2016

Controls on the oxygen isotope ratio of inorganic and biogenic calcium carbonates

Laurent Stéphane John Devriendt

University of Wollongong

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CONTROLS ON THE OXYGEN ISOTOPE RATIO
OF INORGANIC AND BIOGENIC CALCIUM CARBONATES

Laurent Stéphane John Devriendt, MSc

A thesis submitted in fulfilment of
the requirements for the award of the degree

Doctor of Philosophy

from the
University of Wollongong

August 2016
Abstract

The oxygen isotope ratio ($^{18}$O/$^{16}$O) of inorganic and biogenic carbonate minerals is used extensively to reconstruct past temperatures, sea level, ice volume and hydrologic changes. These reconstructions assume that temperature is the dominant controlling factor for the carbonate-water oxygen isotope fractionation ($\alpha_{c/w}$) but there is evidence for temperature-independent variations in $\alpha_{c/w}$. Uncertainties surrounding the reasons for $\alpha_{c/w}$ variations complicate paleoenvironmental reconstructions based on carbonate $^{18}$O/$^{16}$O.

Carbonate-$^{18}$O/$^{16}$O thermometry is based on the principle of equilibrium isotope fractionation but recent work suggests that carbonate-water equilibrium fractionation is the exception in nature rather than the norm. A major advance in understanding oxygen isotopes in carbonates has been to view carbonate-water fractionation as the result of kinetic and/or equilibrium fractionations occurring between water and dissolved inorganic carbon (DIC) species and between the DIC species and carbonate. However, quantifying the intermediate fractionation steps is in its infancy.

This thesis presents a new general model of oxygen isotope fractionations in the CaCO$_3$-DIC-H$_2$O system that quantifies DIC-H$_2$O and CaCO$_3$-DIC fractionation as a function of temperature, pH, salinity, calcite or aragonite saturation state ($\Omega$), DIC residence time in solution and the activity of the enzyme carbonic anhydrase. The model is used with new and previously published oxygen isotope data to explore the cause of $\alpha_{c/w}$ variations for inorganic calcite, ostracod calcite and coral aragonite.

The model assumes that the carbonate ion (CO$_3^{2-}$) is the only oxygen-bearing species directly involved in carbonate precipitation. Thus, the carbonate $^{18}$O/$^{16}$O is thought to reflect the $^{18}$O/$^{16}$O of the CO$_3^{2-}$ ions that participate in CaCO$_3$ nucleation and growth. The bicarbonate ions (HCO$_3^-$) and aqueous carbon dioxide (CO$_2$(aq)) influence the carbonate $^{18}$O/$^{16}$O, where these DIC species are converted into CO$_3^{2-}$ ions shortly before or during carbonate precipitation.

Model results and published data suggest that the inorganic calcite-CO$_3^{2-}$ oxygen isotope fractionation ($\alpha_{c/CO_3}$) is controlled by the solution $\Omega$. For solutions with low ionic strength ($I < 0.05$), the $\alpha_{c/CO_3}$ decreases from $\sim$1.0054 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 suggest that equilibrium $\alpha_{c/CO_3}$ is approached in solutions with low $\Omega$ and ionic strength such as in the cave system of Devil’s Hole, Nevada. The reanalysis of published experimental data with the new model also suggests that $\alpha_{c/CO_3}$ is insensitive to the solution pH and temperature where these parameters do not covary with $\Omega$.

The CO$_3^{2-}$-H$_2$O oxygen isotope fractionation ($\alpha_{CO_3/w}$) deviates from equilibrium values where a change in DIC speciation or an input/output of inorganic carbon with a different $^{18}$O/$^{16}$O than the DIC in solution occurs at a faster rate than the rate of oxygen isotope equilibration between DIC and H$_2$O. Thesis results suggest that CO$_3^{2-}$-H$_2$O disequilibrium fractionation is the main cause of $^{18}$O/$^{16}$O
difference between inorganic and biogenic carbonates precipitated in the same environment. In particular, the high $^{18}\text{O}/^{16}\text{O}$ of ostracods valves relative to inorganic calcite and the low $^{18}\text{O}/^{16}\text{O}$ of corals relative to inorganic aragonite are both explained by the quantitative precipitation of DIC pools that are not isotopically equilibrated with water.

The ~5 to ~6‰ difference in $\alpha_{c/w}$ between ostracod calcite and coralline aragonite formed at the same temperature is explained by different DIC sources used for calcification by these organisms. For ostracods, the DIC originates from the host water and hence ostracod $^{18}\text{O}/^{16}\text{O}$ is highly sensitive to the $^{18}\text{O}/^{16}\text{O}$ of the host water DIC pool (ostracod δ$^{18}$O decreases by ~0.06-0.10‰ per % of [CO$_3$$^2-$]/[DIC]). For corals, the DIC derives from metabolic CO$_2$, leading to a low internal DIC pool $^{18}\text{O}/^{16}\text{O}$. Finally, reported variations in the temperature sensitivity of coral $^{18}\text{O}/^{16}\text{O}$ (0.11 to 0.22‰/°C) are consistent with the effect of a metabolic CO$_2$ source on carbonate $^{18}\text{O}/^{16}\text{O}$.

A strong carbonate ion effect on ostracod $^{18}\text{O}/^{16}\text{O}$ is expected for environments where variations in salinity and/or pH are significant (e.g. closed basins, estuaries). Paleoclimate reconstructions based on ostracod $^{18}\text{O}/^{16}\text{O}$ should therefore assess these potential effects carefully.

For seawater temperature and/or $^{18}\text{O}/^{16}\text{O}$ reconstructions based on shallow corals, it is recommended to target fast growing corals (> 15 mm/yr) to limit variations in mean coral $^{18}\text{O}/^{16}\text{O}$ between different coral colonies. The model predicts that the effect of temperature on coral $^{18}\text{O}/^{16}\text{O}$ may be less variable for corals with low seasonal/interannual variations in coral growth rates.

Overall this thesis reconciles a number of conflicting observations for the $^{18}\text{O}/^{16}\text{O}$ of inorganic carbonate, ostracod calcite and coral aragonite precipitation, and may help explain observations for foraminiferal calcite. A better understanding of oxygen isotope fractionation in these systems will improve proxy system modelling and lead to improved paleoclimate interpretations.
Acknowledgements

I thank my supervisor Helen McGregor for her constant support during the ups and downs of this project. It hasn’t been an easy road and as we say in the language of Molière ‘un long fleuve tranquille, un doctorat n’est pas’. A memorable moment of my PhD was during a field trip at Kiritimati Island, when Helen and I raced to hand saw a submerged coral while the tide was rising. Field work with Helen quickly made me realize that we were not on a tropical island for leisure. Helen’s hard working philosophy; enthusiasm and passion for science have certainly fuelled this PhD project. I am also grateful for the constructive criticism I received, the thorough review of my frenglish writing and for the wise advices that I did not always follow. Thank you Helen for your commitment, I have learnt a lot from you.

Some of the new ideas presented in this thesis greatly benefited from discussions with James Watkins (University of Oregon). The valuable oxygen isotope data from James’ student, Evan Baker, served as a foundation work for this thesis. James’ enthusiasm and scientific inputs certainly brought new light to the project. Allan Chivas (UOW) is thanked for proofreading my thesis chapters and for useful discussions on the oxygen isotope of ostracods, which contributed to some of the findings in this thesis. Exchange of ideas with Stephen Eggins (ANU) and Bärbel Hönisch (Columbia University) also helped to connect the dots during this project.

I wish to thank Mike Gagan, Joan Cowley, Heather Scott-Gagan, Nerilie Abram, and Joe Cali from the Research School of Earth Science (ANU) for showing me what a world-class laboratory is and for the useful training I received in their lab. I have enjoyed and benefited from working with Jian-xin Zaho, Ai Duc Nguyen and Yue-xing Feng from the Radiogenic Isotope Facility (UQ).

Xiangzhong Li (Chinese Academy of Science), Emi Ito (University of Minnesota), Martin Dietzel (Graz University of Technology), and Jianwu Tang (UCLA) are thanked for sharing and/or explaining their useful datasets. “Bear” McPhail (ANU) is thanked for a tutorial on using the PHREEQC software. I was blessed to receive the assistance of Jessica Gaudry during a field trip to Kiritimati Island.

Finally, I want to thank my partner Taran Jenkins and my parents in law Maureen and Jeff Jenkins for their moral support, without which I may not have completed this project.

I dedicate this work to my beloved mother Françoise Vuillet.
Thesis Certification

I, Laurent S. J. Devriendt, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Earth and Environmental Sciences, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. **The thesis has been prepared in journal article compilation style format.**

The document has not been submitted for qualification at any other academic institution.

Laurent S. J. Devriendt

31 August 2016
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Chapter I: INTRODUCTION

Rationale

The use of stable oxygen isotopes to reconstruct environmental and climatic change was founded on the hypothesis that the oxygen isotope ratio ($^{18}\text{O}/^{16}\text{O}$, reported as $\delta^{18}\text{O}$) of carbonates formed in isotopic equilibrium with the parent solution could be used to estimate the temperature and/or $\delta^{18}\text{O}$ of the water in which the minerals formed (Urey, 1947). Subsequently, laboratory experiments with inorganic calcite confirmed Urey’s theoretical predictions (McCrea, 1950) and the analysis of mollusc shells showed no significant difference in $\delta^{18}\text{O}$ with inorganic calcite precipitated in the same conditions (Epstein et al., 1953). Based on these observations, it was assumed that isotopic equilibrium between calcite and water was attained during the McCrea (1950) experiment and the work served as the first benchmark for assessing isotopic equilibrium in biogenic calcite. The $\delta^{18}\text{O}$-temperature relationship for slowly precipitated inorganic calcite was further refined and extended by O’Neil et al. (1969) and Kim and O’Neil (1997), and those studies reinforced the McCrea (1950) finding.

Since the pioneering work of Urey (1947) and McCrea (1950), the principle of equilibrium $\delta^{18}\text{O}$-thermometry has been applied to a wide range of inorganic and biogenic carbonate minerals and led to major advances in the field of paleoclimatology, paleoceanography and tectonics. Notably, cyclic variations in global temperature throughout the Quaternary Period were inferred from the $\delta^{18}\text{O}$ of planktic foraminifers (Emiliani, 1966). Past changes in the Earth’s ice volume and sea level were discovered from the $\delta^{18}\text{O}$ of deep-sea benthic foraminifers (Shackleton, 1967). The benthic foraminifer record also provided the evidence for an orbital control of the Earth’s glacial-interglacial cycles as well as a global chronological framework (Hays et al., 1976). In terrestrial settings, the $\delta^{18}\text{O}$ of carbonates precipitated from groundwater and soils has been used to elucidate temperature variations throughout glacial cycles (Winograd et al., 1992) as well the uplift rate of mountains (Rowley and Currie, 2006). Changes in the geographical position and intensity of global monsoons were inferred from cave calcite $\delta^{18}\text{O}$ (Wang et al., 2001; Cruz et al., 2005). Across shorter timescales, monthly-resolved $\delta^{18}\text{O}$ records from coralline and mollusc aragonite have been used to reconstruct past changes in interannual climatic variability (see Tierney et al. 2015 for a recent synthesis of published works), including the El Niño Southern Oscillation (Cole et al., 1993; Dunbar et al. 1994; Tudhope et al., 2001).

However, it has long been recognised that the $\delta^{18}\text{O}$ of biogenic carbonates can differ from the $\delta^{18}\text{O}$ expected from slowly precipitated inorganic calcite in the same conditions. Early work on benthic foraminifers showed that different species from the same environment had distinct $\delta^{18}\text{O}$ values,
suggesting that some species did not precipitate calcite under isotopic equilibrium conditions (Duplessy et al., 1970). The analysis of 50 coral genera from the same island showed that the δ\(^{18}\)O of coralline aragonite varied with coral species and was depleted by as much as ~ 4 ‰ (i.e. equivalent to a ~ 20°C variation in temperature) relative to the δ\(^{18}\)O of foraminifers living at similar temperatures (Weber and Woodhead, 1970). A common approach used by paleoclimate studies to circumvent these issues has been to target specific calcifying species and assume a time-independent, constant δ\(^{18}\)O offset from inorganic carbonates. Dozens of studies have since calibrated modern biogenic δ\(^{18}\)O with water temperature and δ\(^{18}\)O and have applied these empirical relationships to estimate past temperatures and/or past water δ\(^{18}\)O values. Examples of such calibrations for foraminifers, corals and ostracods are shown on Figure 1 along with results from inorganic calcite and aragonite. As can be seen, there are significant temperature independent variations in δ\(^{18}\)O between inorganic and biogenic CaCO\(_3\), among different taxonomic groups and between specimens from the same species. For example, at the single temperature of 25°C, carbonate δ\(^{18}\)O varies by as much as 5.8‰ (equivalent to a ~ 25-30°C variation in temperature) between ostracod calcite and coral aragonite. The temperature sensitivity of carbonate δ\(^{18}\)O also appears to vary between the different taxonomic groups. Even inorganic calcite and aragonite precipitated under constant conditions display significant variations in δ\(^{18}\)O at the same temperature (cf. Kim and O’Neil, 1997; Kim et al., 2007).

The cause(s) of variable δ\(^{18}\)O among biogenic and inorganic carbonates precipitated at the same water temperature and δ\(^{18}\)O have been investigated by several studies. A decrease in coral δ\(^{18}\)O of up to ~ 3 ‰ with increasing coral extension rates was revealed from the analysis of different sections from a single coral colony (McConnaughey, 1989a). The low δ\(^{18}\)O of corals relative to inorganic carbonates and the growth rate effect on coral δ\(^{18}\)O were first attributed to the contribution of metabolic CO\(_2\) to the precipitating dissolved inorganic carbon (DIC) pool and the incomplete isotopic equilibration between the DIC and water (McConnaughey, 1989b). This model suggests that DIC-H\(_2\)O isotopic equilibrium is promoted by a slow calcification rate, resulting in higher carbonate δ\(^{18}\)O. Conversely, DIC-H\(_2\)O isotopic disequilibrium is facilitated by a fast calcification rate, resulting in in lower carbonate δ\(^{18}\)O. McConnaughey’s model has been widely used or adapted to explain lower coral δ\(^{18}\)O (and δ\(^{13}\)C) relative to the δ\(^{18}\)O expected from slowly precipitated inorganic carbonates (e.g. Cohen and Hart, 1997; Felis et al., 2003; Rollion-Bard et al., 2003; Juillet-Leclerc et al., 2009; Allison and Finch, 2010).

An alternative view to McConnaughey (1989b) hypothesis emerged when experiment results showed lower foraminiferal δ\(^{18}\)O with increasing seawater carbonate ion concentration ([CO\(_3\)\(^{2-}\); Spero et al., 1997). A negative correlation between calcite δ\(^{18}\)O and [CO\(_3\)\(^{2-}\)] was also found for coccoliths and dinoflagellates (Ziveri et al., 2012), suggesting that the ‘carbonate ion effect’ is ubiquitous in planktonic calcifying organisms. The negative dependence of biogenic δ\(^{18}\)O on [CO\(_3\)\(^{2-}\)] has been
explained by a decrease in the precipitating DIC $^{18}\text{O}/^{16}\text{O}$ with increasing host water $\text{CO}_3^{2-}/\text{HCO}_3^{-}$ (Zeebe, 1999). The Zeebe (1999) model differs significantly from the ‘metabolic CO$_2$’ model of McConnaughey (1989b) because in the former, the $^{18}\text{O}$ offset between biogenic and inorganic carbonates is controlled by the environment (via changing DIC speciation) rather than the organism’s biology (e.g. via the effect of growth rate on DIC-H$_2$O isotope equilibration).

![Figure 1](image)

**Figure 1** Difference in $\delta^{18}\text{O}$ between CaCO$_3$ ($\delta^{18}\text{O}_c$ relative to Vienna Pee Dee Belemnite (VDB)) and water ($\delta^{18}\text{O}_w$ relative to Vienna Standard Mean Ocean Water (VSMOW)) as a function of temperature for inorganic and biogenic CaCO$_3$ precipitated in laboratory under constant conditions. Each data point represents a single precipitation experiment for inorganic calcite (Kim and O’Neil, 1997) and aragonite (Kim et al., 2007), multiple specimens grown under the same conditions for planktic foraminifers (Bemis et al., 1998) and benthic foraminifers (Barras et al., 2010) and an individual specimen for ostracods (Candona: Xia et al., 1997, Australocypris: Chivas et al., 2002) and corals (Suzuki et al., 2005). The analytical uncertainty is ~ 0.1-0.2‰ for all studies, which is smaller than the symbol sizes. The $\delta^{18}\text{O}_c-\delta^{18}\text{O}_w$ vs temperature relationships widely considered to represent isotopic equilibrium are indicated by the black line for calcite (Kim and O’Neil, 1997) and the grey line for aragonite (Kim et al., 2007). The coloured lines are linear regressions between $\delta^{18}\text{O}_c-\delta^{18}\text{O}_w$ and temperature for each species in the plot.

Furthermore, inorganic calcite and aragonite growth experiments have shown that the solution pH, salinity, saturation with respect to calcite or aragonite ($\Omega$) and the calcification rate can all affect the carbonate $^{18}\text{O}$ (Kim and O’Neil, 1997; Kim et al., 2006; Dietzel et al., 2009; Gabitov et al., 2012; Wang et al., 2013), yet the effects reported vary in magnitude and/or in direction of change in the different studies. These conflicting results have not been resolved because of covariations between environmental parameters (e.g. pH covaries with $\text{CO}_3^{2-}/\text{HCO}_3^{-}$, $\Omega$ and calcification rate) and an incomplete understanding of the mechanisms responsible for kinetic isotope fractionations. Moreover, the environmental conditions required to precipitate carbonates in isotopic equilibrium with water are still ambiguous (Coplen, 2007; Dietzel et al., 2009). Results from the most recent and well-controlled inorganic carbonate growth experiments (Watkins et al., 2013; Watkins et al., 2014; Baker, 2015)
showed that kinetic isotope effects in carbonates can arise from an isotopically disequilibrated DIC pool and/or during transport of ions to the mineral surface and into the lattice. Separating and quantifying these kinetic effects is fundamental for solving isotopic vital effects in biogenic carbonates and for a sound interpretation of modern and ancient carbonate δ¹⁸O.

In this thesis, oxygen isotope data from inorganic and biogenic CaCO₃ are used to develop models of oxygen isotope fractionation between CaCO₃ and water (α_c/⁰/w). Data from published inorganic calcite experiments are used to quantify the effect of pH, salinity, calcite saturation state, calcification rate and carbonic anhydrase activity on α_c/⁰/w. The model resolves inconsistencies reported in previous studies, such as the variable effect of pH and calcification rate on carbonates δ¹⁸O (e.g. Kim et al., 2006; Dietzel et al., 2009; Watkins et al., 2014) and provides an inorganic framework for interpreting the δ¹⁸O of biogenic carbonates. Knowledge gained from the inorganic model then is used to investigate the causes of kinetic oxygen isotope effects in biogenic calcifiers. This thesis focuses on ostracod calcite and coralline aragonite because these two groups have opposite δ¹⁸O offsets relative to slowly precipitated inorganic calcite and aragonite. The results demonstrate that inorganic processes are sufficient to explain the anomalous δ¹⁸O of ostracods and corals, providing potential for improved paleoenvironmental reconstructions based on the δ¹⁸O of these calcifiers.

**Thesis outline**

**Chapter 2** presents a general model of oxygen isotope fractionation between CaCO₃ and water. The model calculates isotopic fractionations arising from oxygen isotope exchanges between the DIC and H₂O and between the mineral and the precipitating DIC species (i.e. CO₃²⁻). Isotopic exchanges between DIC species and H₂O and related kinetic isotope fractionations are quantified as a function of temperature, reaction pathways and DIC speciation. In the model CO₃²⁻ is the dominant carbonate building block from the DIC pool and isotopic fractionations between the carbonate mineral and CO₃²⁻ are calculated based on calcite precipitation-dissolution kinetic laws. Kinetic isotope fractionations between CaCO₃ and CO₃²⁻ and during the hydroxylation of CO₂ are calibrated using published oxygen isotope data from inorganic carbonate precipitation experiments. Model results indicate that oxygen isotope equilibrium between CaCO₃ and H₂O is the exception in nature rather than the norm. In the model, the effect of pH on carbonate δ¹⁸O is due to disequilibrium isotope effects between the different DIC species, and by a positive correlation between pH and the calcite or aragonite saturation state. No pH effect on carbonate δ¹⁸O is expected where the DIC is isotopically equilibrated and where pH and Ω are not covariant. Isotopic disequilibrium between the DIC and H₂O can result in highly variable carbonate δ¹⁸O-temperaue relationships but isotopic disequilibrium between CaCO₃ and CO₃²⁻ have limited impact on the temperature sensitivity of carbonate δ¹⁸O.
Chapter 3 explores the causes of kinetic oxygen isotope effects in lacustrine and marine ostracod calcite. A compilation of ~ 900 published ostracod oxygen isotope values and associated host water parameters is used to evaluate the effect of DIC speciation, DIC concentration and salinity on ostracod $\delta^{18}O$. Calculations of the host water DIC parameters demonstrate that ostracod $\delta^{18}O$ is mainly controlled by the $^{18}O/^{16}O$ of the sum of host water $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$. This result resolves conflicting observations of variable salinity effects on ostracod $\delta^{18}O$. The chapter also investigates reasons for taxonomic differences in ostracod $\delta^{18}O$. Implications of these results for ostracod biomineralization processes and paleoclimate reconstructions are discussed in detail.

Chapter 4 investigates the relationship between calcification rate and kinetic oxygen isotope effects in Porites sp. corals. Four new Porites microatoll $\delta^{18}O$ records from Kiritimati Island (Central Pacific) spanning the early late and 20th century are presented and compared to previously published coral records from the same location. The results show that Porites microatoll $\delta^{18}O$ is mostly independent of the coral extension rate, in contrast with other Porites $\delta^{18}O$ studies. The mechanisms behind the coral growth rate effect are explored using the oxygen isotope model presented in Chapter 1. Model results suggest that Porites $\delta^{18}O$ and extension rate are negatively correlated over a range of slow extension rates due to increasing isotopic equilibration of the DIC pool in the calcifying fluid with decreasing coral calcification rate. Above a coral extension rate of in between ~ 5 and 15 mm/yr, depending on the coral colony and/or environment, the DIC-H$_2$O isotopic disequilibrium reaches a maximum value and Porites $\delta^{18}O$ is then independent of the extension rate. Variations in the Porites $\delta^{18}O$-extension rate relationships between studies are explained by variations in the rate of DIC-H$_2$O isotopic equilibration rate, which in turn depends on the activity of the enzyme carbonic anhydrase. The model explains why Porites $\delta^{18}O$ is less sensitive to temperature than inorganic aragonite $\delta^{18}O$.

