A13), the relative proportion $X$ of the DIC species is expressed as follows:

$$X_{CO_3^-} = \left(10^{(pK_1^* + pK_2^* - 2pH)} + 10^{(pK_2^* - pH) + 1}\right)^{-1}$$  \hspace{1cm} (A14)

$$X_{HCO_3^-} = 10^{pK_2^* - pH} \left(10^{(pK_1^* + pK_2^* - 2pH)} + 10^{(pK_2^* - pH) + 1}\right)^{-1}$$  \hspace{1cm} (A15)

$$X_{CO_2(aq)} = \left(10^{(2pH - pK_1^* + pK_2^*)} + 10^{(pH - pK_1^*) + 1}\right)^{-1}$$  \hspace{1cm} (A16)

The equilibrium constants $pK_1^*$ and $pK_2^*$ were measured by Millero et al. (2006) for salinities varying from 0 to 50 g/kg:

$$pK_1^* = 13.4191S^{0.5} + 0.0331S - 5.33 \times 10^{-5}S^2 - (530.123S^{0.5} + 6.103S)T^{-1} - 2.0695S^{0.5} \ln T + pK_1^0$$  \hspace{1cm} (A17)

$$pK_2^* = 21.0894S^{0.5} + 0.1248S - 3.687 \times 10^{-4}S^2 - (772.483S^{0.5} + 20.051S)T^{-1} - 3.3336S^{0.5} \ln T + pK_2^0$$  \hspace{1cm} (A18)

With $S$ the salinity and $T$ the temperature in Kelvin. The value of $pK_1^0$ and $pK_2^0$ in (A17) and (A18) is obtained from Harned and Davis (1943) and Harned and Scholes (1941):

$$pK_1^0 = 6320.813T^{-1} + 19.568224\ln T - 126.34048$$  \hspace{1cm} (A19)

$$pK_2^0 = 5143.692T^{-1} + 14.613358\ln T - 90.18333$$  \hspace{1cm} (A20)

A7. Stoichiometric ion product of water $K_w^*$

The ion product of water is used to calculate $[OH^-]$ in equation (43) and (44). Its dependence on temperature and salinity was determined by DOE (1994):

$$\ln K_w^* = 148.96502 - 13847.26/T - 23.6521\ln T + (118.67/T - 5.977 + 1.0495\ln T)S^{1/2} - 0.011615S$$  \hspace{1cm} (A21)
A8. Uncertainties of calculated parameters

Lower and upper uncertainties of calculated parameters from multiple variables with associated uncertainties were calculated assuming no correlations between the different variables. Given a parameter $P_i$ that is a function of $n$ variables $x_1, ..., x_n$ we have:

$$P_i = f(x_1, ..., x_n)$$ (A22)

Then the lower uncertainty of $P_i$ is given by:

$$-\sigma_{P_i} = \sqrt{(P_i - f(x_1 - \sigma_{x_1}, ..., x_n))^2 + \cdots + (P_i - f(x_1, ..., x_n - \sigma_{x_n}))^2}$$ (A23)

Where $\sigma_{x_1}, ..., \sigma_{x_n}$ are the lower uncertainties of the $x_1, ..., x_n$ variables if $x_1, ..., x_n$ are positively correlated with $P_i$ or the upper uncertainties of the $x_1, ..., x_n$ variables if $x_1, ..., x_n$ are negatively correlated with $P_i$.

Similarly, the upper uncertainty of $P_i$ is given by:

$$+\sigma_{P_i} = \sqrt{(P_i - f(x_1 + \sigma_{x_1}, ..., x_n))^2 + \cdots + (P_i - f(x_1, ..., x_n + \sigma_{x_n}))^2}$$ (A24)

Where $\sigma_{x_1}, ..., \sigma_{x_n}$ are the upper uncertainties of the $x_1, ..., x_n$ variables if $x_1, ..., x_n$ are positively correlated with $P_i$ or the lower uncertainties of the $x_1, ..., x_n$ variables if $x_1, ..., x_n$ are negatively correlated with $P_i$. 
Figure 2

A
Lopez et al. (2009)
calcite, I = 0.7
$r^2 = 0.98$

\[ n_2 \]

seawater
NaCl-CaCl$_2$
Z & M (1998)

Temperaure (°C)

B
Zuddas and Mucci (1998)
calcite (25°C)
$r^2 = 0.91$

\[ n_2 \]

Z & M (1998)
this study

Ionic strenght

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Figure 4

A

\[ \varepsilon_{\text{Ba/w}} = \varepsilon_{\text{DIC/w}} \]

Kim et al. (2006)

\[ ^{18}\text{O}_{\text{Ba/w}} (\%e) \]

\[ \% \text{DIC precipitated} \]

\[ ^{18}\text{O}_{\text{Ba/w}} (\%e) \]

\[ ^{18}\text{O}_{\text{Ba/w}} (\%e) \]

B

\[ r^2 = 0.98 \]

1:1 line

\[ \text{measured } ^{18}\text{O}_{\text{Ba/w}} (\%e) \]

\[ \text{model } ^{18}\text{O}_{\text{Ba/w}} (\%e) \]

\[ \text{pH 8.3} \]

\[ \text{pH 10.1} \]

\[ \text{pH 10.7} \]
Figure 6

A

\[ \log(\tau) \text{ (s)} \]

\[ \log(RT_{\text{DIC}}) \text{ (s)} \]

\( E_{\text{DIC}} = 0.01 \), 0.10, 0.50, 0.99

- **Dietzel 5°C**
- **Dietzel 25°C**
- **Dietzel 40°C**
- **Baker 25°C**

B

\[ \varepsilon^{18}O_{c/w} (\%) \]

\[ \text{Temperature (°C)} \]

- **Dietzel et al. (2009), } E_{\text{DIC}} < 0.99**
- **Dietzel et al. (2009), } E_{\text{DIC}} > 0.99**
- **Baker (2015), } E_{\text{DIC}} > 0.99**
- **Coplen (2007)**

Kim and O’Neil (1997)

Dietzel-Baker \( E_{\text{DIC}} > 0.99 \)
Figure 7

A: 'measured' $\varepsilon^{18}O_{c/\text{DIC}}$ vs. $1/\Omega$

- Kinetic limit (Kim et al., 2006)
- Equilibrium limit (Coplen, 2007)

B: average $\Delta^{18}O_{data-model}$ (%)

- $n_2$ range predicted by Z&M (1998)

C: model $\varepsilon^{18}O_{c/w}$ vs. measured $\varepsilon^{18}O_{c/w}$ (%)

$E_{\text{DIC}} > 0.99$

Ionic strength = 0.03 to 0.05
Temperaure = 5 to 40°C
$Ca^{2+}/CO_3^{2-} = 300$ to 4000
$n_2 = 0.2$

$R^2 = 0.96$
Figure 10

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A

$\varepsilon^{18}O_{c/w}$ (%)

$25^\circ C$

K097

B

$\delta^{18}O_c/^{18}C$ (%)

Model simulations

(a) $E_{DIC} = 1$
(b) $E_{DIC} = 0$, no CA
(c) $E_{DIC} = 0$, CA

Measured biogenic carbonates

- Planktic foraminifers
- Benthic foraminifers
- Seawater DIC
- Porites corals