Chapter 5 begins by summarising the inorganic CaCO$_3$-DIC-H$_2$O oxygen isotope model and the kinetic and equilibrium fractionation for CaCO$_3$-DIC and DIC-H$_2$O. The chapter explains the kinetic isotope effects governing ostracod and coral calcification and poses that it is differences in composition of the DIC pool that gives rise to their $\delta^{18}O$ ‘vital effects’ and offsets relative to inorganic carbonates. The new knowledge on $^{18}O$ fractionation in corals and ostracods is applied to foraminiferal calcite. Finally, recommendations are made for the use of ostracods and corals in paleoclimate and paleoenvironmental reconstructions, based on the results of this thesis.
References


Chapter II: OXYGEN ISOTOPE FRACTIONATION IN THE INORGANIC CaCO\textsubscript{3}-DIC-H\textsubscript{2}O SYSTEM

2.1. 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 paleo-environment reconstruction (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, isotope exchanges between chemical phases do not reach equilibrium, and mass-dependent transport of isotopes and the chemical reaction rates contribute to the isotopic fractionations. For oxygen isotopes (\textsuperscript{18}O/\textsuperscript{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\textsubscript{3} precipitation rate, the chemical speciation of the dissolved inorganic carbon (DIC; DIC = CO\textsubscript{2(aq)} + H\textsubscript{2}CO\textsubscript{3} + HCO\textsubscript{3}\textsuperscript{-} + CO\textsubscript{3}\textsuperscript{2-}) and the solution pH (McCrea, 1950; Kim and O'Neil, 1997; Kim et al., 2006; Dietzel et al., 2009; Watkins et al., 2013, 2014). Many natural carbonates grow at rates that likely place them in a non-equilibrium regime and are subject to KIEs, hence to improve interpretations of \textsuperscript{δ\textsuperscript{18}O} data from modern and fossil carbonates there is a need to better understand:

1. Which DIC species contribute to CaCO\textsubscript{3} growth?
2. What controls the isotopic fractionations between the precipitating DIC species and CaCO\textsubscript{3}?
3. How the isotopic composition of DIC species varies prior to and during CaCO\textsubscript{3} precipitation?

A recent advance in understanding the controls on oxygen isotope fractionation between precipitating DIC species and CaCO\textsubscript{3} (point (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\textsubscript{2}, thereby increasing the rate of oxygen isotope exchange between the DIC species and H\textsubscript{2}O and promoting DIC-H\textsubscript{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\textsubscript{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 CaCO₃ (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 fractionations in the CaCO₃-DIC-H₂O system that incorporates the new information on KIE between CaCO₃ and DIC (Watkins et al., 2013; 2014), and accounts for the kinetic isotopic fractionations between the DIC and H₂O. In the model, CO₃²⁻ is the only DIC species that contributes to carbonate nucleation and growth while other DIC species affect the ¹⁸O/¹⁶O of CaCO₃ by conversion to CO₃²⁻ shortly before or during CaCO₃ precipitation. The isotopic fractionation between CaCO₃ and CO₃²⁻ is calculated as a function of the calcite saturation state and solution 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 and theoretical data. These KIFF are used with published equilibrium isotopic fractionation factors (EIFF, Beck et al., 2005) to calculate the time-dependent isotopic composition of CO₃²⁻ and HCO₃⁻ 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 ¹⁸O/¹⁶O of foraminifers and corals to test current hypotheses of oxygen isotope vital effects in biogenic CaCO₃.

2.2. Notation

The ¹⁸O/¹⁶O ratio of a water or carbonate sample (¹⁸Rₛ) is measured as the deviation from the ¹⁸O/¹⁶O ratio of a standard (¹⁸Rstd) and is expressed using the δ¹⁸O notation:

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

(2.1)

where \textit{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 δ¹⁸O value on the VPDB scale is converted to a δ¹⁸O value on the VSMOW scale by using the equation provided by Coplen et al. (1983):

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

(2.2)
The oxygen isotope fractionation factor between any two phases A and B \((\alpha_{A/B})\) is expressed as:

\[
\alpha_{A/B} = \frac{^{18}R_A}{^{18}R_B} = \frac{1000 + \delta^{18}O_A}{1000 + \delta^{18}O_B}
\]  

(2.3)

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 \(\epsilon\):

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

(2.4)

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

2.3. Model background

2.3.1. 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 consider spontaneous nucleation of CaCO_3 minerals in solution separately from subsequent mineral growth via ion adsorption to the mineral surface, because nucleation has a higher energy barrier than surface growth (Morse et al., 2007).

Several lines of evidence suggest that \(\text{CO}_3^{2-}\), rather than bicarbonate, is the dominant DIC species during CaCO_3 nucleation. For example, negligible bicarbonate ion concentrations were reported in amorphous calcium carbonate (ACC), the precursor to calcite or aragonite precipitation, suggesting that \(\text{HCO}_3^-\) ions do not contribute to CaCO_3 nucleation (Nebel et al., 2008). Similarly, numerical simulations of calcite (pre-) nucleation, showing that \(\text{HCO}_3^-\) ions 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 \(\text{HCO}_3^-\) and \(\text{CO}_3^{2-}\) 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). Here for example, quasi-instantaneous precipitation of witherite (\(\text{BaCO}_3\)) showed that \(\delta^{18}O_{\text{witherite}}\) reflects the \(\delta^{18}O\) of \(\text{CO}_3^{2-}\) ions unless the amount of DIC consumed was higher than the initial amount of \(\text{CO}_3^{2-}\) in solution, and demonstrated that \(\text{HCO}_3^-\) ions do not directly contribute to witherite nucleation (Kim et al., 2006). In the experiments, the reaction was considered strictly forward, and the oxygen isotopic ratio of the mineral reflected that of the DIC species consumed during the reaction.
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 δ$^{18}$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 chapter therefore assumes that calcite precipitates from CO$_3^{2-}$ ions exclusively and that the δ$^{18}$O of calcite reflects the $^{18}$O/$^{16}$O of the carbonate ions consumed during mineral precipitation.

2.3.2. 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). 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 $r_\text{c}/r_\text{c+}$ ($R_\text{b}/R_\text{f}$ in DePaolo, 2011). Fractionation varies between an equilibrium limit at $r_\text{c}/r_\text{c+} = 1$ and a kinetic limit at $r_\text{c}/r_\text{c+} = 0$. The ratio is obtained from calcite dissolution rate estimates and the measured net calcite precipitation rate $r_\text{c}$ ($r_\text{c+} = r_\text{c+} - r_\text{c}$). The $r_\text{c}/r_\text{c+}$ 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 $r_\text{c}/r_\text{c+}$ 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 in this chapter 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 2.3.1). Moreover, a new expression for deriving the CaCO$_3$ dissolution/precipitation ratio is derived from the Zhong and Mucci (1993) classical crystal growth rate expression (Section 2.4.2).

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$_3$ and of inorganic CaCO$_3$ precipitating in natural environments under high pH conditions (McConnaughey, 1989b, Clark et al., 1992, Rollion-Bard et al., 2003, Allison et al., 2010, Ziveri et al., 2012, Saenger et al., 2012, Hermoso et al., 2016). Several studies (McConnaughey, 1989b, Clark et al., 1992, Dietzel et al., 2009, Watkins et al., 2013) have shown that inorganic calcite precipitated at fast rates from a DIC pool deriving from gaseous CO$_2$ is always depleted in $^{18}$O relative to slowly precipitated inorganic calcite (e.g. Kim and O’Neil, 1997, Coplen, 2007). Under such conditions, calcite $^{18}$O/$^{16}$O also strongly decreases with the solution pH (Dietzel et al., 2009), and can exhibit large negative offsets in $^{18}$O of $\sim$14‰ or more relative to slowly precipitated calcite grown at more neutral pH values (Clark et al., 1992; Dietzel et al., 2009; Watkins et al., 2013, 2014). These KIE are thought to be caused by (1) the preferential reaction of isotopically light CO$_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 molecules and OH$^-$ ions into newly formed HCO$_3^-$ and CO$_3^{2-}$ (Clark et al., 1992). To better understand and accurately predict KIE related to CO$_2$ 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 H₂O prior to calcite precipitation and because KIE between DIC and H₂O could not be isolated from the overall CaCO₃-H₂O fractionation factor.

The model presented in this chapter is used to distinguish and quantify CaCO₃-CO₃²⁻ and DIC-H₂O KIE by estimating the level of DIC-H₂O isotopic equilibrium based on solution parameters (Section 2.4.3). In turn, this permits quantifying the different factors contributing to the observed KIE between DIC and H₂O.

2.4. Model

2.4.1. Overview

The model integrates oxygen isotopic fractionations arising from the mineral growth reaction and isotopic exchanges between the DIC species and H₂O (Fig. 2.1). The CaCO₃-H₂O fractionation factor, \( \alpha_{cw} \) is expressed as:

\[
\alpha_{cw} = \frac{^{18}R_c}{^{18}R_w} \tag{2.5}
\]

Since CO₃²⁻ is assumed to be the only precipitating DIC species, the numerator and denominator of equation (2.5) are divided by \( ^{18}R_{CO_3^{2-}} \) (the \(^{18}O/^{16}O\) of CO₃²⁻) to express \( \alpha_{cw} \) as the product of the CaCO₃-CO₃²⁻ (\( \alpha_{c/CO_3^{2-}} \)) and CO₃²⁻-H₂O (\( \alpha_{CO_3^{2-}/w} \)) fractionation factors:

\[
\alpha_{cw} = \frac{^{18}R_c}{^{18}R_{CO_3^{2-}}} = \alpha_{c/CO_3^{2-}} \cdot \alpha_{CO_3^{2-}/w} \tag{2.6}
\]
Figure 2.1. Factors controlling the $\delta^{18}O$ 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 $\delta^{18}O$ of inorganic CaCO$_3$ depends. The arrows indicate the cause and effect relations between the input and output parameters (e.g. $\Omega$ is controlled by $[\text{Ca}^{2+}]$, $[\text{DIC}]$, DIC speciation 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; “[Ca$^{2+}$]”: Ca$^{2+}$ concentration (µmol/kg); “$\Delta_{\text{DIC}}$”: isotopic equilibration level between DIC and water (0 to 1); “$\Omega$”: calcite or aragonite saturation state (>1); “$n_2$”: partial reaction order with respect to the solution CO$_3^{2-}$ concentration; $^{18}R$: $^{18}O/^{16}O$ 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 $E_{\text{DIC}} = 1$, $\alpha_{\text{CO}_3^{2-}/w}$ only depends on temperature and $\alpha_{c/w}$ only depends on temperature and $E_c$. Where $E_{\text{DIC}} < 1$, $\alpha_{\text{CO}_3^{2-}/w}$ and $\alpha_{c/w}$ also depend on the $\delta^{18}O$ of the DIC source, $E_{\text{DIC}}$, pH and DIC speciation.

In the model (Fig. 2.1), the $\delta^{18}O$ of a calcium carbonate mineral ($\delta^{18}O_{c}$) is calculated from $^{18}R_{CO_3^{2-}}$ and the fractionation factor $\alpha_{c/CO_3^{2-}}$, the latter being a function of temperature ($T$) and the degree of isotopic equilibrium between the mineral and the carbonate ion pool ($E_c$). The fractionation factor $\alpha_{c/CO_3^{2-}}$ 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 ($n_2$).

The $^{18}R_{CO_3^{2-}}$ value (on which $\delta^{18}O_c$ depends) is dependent on the $\delta^{18}O$ of water ($\delta^{18}O_w$) and the fractionation factor $\alpha_{CO_3^{2-}/w}$. The value of $\alpha_{CO_3^{2-}/w}$ also varies between a kinetic and an equilibrium limit. At isotopic equilibrium, $\alpha_{CO_3^{2-}/w}$ only depends on temperature (Beck et al., 2005). Under non-
equilibrium conditions, $\alpha_{CO_3^{2-}/w}$ also depends on the $\delta^{18}O$ value 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 ($E_{DIC}$). In turn, $E_{DIC}$ varies between 0 and 1 and is a function of the DIC residence time in solution (calculated from the calcification rate ($r_c$), solution volume ($V$) and the DIC concentration ([DIC])) and the rate of oxygen isotope exchange between DIC and water (calculated from the solution pH, 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 ($h^+2$) and hydroxylated ($h^+4$) CO$_2$. These reactions initially produce HCO$_3^-$ and CO$_3^{2-}$ ions with low $^{18}O/^{16}O$ 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 $\alpha_{CO_3^{2-}/w}$ and $R_{CO_3^{2-}}$ towards equilibrium values.

The rates of reactions in the CaCO$_3$-DIC-H$_2$O system are such that the carbonate ion pool can be isotopically equilibrated with H$_2$O ($E_{DIC} = 1$) but not with CaCO$_3$ ($E_c < 1$). 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 kinetic fractionation. In Section 2.4.2 equations for calculating the level of isotopic equilibration between calcite and CO$_3^{2-}$ ($\alpha_{c/CO_3^{2-}}$) are derived, and then the $\alpha_{c/CO_3^{2-}}$ kinetic (disequilibrium) and equilibrium limits are quantified. Section 2.4.3 presents equations for calculating the level of isotopic equilibration between CO$_3^{2-}$ and H$_2$O ($\alpha_{CO_3^{2-}/w}$), followed by the quantification of the $\alpha_{CO_3^{2-}/w}$ kinetic and equilibrium limits. An Excel version of the model is available (Excel Macro ‘OCD18’ in the electronic appendix). Symbols and abbreviations used in this chapter are compiled in Appendix A1.

2.4.2. Isotopic fractionation between CaCO$_3$ and CO$_3^{2-}$ ($\alpha_{c/CO_3^{2-}}$)

2.4.2.1. Kinetic vs equilibrium isotope fractionation

As discussed in section 2.3.1, it is assumed that calcite forms via the following reaction pathway:

$$Ca^{2+} + CO_3^{2-} \xrightleftharpoons[k_e-k_f]{k_f+k_e} CaCO_3$$  \hspace{1cm} (2.7)
where $k_c$ and $k_e$ 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 $\alpha_{c/CO_3^2-}$:

$$\alpha_{c/CO_3^2-} = \frac{\alpha_{c/CO_3^2-}^{eq}}{\alpha_{c/CO_3^2-}^{eq} + \frac{r_e}{r_c} - 1}$$  \hspace{1cm} (2.8)

where $\alpha_{c/CO_3^2-}^{eq}$ and $\alpha_{c/CO_3^2-}^{eq}$ are the kinetic and equilibrium limits of $\alpha_{c/CO_3^2-}$ and $r_e$ and $r_c$ are the rates of the backward and forward reaction, respectively. Equation (2.8) shows that the $r_e/r_c$ ratio determines the degree of isotopic equilibration between CaCO$_3$ and carbonate ions ($E_c$). Where $r_e$ is much smaller than $r_c$, then $E_c \approx 0$ and $\alpha_{c/CO_3^2-}^{eq}$ approaches $\alpha_{c/CO_3^2-}^{eq}$. Where $r_e \approx r_c$, then $E_c \approx 1$ and $\alpha_{c/CO_3^2-}^{eq}$ approaches $\alpha_{c/CO_3^2-}^{eq}$. Here, the $r_e/r_c$ ratio is derived from classic calcite growth kinetic laws. According to the reaction pathway (2.7), the net reaction rate $r_c$ is expressed as the difference between $r_c$ and $r_e$ (Lasaga, 1981):

$$r_c = r_c - r_e = k_{+c}\{Ca^{2+}\}^{n_1}\{CO_3^{2-}\}^{n_2} - k_{-c}\{CaCO_3\}^{n_3}$$  \hspace{1cm} (2.9)

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 (2.9) can be simplified as (Zhong and Mucci, 1993):

$$r_c = K_{+c}\{CO_3^{2-}\}^{n_2} - k_{-c}$$  \hspace{1cm} (2.10)

with

$$K_{+c} = k_{+c}\{Ca^{2+}\}^{n_1}\gamma_{CO_3^{2-}}^{n_2}$$  \hspace{1cm} (2.11)

where $[\ ]$ denotes concentration (moles/kg), and $\gamma_{CO_3^{2-}}$ 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):

$$k_{-c} = K_{+c}\{CO_3^{2-}\}^{n_2}_{eq}$$  \hspace{1cm} (2.12)
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 $\Omega$), the backward and forward reaction rate ratio are expressed as follows:

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

(2.13)

Simplifying equation (2.13) and multiplying the numerator and denominator by $\frac{[Ca^{2+}]}{K_{sp}^*}$, where $K_{sp}^*$ is the stoichiometric solubility product of a CaCO$_3$ mineral (Mucci, 1983, Appendix A2), yields the following relationship:

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

(2.14)

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 (2.14) equals 1 regardless of the $[Ca^{2+}]$ value and equation (2.14) simplifies to:

$$\frac{r_{-c}}{r_{+c}} = \frac{1}{[CO_3^{2-}][Ca^{2+}]}$$

(2.15)

Equation (2.15) 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 $n_2$.

2.4.2.2. The partial reaction order $n_2$

The value of the partial reaction order $n_2$ is determined by the logarithmic expression of equation (2.10) (Zhong and Mucci, 1993):
\[
\log(r_c + k_{-c}) = n_2 \log[CO_3^{2-}] + \log(K_{+c})
\] (2.17)

When crystal growth is far from chemical equilibrium \((r_c \gg k_{-c})\), equation (2.17) can be approximated by:

\[
\log(r_c) = n_2 \log[CO_3^{2-}] + \log(K_{+c})
\] (2.18)

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. 2.2A and 2B, Zuddas and Mucci, 1998, Lopez et al., 2009).

![Figure 2.2](image)

**Figure 2.2.** 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 0.21 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\(_3^{2-}\) (\(E_i\)) can be calculated.

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. 2.2A) 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):

\[
n_2 = 0.045(\pm 0.002) T(°C) + 2.0(\pm 0.1) \quad \text{(for seawater, I=0.7)}
\] (2.19)

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, 1993; Zuddas and Mucci, 1994, 1998). The 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. 2.2B, Zuddas and Mucci, 1998):

\[
n_2 = 3.5(\pm 0.6) I + 0.16(\pm 0.37) \quad \text{at } 25^\circ \text{C} \quad \text{(2.20)}
\]

Substituting equation (2.19) or (2.20) into equation (2.15), the level of isotopic equilibrium between calcite and CO\(_3^{2-}\) \( (E_c = r_c/r_{c+}) \) 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 2.3.

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

According to equation (2.6), the oxygen-isotope equilibrium fractionation factor between CaCO\(_3\) and CO\(_3^{2-}\) \( (\alpha_{c/CO_3^{2-}}) \) is equal to the ratio of the equilibrium fractionation factor between CaCO\(_3\) and water \( (\alpha_{c/w}) \) and the equilibrium fractionation factor between CO\(_3^{2-}\) and water \( (\alpha_{CO_3^{2-}/w}) \):

\[
\alpha_{c/CO_3^{2-}}^{eq} = \frac{\alpha_{c/w}^{eq}}{\alpha_{CO_3^{2-}/w}^{eq}} \quad \text{(2.21)}
\]

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 (2.15), isotopic equilibrium is approached in solutions with low \( \Omega \) and low ionic strength (Fig. 2.3). 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 (2.21), and the expression of Beck et al. (2005) for \( \alpha_{CO_3^{2-}/w}^{eq} \) (Table 2.1), yields an \( \alpha_{c/CO_3^{2-}}^{eq} \) of 1.00542 at 33.7°C. Available data (Dietzel et al., 2009; Baker et al., 2015, see Section 2.5.2) suggest that \( \alpha_{c/CO_3^{2-}}^{eq} \) does not vary significantly between 5 and 40°C, and therefore \( \alpha_{c/CO_3^{2-}}^{eq} \) is assumed to be constant. Note that an accurate determination of the temperature sensitivity of \( \alpha_{c/CO_3^{2-}}^{eq} \) would require additional oxygen isotope data on inorganic calcite growing at low supersaturation solution (i.e., under equilibrium conditions) and under various temperatures.
Figure 2.3. Modelled isotopic equilibrium level ($E_c$) between calcite and CO$_3^{2-}$ ($E_c = r_c/r_{c+}$; Eq. 2.15) at 25°C as a function of the solution $\Omega$ and for different ionic strengths ($I$). The lines showing $E_c$ as a function of $1/\Omega$ were calculated using equations (2.15) and (2.20). Dotted lines are extrapolations of equation (2.20) for $I < 0.1$. The expectation is that $E_c$ will approach 1 where calcite precipitates at low $\Omega$ and low ionic strength (e.g. Devil’s Hole calcite, $I < 0.01$, $\Omega < 1.6$; Coplen, 2007) and will approach 0 where calcite precipitates at high $\Omega$ and high ionic strength (e.g. calcite secreted by marine organisms, $0.5 < I < 1.0$, $\Omega > 5$; 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, $n_2 = 0.21$, c.f. Section 2.5.2 and Figure 2.7). In comparison, $E_c$ is independent of the ionic strength in the model of Watkins et al. (2014) (grey line).

Table 2.1. Equilibrium fractionation factors used in this chapter.

<table>
<thead>
<tr>
<th>Equilibrium $\alpha$</th>
<th>Equation ($T$ in Kelvin)</th>
<th>25°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_3^{2-}$ – water</td>
<td>$\alpha^e_{CO_3^{2-}/w}$ exp(2390 $T^2$ - 0.00270)</td>
<td>1.02448</td>
<td>Beck et al. (2005)</td>
</tr>
<tr>
<td>HCO$_3^{-}$ – water</td>
<td>$\alpha^e_{HCO_3^{-}/w}$ exp(2590 $T^2$ + 0.00189)</td>
<td>1.03151</td>
<td>Beck et al. (2005)</td>
</tr>
<tr>
<td>CO$_2$(aq) – water</td>
<td>$\alpha^e_{CO_2/w}$ exp(2520 $T^2$ + 0.01212)</td>
<td>1.04130</td>
<td>Beck et al. (2005)</td>
</tr>
<tr>
<td>CO$_3^{2-}$ – HCO$_3^{-}$</td>
<td>$\alpha^e_{CO_3^{2-}/HCO_3^{-}}$ $\alpha^e_{CO_3^{2-}/w} / \alpha^e_{HCO_3^{-}/w}$</td>
<td>0.99318</td>
<td>Calculated after Beck et al. (2005)</td>
</tr>
<tr>
<td>calcite – CO$_3^{2-}$</td>
<td>$\alpha^e_{c/CO_3^{2-}}$ constant</td>
<td>1.00542</td>
<td>calculated after Coplen (2007) and Beck et al. (2005)</td>
</tr>
<tr>
<td>calcite – water</td>
<td>$\alpha^e_{c/w}$ $\alpha^e_{CO_3^{2-}/w} / \alpha^e_{c/CO_3^{2-}}$</td>
<td>1.03002</td>
<td>calculated after Coplen (2007) and Beck et al. (2005)</td>
</tr>
<tr>
<td>OH$^-$ – water</td>
<td>$\alpha^e_{OH^{-}/w}$ exp(0.00048 $T$ - 0.1823)</td>
<td>0.96157</td>
<td>calculated after Green and Taube (1963)</td>
</tr>
</tbody>
</table>
### Table 2.2. Kinetic isotope fractionation factors used in this chapter.

<table>
<thead>
<tr>
<th>Kinetic isotope fractionation</th>
<th>25°C</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃ - CO₃²⁻</td>
<td>¹⁸kₑ/¹⁶kₑ</td>
<td>0.9990 ± 0.0003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>calculated after Kim et al. (2006)</td>
</tr>
<tr>
<td>HCO₃⁻ - (CO₂ + H₂O)</td>
<td>¹⁸kₑ²/¹⁶kₑ²</td>
<td>0.9994 ± 0.0010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>calculated after Zeebe (2014)</td>
</tr>
<tr>
<td>HCO₃⁻ - (CO₂ + OH)</td>
<td>¹⁸kₑ₄/¹⁶kₑ₄</td>
<td>0.9970 ± 0.0011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>model parameter</td>
</tr>
</tbody>
</table>

*For example, a $\alpha_{C/O}^{+c}$ of 0.9990 ± 0.0003 at 25°C indicates that the product (CaCO₃) has a lower $^{18}$O/$^{16}$O than the reactant (CO₃²⁻).

#### 2.4.2.4. Kinetic fractionation between CaCO₃ and CO₃²⁻

Keeping in mind the framework where only CO₃²⁻ participates directly in calcite growth (pathway 2.7), 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):

$$\frac{^{18}k_{+c}}{^{16}k_{+c}} = \alpha_{c/CO₃²⁻}^{+c}$$  \hspace{1cm} (2.22)

where $\alpha_{c/CO₃²⁻}^{+c}$ is the kinetic limit of $\alpha_{c/CO₃²⁻}$ during fast calcite precipitation. Under closed system conditions, there are isotopic distillation effects that reduce the kinetic fractionations between product and reactant of a unidirectional reaction (Rayleigh, 1896; Hoefs, 2015). In this case, the isotopic ratio of instantaneously precipitated CaCO₃ formed from a finite CO₃²⁻ pool is (Rayleigh, 1896):

$$^{18}R_{c} = \frac{^{18}R_{CO₃²⁻}^0}{^{18}R_{CO₃²⁻}} \frac{1 - (1 - X_{CO₃²⁻}) \alpha_{c/CO₃²⁻}^{+c}}{X_{CO₃²⁻}}$$  \hspace{1cm} (2.23)

where $^{18}R_{CO₃²⁻}^0$ is the initial $^{18}R_{CO₃²⁻}$ prior to calcite precipitation and $X_{CO₃²⁻}$ is the proportion of CO₃²⁻ ions consumed during calcite precipitation. Note that when all carbonate ions are consumed $X_{CO₃²⁻} = 1$ and $^{18}R_{c} = ^{18}R_{CO₃²⁻}$. Dividing equation (2.23) by $^{18}R_w$, the oxygen isotope fractionation between instantaneously precipitated calcite and water is obtained:

$$\alpha_{c/w} = \frac{^{18}R_{CO₃²⁻}^0}{^{18}R_w} \frac{1 - (1 - X_{CO₃²⁻}) \alpha_{c/CO₃²⁻}^{+c}}{X_{CO₃²⁻}}$$  \hspace{1cm} (2.24)

Oxygen isotopic results from witherite (i.e. BaCO₃) precipitated quasi-instantaneously from isotopically equilibrated CO₃²⁻ (Kim et al., 2006) can be used to quantify $\alpha_{c/CO₃²⁻}^{+c}$ assuming that the
\(^{18}\)O-\(^{16}\)O difference in reaction rates during calcite precipitation are similar to that of witherite precipitation. Accordingly, equations (2.24) is rewritten for the BaCO\(_3\)-H\(_2\)O \((\alpha_{Ba/w})\) and BaCO\(_3\)-CO\(_3^{2-}\) \((\alpha_{Ba/CO_3^{2-}})\) fractionation factors:

\[
\alpha_{Ba/w} = \frac{\alpha_{CO_3^{2-}/w}^0}{1 - (1 - X_{CO_3^{2-}})\alpha_{Ba/CO_3^{2-}}}
\]

(2.25)

**Figure 2.4.** Oxygen isotope fractionation between BaCO\(_3\) and water \((\varepsilon_{Ba/w})\) at 25°C as a function of the fraction of CO\(_3^{2-}\) ions precipitated \((X_{CO_3^{2-}})\). The data are from Kim et al. (2006) and were replotted as a function of \(X_{CO_3^{2-}}\) for witherite that precipitated instantaneously from isotopically equilibrated CO\(_3^{2-}\) ions exclusively. Where all CO\(_3^{2-}\) ions are consumed, the \(^{18}\)O/\(^{16}\)O of BaCO\(_3\) is equal to that of the CO\(_3^{2-}\) pool \((\varepsilon_{Ba/w} = \varepsilon_{CO_3^{2-}/w} = 24.5 \pm 0.3\%\,\text{o},\) Beck et al., 2005; Kim et al., 2006, 2014). Where the CO\(_3^{2-}\) ions are not fully consumed during precipitation, BaCO\(_3\) is depleted in \(^{18}\)O relative to the CO\(_3^{2-}\) pool \((\varepsilon_{Ba/w} < \varepsilon_{CO_3^{2-}/w})\) due to the preferential precipitation of isotopically light CO\(_3^{2-}\) ions. A Rayleigh fractionation model fitted to this data (dashed line, \(R^2 = 0.71, p\)-value < 0.01) predicts a \(\varepsilon_{18O_{Ba/w}}\) of 23.5 \(\pm 0.2\%\) for \(X_{CO_3^{2-}}\) approaching 0%. This data suggest a kinetic isotope fractionation of -1.0 \(\pm 0.3\%\) between BaCO\(_3\) and the CO\(_3^{2-}\) ion pool during instantaneous BaCO\(_3\) precipitation (blue double-headed arrow at \(X_{CO_3^{2-}} = 0\%\)).

Kim et al. (2006) found that \(\alpha_{Ba/w}\) increased with increasing fractions of the CO\(_3^{2-}\) pool consumed \((X_{CO_3^{2-}})\), suggesting that isotopically light CO\(_3^{2-}\) ions are preferentially incorporated into BaCO\(_3\) (Fig. 2.4). The \(\alpha_{Ba/CO_3^{2-}}\) value can be estimated by fitting equation (2.25) to the data shown in Figure 2.4. Substituting \(\alpha_{CO_3^{2-}/w}^0\) with \(\alpha_{CO_3^{2-}/w}^{eq}\) \((\alpha_{CO_3^{2-}/w}^{eq} = 1.0245 \pm 0.0003\) at 25°C, Beck et al., 2005) in equation (2.25), the best data-model agreement is found for a \(\alpha_{Ba/CO_3^{2-}}^{+}\) of 0.9990 \(\pm 0.0003\) (Fig. 2.4, \(R^2 = 0.71, p\)-value < 0.01). This value is closer to unity than the only available estimate for the
CaCO$_3$-CO$_3^{2-}$ kinetic fractionation ($\alpha_{c/CO_3^{2-}}^{+c} = 0.9980$), which was deduced from an isotopic ion-by-ion growth model and $\alpha_{c/w}$ versus growth rate data (Watkins et al., 2014). Watkins et al. (2014) estimated $\alpha_{c/CO_3^{2-}}^{+c}$ using a $\alpha_{CO_3^{2-}/w}^{eq}$ value of 1.0268 (at 25°C), based on the equation of Wang et al. (2013), whereas three experimental studies have now reported consistent $\alpha_{CO_3^{2-}/w}^{eq}$ values between 1.0240 and 1.0245 (Beck et al., 2005; Kim et al., 2006; Kim et al., 2014). Adjusting the result of Watkins et al. (2014) for a $\alpha_{CO_3^{2-}/w}^{eq}$ value of 1.0245 (Beck et al., 2005) yields $\alpha_{c/CO_3^{2-}}^{+c} = 1.0003$, which is 1.3‰ higher than our estimate based on the wetherite experiments and is inconsistent with a preferential precipitation of isotopically light CO$_3^{2-}$ ions (Kim et al., 2006). Our results suggest that the transfer of carbonate ions from the solution to the carbonate mineral induces a small oxygen isotopic fractionation of ~1‰ at the kinetic limit.

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

#### 2.4.3.1. 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 exchanges between DIC species and water occurs via the hydration and hydroxylation reactions (McConnaughey, 1989b; Usdowski et al., 1991):

\[
\text{CO}_2 + H_2O \xrightleftharpoons[k^-2, k^+2]{k_{-2}, k_{+2}} H_2CO_3 \leftrightarrow HCO_3^- + H^+ \quad \text{(hydration)}
\]  

\[
\text{CO}_2 + OH^- \xrightleftharpoons[k^-4, k^+4]{k_{-4}, k_{+4}} HCO_3^- \quad \text{(hydroxylation)}
\]  

where $k_{-2}$, $k_{+2}$ and $k_{-4}$, $k_{+4}$ are the backward and forward reaction rate constants for CO$_2$ hydration and hydroxylation, respectively (see Appendix A3 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:

\[
\ln \left( \frac{^{18}R_{DIC}}{^{18}R_{DIC}} - \frac{^{18}R_{DIC}^{eq}}{^{18}R_{DIC}^{eq}} \right) = -\frac{t}{\tau}
\]  

where $^{18}R_{DIC}$ is the oxygen isotope ratio of DIC at time $t$, and $\tau$ is the time constant for equilibration.
where $t$ is the time spent by the DIC pool in solution, $\tau$ is the time constant and $^{18}R_{DIC}^t$, $^{18}R_{DIC}^0$ and $^{18}R_{DIC}^{eq}$ are the oxygen isotope ratios of DIC at time $t$, $t=0$ and at isotopic equilibrium. Equation (2.28) can be rewritten to express the oxygen isotope ratio of DIC:

$$^{18}R_{DIC} = e^{(-t/\tau)} \left( {^{18}R_{DIC}^0 - ^{18}R_{DIC}^{eq}} \right) + ^{18}R_{DIC}^{eq}$$ (2.29)

Dividing equation (2.29) by $^{18}R_w$ provides an equation for the oxygen isotope fractionation between the DIC pool and water:

$$\alpha_{DIC/w} = e^{(-t/\tau)} \left( \alpha_{DIC/w}^0 - \alpha_{DIC/w}^{eq} \right) + \alpha_{DIC/w}^{eq}$$ (2.30)

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, the model assumes that all the DIC species remain at isotopic equilibrium with each other (but not with $H_2O$) over the course of DIC-$H_2O$ isotopic equilibration. Consequently, equation (2.30) can be rewritten for any of the DIC species ($i$):

$$\alpha_{i/w} = e^{(-t/\tau)} \left( \alpha_{i/w}^0 - \alpha_{i/w}^{eq} \right) + \alpha_{i/w}^{eq}$$ (2.31)

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

$$E_{DIC} = 1 - e^{(-t/\tau)}$$ (2.32)

The time constant $\tau$ in equation (2.31) and (2.32) is a function of the hydration and hydroxylation reaction kinetics (Usdowski et al., 1991, Uchikawa and Zeebe, 2012):

$$\tau^{-1} = \frac{1}{2} \cdot \left[ k_{+2}^{+2} + k_{+4}^{-} [OH^-] \right] \cdot \left[ 1 + \frac{[CO_2]}{[DIC] - [CO_2]} - \sqrt{1 + \frac{2}{3} \cdot \frac{[CO_2]}{[DIC] - [CO_2]} + \left( \frac{[CO_2]}{[DIC] - [CO_2]} \right)^2} \right]$$ (2.33)

with
\[ k_{+2} = k_{+2} + \frac{k_{\text{Cat}}}{K_M} [CA] \]  

(2.34)

where \( k_{\text{Cat}} \) 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). Solving equation (2.31) requires knowledge of the residence time of the DIC in solution (\( RT_{DIC} \)). In steady state conditions, \( RT_{DIC} \) is equal to the molar quantity of DIC divided by the calcite growth rate in moles/s:

\[ RT_{DIC} = \frac{[DIC]V}{\tau_c} \]  

(2.35)

Where \( V \) is the volume of the precipitating solution. The following sections present equations for the equilibrium (\( \alpha^{eq}_{i/w} \)) and kinetic (\( \alpha^0_{i/w} \)) end members of equation (2.31).

### 2.4.3.2. Equilibrium fractionations 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 2.1). 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 chapter (Table 2.1).

### 2.4.3.3. Kinetic isotope fractionation during the hydration and hydroxylation of CO₂

When gaseous CO₂ dissolves in water with a pH higher than 7, most of the CO₂ is rapidly converted into HCO\(_3^-\) and CO\(_3^{2-}\) ions via the hydration and/or hydroxylation reaction pathways (Section 2.4.3.1). The initial oxygen isotope ratios of ‘HCO\(_3^-\)’ plus CO\(_3^{2-}\) (\( R_{(\text{CO}_3^{2-} + \text{HCO}_3^-)}^0 \)) reflects the oxygen atoms from the molecules or ions involved in hydration and/or hydroxylation reactions. The parameter \( \alpha^0_{(\text{CO}_3^{2-} + \text{HCO}_3^-)/w} \) is defined as the initial (kinetic) oxygen isotope fractionation between hydrated/hydroxylated CO₂ and water:

\[ \alpha^0_{(\text{CO}_3^{2-} + \text{HCO}_3^-)/w} = \frac{18R_{(\text{CO}_3^{2-} + \text{HCO}_3^-)}^0}{18R_w} \]  

(2.36)
In turn, $^{18}R_{(CO_3^{2-}+HCO_3^-)}^0$ is equal to the isotopic mass-balance between the initial oxygen isotopic ratios of hydrated and hydroxylated CO₂. Applying the isotopic mass balance formulation of Hayes (1982), $^{18}R_{(CO_3^{2-}+HCO_3^-)}^0$ is expressed as:

$$^{18}R_{(CO_3^{2-}+HCO_3^-)}^0 = \left[ \frac{^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+2}}{^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+4}} \cdot X_{+2} + \frac{^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+4}}{^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+2}} \cdot X_{+4} \right]^{-1} - 1 \quad (2.37)$$

Because $^{18}O \ll ^{16}O$, $^{18}R_{(CO_3^{2-}+HCO_3^-)}^0$ can be approximated as (Zeebe and Wolf-Gladrow, 2001):

$$^{18}R_{(CO_3^{2-}+HCO_3^-)}^0 \approx \frac{^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+2}}{^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+4}} \cdot X_{+2} + \frac{^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+4}}{^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+2}} \cdot X_{+4} \quad (2.38)$$

Where $^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+2}$ and $^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+4}$ are the initial oxygen isotopic ratios of hydrated and hydroxylated CO₂, respectively, and where $X_{+2}$ and $X_{+4}$ are the relative proportions of hydrated and hydroxylated CO₂, respectively. The relative importance of CO₂ hydration versus CO₂ hydroxylation depends on solution pH (Johnson, 1982). According to reactions pathways (2.26) and (2.27), $X_{+2}$ and $X_{+4}$ are expressed as follows:

$$X_{+2} = \frac{k^{+2}}{k^{+2} + k^{+4} [OH^-]} \quad (2.39)$$

and

$$X_{+4} = \frac{k^{+4} [OH^-]}{k^{+2} + k^{+4} [OH^-]} \quad (2.40)$$

The concentration of hydroxyl ions $[OH^-]$ in equation (2.40) and (2.41) is obtained from the stoichiometric ion product of water $K_w^*$ (DOE, 1994) and pH. Solving (2.38) requires knowledge of $^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+2}$ and $^{18}R_{(CO_3^{2-}+HCO_3^-)}^{+4}$. 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 ‘CO₂(aq) and H₂O’ and hydrated CO₂ (i.e. mainly the sum of HCO₃⁻ and CO₃²⁻). Where the reaction is strictly forward the $^{18}k_{+2}/^{16}k_{+2}$ ratio is related to the oxygen isotopic ratios of reactants (CO₂(aq) + H₂O) and products (HCO₃⁻ and CO₃²⁻):
\[
\frac{^{18}k_{+2}}{^{16}k_{+2}} = \frac{^{18}R_{(CO^3_-+HCO^-)}^{+2}}{^{18}R_{(CO_2+w)}} \tag{2.41}
\]

where \(^{18}R_{(CO_2+w)}\) is the oxygen isotopic ratio of ‘\(CO_{2(aq)} + H_2O\)’. Rearranging (2.41) provides an equation for \(^{18}R_{(CO^3_-+HCO^-)}^{+2}\) as a function of the \(^{18}k_{+2}/^{16}k_{+2}\) ratio:

\[
^{18}R_{(CO^3_-+HCO^-)}^{+2} = ^{18}R_{(CO_2+w)} \cdot \frac{^{18}k_{+2}}{^{16}k_{+2}} \tag{2.42}
\]

with a contribution of two oxygen atoms from \(CO_{2(aq)}\) and one from \(H_2O\), \(^{18}R_{(CO_2+w)}\) is expressed as:

\[
^{18}R_{(CO_2+w)} \cong ^{18}R_{CO_2} \cdot \frac{2}{3} + ^{18}R_w \cdot \frac{1}{3} \tag{2.43}
\]

The value of \(^{18}k_{+2}/^{16}k_{+2}\) in equation (2.42) 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 \(CO_{2(aq)}\) (\(\alpha_{(CO^3_-+HCO^-)/CO_2}\)) of 0.986 ± 0.001 (Zeebe, 2014). Note that Zeebe (2014) presented results for the kinetic fractionation factor between \(CO_{2(aq)}\) and hydrated \(CO_2\) (1.014 ± 0.001), thus the fractionation factor between hydrated \(CO_2\) and \(CO_{2(aq)}\) is the inverse of 1.014. The initial oxygen isotope ratio of hydrated \(CO_2\) can therefore be expressed as a function of \(\alpha_{(CO^3_-+HCO^-)/CO_2}\):

\[
^{18}R_{(CO^3_-+HCO^-)}^{+2} = ^{18}R_{CO_2} \cdot \alpha_{(CO^3_-+HCO^-)/CO_2} \tag{2.44}
\]

where \(^{18}R_{CO_2}\) is the oxygen isotopic ratio of \(CO_{2(aq)}\). Substituting (2.44) into (2.42) yields an equation for \(^{18}k_{+2}/^{16}k_{+2}\) as a function of \(\alpha_{(CO^3_-+HCO^-)/CO_2}\):

\[
\frac{^{18}k_{+2}}{^{16}k_{+2}} = \frac{\alpha_{(CO^3_-+HCO^-)/CO_2}}{2/3 + 1/3 \cdot (\alpha_{CO_2/w})^{-1}} \tag{2.45}
\]

Using the relation of Beck et al. (2005) for \(\alpha_{CO_2/w}\) (Table 2.1) and a value of 0.986 ± 0.001 for \(\alpha_{(CO^3_-+HCO^-)/CO_2}\) (Zeebe, 2014) yields a \(^{18}k_{+2}/^{16}k_{+2}\) ratio of 0.9994 ± 0.0010 at 25°C. This calculation suggests that the mass-related kinetic isotope effect during \(CO_2\) hydration is on the order of 1‰ or
less. The 14‰ depletion in $^{18}$O between hydrated CO$_2$ and CO$_2$(aq) ($\alpha_{(CO_2^{\text{aq}}+HCO_3^-)/CO_2} = 0.986 \pm 0.001$, Zeebe, 2014) is therefore mainly caused by the contribution of oxygen atoms from water molecules.

Similar to the hydration reaction above, we define $^{18}k_{+4}$ and $^{16}k_{+4}$ 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$_2$(aq) and OH$^-$:

$$\frac{^{18}k_{+4}}{^{16}k_{+4}} = \frac{^{18}R^{+4}_{(CO_2^{3-}+HCO_3^-)}}{^{18}R_{(CO_2+OH^-)}}$$  \hspace{1cm} (2.46)

where $^{18}R_{(CO_2+OH^-)}$ is the oxygen isotopic ratio of ‘CO$_2$(aq) + OH$^-$’. Rearranging equation (2.46), we have:

$$^{18}R^{+4}_{(CO_2^{3-}+HCO_3^-)} = \frac{^{18}R_{(CO_2+OH^-)}}{^{16}k_{+4}} \cdot \frac{^{18}k_{+4}}{^{16}k_{+4}}.$$  \hspace{1cm} (2.47)

With a contribution of two oxygen atoms from CO$_2$(aq) and one from OH$^-$, $^{18}R_{(CO_2+OH^-)}$ is expressed as:

$$^{18}R_{(CO_2+OH^-)} \approx \frac{^{18}R_{CO_2}}{3} + \frac{^{18}R_{OH^-}}{3},$$  \hspace{1cm} (2.48)

where $^{18}R_{OH^-}$ is the oxygen isotope ratio of OH$^-$ ions. The temperature dependence of the equilibrium oxygen isotope fractionation between OH$^-$ and H$_2$O ($a_{OH^-/H_2O}^\theta$) was estimated by Green and Taube (1963) (Table 2.1). The $^{18}k_{+4}/^{16}k_{+4}$ ratio has not been 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$_3^{2-}$ and HCO$_3^-$ but not of CO$_3^{2-}$ or HCO$_3^-$ individually. The parameter $^{18}R_{CO_2^{3-}+HCO_3^-}^0$ in equation (2.38) can be expressed as the isotopic mass balance between the initial oxygen isotope ratio of CO$_3^{2-}$ ($^{18}R_{CO_3^{2-}}^0$) and HCO$_3^-$ ($^{18}R_{HCO_3^-}^0$):

$$^{18}R_{(CO_3^{2-}+HCO_3^-)}^0 = ^{18}R_{CO_3^{2-}}^0 \cdot X_{CO_3^{2-}} + ^{18}R_{HCO_3^-}^0 \cdot X_{HCO_3^-}.$$  \hspace{1cm} (2.49)
where $X_{CO_3^{2-}}$ and $X_{HCO_3^{-}}$ are the relative proportions of $CO_3^{2-}$ and $HCO_3^{-}$ ions respectively and are obtained from the first and second dissociation constants of carbonic acid (Millero et al., 2006, Appendix A4). As mentioned in Section 2.4.3.1, $CO_3^{2-}$ and $HCO_3^{-}$ are considered to be at isotopic equilibrium with each other due to the fast rate of protonation and deprotonation between these species relative to the rate of hydration and hydroxylation reactions. The ratio of $^{18}R_{CO_3^{2-}}^0$ to $^{18}R_{HCO_3^{-}}^0$ is therefore equal to the equilibrium fractionation factor between $CO_3^{2-}$ and $HCO_3^{-}$ ($\alpha_{CO_3^{2-}/HCO_3^{-}}^{eq}$):

$$\frac{^{18}R_{CO_3^{2-}}^0}{^{18}R_{HCO_3^{-}}^0} = \alpha_{CO_3^{2-}/HCO_3^{-}}^{eq}$$  \hspace{1cm} (2.50)

Substituting (50) into (49) and dividing each isotopic ratio by $^{18}R_w$, expressions for $\alpha_{CO_3^{2-}/w}^0$ and $\alpha_{HCO_3^{-}/w}^0$ are as follows:

$$\alpha_{CO_3^{2-}/w}^0 \approx \frac{\alpha_{CO_3^{2-}/w}^{eq} (X_{CO_3^{2-}} + X_{HCO_3^{-}})X_{HCO_3^{-}}}{\alpha_{CO_3^{2-}/w}^{eq} X_{CO_3^{2-}} + X_{HCO_3^{-}} \left(\frac{\alpha_{CO_3^{2-}/HCO_3^{-}}^{eq}}{\alpha_{CO_3^{2-}/HCO_3^{-}}^{eq}}\right)^{-1}}$$  \hspace{1cm} (2.51)

and

$$\alpha_{HCO_3^{-}/w}^0 \approx \frac{\alpha_{HCO_3^{-}/w}^{eq} X_{CO_3^{2-}} + X_{HCO_3^{-}}}{\alpha_{HCO_3^{-}/w}^{eq} X_{CO_3^{2-}} + X_{HCO_3^{-}}}$$  \hspace{1cm} (2.52)

The value of $\alpha_{CO_3^{2-}/HCO_3^{-}}^{eq}$ in equation (2.51) and (2.52) is obtained from the equilibrium isotopic fractionation factors $\alpha_{CO_3^{2-}/w}^{eq}$ and $\alpha_{HCO_3^{-}/w}^{eq}$ (Beck et al., 2005; Table 2.1):

$$\alpha_{CO_3^{2-}/HCO_3^{-}}^{eq} = \frac{\alpha_{CO_3^{2-}/w}^{eq}}{\alpha_{HCO_3^{-}/w}^{eq}}$$  \hspace{1cm} (2.53)

From this set of equations, it is possible to calculate, and display graphically, the kinetic limits $\alpha_{CO_3^{2-}/w}^0$ and $\alpha_{HCO_3^{-}/w}^0$ as a function of temperature and chemical speciation (Fig. 2.5). The increasing contribution of the hydroxylation reaction and increasing $CO_3^{2-}/HCO_3^{-}$ ratio with increasing pH (Fig. 2.5A) make $\alpha_{CO_3^{2-}/w}^0$ and $\alpha_{HCO_3^{-}/w}^0$ highly sensitive to changes in solution pH (Fig. 2.5B). Overall, both $\alpha_{CO_3^{2-}/w}^0$ and $\alpha_{HCO_3^{-}/w}^0$ decrease with increasing pH, although minimum values are attained when
the hydroxylation/hydration reaction rate ratio is near the maximum value but the CO$_3^{2-}$/HCO$_3^-$ ratio is low. For a solution at 25°C and salinity of 2.5, both $\alpha_{CO_3^{2-}/w}^0$ and $\alpha_{HCO_3^-/w}^0$ reach minimum values at pH ~ 9.6 (Fig. 2.5B). Since in our model CO$_3^{2-}$ is the only precipitating DIC species, the kinetic limit of $\alpha_{c/w}$ is always 1.0 % lower than $\alpha_{CO_3^{2-}/w}^0$ (see Section 2.4.2.4). At high pH, the $\alpha_{CO_3^{2-}/w}^0$ and $\alpha_{HCO_3^-/w}^0$ values and the kinetic limit of $\alpha_{c/w}$ depend on the $\frac{k_{+4}}{k_{+3}}$ ratio, which is constrained with experimental data in Section 2.5.3.

2.5. Data-model comparison

2.5.1. Experimental data

We used the temperature, pH, salinity, [DIC], [Ca$^{2+}$], calcite growth rate and carbonic anhydrase activity from the calcite growth experiments of Dietzel et al. (2009) and Baker (2015) to calculate the calcite-CO$_3^{2-}$ and CO$_3^{2-}$-H$_2$O fractionations using our model. The model estimates were compared to the measured calcite-CO$_3^{2-}$ and CO$_3^{2-}$-H$_2$O fractionations from the Dietzel and Baker experiments. 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 $\delta^{18}$O of the incoming CO$_2$(g) is known for the experiments of Baker (2015) but not for those of Dietzel et al. (2009). We assumed however, that CO$_2$(aq) entered the precipitating solution at isotopic equilibrium with water during the experiments of Dietzel et al. (2009) 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 this chapter, 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 ± 1/3 of the initial [DIC] reported by Dietzel et al. (2009) (i.e. 33 to 100% of the reported maximum [DIC]).

We calculated level of isotopic equilibrium between DIC and water ($E_{DIC}$, equation 2.33, Table 2.3 and Fig. 2.6A) and the calculations 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).
Figure 2.5. Kinetic isotope effects in the CaCO₃-DIC-H₂O system during the hydration and hydroxylation of CO₂.

(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 \( f = 0.05 \). (B) Initial oxygen isotope fractionation (kinetic limit) relative to water for CO₃²⁻, HCO₃⁻ and CaCO₃ following the hydration and hydroxylation of CO₂ in the solution defined in (A). In (B), the CO₃²⁻ (red) and HCO₃⁻ (light blue) lines were constructed with a fractionation factor between CO₃²⁻ and HCO₃⁻ of 0.9932 (see Section 2.4.1) and a pH-dependent fractionation factor between hydrated/hydroxylated CO₂ (i.e., CO₃²⁻ + HCO₃⁻, dash line) and water varying from 1.0269 to 1.0105. The mass dependent kinetic isotope fractionation during hydration (\( \frac{18k_{+2}}{16k_{+2}} = 0.9994 \)) is seen in the difference between the “CO₃²⁻ + HCO₃⁻” and “CO₂(aq) + H₂O” lines at low pH values. For the hydroxylation reaction, the mass dependent kinetic fractionation (\( \frac{18k_{+4}}{16k_{+4}} = 0.9959 \)) is seen in the difference between the “CO₃²⁻ + HCO₃⁻” and “CO₂(aq) +OH⁻” lines at high pH values. Instantaneously precipitated CaCO₃ from a small fraction of the CO₃²⁻ pool would be depleted by ~ 1.0 ‰ (\( \frac{18k_{+c}}{16k_{+c}} = 0.9990 \)) relative to the CO₃²⁻ pool (black continuous line). The fractionations relative to water for CO₃²⁻, HCO₃⁻ and CaCO₃ are lowest where the hydroxylation/hydration reaction rate ratio is high but the CO₃²⁻/HCO₃⁻ ratio is low (vertical line in panel A and B). For a CO₂-fed solution at 25°C, the kinetic limit of the oxygen isotope fractionation between CaCO₃ and water depends on the solution pH and varies from 19 to 8‰ (i.e. 1.019 to 1.008) between pH 7 and 9.6.
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 2.3). A plot of $\alpha_{c/w}$ versus temperature (Fig. 2.6B) 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 calcite precipitation from a non-equilibrium DIC pool ($E_{DIC} < 0.99$). 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. 2.6B). Also of note is that the temperature sensitivity of $\alpha_{c/w}$ obtained using Dietzel’s and Baker’s data with $E_{DIC} > 0.99$ is slightly lower than that reported by Kim and O’Neil (1997). The potential reasons for this difference are explored in Section 2.7.

In the following sections, the measured $\alpha_{c/w}$ values of Dietzel and Baker for the experiments where $E_{DIC} > 0.99$ and calculated equilibrium $\alpha_{CO_3^{2-}/w}$ values (Beck et al., 2005) 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 to investigate and quantify KIE between DIC and H$_2$O for experiments where $E_{DIC} < 0.99$.

**Figure 2.6.** 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 ($\varepsilon_{c/w}$) 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.
Table 2.3. Model input and output parameters for the calcite growth experiment of Baker (2015) and Dietzel et al. (2009).

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<th>σ</th>
<th>[Ca(^{2+})] μmol/kg</th>
<th>(R_s) nmol/s/L</th>
<th>[CA] μmol/kg</th>
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<td>25</td>
<td>8.30</td>
<td>840 420</td>
<td>9210</td>
<td>6.42</td>
<td>0.00</td>
<td>11.18</td>
<td>1.00</td>
<td>0.60</td>
<td>28.09</td>
<td>0.15</td>
<td>27.59</td>
<td>0.27</td>
<td>0.65</td>
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</tr>
<tr>
<td>D14b</td>
<td>25</td>
<td>8.30</td>
<td>560 280</td>
<td>9220</td>
<td>3.92</td>
<td>0.00</td>
<td>7.46</td>
<td>1.00</td>
<td>0.66</td>
<td>28.66</td>
<td>0.15</td>
<td>27.94</td>
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<tr>
<td>D15</td>
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<td>8.30</td>
<td>293 147</td>
<td>9270</td>
<td>1.01</td>
<td>0.00</td>
<td>3.91</td>
<td>1.00</td>
<td>0.75</td>
<td>29.50</td>
<td>0.15</td>
<td>28.57</td>
<td>0.34</td>
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<td>D16</td>
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<td>493 247</td>
<td>9530</td>
<td>6.64</td>
<td>0.00</td>
<td>6.74</td>
<td>1.00</td>
<td>0.67</td>
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<td>0.15</td>
<td>28.04</td>
<td>0.30</td>
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<tr>
<td>D17</td>
<td>25</td>
<td>8.30</td>
<td>287 144</td>
<td>9590</td>
<td>0.59</td>
<td>0.00</td>
<td>3.95</td>
<td>1.00</td>
<td>0.75</td>
<td>28.30</td>
<td>0.15</td>
<td>28.56</td>
<td>0.34</td>
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<tr>
<td>D18</td>
<td>25</td>
<td>8.30</td>
<td>313 157</td>
<td>9100</td>
<td>1.19</td>
<td>0.00</td>
<td>4.13</td>
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<td>0.74</td>
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<td>0.15</td>
<td>28.51</td>
<td>0.33</td>
<td>0.81</td>
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</table>
Table 2.3. (continued)

| ID<sup>(b)</sup> | T<sup>(c)</sup> | pH<sub>NBS</sub> | [DIC]<sup>(b)</sup> | [Ca<sup>2+</sup>]<sup>(b)</sup> | R<sub>e</sub> | [CA]<sup>(c)</sup> | Ω<sup>(c)</sup> | E<sub>DIC<sup>(c)</sup></sup> | E<sub>c</sub> | measured ε<sup>(c</sup>)<sup>(c</sup>)<sup>(c</sup>) | σ | modelled ε<sup>(c</sup>)<sup>(c)</sup>(%o) | pos σ | neg σ |
|---------------|----------------|----------------|----------------------|----------------|--------|----------------|--------|-----------------|--------|---------------------|--------|--------|--------|
| D19b          | 25             | 8.30           | 1033 517             | 9470           | 79.60  | 0.00           | 14.07  | 0.84            | 0.57   | 27.58               | 0.15   | 26.07             | 0.99   | 1.62   |
| D20b          | 25             | 8.30           | 833 417              | 9540           | 51.20  | 0.00           | 11.41  | 0.90            | 0.60   | 26.97               | 0.15   | 26.73             | 0.73   | 1.37   |
| D21b          | 25             | 8.30           | 1087 544             | 9670           | 87.60  | 0.00           | 15.01  | 0.82            | 0.57   | 27.25               | 0.15   | 25.90             | 1.04   | 1.67   |
| D22b          | 25             | 8.30           | 767 384              | 9210           | 54.60  | 0.00           | 10.21  | 0.86            | 0.61   | 27.21               | 0.15   | 26.52             | 0.90   | 1.52   |
| D23           | 25             | 8.30           | 387 194              | 9450           | 0.90   | 0.00           | 5.26   | 1.00            | 0.71   | 28.08               | 0.15   | 28.27             | 0.31   | 0.77   |
| D24           | 40             | 9.00           | 67 34                | 8620           | 3.56   | 0.00           | 4.64   | 0.60            | 0.72   | 24.04               | 0.15   | 21.15             | 3.93   | 2.18   |
| D25           | 40             | 9.00           | 87 44                | 8980           | 3.66   | 0.00           | 6.22   | 0.69            | 0.68   | 23.17               | 0.15   | 21.83             | 3.37   | 2.33   |
| D26           | 40             | 9.00           | 53 27                | 9660           | 0.58   | 0.00           | 4.03   | 0.99            | 0.75   | 24.77               | 0.15   | 25.61             | 0.34   | 0.47   |
| D27           | 40             | 9.00           | 107 54               | 9450           | 4.24   | 0.00           | 7.99   | 0.71            | 0.65   | 20.01               | 0.15   | 21.85             | 3.21   | 2.37   |
| D28           | 40             | 9.00           | 100 50               | 9740           | 1.65   | 0.00           | 7.64   | 0.95            | 0.65   | 23.61               | 0.15   | 24.58             | 0.61   | 1.41   |
| D29           | 40             | 9.00           | 113 57               | 9310           | 7.78   | 0.00           | 8.34   | 0.51            | 0.64   | 21.57               | 0.15   | 19.56             | 4.31   | 2.02   |
| D30           | 40             | 9.00           | 100 50               | 9670           | 2.46   | 0.00           | 7.61   | 0.86            | 0.65   | 22.65               | 0.15   | 23.63             | 1.65   | 2.11   |
| D31           | 40             | 9.00           | 113 57               | 9800           | 3.08   | 0.00           | 8.67   | 0.83            | 0.64   | 22.13               | 0.15   | 23.18             | 1.99   | 2.24   |
| D32           | 40             | 9.00           | 100 50               | 9680           | 4.14   | 0.00           | 7.6    | 0.69            | 0.65   | 21.65               | 0.15   | 21.71             | 3.34   | 2.35   |
| D33           | 40             | 8.30           | 247 124              | 8790           | 3.42   | 0.00           | 3.81   | 1.00            | 0.76   | 25.73               | 0.15   | 25.80             | 0.44   | 0.74   |
| D34           | 40             | 8.30           | 433 217              | 4230           | 2.88   | 0.00           | 3.74   | 1.00            | 0.76   | 25.87               | 0.15   | 25.81             | 0.42   | 0.78   |
| D35           | 40             | 8.50           | 93 47                | 9610           | 0.15   | 0.00           | 2.42   | 1.00            | 0.83   | 25.70               | 0.15   | 26.27             | 0.48   | 0.86   |
| D36           | 40             | 8.70           | 160 80               | 9930           | 2.22   | 0.00           | 6.6    | 0.99            | 0.67   | 24.03               | 0.15   | 25.23             | 0.36   | 0.27   |
| D37           | 40             | 9.60           | 60 30                | 19500          | 7.94   | 0.00           | 19.27  | 0.16            | 0.54   | 15.31               | 0.15   | 13.56             | 3.29   | 0.61   |
| D38b          | 40             | 8.30           | 547 274              | 9280           | 144.40 | 0.00           | 8.84   | 0.41            | 0.63   | 24.99               | 0.15   | 21.08             | 2.00   | 1.12   |
| D39b          | 40             | 8.30           | 480 240              | 8900           | 185.20 | 0.00           | 7.49   | 0.30            | 0.66   | 24.77               | 0.15   | 20.51             | 1.61   | 0.98   |
| D40b          | 40             | 8.30           | 213 107              | 9190           | 1.23   | 0.00           | 3.41   | 1.00            | 0.77   | 25.91               | 0.15   | 25.91             | 0.45   | 0.80   |

<sup>(a)</sup>“B” refers to Baker (2015), “D” refers to Dietzel et al. (2009)

<sup>(b)</sup>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 2.3.1).

<sup>(c)</sup>Model output parameters.

<sup>(d)</sup>Calculated using a partial reaction order n<sub>2</sub> of 0.2
2.5.2. 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 2.1, 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 $\alpha_{CO_3^{2-}/w}$ value (equation 2.6). Calculated $\alpha_{c/CO_3^{2-}}$ values for experimental conditions where $E_{DIC} > 0.99$ vary from 1.0028 to 1.0049 (Fig. 2.7A, ‘measured’ $\epsilon^{18}$O$_{c/CO_3^{2-}}$) and appear to be independent of temperature and experimental setup. Importantly, the $\alpha_{c/CO_3^{2-}}$ values are negatively correlated with the calcite saturation state $\Omega$ ($r^2 = 0.34$, 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 ($\alpha_{c/CO_3^{2-}}^{+c} = 0.9990$). The lack of a significant temperature effect on $\alpha_{c/CO_3^{2-}}$ (Fig. 2.7A) implies that the $\alpha_{c/CO_3^{2-}}^{eq}$ and $\alpha_{c/CO_3^{2-}}^{+c}$ 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 $\alpha_{CO_3^{2-}/w}$ and constant values for $\alpha_{c/CO_3^{2-}}^{eq}$ and $\alpha_{c/CO_3^{2-}}^{+c}$ (Table 2.1 and Table 2.2), the $\alpha_{c/w}^{eq}$ and $\alpha_{c/w}^{+c}$ can be expressed as a function of temperature:

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

and

$$\alpha_{c/w}^{+c} = \exp(2390 T^{-2} - 0.0027) \cdot 0.999 \quad \text{(for an equilibrated DIC pool only)}$$

In the model, $\alpha_{c/w}$ varies between $\alpha_{c/w}^{eq}$ and $\alpha_{c/w}^{+c}$ as a function of $\Omega$ and the partial reaction order $n_2$ (Fig. 2.3, Section 2.4.2.2). 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. 2.7B). Measured and modelled $\alpha_{c/w}$ values agree best at $n_2 = 0.20 \pm 0.02$ (Fig. 2.7B and 2.7C, average $|\Delta^{18}$O$_{data-model}| = 0.25\%$, $r^2 = 0.96$, 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. 2.7B).
Figure 2.7. Measured versus modelled oxygen isotope fractionation between calcite and water for experimental conditions where the DIC pool was isotopically equilibrated. (A) 'Measured' (data points) and modelled (lines) oxygen isotope fractionation between calcite and CO$_3^{2-}$ ($\epsilon_{c/CO_3^{2-}}$) versus $1/\Omega$ for the experiments of Dietzel et al. (2009) and Baker (2015). 'Measured' $\epsilon_{c/CO_3^{2-}}$ values were inferred from oxygen isotope fractionation between calcite and water and the theoretical 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 $\epsilon_{c/CO_3^{2-}}$ vs $1/\Omega$ (continuous line) with its uncertainties (dashed lines). Modelled $\epsilon_{c/CO_3^{2-}}$ values assume an equilibrium limit of $+5.5 \pm 0.2$ ‰ (inferred from Coplen, 2007) and a kinetic limit of $-1.0 \pm 0.3$ ‰ (inferred 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 $n_2 = 0.20 \pm 0.02$ 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) Modelled versus measured $\epsilon_{c/w}$ values using $n_2 = 0.2$. Uncertainties on modelled $\epsilon_{c/w}$ values (error bars) are mostly caused by the uncertainties on the solution $\Omega$ during calcite precipitation. Where the DIC pool is isotopically equilibrated, the oxygen isotope fractionation between calcite and the CO$_3^{2-}$ pool ($\epsilon_{c/CO_3^{2-}}$) appears to be independent of temperature. The solution $\Omega$ seems to have a weak negative effect on $\epsilon_{c/CO_3^{2-}}$ with $\epsilon_{c/CO_3^{2-}}$ decreasing from $\sim +4.1$ ‰ to $\sim +2.9$ ‰ between the 3-12 range in $\Omega$ (i.e. 0.4-0.1 range in $1/\Omega$).
The sensitivity analysis presented in Figure 2.7B, 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 \(^{18}\text{O}/^{16}\text{O} \) 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 \( \delta^{18}\text{O} \) of calcite precipitated in CO₂-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.

### 2.5.3. Calcite precipitated from isotopically non-equilibrated DIC

Kinetic isotope effects related to the CO₂ 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 CO₃²⁻ (Section 2.5.2), and the only model unknown remaining to quantify DIC-H₂O kinetic effects is the kinetic isotope fractionation related to the hydroxylation of CO₂ (\(^{18}\text{O}_{16}\text{O}^{18}\text{O}/^{16}\text{O}^{16}\text{O} \)). Similar to the treatment of \( n_2 \) in Section 2.5.2, a sensitivity analysis of data-model agreement was used to determine \(^{18}k_{+\phi} /^{16}k_{+\phi} \) (not shown). Measured and modelled \( \alpha_{c/w} \) agree best at \(^{18}k_{+\phi} /^{16}k_{+\phi} = 0.9959 \) (average \( |\Delta^{18}\text{O}_{\text{data-model}}| = 1.08 \%_o, r^2 = 0.89, \text{p-value} < 0.001 \)), although similar data-model agreement (\( |\Delta^{18}\text{O}_{\text{data-model}}| = 1.08 \text{ to } 1.14\%_o \)) is obtained where \(^{18}k_{+\phi} /^{16}k_{+\phi} \) ranges from 0.9959 up to 0.9980. Hence, a \(^{18}k_{+\phi} /^{16}k_{+\phi} \) of 0.9970 ±0.0011 is a reasonable estimate. The low precision of the estimated \(^{18}k_{+\phi} /^{16}k_{+\phi} \) is due to the low number (\( n = 3 \)) of available \( \alpha_{c/w} \) values for calcite precipitated at high pH from a non-equilibrated DIC pool (\( E_{\text{DIC}} < 0.1 \)), as well as uncertainties in the DIC concentration during the calcite precipitation experiments of Dietzel et al. (2009). Nevertheless, a comparison of experimental data with model outputs using \(^{18}k_{+\phi} /^{16}k_{+\phi} = 0.9959 \) (Fig. 2.8, Table 2.3) shows that the model captures the full range of measured \( \alpha_{c/w} \), with 40 of the 48 measured \( \alpha_{c/w} \) values within error of model outputs. This result gives confidence in the ability of the model to quantify the oxygen isotope fractionation between CaCO₃ and CO₃²⁻ and between CO₃²⁻ and H₂O over a wide range of temperature, pH, \( \Omega \) and DIC residence times.
Figure 2.8. Measured versus modelled oxygen isotope fractionation between calcite and water (ε_{c/w}) for all experimental conditions at (A) 5°C, (B) 25°C and (C) 40°C. The experimental data include all the ε_{c/w} values presented in Figure 2.7 and additional ε_{c/w} values from the experiments of Dietzel et al. (2009) where calcite precipitated from non-isotopically equilibrated DIC (cf. Figure 2.6). Modelled ε_{c/w} values depend on the oxygen isotope fractionation between CO_3^{2-} and water (ε_{CO_3^{2-}/w}) and the oxygen isotope fractionation between calcite and CO_3^{2-} (ε_{c/CO_3^{2-}}). All modelled ε_{c/w} were calculated using a partial reaction order n_2 value of 0.2 (cf. Figure 2.7 and Section 2.5.2). The model assumes that the equilibrium limit of ε_{c/w} (upper horizontal line) is independent of pH while the kinetic limit of ε_{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 range of possible ε_{CO_3^{2-}/w} values (grey shaded area) decreases with temperature and is always smaller than the range of possible ε_{c/w} values. (D) Compilation of measured versus modelled ε_{c/w} values at 5°C, 25°C and 40°C temperatures. A linear regression between modelled and measured ε_{c/w} values (pink dash line) yields an r^2 value of 0.89. In each plot, uncertainties on modelled ε_{c/w} values (error bars) were calculated as the square root of the sum of square uncertainties from each model input parameter (cf. Appendix A5). The good data-model agreement suggests that kinetic isotope effects occurring between DIC and H_2O and between calcite and CO_3^{2-} are well predicted by the model.
2.6. Discussion

2.6.1. 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. 2.7A), suggesting that one or more parameter, in addition to temperature, affects the calcite-CO\(_3^{2-}\) (and possibly calcite-HCO\(_3^{-}\)) fractionation and/or the relative proportion of HCO\(_3^{-}\) and CO\(_3^{2-}\) precipitating.

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 chapter). 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. 2.6).

In the study of Baker (2015), \( \alpha_{c/w} \) decreases by ~ 0.7‰ between pH 7.5 and 9.3 (Fig. 2.9A), which would seem to support the model of Watkins et al. (2014) that suggests \( \alpha_{c/w} \) decreases with increasing pH. However, the study of Dietzel et al. (2009) shows that \( \alpha_{c/w} \) varies by 1.5‰ at the single pH value of 8.3 (Fig. 2.9A). A similar result is obtained when \( \alpha_{c/w} \) is plotted against the solution \([\text{CO}_3^{2-}] / [\text{CO}_3^{2-} + \text{HCO}_3^-]\) molar ratios (Fig. 2.9B), suggesting that neither pH nor DIC speciation explain the scatter in the study of Dietzel et al. (2009).

There are several reasons that may explain why in the study of Baker (2015) pH and DIC speciation are not the primary parameters causing \( \alpha_{c/w} \) to vary. If \( \alpha_{c/w} \) were affected by increased contribution
of HCO$_3^-$ to calcite growth as pH decreased (Watkins et al., 2014), one would expect a larger decrease in $\alpha_{c/w}$ than 0.7‰ (between pH 7.5 and 9.3) due to the ~ 7‰ difference in $^{18}$O/$^{16}$O between isotopically equilibrated CO$_3^{2-}$ and HCO$_3^-$ (Beck et al., 2005). In fact, the surface speciation model of Wolthers et al. (2012), which is the basis for the Watkins et al. (2014) model, predicts that between pH 7.5 and 9.3, the relative abundance of HCO$_3^-$ ions adsorbed to calcite decreases from 93% to 17% while the CO$_3^{2-}$ contribution increases from 7 to 83% (parameter $\Theta$ in Watkins et al., 2014). A shift from HCO$_3^-$ to CO$_3^{2-}$ as the dominant precipitating species should therefore be accompanied by a substantial decrease in $\alpha_{c/w}$, which does not occur (Fig. 2.9A). This observation is also consistent with inorganic aragonite precipitation experiments (Kim et al., 2006) showing no significant pH effect on the oxygen isotope fractionation between rapidly precipitated aragonite and water. Hence, the available data supports the notion that CO$_3^{2-}$ is the main contributing DIC species to calcite and aragonite growth.

The model of Watson (2004) suggests that $\alpha_{c/w}$ decreases with increasing net calcite growth rate. Although both Watson’s model and the model presented in this chapter involve calcite growth rate as the main controlling factor of $\alpha_{c/w}$, the mechanism involved for the isotopic equilibration between calcite and the precipitating DIC species differ. In the model of Watson (2004), the level of isotopic equilibration is determined by a competition between calcite surface growth rate and diffusive processes on the solid side of the solid-fluid interface, while in our model, it is the ratio between the backward and the forward reaction ($r_c/r_+\alpha$) that controls isotopic equilibration (DePaolo, 2011). A plot of $\alpha_{c/w}$ against calcite growth rate normalised to the calcite surface (Fig. 2.9C) shows no apparent relationship for growth rates varying from 0.05 to 1.05 µmol/m$^2$/s, suggesting that $\alpha_{c/w}$ is not directly controlled by the calcite net growth rate.

In the model presented in this chapter, CO$_3^{2-}$ is the only precipitating DIC species and the fractionation between calcite and CO$_3^{2-}$ ($\alpha_{c/CO_3^{2-}}$) is determined by the reaction rates ratio $r_c/r_+\alpha$, which in turn is a function of the solution $\Omega$ and the partial reaction order $n_2$ (Section 2.4.2). 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. 2.9D, $r^2 = 0.30$, p-value = 0.03), although large uncertainties in the $\Omega$ values limit any conclusive result. If the relation between $\alpha_{c/w}$ and $1/\Omega$ were linear, this would suggest first order reaction kinetics ($n_2 = 1$), contrasting with the $n_2$ value of 0.2 obtained from our sensitivity test (Fig. 2.7B). However, noteworthy is that the result of the sensitivity test depends on the accuracy of other model parameters, namely the equilibrium and kinetic limits of $\alpha_{c/CO_3^{2-}}$ ($\alpha_{c/CO_3^{2-}}^{eq}$ and $\alpha_{c/CO_3^{2-}}^{+\alpha}$). It is possible that $\alpha_{c/CO_3^{2-}}^{eq}$
was underestimated, since full isotopic equilibrium between calcite and water should only occur at chemical equilibrium (DePaolo, 2011). Because net crystal growth is inherently a non-equilibrium process, the true value of $\alpha_{c/w}^{eq}$ may be higher than reported by Coplen (2007). There are also uncertainties regarding $\alpha_{c/CO_3^{2-}}^{+}$, since it was estimated from the oxygen isotope fractionation between instantaneously precipitated witherite and water (Section 2.4.2.4). At the fast growth limit, calcite and witherite may behave differently with regards to isotopic fractionation. Finally, results from instantaneously precipitated minerals may not apply to minerals formed via surface growth processes. Resolution of these issues would benefit from experiments in which calcite is grown in solutions near chemical equilibrium, in highly saturated solutions, and in solutions with variable ionic strength. Nevertheless, the model presented here suggests that $\alpha_{c/w}$ is insensitive to pH when $\Omega$ is constant and therefore goes some way to explain the variable effect of pH on $\alpha_{c/w}$ reported previously.

![Figure 2.9](image)

**Figure 2.9.** Measured oxygen isotope fractionation between calcite and water ($\varepsilon_{c/w}$) at 25°C for experimental conditions with isotopically equilibrated DIC. (A) $\varepsilon^{18}$O$_{c/w}$ 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 ($\Omega$).
2.6.2. 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., 2.8A, 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 2.6.1). 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 CO$_2$ (McConnaughey, 1989b). In this case, 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. 2.5) because OH$^-$ has a low $^{18}\text{O}/^{16}\text{O}$ value (~39‰ relative to H$_2$O at 25°C, Green and Taube, 1963). In other words, strong KIE between the DIC species and water are more likely at high pH, and the kinetic limit of $\alpha_{c/w}$ decreases with pH (Fig. 2.5 and Fig. 2.8).

In the study of Dietzel et al. (2009), the 19‰ and 11‰ variations in measured $\alpha_{c/w}$ at 5°C and 40°C are explained almost entirely by the variations in the $^{18}\text{O}/^{16}\text{O}$ of the carbonate ion pool (Fig. 2.8, 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 significant decrease in the range of possible $\alpha_{c/w}$ and $\alpha_{\text{CO}_3^{2-}/w}$ values 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 $^{18}\text{O}/^{16}\text{O}$ of hydrated and hydroxylated CO$_2$. In other words, the difference between the equilibrium and the kinetic limit of $\alpha_{\text{CO}_3^{2-}/w}$ and $\alpha_{c/w}$ is reduced with increasing temperature.

2.7. Implications

2.7.1. 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) (KO) has been widely used to assess isotopic equilibrium in biogenic calcite (e.g. Bemis et al., 1998; von Grafen Stein et al., 1999; Barras et al., 2010; Decrouy et al., 2011; Candelier et al., 2013; Marchitto et al., 2014; Rollion-Bard et al., 2016 and many others). However, in the KO experiments calcite precipitation was triggered by CO$_2$ degassing, which can lead to KIE between the DIC and H$_2$O. The degassing of CO$_2$ elevates the solution pH, causes the dehydration of carbonic acid and
shifts the DIC speciation towards carbonate ions. 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). Importantly, the dehydration of carbonic acid is expected to increase the $^{18}\text{O} / ^{16}\text{O}$ ratio of the precipitating $\text{CO}_3^{2-}$ ions, which would increase the $\alpha_{c/w}$. Interestingly, KO reported a 1 to 2‰ increase in $\alpha_{c/w}$ with increasing Ca$^{2+}$ 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 2.4.2, Fig. 2.7A). We postulate that the positive relationship between $\alpha_{c/w}$ and $\Omega$ reported by KO is due to a negative correlation between $\Omega$ and the DIC residence time in solution. The time available for DIC-H$_2$O isotopic equilibration likely decreases with $\Omega$ because the rate of calcite precipitation commonly increases with the solution $\Omega$. As a result, KIEs between DIC and H$_2$O are likely to increase with $\Omega$. Another supporting observation for the imprint of DIC-H$_2$O kinetic isotope effects on $\alpha_{c/w}$ during these experiments is the reducing effect of $\Omega$ on $\alpha_{c/w}$ with increasing temperature (cf. Fig. 2.6 in Kim et al., 1997). DIC-H$_2$O 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 Ca$^{2+}$ and HCO$_3^-$ concentrations of 5 mM for the less concentrated solution of KO 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 condition far from chemical equilibrium). Hence, the $\alpha_{c/w}$ reported by Kim and O’Neil (1997) most likely reflects KIEs between calcite and CO$_3^{2-}$ and perhaps KIEs between CO$_3^{2-}$ and H$_2$O.

Based on theoretical constraints presented in Section 2.4.2 and Figure 2.3 (i.e. isotopic equilibrium is approached in solution of low $\Omega$ and low ionic strength), we support previous suggestions that the natural inorganic calcite from Devil’s 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 Devil’s Hole (1.02849 at 33.7°C, Coplen, 2007) remains uncertain because of uncertainties in the water temperature (±2.6°C, Kluge et al., 2014) and $\delta^{18}\text{O}$ 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 Devil’s 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 $\Omega$ and ionic strength on the isotopic equilibration between CaCO$_3$ and CO$_3^{2-}$. Until new
2.7.2. The temperature sensitivity of $\alpha_{c/w}$

The temperature dependence of $\delta^{18}O_c$ (and $\varepsilon_{c/w}$) for slowly precipitated inorganic calcite and aragonite averages $-0.21 \pm 0.02\%$ between 0 and 30°C (O'Neil et al., 1969; Kim and O'Neil, 1997; Kim et al., 2007; Watkins et al., 2013). Based on the observation that the temperature sensitivities of $\varepsilon_{c/w}$, $\varepsilon_{CO_3^{2-}/w}$ and $\varepsilon_{HCO_3^-/w}$ are similar, it has been suggested that the temperature dependence of $\delta^{18}O_c$ is caused by the effect of temperature on the carbonate and bicarbonate ions $^{18}O/^{16}O$ (Wang et al., 2013). Our investigation of the calcite-$CO_3^{2-}$ oxygen isotope fractionation ($\varepsilon_{c/CO_3^{2-}}$; Fig. 2.7) shows for the first time that $\varepsilon_{c/CO_3^{2-}}$ is not significantly affected by temperature, confirming the Wang et al. (2013) hypothesis. An important implication of our result is that the temperature dependence of $\varepsilon_{CO_3^{2-}/w}$ and $\varepsilon_{c/w}$ should deviate from $-0.21 \pm 0.02\%/\degree C$ when the precipitating $CO_3^{2-}$ ions are not at isotopic equilibrium with water. On the other hand, isotopic disequilibrium effects between calcite and $CO_3^{2-}$ should have limited impact on the temperature sensitivity of $\varepsilon_{c/w}$. 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).

2.8. 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 DIC and water ($\alpha_{CO_3^{2-}/w}$ and $\alpha_{HCO_3^-/w}$). 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 DIC and $H_2O$ 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. Oxygen isotope equilibration between CaCO$_3$ and the carbonate ion pool is enhanced in solutions with low $\Omega$ and ionic strength. This implies that inorganic calcite from Devils Hole cave system
should have formed near isotopic equilibrium conditions while 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 sensitivity of $\alpha_{c/w}$ depends on the level of isotopic equilibration between the precipitating carbonate pool and water. When the precipitating carbonate ion pool is at isotopic equilibrium with water, a small negative pH effect on $\alpha_{c/w}$ occurs where pH is positively correlated to $\Omega$. Hence, where the DIC pool is fully equilibrated with H$_2$O during CaCO$_3$ precipitation, the pH dependence of $\alpha_{c/w}$ can be explained without the contribution of HCO$_3^-$ ions to calcite growth. On the other hand, disequilibrium effects between the DIC species and water can lead to strong positive or negative pH effects on $\alpha_{c/w}$. Such disequilibrium effects include the isotopic imprint of HCO$_3^-$ into CaCO$_3$ where the solution pH increases rapidly (i.e. fast HCO$_3^-$ conversion into CO$_3^{2-}$) and is followed by rapid CaCO$_3$ precipitation (e.g. calcification by foraminifers and corals).

3. Particularly low $\alpha_{c/w}$ values occur where the carbonate ion pool derives from gaseous CO$_2$ and the residence time of the DIC pool in solution is short. These conditions also favour strong correlations between $\alpha_{c/w}$ and pH due to the positive effect of pH on the rate of CO$_2$ hydroxylation and the negative effect of pH on the rate of isotopic equilibration between the DIC species and water. Light isotope enrichments of up to $\sim 25\%$ may occur where gaseous CO$_2$ dissolves in alkaline environments due to the contribution of OH$^-$ (39‰ in $^{18}$O/$^{16}$O relative to H$_2$O) in the hydroxylation reaction.

4. The temperature dependence of $\alpha_{c/w}$ appears to originate from the effect of temperature on the $^{18}$O/$^{16}$O ratio of carbonate ions in solution. This implies that isotopic disequilibrium effects between CaCO$_3$ and CO$_3^{2-}$ ions 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 between -0.19 and -0.23 $\%$/°C when carbonate ions do not reach isotopic equilibrium with water prior to CaCO$_3$ precipitation.
A2 Appendices

A2.1. Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>DIC</td>
<td>Dissolved inorganic carbon</td>
</tr>
<tr>
<td>CA</td>
<td>Enzyme carbonic anhydrase</td>
</tr>
<tr>
<td>KIE</td>
<td>Kinetic isotope effect</td>
</tr>
<tr>
<td>KIF</td>
<td>Kinetic isotope fractionation</td>
</tr>
<tr>
<td>EIF</td>
<td>Equilibrium isotope fractionation</td>
</tr>
<tr>
<td>Ω</td>
<td>Solution saturation state with respect to a CaCO$_3$ mineral</td>
</tr>
<tr>
<td>$K_{sp}^*$</td>
<td>Stoichiometric solubility product of a CaCO$_3$ mineral</td>
</tr>
<tr>
<td>$n_2$</td>
<td>Partial reaction order for CO$_3^{2-}$ during CaCO$_3$ precipitation</td>
</tr>
<tr>
<td>$I$</td>
<td>Ionic strength</td>
</tr>
<tr>
<td>$r_{-c}$</td>
<td>Rate of CaCO$_3$ dissolution (backward rate)</td>
</tr>
<tr>
<td>$r_{+c}$</td>
<td>Rate of CaCO$_3$ precipitation (forward rate)</td>
</tr>
<tr>
<td>$r_c$</td>
<td>Net rate of CaCO$_3$ precipitation</td>
</tr>
<tr>
<td>$E_c$</td>
<td>Level of isotopic equilibration between CaCO$_3$ and CO$_3^{2-}$</td>
</tr>
<tr>
<td>$E_{DIC}$</td>
<td>Level of isotopic equilibration between DIC and water</td>
</tr>
<tr>
<td>$RT_{DIC}$</td>
<td>Residence time of DIC in solution</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Time constant</td>
</tr>
<tr>
<td>$k_{cat}$</td>
<td>Catalytic rate constant</td>
</tr>
<tr>
<td>$K_M$</td>
<td>Michaelis-Menten constant</td>
</tr>
<tr>
<td>$^{18}R_W$</td>
<td>$^{18}$O/$^{16}$O ratio of water</td>
</tr>
<tr>
<td>$^{18}R_C$</td>
<td>$^{18}$O/$^{16}$O ratio of CaCO$_3$</td>
</tr>
<tr>
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<td>$^{18}$O/$^{16}$O ratio of CO$_3^{2-}$</td>
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<tr>
<td>$^{18}R_{CO_3^{2-}}^0$</td>
<td>$^{18}$R$_{CO_3^{2-}}$ at $t = 0$</td>
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<tr>
<td>$^{18}R_{HCO_3^-}$</td>
<td>$^{18}$O/$^{16}$O ratio of HCO$_3^-$</td>
</tr>
<tr>
<td>$^{18}R_{HCO_3^-}^0$</td>
<td>$^{18}$R$_{HCO_3^-}$ at $t = 0$</td>
</tr>
<tr>
<td>$^{18}R_{CO_2}$</td>
<td>$^{18}$O/$^{16}$O ratio of CO$_2$</td>
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<tr>
<td>Term</td>
<td>Description</td>
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<td>-----------------------------------------------------------------------------</td>
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<tr>
<td>$^{18}R_{\text{DIC}}$</td>
<td>$^{18}$O/$^{16}$O ratio of DIC</td>
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<tr>
<td>$^{18}R_{(\text{CO}_3^{2-}+\text{HCO}_3^-)}$</td>
<td>$^{18}$O/$^{16}$O ratio of $\text{CO}_3^{2-} + \text{HCO}_3^-$</td>
</tr>
<tr>
<td>$^{18}R_{(\text{CO}_2+w)}$</td>
<td>$^{18}$O/$^{16}$O ratio of $\text{CO}_2 + \text{H}_2\text{O}$</td>
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<td>$^{18}R_{(\text{CO}_2+\text{OH}^-)}$</td>
<td>$^{18}$O/$^{16}$O ratio of $\text{CO}_2 + \text{OH}^-$</td>
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<tr>
<td>$\alpha_{c/w}$</td>
<td>Oxygen isotope fractionation between CaCO$_3$ and water</td>
</tr>
<tr>
<td>$\alpha_{c/w}^{eq}$</td>
<td>Equilibrium limit of $\alpha_{c/w}$</td>
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<tr>
<td>$\alpha_{c/\text{CO}_3^{2-}}$</td>
<td>Oxygen isotope fractionation between CaCO$_3$ and $\text{CO}_3^{2-}$</td>
</tr>
<tr>
<td>$\alpha_{c/\text{CO}_3^{2-}}^{eq}$</td>
<td>Equilibrium limit of $\alpha_{c/\text{CO}_3^{2-}}$</td>
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<tr>
<td>$\alpha_{c/\text{CO}_3^{2-}}^{+}$</td>
<td>Kinetic limit of $\alpha_{c/\text{CO}_3^{2-}}$</td>
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<tr>
<td>$\alpha_{\text{CO}_3^{2-}/w}$</td>
<td>Oxygen isotope fractionation between $\text{CO}_3^{2-}$ and water</td>
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<tr>
<td>$\alpha_{\text{CO}_3^{2-}/w}^0$</td>
<td>$\alpha_{\text{CO}_3^{2-}/w}$ at $t = 0$</td>
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<tr>
<td>$\alpha_{\text{HCO}_3^-/w}$</td>
<td>Oxygen isotope fractionation between HCO$_3^-$ and water</td>
</tr>
<tr>
<td>$\alpha_{\text{HCO}_3^-/w}^0$</td>
<td>$\alpha_{\text{HCO}_3^-/w}$ at $t = 0$</td>
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<tr>
<td>$\alpha_{\text{CO}_2/w}$</td>
<td>Oxygen isotope fractionation between $\text{CO}_2$ and water</td>
</tr>
<tr>
<td>$\alpha_{(\text{CO}_3^{2-}+\text{HCO}_3^-)/w}$</td>
<td>Oxygen isotope fractionation between $\text{CO}_3^{2-} + \text{HCO}_3^-$ and water</td>
</tr>
<tr>
<td>$\alpha_{(\text{CO}_3^{2-}+\text{HCO}_3^-)/w}^0$</td>
<td>$\alpha_{(\text{CO}_3^{2-}+\text{HCO}_3^-)/w}$ at $t = 0$</td>
</tr>
<tr>
<td>$\alpha_{(\text{CO}_3^{2-}+\text{HCO}_3^-)/\text{CO}_2}^{+2}$</td>
<td>Oxygen isotope fractionation between $\text{CO}_3^{2-} + \text{HCO}_3^-$ and $\text{CO}_2$ following CO$_2$ hydration</td>
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<tr>
<td>$\alpha_{(\text{CO}_3^{2-}+\text{HCO}_3^-)/\text{CO}_2}^{+4}$</td>
<td>Oxygen isotope fractionation between $\text{CO}_3^{2-} + \text{HCO}_3^-$ and CO$_2$ following CO$_2$ hydroxylation</td>
</tr>
<tr>
<td>$^{16}k_{+c}$</td>
<td>Rate coefficient of $^{16}$O transfer between $\text{CO}_3^{2-}$ and CaCO$_3$ during CaCO$_3$ precipitation</td>
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<tr>
<td>$^{18}k_{+c}$</td>
<td>Rate coefficient of $^{18}$O transfer between $\text{CO}_3^{2-}$ and CaCO$_3$ during CaCO$_3$ precipitation</td>
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<tr>
<td>$^{16}k_{+2}$</td>
<td>Rate coefficient of $^{16}$O transfer between $\text{CO}_2$ and hydrated $\text{CO}_2$ ($\text{HCO}_3^- + \text{CO}_3^{2-}$) during CO$_2$ hydration</td>
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<tr>
<td>$^{18}k_{+2}$</td>
<td>Rate coefficient of $^{18}$O transfer between $\text{CO}_2$ and hydrated $\text{CO}_2$ ($\text{HCO}_3^- + \text{CO}_3^{2-}$) during CO$_2$ hydration</td>
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<tr>
<td>$^{16}k_{+4}$</td>
<td>Rate coefficient of $^{16}$O transfer between $\text{CO}_2$ and hydroxylated $\text{CO}_2$ ($\text{HCO}_3^- + \text{CO}_3^{2-}$) during CO$_2$ hydroxylation</td>
</tr>
</tbody>
</table>
Rate coefficient of $^{18}$O transfer between CO$_2$ and hydroxylated CO$_2$ (HCO$_3^-$ + CO$_3^{2-}$) during CO$_2$ hydroxylation

Proportion of CO$_3^{2-}$ consumed during CaCO$_3$ precipitation

Relative proportion of CO$_2$ hydration

Relative proportion of CO$_2$ hydroxylation

### A2.2. The relative abundances of DIC species

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

$$CO_2(g) + H_2O \overset{K_0}{\rightarrow} CO_2(aq) + H_2O \overset{K_1}{\rightarrow} HCO_3^- + H^+ \overset{K_2}{\rightarrow} CO_3^{2-} + 2H^+$$  \hspace{1cm} (A2.1)

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:

$$K_1^* = \frac{[HCO_3^-][H^+]}{[CO_2(aq)]} \ ; \ pK_1^* = pH + log[CO_2(aq)] - log[HCO_3^-]$$  \hspace{1cm} (A2.2)

$$K_2^* = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \ ; \ pK_2^* = pH + log[HCO_3^-] - log[CO_3^{2-}]$$  \hspace{1cm} (A2.3)

Where $pK_1^*$ and $pK_2^*$ are the negative log$_{10}$ of the first and second dissociation constants of carbonic acid respectively.

Using equations (A2.2) and (A2.3), the relative proportion $X$ of the DIC species is expressed as follows:

$$X_{CO_3^{2-}} = \left(10^{(pK_1^*+pK_2^*-2pH)} + 10^{(pK_2^*-pH)} + 1\right)^{-1}$$  \hspace{1cm} (A2.4)

$$X_{HCO_3^-} = 10^{pK_2^*-pH} \cdot \left(10^{(pK_1^*+pK_2^*-2pH)} + 10^{(pK_2^*-pH)} + 1\right)^{-1}$$  \hspace{1cm} (A2.5)

$$X_{CO_2(aq)} = \left(10^{(2pH-pK_1^*-pK_2^*)} + 10^{(pH-pK_1^*)} + 1\right)^{-1}$$  \hspace{1cm} (A2.6)

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

$$pK_1^* = 13.4191S^{0.5} + 0.0331S - 5.33 \cdot 10^{-5}S^2 - (530.12S^{0.5} + 6.103S)T^{-1} - 2.0695S^{0.5} \ln T + pK_1^0$$  \hspace{1cm} (A2.7)
\[ pK_2^* = 21.0894S^{0.5} + 0.1248S - 3.687.10^{-4}S^2 - (772.483S^{0.5} + 20.051.5)T^{-1} - 3.3336S^{0.5}\ln T + pK_2^0 \]  

(A2.8)

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

\[ pK_1^0 = 6320.813T^{-1} + 19.568224\ln T - 126.34048 \]  

(A2.9)

\[ pK_2^0 = 5143.692T^{-1} + 14.613358\ln T - 90.18333 \]  

(A2.10)

**A2.3. Reaction rate constants for CO₂ 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):

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

(A2.11)

\[ k_{+4} = 4.7 \times 10^7\exp(-23200/(8.314T)) \]  

(A2.12)

**A2.4. 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 \( x_1, \ldots, x_n \) we have:

\[ P_i = f(x_1, \ldots, x_n) \]  

(A2.1)

Then the lower uncertainty of \( P_i \) is given by:

\[ -\sigma_{P_i} = \sqrt{\left(P_i - f(x_1 - \sigma_{x_1}, \ldots, x_n)\right)^2 + \cdots + \left(P_i - f(x_1, \ldots, x_n - \sigma_{x_n})\right)^2} \]  

(A2.2)

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

Similarly, the upper uncertainty of \( P_i \) is given by:

\[ +\sigma_{P_i} = \sqrt{\left(P_i - f(x_1 + \sigma_{x_1}, \ldots, x_n)\right)^2 + \cdots + \left(P_i - f(x_1, \ldots, x_n + \sigma_{x_n})\right)^2} \]  

(A2.3)
Where $\sigma_{x_1}, \ldots, \sigma_{x_n}$ are the upper uncertainties of the $x_1, \ldots, x_n$ variables if $x_1, \ldots, x_n$ are positively correlated with $P_i$ or the lower uncertainties of the $x_1, \ldots, x_n$ variables if $x_1, \ldots, x_n$ are negatively correlated with $P_i$.

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Chapter III: OXYGEN ISOTOPE SYSTEMATICS
OF OSTRACOD CALCITE

3.1. Introduction

Ostracods are microcrustaceans inhabiting a wide range of aquatic environments and the oxygen isotope ratios of their valves ($\delta^{18}$O$_{ostr}$) provide important records of past changes in regional evaporation/precipitation ratios (e.g. Lister et al., 1991b; Chivas et al., 1993; Schwalb et al., 1999b; Bahr et al., 2006), and estimates of the $\delta^{18}$O value of continental precipitation (e.g. von Grafenstein et al., 1999a; von Grafenstein et al., 2013). It is critical to identify the physical and/or chemical parameters affecting the oxygen isotope fractionation between ostracod calcite and water to reduce uncertainties in palaeoenvironmental reconstruction based on the $\delta^{18}$O$_{ostr}$ proxy.

Ostracod calcite $\delta^{18}$O is unusual in that it is enriched in $^{18}$O (Xia et al., 1997a) relative to slowly precipitated inorganic calcite (Kim and O'Neil, 1997), whereas most other calcifying organisms are depleted in $^{18}$O (McConnaughey, 1989a). The deviations between $\delta^{18}$O$_{ostr}$ and the $\delta^{18}$O value expected for inorganic calcite ($\Delta^{18}$O$_{ostr-c}$) is dependent on taxonomy, and ranges between +1.5‰ and +3‰ depending on the species (von Grafenstein et al., 1999b; Holmes and Chivas, 2002; Decrouy et al., 2011a). Furthermore, a comparison of $\delta^{18}$O$_{ostr}$ data from multiple sites suggests that the degree of $\Delta^{18}$O$_{ostr-c}$ for a given species changes with changing environmental conditions (Decrouy et al., 2011a). Explanations for $\delta^{18}$O ‘vital offsets’ for other marine calcifiers cannot explain ostracod $\delta^{18}$O. For most marine calcifiers, dissolved inorganic carbon (DIC) is thought to be derived from metabolic CO$_2$ (McConnaughey, 1989a,b; Rollion-Bard et al., 2003), and/or from a higher CO$_3^{2-}$/HCO$_3^-$ ratio in the calcifying fluid relative to the host water due to a biologically elevated calcifying fluid pH (Zeebe, 1999; Adkins et al., 2003; Rollion-Bard et al., 2003). Both these processes are thought to result in CaCO$_3$ depleted in $^{18}$O relative to slowly precipitated inorganic calcite (Kim and O’Neil, 1997), the opposite to the $^{18}$O enrichment of ostracods.

Aside from the average $^{18}$O enrichment of ostracod relative to inorganic calcite, the host water temperature is assumed to be the main driver of oxygen isotope fractionation between ostracod calcite and water (reported in ‰ with the $\varepsilon_{ostr/w}$ notation). However, results from culture experiments and comparisons of field and laboratory studies suggest that the $\varepsilon_{ostr/w}$ may also be sensitive to the host water pH (Chivas et al., 2002; Marco-Barba et al., 2012), salinity and/or ionic composition (Li and Liu, 2010a; Decrouy and Vennemann, 2013). Yet the sensitivity of $\varepsilon_{ostr/w}$ to these variables greatly varies among studies, even where results are compared for ostracods that are closely related taxonomically. The host water pH and salinity both affect the host water CO$_3^{2-}$/HCO$_3^-$ ratio, and the
latter is known to affect the $\delta^{18}O$ of marine planktic calcifiers (Spero et al., 1997; Zeebe, 1999, 2007, Ziveri et al., 2012) but the effect of $CO_3^{2-}/HCO_3^-$ on the $\delta^{18}O$ of ostracod valves is unclear.

In this chapter, published field-based and laboratory data are used to investigate the origins of ostracod $^{18}O$ enrichment, taxonomic differences, and the factors controlling $\varepsilon_{ostr/w}$. We find that the ostracod $^{18}O/^{16}O$ ratio is negatively correlated with the host water carbonate ion concentration to dissolved inorganic carbon ratio ($[CO_3^{2-}]/[DIC]$), and present a model for the oxygen isotope fractionation between ostracod calcite and water. The results reconcile the variable effect of host water pH and salinity on ostracod $\delta^{18}O$ found in previous studies. A hypothesis for ostracod taxonomic differences in $\delta^{18}O$ is also presented. The model can be applied to fossil ostracod $\delta^{18}O$ records to provide a more complete picture of palaeoenvironmental change.

Background on ostracod ecology, life cycle and calcification

Ostracods are small crustaceans that secrete a calcified bivalved carapace of the order of a millimetre long in the adult stage. They represent the major group of calcareous microorganisms and microfossils on the continents and are extremely diverse with more than 20,000 living species (Smith and Horne, 2002). Among all the Arthropods, ostracods have the best fossil record for the Phanerozoic eon. They inhabit various aquatic environments from the deep ocean to freshwater lakes and rivers (Horne et al., 2002). Non-marine ostracod species are commonly adapted to $Ca^{2+}, HCO_3^-$ dominated water, although some non-marine species thrive in $Na^+, Cl^-$ dominated water (e.g. *Cyprideis* sp., *Australocypris* sp., *Limnocythere* sp.).

For podocopan ostracods (the taxonomic subclass investigated in this chapter), ontogeny usually consists of nine instars including eight juveniles named “A-8” to “A-1” (first to last) and one adult abbreviated “A”. At each stage of development, the animal abandons the previous carapace (mouling), increases its body size and produces a new carapace. Total life span is from a few months to as long as four years. In mid to high latitude, most non-marine ostracods have a single generation per year, development taking place mainly in spring and summer, with delayed development of eggs or instars during the winter months. However, some species manage four or five generations during the warmer part of the year (Horne et al., 2002).

Podocopan valves are formed by the secretion of amorphous calcium carbonate by the epidermis, which then crystallises into low Mg-calcite (Harding, 1964; Keyser and Walter, 2004). Laboratory experiments with $^{45}Ca$ labelling showed that the calcium used for the formation of the shells is taken directly from the water without build up or storage of calcium within the body of the animal prior to mouling (Turpen and Angell, 1971). Heavily calcified valves are formed in waters that are supersaturated with respect to calcite, such as near the shore of a lake. In contrast, thinly calcified
valves commonly form in water poorly saturated with respect to calcite such as cold water in a deep lake (De Deckker, 2002). This chapter investigates ostracods living in a range of salinity and carbonate saturation states.

3.2. Methods

3.2.1. Data selection

A database of ostracod-water oxygen isotope fractionation ($\epsilon_{ostr/w}$) was compiled (Table A1). All data are from studies that reported $\delta^{18}O_{ostr}$ values along with the $\delta^{18}O_{w}$, temperature, pH and major ion concentrations (hereafter referred as the water parameters) at the time of ostracod moulting or ostracod sampling; or from ostracod studies where the water parameters could be estimated from other sources. The dataset includes $\delta^{18}O_{ostr}$ values from ostracods that calcified their carapaces in varied marine and terrestrial settings, and in laboratory culture experiments (Fig. 3.1; Table 3.1). The pH range of water measurements in the dataset is 6.9 to 10.4, temperatures range from -1 to 29°C and salinities range from 0 to 65 g/kg. DIC speciation and the DIC $\delta^{18}O$ value in the host water were calculated from these parameters (see Section 2.4.2). Where studies reported the water DIC concentration or alkalinity, concentrations of the DIC species in water were estimated. The following sections provide details on data selection and estimates of data uncertainties.

![Figure 3.1](image_url)  
**Figure 3.1** Geographic locations of the ostracod and water sampling sites. Filled circles indicate field studies where living ostracods and water samples were collected in tandem while empty circles indicate the locations of water sampling for the ostracod culture experiments. In the legend, capital letters in brackets designate ostracod studies: C: Chivas et al. (2002), D&B: Didié and Bauch (2002), B: Bornemann et al. (2012), L&L: Li and Liu (2010), X: Xia et al. (1997a,b), VDM: (Van der Meeren et al., 2011), MB: Marco-Barba et al. (2012), VG: Von Grafenstein et al. (1999b), K: Keatings et al. (2002), D: Decrouy et al. (2011a,b).
Table 3.1 List of references and ranges of environmental conditions for the ostracod data included in this chapter.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Genus</th>
<th>Study site</th>
<th>Data included</th>
<th>Temperature (°C)</th>
<th>Salinity (g/kg)</th>
<th>pH (scale)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chivas et al. (2002)</td>
<td>Australocypris</td>
<td>laboratory</td>
<td>fully calcified valves</td>
<td>12 and 25</td>
<td>15 to 65</td>
<td>7.85 to 8.57&lt;sup&gt;a&lt;/sup&gt; (NBS)</td>
</tr>
<tr>
<td>Li and Liu (2010)</td>
<td>Eucypris</td>
<td>laboratory</td>
<td>all</td>
<td>10 to 19</td>
<td>10.4 to 16.5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.91 to 9.38&lt;sup&gt;c&lt;/sup&gt; (NBS)</td>
</tr>
<tr>
<td>Xia et al. (1997b)</td>
<td>Candonina</td>
<td>laboratory</td>
<td>ostracods grown in 100% natural water</td>
<td>15.9 to 24.8</td>
<td>3.15 to 3.58</td>
<td>8.55 to 8.91 (NBS)</td>
</tr>
<tr>
<td>Xia et al. (1997a)</td>
<td>Candonina</td>
<td>Coldwater and Roselyn lakes (S. Dakota, USA)</td>
<td>juvenile ostracods</td>
<td>15 and 25</td>
<td>2.9</td>
<td>8.6 (NBS)</td>
</tr>
<tr>
<td>Keatings et al. (2002)</td>
<td>Candonina, Pseudocandona, Herpetocypris</td>
<td>Ponds of Greywell Moor Nature Reserve (England)</td>
<td>all</td>
<td>10 to 12</td>
<td>0.5</td>
<td>6.9 (NBS)</td>
</tr>
<tr>
<td>Marco-Barba et al. (2012)</td>
<td>Cyprideis</td>
<td>Non-marine water bodies of the eastern Iberian Peninsula (Spain)</td>
<td>juvenile ostracods</td>
<td>12.9 to 31.7</td>
<td>0.6 to 71.8</td>
<td>7.6 to 9.0 (NBS)</td>
</tr>
<tr>
<td>von Grafensteine (1999b)</td>
<td>Candonina, Fabaformiscandona, Cytherissa</td>
<td>Ammersee and Starnberger See (Germany)</td>
<td>all</td>
<td>5.6 to 17.7</td>
<td>0.17&lt;sup&gt;d&lt;/sup&gt;</td>
<td>8.3&lt;sup&gt;d&lt;/sup&gt; (NBS)</td>
</tr>
<tr>
<td>Decrouy et al. (2011a)</td>
<td>13 genera</td>
<td>Lake Geneva (Switzerland)</td>
<td>all</td>
<td>4.7 to 25.9</td>
<td>0.3&lt;sup&gt;e&lt;/sup&gt;</td>
<td>7.6 to 8.9&lt;sup&gt;f&lt;/sup&gt; (NBS)</td>
</tr>
<tr>
<td>Van der Meeren et al. (2011)</td>
<td>Limnocythere</td>
<td>Ponds and lakes of western Mongolia</td>
<td>all</td>
<td>12 to 23</td>
<td>0.2 to 24.7</td>
<td>7.8 to 10.4 (NBS)</td>
</tr>
<tr>
<td>Didié and Bauch (2002)</td>
<td>Henryhowella, Krithe</td>
<td>Surface sediment of the Iceland Plateau</td>
<td>all</td>
<td>-0.9</td>
<td>34.9&lt;sup&gt;f&lt;/sup&gt;</td>
<td>7.98 to 8.02&lt;sup&gt;j&lt;/sup&gt; (SW)</td>
</tr>
<tr>
<td>Bornemann et al. (2012)</td>
<td>Henryhowella, Bairdia, Bosquetina</td>
<td>Surface sediment from Gulf of Taranto (southern Italy)</td>
<td>all</td>
<td>13&lt;sup&gt;i&lt;/sup&gt;</td>
<td>38.7&lt;sup&gt;i&lt;/sup&gt;</td>
<td>8.11&lt;sup&gt;i&lt;/sup&gt; (T)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Represent maximum values since the water pH decreased following ostracod calcification.
<sup>b</sup> Calculated from the δ<sup>18</sup>O of culture water resulting from the mixing of water from Lake Qinghai with salinity 16.5 and δ<sup>18</sup>O of +3.43 ‰ and deionised water with salinity 0 and δ<sup>18</sup>O of -9.90 ‰.
<sup>c</sup> Represent minimum values since the water pH was only measured after ostracod calcification.
<sup>d</sup> From Funk (2004).
<sup>e</sup> From Ramuz (1957).
<sup>f</sup> From Decrouy et al. (2011b).
<sup>g</sup> From Brewer et al. (1986).
<sup>h</sup> From Brewer et al. (1995) recalculated for -0.9°C using CO2sys software of Lewis and Wallace (1998).
<sup>i</sup> From Sellschopp and Alvarez (2003).
<sup>j</sup> From Álvarez et al. (2014) recalculated for 13°C using CO2sys software of Lewis and Wallace (1998).
Culture experiments

Laboratory culture experiments allow the study of ostracod isotopic fractionation in controlled environments. The water δ\(^{18}\)O (δ\(^{18}\)O\(_w\)), temperature and salinity are assumed to be constant for each experiment, unless the authors reported some variations during their experiments. Published culture experiments to date have not evaluated the effect of DIC speciation on ostracod δ\(^{18}\)O (Xia et al., 1997a; Chivas et al., 2002; Li and Liu, 2010a). DIC speciation is pH dependent and these experiments did not maintain constant pH conditions in the culturing tanks. A decrease in water pH following ostracod calcification was reported by Chivas et al. (2002) while Xia et al. (1997a) did not measure the water pH after ostracod moulting and Li and Liu (2010a) only measured the water pH at the end of their culturing experiment. As CaCO\(_3\) precipitation decreases the surrounding water pH in a closed system (cf. Zeebe and Wolf-Gladrow, 2001), pH measurements performed before ostracod calcification were considered maximum values, while pH measurements performed after ostracod calcification were considered minimum values.

Field studies

Most field-based studies included in the database are from studies where the water parameters were monitored monthly. This is important because variations in water parameters over short time scales (e.g. daily, monthly and seasonal) can lead to significant errors in the determination of ε\(\text{ostr/w}\). One exception is the study of Van der Meeren et al. (2011) where the water parameters were measured only once at the time of ostracod sampling. This study was included however, as it provides unique ε\(\text{ostr/w}\) data in highly alkaline environments. Moreover, the study reported low variability in δ\(^{18}\)O\(_{\text{ostr}}\) values between replicate samples at each site, suggesting relatively stable environmental conditions over the time represented by the ostracod living populations. We also used a conservative uncertainty in water temperature of ±3.4°C, which is the maximum range in mean monthly air temperature during the ostracod moulting season (Van der Meeren et al., 2011).

Where ostracods were sampled live in the field, larger uncertainties regarding the time of ostracod moulting are expected with adult ostracods compared to juveniles due to the longer life span of adult ostracods (typically several months to multiple seasons) relative to the time elapsed between the juvenile moulting stages (typically weeks to a few months, Whatley, 1988). Taking this difference into account and knowing that the ε\(\text{ostr/w}\) values of adult and A-1 juvenile ostracod valves are similar where these valves precipitate at the same temperature (von Grafenstein et al., 1999b; Chivas et al., 2002), we employed the following strategies to minimize uncertainties related to the water parameters:
i) For environments where the annual variability was > 5°C for temperature or > 1‰ for δ\(^{18}\)O\(_w\), only data from A-1 juvenile ostracods were selected.

ii) All ostracod data were discarded for sampling batches where the standard deviation (s) of δ\(^{18}\)O\(_{ostr}\) values was > 1‰ for contemporaneous living adult or juvenile ostracods.

iii) For studies where the short-term environmental variability was significant (e.g. surface waters or shallow water bodies), each water parameter ascribed to the ostracod data was the average value obtained from the measurement performed at the time of ostracod sampling and the measurement one month prior to the ostracod sampling, as reported in the published study. The uncertainty range of each water parameter was calculated conservatively as the difference in value between the two measurements.

Where ostracods were sampled from the deep sea or deep lakes with near-constant water parameters all year round, both adult and A-1 juvenile ostracods were selected and a single set of water parameters was associated with the ostracod data.

3.2.2. Calculation of DIC speciation

The host water DIC speciation affects the δ\(^{18}\)O of marine planktic calcifiers (Spero et al., 1997; Zeebe, 1999; Ziveri et al., 2012) and is therefore a potential factor of δ\(^{18}\)O\(_{ostr}\) variability. To investigate the effect of DIC speciation on δ\(^{18}\)O\(_{ostr}\), the relative and absolute concentrations of the DIC species in the host waters were calculated in two different ways depending on the chemical composition of the waters:

i) The CO2sys program (Lewis and Wallace, 1998) was used for DIC speciation calculations in aquatic environments with salinities < 1 g/kg or with seawater-type water. Water pH, salinity, temperature and pressure were input variables. The carbonic acid dissociation constants of Millero et al. (2006) were used for the computation and appropriate pH scales were selected for each study. The effect of pressure on DIC speciation was only noticeable for the deep-sea water of the Iceland plateau (Didié and Bauch, 2002) and the Mediterranean bottom water (Borneman et al., 2012).

ii) DIC speciation was calculated using the program Phreeqc v3.1.7 (database ‘Phreeqc.dat’, Parkhurst and Appelo, 2005) for aquatic environments with salinities > 1 g/kg and with ionic composition different to that of seawater. Water temperature, pH (expressed on the NBS scale) and major ion concentrations were used as input parameters.
3.3. Results

The calculated $\varepsilon_{ostr/w}$ values for all ostracod data in Table A3.1 are presented in Figure 3.2A, along with the oxygen isotope fraction factors relative to water for slowly precipitated inorganic calcite ($\varepsilon_c/w$; Kim and O’Neil, 1997), CO$_3^{2-}$ ($\varepsilon_{CO_3^{2-}}/w$; Beck et al., 2005) and HCO$_3^-$ ($\varepsilon_{HCO_3^-}/w$; Beck et al., 2005). The $\varepsilon_{ostr/w}$ varies from $+37.1\%$ to $+26.6\%$ across the -1 to 29 °C temperature range. For $\varepsilon_{ostr/w}$ values with uncertainties $< 1\%$, 97% of the $\varepsilon_{ostr/w}$ values are higher than $\varepsilon_c/w$ at respective temperatures, with positive differences between $\varepsilon_{ostr/w}$ and $\varepsilon_c/w$ of up to 4‰. A minority (1.7%) of $\varepsilon_{ostr/w}$ values are lower than $\varepsilon_c/w$ by more than 1‰ (i.e. the uncertainty threshold for the selected data) and the maximum negative difference between $\varepsilon_{ostr/w}$ and $\varepsilon_c/w$ is 3‰. Most of the $\varepsilon_{ostr/w}$ values (70%) are within 1‰ of $\varepsilon_{HCO_3^-}/w$, although some $\varepsilon_{ostr/w}$ are close in value to $\varepsilon_{CO_3^{2-}}/w$. Overall, the variation in $\varepsilon_{ostr/w}$ is contained between the $\varepsilon_{CO_3^{2-}}/w$ and $\varepsilon_{HCO_3^-}/w$ values.

Taxonomic differences in $\varepsilon_{ostr/w}$ are apparent (Fig. 3.2B) with Candonids generally having the highest $\varepsilon_{ostr/w}$ values and Limnocytherids having the lowest $\varepsilon_{ostr/w}$ values. Cyprid and Cytherid $\varepsilon_{ostr/w}$ values are between those of Candonids and Limnocytherids. Each non-marine ostracod taxon displays temperature independent variations in $\varepsilon_{ostr/w}$ (Fig. 3.2B). The largest range in $\varepsilon_{ostr/w}$ for a (near) constant temperature is 4.8‰ for Cypriods (at 18-20°C), 3.7‰ for Limnocytherids (at 20°C), 3.0‰ for Cytherids (at 23°C) and 2.1‰ for Candonids (at 24°C). Temperature-independent variations in $\varepsilon_{ostr/w}$ are also evident for the marine Trachileberidids, with an average $\varepsilon_{ostr/w}$ offset relative to $\varepsilon_c/w$ of $\sim 1.4 \pm 0.1\%$ (1σ) in the North Atlantic (-1°C on Fig. 3.2B) and 0.7 ±0.2 ‰ (1σ) in the Mediterranean Sea (13°C on Fig. 3.2B). Although uncertainties in $\delta^{18}O_w$ values and temperature may contribute to the scatter in $\varepsilon_{ostr/w}$ for ostracods collected in the field, these uncertainties cannot explain the large variations in $\varepsilon_{ostr/w}$ of up to 3.8‰ for ostracods belonging to the same species and grown in controlled laboratory environments, with near-constant $\delta^{18}O_w$ values and temperatures (e.g. Cyprididae in Fig. 3.2B; Chivas et al., 2002; Li and Liu, 2010a).

In addition to these taxonomic effects, the $\varepsilon_{ostr/w}$ also varies with environmental conditions (Fig. 3.2C). Overall, $\varepsilon_{ostr/w}$ is lowest in brackish and saline lakes (i.e. salinity 3 to 25 g/kg) and highest in freshwater lakes. The $\varepsilon_{ostr/w}$ of marine ostracods (salinity $\sim$ 35 g/kg) fits between the $\varepsilon_{ostr/w}$ of ostracods from saline and freshwater lakes. The largest negative offsets between $\varepsilon_{ostr/w}$ and $\varepsilon_c/w$ are for Limnocytherids that calcified in Mongolian saline lakes (Van der Meeren et al., 2011), and for Cypridids cultured in tanks filled with saline water obtained from Lake Qinghai (Li and Liu, 2010a).
3.4. Discussion

3.4.1. The effect of DIC speciation on ostracod δ18O

The similarity between $\epsilon_{ostr/w}$ and the calculated $\epsilon_{HCO_3^-/w}$ (i.e. the HCO$_3^-$-H$_2$O oxygen isotope fractionation) for most of the ostracod dataset (Fig. 3.2) suggests that $\delta^{18}$O$_{ostr}$ most commonly reflects the $^{18}$O/$^{16}$O of the bicarbonate ion in water. The bicarbonate ion is the dominant DIC species in most terrestrial and marine aquatic environments (Stumm and Morgan, 1996) and thus the similarity between $\epsilon_{ostr/w}$ and $\epsilon_{HCO_3^-/w}$ supports an environmental source of DIC for ostracod calcification. However, the bicarbonate ion $^{18}$O/$^{16}$O alone cannot explain all of the $\epsilon_{ostr/w}$ values observed in Figure 3.2, such as the comparatively low $\epsilon_{ostr/w}$ reported by Li and Liu (2010a) and van der Meeren et al. (2010).

Calculated proportions of DIC species for the ostracod host waters indicate that carbonate ions represent up to 70% of the DIC pool in some brackish and saline lakes (Fig. 3.3A). To investigate the potential effect of carbonate ions on $\epsilon_{ostr/w}$, the differences between the $\epsilon_{ostr/w}$ and $\epsilon_{HCO_3^-/w}$ values for equivalent temperatures ($\Delta_{ostr-HCO_3^-}$), were plotted against the host water [CO$_3^{2-}$/DIC] molar ratio (Fig. 3.4A and 3.4B) and the host water [CO$_3^{2-}$] molar concentration (Fig. 3.4C and 3.4D). Using $\Delta_{ostr-HCO_3^-}$ instead of $\epsilon_{ostr/w}$ means temperature independent variation in ostracod $^{18}$O/$^{16}$O can be investigated, since $\epsilon_{ostr/w}$ and $\epsilon_{HCO_3^-/w}$ have similar temperature sensitivities ($\sim 0.21 \pm 0.02$‰/°C; Beck et al., 2005; Decrouy et al., 2011a; Fig. 3.2B).
Figure 3.3 Relationships between DIC speciation, pH and salinity for each ostracod sampling site (filled circles) and water used in ostracod culturing experiment (unfilled circles). The molar proportion of (A) carbonate ions ([CO$_3^{2-}$]/[DIC]), (B) bicarbonate ions ([HCO$_3^-$]/[DIC]) and (C) aqueous carbon dioxide plus carbonic acid ([CO$_2(aq)$]/[DIC]) are presented as a function of pH and salinity. The relationship between DIC speciation and pH for seawater at 25°C and for salinities ranging from 0 to 50 g/kg is indicated by the continuous black lines (computed using the chemical equilibrium constants of Millero et al., 2006; salinity values written on each line). Dashed lines represent extrapolations of Millero’s equilibrium constants for a salinity of 65 g/kg. In the legend, capital letters in parentheses designate ostracod studies and have the following meaning: C: Chivas et al. (2002), D&B: Didié and Bauch (2002), B: Bornemann et al. (2012), L&L: Li and Liu (2010a), X: Xia et al. (1997a,b), VDM: (Van der Meeren et al., 2011), MB: Marco-Barba et al. (2012), VG: von Grafenstein et al. (1999), K: Keatings et al. (2002), D: Decrouy et al. (2011a,b).
Figure 3.4 Carbonate ion effects on the difference between the \( \varepsilon_{\text{ostr}} \) and \( \varepsilon_{\text{HCO}_3^-} \) values (\( \Delta_{\text{ostr-HCO}_3^-} \)). (A) \( \Delta_{\text{ostr-HCO}_3^-} \) as a function of the calculated carbonate ions molar proportion to the DIC pool in the host water ([\( \text{CO}_3^{2-} \])/[DIC]). The data are shaded by the uncertainty on \( \Delta_{\text{ostr-HCO}_3^-} \) and [\( \text{CO}_3^{2-} \)]/[DIC] (\( \Delta_{\text{ostr-HCO}_3^-} < 1 \)‰ and [\( \text{CO}_3^{2-} \)]/[DIC] < 10 % black; \( \Delta_{\text{ostr-HCO}_3^-} > 1 \)‰ or [\( \text{CO}_3^{2-} \)]/[DIC] > 10 % white; see Method for calculations of uncertainties). (B) Same as (A) but for data with low uncertainties in \( \Delta_{\text{ostr-HCO}_3^-} \) and [\( \text{CO}_3^{2-} \)]/[DIC] and colour shaded with respect to the ostracod taxonomic family. (C) Same as (B) but with \( \Delta_{\text{ostr-HCO}_3^-} \) plotted as a function of the carbonate ion molar concentration in water ([\( \text{CO}_3^{2-} \])]. (D) Same as (C) but for [\( \text{CO}_3^{2-} \)] < 1.6 mmol/kg. In each panel, the error bars represent the uncertainties in \( \Delta_{\text{ostr-HCO}_3^-} \) and [\( \text{CO}_3^{2-} \)]/[DIC]. Data for which uncertainties in \( \Delta_{\text{ostr-HCO}_3^-} \) and [\( \text{CO}_3^{2-} \)]/[DIC] could not be fully assessed are indicated by black centred diamonds in (B), (C) and (D). Each panel also shows the \( \Delta_{\text{HCO}_3^-} \) (0 ‰ by definition, dark blue line), \( \Delta_{\text{CO}_3^{2-}} \) (light blue line) and \( \Delta_{\text{CaCO}_3} \) (dark line) values calculated using the \( \varepsilon_{\text{w}} \) from Kim and O’Neil (1997) and the \( \varepsilon_{\text{w}} \) from Beck et al. (2005); the line thicknesses represent the uncertainties in \( \Delta_{x-HCO}_3^- \). In (A) and (B), the grey line represents the \( \Delta_{\text{calcite}} \) expected for calcite precipitating instantaneously and quantitatively from the sum of carbonate and bicarbonate ions in water (dashed grey lines indicate the upper and lower uncertainty of the latter mixing line). These data suggest that \( \Delta_{\text{ostr-HCO}_3^-} \) is a function of the [\( \text{CO}_3^{2-} \)]/[DIC] concentration ratio of the host water rather than the absolute [\( \text{CO}_3^{2-} \)] concentration.
Considering data with uncertainties in $\Delta_{\text{ostr}-\text{HCO}_3^-} < 1\%$ and uncertainties in $[\text{CO}_3^{2-}]/[\text{DIC}] < 10\%$, the $\Delta_{\text{ostr}-\text{HCO}_3^-}$ is significantly correlated with $[\text{CO}_3^{2-}]/[\text{DIC}]$ (Fig. 3.4A, $r^2 = 0.56$, p-value < 0.01) and less well correlated to the host water $[\text{CO}_3^{2-}]$ (Fig. 3.4C, $r^2 = 0.22$, p-value < 0.01). This suggests that the offset in $^{18}$O/$^{16}$O between ostracod calcite and the host water $\text{HCO}_3^-$ is controlled by the relative contribution of carbonate ion to the DIC pool. Overall, the $\Delta_{\text{ostr}-\text{HCO}_3^-}$ decreases by ~ 5-6‰ between 0 and 70% in $[\text{CO}_3^{2-}]/[\text{DIC}]$ (Fig. 3.4A), corresponding to a 0.07-0.09‰ decrease in $\Delta_{\text{ostr}-\text{HCO}_3^-}$ per % of $[\text{CO}_3^{2-}]/[\text{DIC}]$. The host water $[\text{CO}_3^{2-}]/[\text{DIC}]$ is therefore a major cause of ostracod $\delta^{18}$O variability.

The relationship between $\Delta_{\text{ostr}-\text{HCO}_3^-}$ and $[\text{CO}_3^{2-}]/[\text{DIC}]$ suggests that the common $^{18}$O enrichment of ostracod calcite relative to slowly precipitated inorganic calcite originates from the $^{18}$O/$^{16}$O ratio of the bicarbonate ion in water. In fact, where the water $[\text{CO}_3^{2-}]/[\text{DIC}]$ ratio is higher than ~ 30 ±10%, ostracod $\delta^{18}$O becomes lower than the predicted $\delta^{18}$O value for slowly precipitated inorganic calcite (Fig. 3.4A). The sensitivity of $\Delta_{\text{ostr}-\text{HCO}_3^-}$ to $[\text{CO}_3^{2-}]/[\text{DIC}]$ is similar to that of the oxygen isotope fractionation between the sum of ‘$\text{HCO}_3^-$’ and $\text{CO}_3^{2-}$’ and $\text{H}_2\text{O}$ (grey line in Fig. 3.4A and 3.4B), indicating that ostracod $^{18}$O/$^{16}$O may be a function of the $^{18}$O/$^{16}$O from the sum of host water carbonate and bicarbonate ions. In turn, this further supports the idea that the DIC consumed during ostracod calcification derives from the host water. Such a model of biocalcification and oxygen isotopic fractionation was proposed by Zeebe (1999, 2007) to explain the dependence of planktic foraminifers on the $[\text{CO}_3^{2-}]$ concentration of seawater (Spero et al., 1997). The Zeebe (1999, 2007) model suggests that foraminiferal calcite $^{18}$O/$^{16}$O is determined by the $^{18}$O/$^{16}$O of the sum of all DIC species in seawater. Therefore, if ostracod $^{18}$O/$^{16}$O was to be explained by the Zeebe (1999) model, one may expect that $\Delta_{\text{ostr}-\text{HCO}_3^-}$ is also affected by the contribution of dissolved $\text{CO}_2$ ($\text{CO}_2(\text{aq})$) to the host water DIC pool ([CO$_2$]([DIC]). This would be expected if the entire DIC pool was consumed during ostracod calcification. There is one study in which ostracods calcified from an environment with a [CO$_2$]([DIC] of ~ 26% (ponds from S-E England, Keatings et al., 2002) while in all the other studies considered here, the host water [CO$_2$]([DIC] was < 7% (Fig. 3.3C). Within the 0 to 26% range in [CO$_2$]([DIC] and for environments where the DIC is mostly composed of CO$_2$ and HCO$_3^-$ ions (i.e. [CO$_2$] - [HCO$_3^-$] $\gg$ [CO$_3^{2-}$]), the $\Delta_{\text{ostr}-\text{HCO}_3^-}$ of Candonid and Cyprid ostracods appear insensitive to the [CO$_2$]([DIC] ratio (Fig. 3.5, $r^2 < 0.1$, p-value > 0.4). In fact, ostracods that calcified in waters with a DIC composed almost entirely of bicarbonate ions have very similar average $\Delta_{\text{ostr}-\text{HCO}_3^-}$ (Candonidae: +0.2 ±0.3‰; Cyprididae: -0.4 ±0.3‰) to that of ostracods that calcified in waters with a [CO$_2$]([DIC] of 26% (Candonidae: -0.1 ±0.3‰; Cyprididae: -0.3 ±0.3‰).

The fact that $\Delta_{\text{ostr}-\text{HCO}_3^-}$ is independent of the host water [CO$_2$]([DIC] (Fig. 3.5) but is linearly related the host water [CO$_3^{2-}$][DIC] ratio (Fig. 3.4A) suggests that ostracod $^{18}$O/$^{16}$O is a function of
the $^{18}\text{O}/^{16}\text{O}$ from the sum of host water $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$, rather than from the $^{18}\text{O}/^{16}\text{O}$ of DIC ($\text{CO}_3^{2-}$, $\text{HCO}_3^-$ and $\text{CO}_2(\text{aq})$). Accordingly, the $\Delta_{\text{ostr-HCO}_3^-}$ is expressed as a function of the host water $[\text{CO}_3^{2-}]/([\text{CO}_3^{2-}] + [\text{HCO}_3^-])$:

$$\Delta_{\text{ostr-HCO}_3^-} = \Delta + \frac{\gamma[\text{CO}_3^{2-}]}{[\text{CO}_3^{2-}] + [\text{HCO}_3^-]}$$

(3.1)

Where $\Delta$ is the $\Delta_{\text{ostr-HCO}_3^-}$ value at $[\text{CO}_3^{2-}]/([\text{CO}_3^{2-}] + [\text{HCO}_3^-]) = 0$ and $\gamma$ is the sensitivity of $\Delta_{\text{ostr-HCO}_3^-}$ to $[\text{CO}_3^{2-}]/([\text{CO}_3^{2-}] + [\text{HCO}_3^-])$.

Figure 3.5 The effect of dissolved carbon dioxide and carbonic acid ($[\text{CO}_2(\text{aq})]/[\text{DIC}]$) on the difference between the $\varepsilon_{\text{ostr/w}}$ and $\varepsilon_{\text{HCO}_3^-/w}$ values ($\Delta_{\text{ostr-HCO}_3^-}$). Uncertainties in $\Delta_{\text{ostr-HCO}_3^-}$ and $[\text{CO}_2(\text{aq})]/[\text{DIC}]$ are indicated by the error bars (see Method section for calculations of uncertainties). The $\Delta_{\text{ostr-HCO}_3^-}$ values are compared to the $\Delta_{\text{HCO}_3^-/w}$ (0‰ by definition, dark blue line), the $\Delta_{\text{HCO}_3^-}$ value for slowly precipitated inorganic calcite as in Kim and O’Neil (1997) (black line) and the maximum $\Delta_{\text{HCO}_3^-}$ values expected for inorganic calcite precipitated instantaneously and assuming complete consumption of the DIC pool (grey field). The latter values are calculated from an isotopic mass balance between bicarbonate ions and hydrated CO$_2$. These data suggest that $\Delta_{\text{ostr-HCO}_3^-}$ is insensitive to the host water $[\text{CO}_2(\text{aq})]/[\text{DIC}]$ ratio.

Equation (3.1) can be used to derive an expression for the ostracod-water oxygen isotope fractionation ($\varepsilon_{\text{ostr/w}}$):

$$\varepsilon_{\text{ostr/w}} = \varepsilon_{\text{HCO}_3^-/w} + \Delta + \frac{\gamma[\text{CO}_3^{2-}]}{[\text{CO}_3^{2-}] + [\text{HCO}_3^-]}$$

(3.2)

Figure 3.4B suggests there are taxonomic-related differences in $\Delta$ and $\gamma$. For each ostracod genus, the $\Delta$ value was estimated from the average $\Delta_{\text{ostr-HCO}_3^-}$ value of ostracods that calcified in waters with
Table 3.2 Intercept (Δ) and slope (γ) of the least squares regression between Δ_{ostr−HCO_3^{-}} and [CO_3^{2-}]/[DIC] for each ostracod genus/family included in this chapter.

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<th>ref</th>
<th>n</th>
<th>Δ</th>
<th>γ</th>
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<tr>
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<td>-1.12 ± 0.05</td>
<td>-0.058 ± 0.005</td>
</tr>
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Trachyleberidae  Henryhowella  D&B, B  17  -1.08 ± 0.17n  -0.124 ± 0.022

| Average difference (± 1σ) in ‰ between ε_{ostr/w} and ε_{HCO_3^{-}/w} (Δ_{ostr−HCO_3^{-}}) for ostracod calcite that precipitated in environments where the carbonate ions represent < 2% of the DIC pool (ε_{HCO_3^{-}/w} calculated from Beck et al., 2005).
| Slope (± 1SE) of the linear regression between Δ_{ostr−HCO_3^{-}} and [CO_3^{2-}]/[DIC] for ostracod data belonging to the same family and with the intercept of the linear regression forced to equal the family mean Δ value.
| Calculated by extrapolating the Δ_{ostr−HCO_3^{-}} vs [CO_3^{2-}]/[DIC] linear regression to [CO_3^{2-}]/[DIC] = 0.

[CO_3^{2-}]/[CO_3^{2-} + HCO_3^{-}] lower than 2% (Fig. 3.6, Table 3.2). The 2% limit for [CO_3^{2-}]/[CO_3^{2-} + HCO_3^{-}] was chosen as it constrains the effect of [CO_3^{2-}]/[CO_3^{2-} + HCO_3^{-}] on Δ_{ostr−HCO_3^{-}} to less than 0.15‰. The genus-specific Δ values vary from +0.2‰ to -1.3‰ and are similar for ostracod genera belonging to the same taxonomic family. The Δ value of Candonids is very close to 0‰, indicating that the ^18O/^16O of these ostracods is almost identical to that of the bicarbonate ^18O/^16O where there are no carbonate ions in the host water (Fig. 3.6B). For all the other ostracod families, the Δ is negative. In detail, Cyprids may be separated in two groups with Herpetocypris, Isocypris and Prionocypris having a Δ value of -0.3 to -0.4‰, while the Δ value of Plesiocypridopsis,
Potamocypris, Cyridopsis and Cypria varies from -0.7 to -1.0‰. The Δ value varies from -0.8 to -1.3‰ for Cytherids and from -1.1 to -1.2‰ for Limnocytherids. Extrapolation of the linear regression between the Δ_ostr−HCO_3^- value of the Henryhowella marine ostracods and the [CO_3^{2-}]/[CO_3^{2-} + HCO_3^-] to a [CO_3^{2-}]/[CO_3^{2-} + HCO_3^-] ratio of 0 suggests a Δ value of -1.1 ±0.2‰ for these marine ostracods.

The γ value in equation (3.1) and (3.2) was estimated for each ostracod family (Table 3.2) rather than for each ostracod genus because there were insufficient data to obtain genus-specific γ values. Given that ostracods from the same family appear to have similar Δ values, it is assumed that the γ value is also similar among ostracods from the same taxonomic family. The γ value was estimated for each ostracod family from the slope of the linear regression between the Δ_ostr−HCO_3^- value and the [CO_3^{2-}]/[CO_3^{2-} + HCO_3^-] (Table 3.2). Candonids, which have the highest Δ value, also have the highest γ value. On the other hand, Cytherids and Limnocytherids, which have the lowest Δ value have the lowest γ value. The few data on marine ostracods suggest that Trachyleberids have a higher γ value than any of the non-marine ostracod families.

Figure 3.6 Taxonomic variations in Δ_ostr−HCO_3^- for environments with negligible carbonate ions ([CO_3^{2-}]/[DIC] < 2%). (A) Box plot summary of Δ_ostr−HCO_3^- values for various ostracod genera and studies. Each box plot represents the minimum, 1st quartile, median, 3rd quartile and maximum value. Data from Candonids are in purple, Cyprids in red, Cytheroids in orange and Limnocytherids in yellow. The Δ_HCO_3^-−HCO_3^- value (0 ‰) is indicated by the horizontal line. Capital letters in parentheses on the x-axis refer to the following studies: D: Decrouy et al. (2011b), K: Keatings et al. (2002), VG: von Grafenstein et al. (1999), MB: Marco-Barba et al. (2012). (B) Measured δ^{18}O_Candonid vs estimated δ^{18}O_bicarbonate. The δ^{18}O_bicarbonate value was estimated from measured δ^{18}O_w and the equilibrium oxygen isotope fractionation factor between bicarbonate ions and water (as in Beck et al., 2005). When the contribution of carbonate ions to the host water DIC pool is negligible, the Δ_ostr−HCO_3^- value is primarily determined by the ostracod taxonomic family or genus.
The $\varepsilon_{ostr/w}$ values are modelled using equation (3.2) and the $\Delta$ and $\gamma$ values of each ostracod genus/family as listed in Table 3.2, and show good agreement with measured $\varepsilon_{ostr/w}$ (Fig. 3.7A, $r^2 = 0.96$, p-value < 0.01). The average difference between the measured and modelled $\varepsilon_{ostr/w}$ value is 0.2 ±0.9‰ (2σ), which is within the uncertainty of the modelled $\varepsilon_{ostr/w}$ values (Fig. 3.7B). Candonidae is the only ostracod family with a significant data-model offset in $\varepsilon_{ostr/w}$. This disagreement mostly originates from Candonid ostracods extracted from a single site in Lake Geneva (-70 m, Decrouy et al., 2011a). The cause of this $\varepsilon_{ostr/w}$ offset for this site is unknown.

Figure 3.7 Comparison of measured and modelled $\varepsilon_{ostr/w}$ values. (A) Measured vs modelled $\varepsilon_{ostr/w}$ values for data with uncertainties in measured $\varepsilon_{ostr/w} < 1$‰ and uncertainties in $[\text{CO}_3^{2-}]/[\text{DIC}] < 10$ %. (B) Difference between measured and modelled $\varepsilon_{ostr/w}$ values ($\Delta_{\text{data-model}}$) as a function of the $[\text{CO}_3^{2-}]/[\text{DIC}]$ ratio. On the right side of panel (B) is shown the frequency distribution of the $\Delta_{\text{data-model}}$ values colour shaded with respect to the ostracod taxonomic family. Uncertainties in measured and modelled $\varepsilon_{ostr/w}$ and in the $[\text{CO}_3^{2-}]/[\text{DIC}]$ ratio are indicated by the error bars. Data for which uncertainties in measured $\varepsilon_{ostr/w}$ and $[\text{CO}_3^{2-}]/[\text{DIC}]$ could not be fully assessed are indicated by black centred diamonds.
3.4.2. The origin of taxonomic variations in ostracod $\delta^{18}O$

Differences in $\delta^{18}O$ among ostracod species inhabiting the same natural environment were identified in the late 1990s (von Grafenstein et al., 1999) but the causes of these differences have remained elusive. The $\delta^{18}O_{\text{ostr}}$ values vary with the $[\text{CO}_3^{2-}]/[\text{CO}_3^{2-} + \text{HCO}_3^-]$ ratio in water, therefore the effect of taxonomy on the $\delta^{18}O_{\text{ostr}}$ value is easier to evaluate in environments where carbonate ions are negligible. In these conditions, the relative differences in $\delta^{18}O$ between the ostracod families can be inferred on Figure 3.6. These relative taxonomic differences are in good agreement with the results of Decrouy et al. (2011a) because these authors reported ostracod-water fractionation factors for ostracods that calcified in an environment where the proportion of carbonate ions to the DIC pool was negligible.

Candonids have a $\delta^{18}O$ value almost identical to the $\delta^{18}O$ value of the bicarbonate ion where the contribution of carbonate ions to the DIC pool is negligible (i.e. $[\text{CO}_3^{2-}]/[\text{DIC}] < 2 \%$; Fig. 3.6B). The other ostracod taxa are systematically depleted in $18O$ relative to the bicarbonate ion. In the absence of carbonate ions in the host water, the offset in $^{18}O/^{16}O$ between ostracod calcite and the bicarbonate ion ($\Delta_{\text{ostr-HCO}_3^-}$) must originate from isotopic fractionations occurring between the calcite mineral and the DIC pool in the ostracod calcifying fluid (CF) and/or a modification of the DIC pool $^{18}O/^{16}O$ ratio during its transfer from the host water to the calcifying site. We reject calcite-DIC isotope exchange as a potential cause for the taxonomic differences in $\delta^{18}O_{\text{ostr}}$ because isotopic equilibration between calcite and water enriches rather than depletes calcite in $^{18}O$ (Coplen, 2007, Watkins et al., 2013). Thus, the taxonomic differences are likely to originate from an isotopic alteration of the DIC pool prior to or during calcite precipitation. Here, three known mechanisms that decrease the $^{18}O/^{16}O$ ratio of a precipitating DIC pool are reviewed and assessed. These include: (1) a contribution of DIC derived from metabolic CO$_2$ (McConnaughey, 1989b), (2) the deprotonation and consumption of a fraction of the bicarbonate ion pool in the CF (Kim et al., 2006) and (3) a partial isotopic equilibration between deprotonated bicarbonate ions and water (Beck et al., 2005).

Some of the ostracod taxa may use metabolic CO$_2$ to increase the DIC concentration of the CF (DIC$_{cf}$) and promote rapid calcification. Kinetic effects related to the hydration and hydroxylation of CO$_2$ are known to decrease the $^{18}O/^{16}O$ ratio of the DIC (McConnaughey, 1989b; Clark et al., 1992; Watkins et al., 2013, 2014) and are thought to cause the low $^{18}O/^{16}O$ ratio of corals and other marine calcifiers (McConnaughey, 1989a) relative to slowly precipitated inorganic CaCO$_3$. These kinetic isotope effects also affect the $^{13}C/^{12}C$ ratio of the DIC pool and result in CaCO$_3$ minerals with covariant $\delta^{18}O$ and $\delta^{13}C$ values (McConnaughey, 1989b). Although a correlation between the $\delta^{18}O$ and $\delta^{13}C$ values was previously reported for marine ostracods from the Mediterranean Sea (Bornemann et al., 2012), such a correlation was not found for lacustrine ostracods that calcified within the same environment.
with no carbonate ions, near-constant $\delta^{18}O_{w}$ value and temperature (Fig. 3.8). Thus, possibility (1) may explain the low $\delta^{18}O$ of marine ostracod relative to lacustrine ostracods but is unlikely to explain the taxonomic differences in $\delta^{18}O$ between non-marine ostracod taxa.

The deprotonation and consumption of a fraction of the bicarbonate ion pool during fast calcification leads to CaCO$_3$ depleted in $^{18}O$ relative to the initial $^{18}O/^{16}O$ of the bicarbonate ion pool (Kim et al., 2006, Watkins et al., 2013). This is due to the preferential deprotonation of the isotopically light bicarbonate ions (Kim et al., 2006). Assuming that ostracod calcite precipitation is triggered by a high calcite saturation state in the ostracod CF and follows processes similar to that of inorganic calcite formation, then the carbonate ion should be the dominant DIC species directly involved in CaCO$_3$ precipitation (i.e. other DIC species indirectly contribute to calcification where they are converted into carbonate ions, Kim et al., 2006; Chapter 2) and the sensitivity of calcite $^{18}O/^{16}O$ ratio to the environment $[CO_3^{2-}]/[CO_3^{2-} + HCO_3^-]$ should increase with decreasing fraction of DIC pool precipitated. Thus, if possibility (2) was correct, one should expect that ostracods with the lowest $\delta^{18}O$ value in the absence of carbonate ions in water (i.e. the lowest $\Delta$ value) should have a $\delta^{18}O$ value which is most sensitive to the environment $[CO_3^{2-}]/[CO_3^{2-} + HCO_3^-]$ (i.e. the lowest $\gamma$ value). Since the opposite pattern is observed for the non-marine ostracod taxa (i.e. $\Delta$ and are $\gamma$ are negatively related, Table 3.2), possibility (2) is therefore unlikely to explain the ostracod taxonomic differences in $\delta^{18}O$.

![Figure 3.8](image_url)

**Figure 3.8** $\delta^{18}O$ vs $\delta^{13}C$ for contemporaneous ostracods that calcified in a single environment with negligible carbonate ions ($[CO_3^{2-}]/DIC < 2\%$), near constant water $\delta^{18}O$ (-12.5 ±0.25 ‰), temperature (5 ±1 °C), salinity (< 0.3 g/kg) and DIC $\delta^{13}C$ (-8.0 ±1.0 ‰). The data represent living ostracods sampled at a 70 m water depth in Lake Geneva (from Decrouy et al., 2011a). Individual measurements (small diamonds) and the average $\delta^{18}O$ and $\delta^{13}C$ values of each ostracod species (large diamonds) are shown. The modern range of $\delta^{13}C_{DIC}$ values (grey bar) is shown for comparison. The absence of correlation between ostracod $\delta^{18}O$ and $\delta^{13}C$ among individuals of the same species and between ostracods from different species suggests that kinetic isotope effects related to the hydration or hydroxylation of metabolic CO$_2$ are unlikely to explain taxonomic differences in ostracod $\delta^{18}O$. 

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Partial isotopic equilibration between deprotonated bicarbonate ions and water could in theory lead to the formation of calcite with a lower $^{18}$O/$^{16}$O ratio than the initial bicarbonate ion pool. This is expected to occur if the rate of isotopic exchange between carbonate ion and water is of similar magnitude than the rate of carbonate ion consumption during calcite precipitation or if a fraction of the bicarbonate ion pool is deprotonated prior to the onset of calcite precipitation (these possibilities contrast with a very fast carbonate precipitation described in the paragraph above). Isotopic equilibration between deprotonated bicarbonate ions and water could also be facilitated by the presence of the enzyme carbonic anhydrase in the ostracod CF. This enzyme, which enhances the isotopic exchanges between the DIC species and water (Uchikawa and Zeebe, 2012), has been located in the tissues of several crustaceans (e.g. Henry, 2001) and may be present in or near the ostracod CF. Regardless of the presence/absence of carbonic anhydrase in the ostracod CF, an increasing isotopic equilibration between deprotonated bicarbonate ions and water should be accompanied by a decreasing sensitivity of the ostracod $^{18}$O/$^{16}$O ratio to the environment $[CO_3^{2-}]/[CO_3^{2-} + HCO_3^-]$ ratio. This is because isotopic exchanges between deprotonated bicarbonate ions and water lower the $^{18}$O/$^{16}$O ratio of these ions towards the $^{18}$O/$^{16}$O ratio of isotopically equilibrated carbonate ions. As the $^{18}$O/$^{16}$O of the deprotonated bicarbonate ions tends towards the $^{18}$O/$^{16}$O of equilibrated carbonate ions, the sensitivity of calcite $^{18}$O/$^{16}$O to the $[CO_3^{2-}]/[CO_3^{2-} + HCO_3^-]$ (i.e. the $\gamma$ value) should decrease. If this hypothesis is correct and DIC precipitation is quantitative, then the ostracod-water oxygen isotope fractionation ($\varepsilon_{o/w}$) may be approximated by an isotopic mass balance between partially equilibrated deprotonated bicarbonate ions and isotopically equilibrated carbonate ions:

$$\varepsilon_{ostr/w} \cong \varepsilon_{CO_3^{2-}/w} \cdot \frac{[CO_3^{2-}]}{[CO_3^{2-} + HCO_3^-]} + \left[ \varepsilon_{CO_3^{2-}/w} \cdot E_{DIC} + \varepsilon_{HCO_3^-/w} \cdot (1 - E_{DIC}) \right] \cdot \frac{[HCO_3^-]}{[CO_3^{2-} + HCO_3^-]}$$

(3.3)

Where $E_{DIC}$ is the level of DIC-H$_2$O isotopic equilibration in the ostracod CF (i.e. the fraction of isotopically equilibrated carbonate ions deriving from deprotonated bicarbonate ions). Where $E_{DIC} = 0$, ostracod $^{18}$O/$^{16}$O reflects the $^{18}$O/$^{16}$O of host water ‘$CO_3^{2-} + HCO_3^-$’ while at $E_{DIC} = 1$, ostracod $^{18}$O/$^{16}$O reflects the $^{18}$O/$^{16}$O of isotopically equilibrated $CO_3^{2-}$. The similarity between ostracod $^{18}$O/$^{16}$O and the $^{18}$O/$^{16}$O of host water ‘$CO_3^{2-} + HCO_3^-$’ (Fig. 3.3A and 3.3B) suggests $E_{DIC}$ close to 0 in most ostracod CF. This expression differs from Eq. (3.2) in that the $\varepsilon_{ostr/w}$ value is constrained between the $\varepsilon_{CO_3^{2-}/w}$ and $\varepsilon_{HCO_3^-/w}$ values. According to this equation, the differences in $\varepsilon_{ostr/w}$ values between ostracod taxa should decrease with increasing host water $[CO_3^{2-}]/[CO_3^{2-} + HCO_3^-]$ and should become 0 where $[CO_3^{2-}]/[CO_3^{2-} + HCO_3^-]$ is 100%. Although additional data are needed to test this model, the $\Delta$ and $\gamma$ values of non-marine ostracods are within error of the $\Delta$ and $\gamma$ values expected from Eq. (3.3) (Fig. 3.9; Table 3.2). It is worth emphasizing that this model does not indicate whether $CO_3^{2-}$ is the dominant DIC species contributing to ostracod calcite or if both $CO_3^{2-}$ and $HCO_3^-$ are
directly involved during calcite growth. Both possibilities are compatible with our model because the isotopic imprint of $\text{HCO}_3^-$ would be recorded in ostracod calcite if $\text{HCO}_3^-$ directly contributes to calcite growth (as in the Zeebe, 1999 biogenic model) or if $\text{HCO}_3^-$ converts to $\text{CO}_3^{2-}$ prior to calcification due to an increase in pH (as observed for inorganic carbonates, Kim et al., 2006). For practical purposes, ostracod $\delta^{18}O$ reflects the $^{18}O/^{16}O$ of the DIC in the ostracod calcifying fluid, which is equal to or slightly lower than the $^{18}O/^{16}O$ of the host water DIC.

Figure 3.9. $\gamma$ versus $\Delta$ for Candonids (purple), Cyprids (red), Cytherids (orange), Limnocytherids (yellow) and Trachyleberids (green). The $\gamma$ versus $\Delta$ relationship expected from Eq. (3.3) is the grey line whose width integrates the uncertainties ($1\sigma$) of $\varepsilon_{\text{CO}_3^{2-}/w}$ and $\varepsilon_{\text{HCO}_3^-/w}$ as in Beck et al. (2005). Variations in the sensitivity of $\delta^{18}O_{\text{ostr}}$ to $[\text{CO}_3^{2-}]/[\text{CO}_3^{2-} + \text{HCO}_3^-]$ between different taxa (Table 3.2) may offer the possibility to reconstruct the DIC speciation of the host water. Because the $\delta^{18}O_{\text{ostr}}$ offsets between ostracod taxa that calcified in the same environment vary with the host water $[\text{CO}_3^{2-}]/[\text{CO}_3^{2-} + \text{HCO}_3^-]$, one may be able to estimate the water $[\text{CO}_3^{2-}]/[\text{CO}_3^{2-} + \text{HCO}_3^-]$ by measuring $\delta^{18}O_{\text{ostr}}$ from two or more ostracod taxa with different sensitivities to $[\text{CO}_3^{2-}]/[\text{CO}_3^{2-} + \text{HCO}_3^-]$.

3.4.3. An explanation for the effect of salinity on the ostracod $^{18}O/^{16}O$ ratio

Significant negative correlations between $\varepsilon_{\text{ostr}/w}$ and salinity were reported for Cypridid ostracods grown in controlled laboratory environments (Chivas et al., 2002; Li and Liu, 2010a; Decrouy and Vennemann, 2013). A plot of $\Delta_{\text{ostr}-\text{HCO}_3^-}$ against salinity shows a weak negative trend with increasing salinity (Fig. 3.10, $r^2 = 0.37$, $p < 0.01$). The effect of salinity on $\Delta_{\text{ostr}-\text{HCO}_3^-}$ is clearer and stronger for Cypridids in the study of Chivas et al. (2002) ($r^2 = 0.46$, p-value < 0.01) and for Li and Liu (2010a) ($r^2 = 0.73$, p-value < 0.01), but when these data are combined the $\Delta_{\text{ostr}-\text{HCO}_3^-}$ of Cyprids do not correlate with salinity ($r^2 = 2 \times 10^{-3}$, p-value = 0.5).
Figure 3.10 Difference between the $\varepsilon_{\text{oss}/w}$ and $\varepsilon_{\text{HCO}_3^-/w}$ values ($\Delta_{\text{oss}-\text{HCO}_3^-}$) as a function of salinity. Uncertainties in $\Delta_{\text{oss}-\text{HCO}_3^-}$ and salinity are indicated by the error bars (see method section for calculations of uncertainties). Data for which uncertainties in $\Delta_{\text{oss}-\text{HCO}_3^-}$ and salinity could not be fully assessed are indicated by black centred diamonds. The $\Delta_{\text{oss}-\text{HCO}_3^-}$ data are compared to the $\Delta_{\text{HCO}_3^-/w}$ (0 ‰ by definition, dark blue line), $\Delta_{\text{CO}_3^{2-}-\text{HCO}_3^-}$ (light blue line, calculated from Beck et al., 2005), and the $\Delta_{\text{CaCO}_3-\text{HCO}_3^-}$ value for slowly precipitated inorganic calcite as in Kim and O’Neil (1997) (dark line); the line thicknesses represent the uncertainties in $\Delta_{x-\text{HCO}_3^-}$. Arrows indicate results from the culture experiments of Chivas et al. (2002) and Li and Liu (2010a). These data suggest that variation in salinity do not fully explain the $\Delta_{\text{oss}-\text{HCO}_3^-}$ value.

These results suggest that salinity is not a primary driver of $\delta^{18}O_{\text{ostr}}$, as previously suggested by Decrouy and Vennemann (2013). The sensitivity of $\varepsilon_{\text{oss}/w}$ to salinity can be explained by the positive effect of salinity on the host water $[\text{CO}_3^{2-}]/[\text{CO}_3^{2-} + \text{HCO}_3^-]$ (Fig. 3.3A). Here, higher salinities increase $[\text{CO}_3^{2-}]/[\text{CO}_3^{2-} + \text{HCO}_3^-]$, which leads to a decrease in the $^{18}O/^{16}O$ of host water DIC, and in turn results in lower $\delta^{18}O_{\text{oss}}$ values. Another contributing factor to the negative $\varepsilon_{\text{oss}/w}$-salinity relationship comes from the positive correlations between salinity and alkalinity in the culturing solutions. The solutions used for ostracod culturing in Chivas et al. (2002) and Li and Liu (2010a) were obtained from the mixing of a saline solution with freshwater or distilled water to create solutions at different salinities. Alkalinity was significantly lower in the freshwater/distilled water relative to the saline water, thus the solutions’ alkalinity also covaried with salinities. After a CaCO$_3$ precipitation event, the decrease in solution pH is more pronounced when the initial alkalinity of the solution is lower. In other words, the magnitude of the pH decrease depends on the ratio between the amount of CaCO$_3$ precipitation and the initial amount of carbonate ions in solution. Thus, in a closed system with a finite DIC pool such as in culturing jars, the DIC $^{18}O/^{16}O$ shifts more readily towards the bicarbonate ion $^{18}O/^{16}O$ following CaCO$_3$ precipitation where alkalinity is lower. This also explains why the ostracod $\delta^{18}O$ is more correlated to $[\text{CO}_3^{2-}]$ (Fig. 3.4C and 3.4D) than $[\text{CO}_3^{2-}]/[\text{DIC}]$ (Fig. 3.4B) in the culturing experiments of Chivas et al. (2002) and Li and Liu (2010a).
3.4.4. Ostracod biomineralization

The small difference in $^{18}$O/$^{16}$O ratio between ostracod calcite and an isotopic mass balance between the sum of the host water bicarbonate and carbonate ions (Fig. 3.4A) implies that isotopic fractionation between the DIC$_{cf}$ and the host water DIC (DIC$_{w}$) and between the DIC$_{cf}$ and ostracod calcite must be limited. This has several important implications for the ostracod calcification processes:

i) The isotopic composition of DIC$_{cf}$ is not significantly modified by biological processes. Thus, metabolic CO$_2$ is not a significant DIC source for ostracod calcification, otherwise ostracod calcite would be systematically and significantly depleted in $^{18}$O relative to bicarbonate ions due to kinetic isotope effects during the hydration and/or hydroxylation of CO$_2$(aq) in the CF (McConnaughey, 1989b).

ii) Calcite precipitation must occur at a very fast rate under a high calcite saturation state to prevent the isotopic equilibration between calcite and water (McCrea, 1950; Beck et al., 2005; Kim et al., 2006). In fact, the formation of a whole new ostracod carapace can take less than 12 hours (Chivas et al., 1983).

iii) The DIC$_{cf}$ pool is likely be consumed almost entirely since carbonate ions are thought to be consumed preferentially over bicarbonate ions when DIC consumption is not total (Kim et al., 2006).

In turn, a fast and quantitative precipitation of the DIC$_{cf}$ implies a high pH in the ostracod CF (pH$_{cf}$). The ostracod pH$_{cf}$ has not yet been measured but high pH$_{cf}$ conditions (~ 8.5 to ~ 9.5) have been reported for corals (Al-Horani et al., 2003; Cai et al., 2016), foraminifers (de Nooijer et al., 2009; Bentov et al., 2009) and coccolithophores (Stoll et al., 2012), suggesting that pH elevation is ubiquitous in biogenic calcifiers. A higher pH in the ostracod CF than in the host water is expected since ostracods are able to calcify in host waters undersaturated with calcite and with pH values as low as ~ 6.8 (e.g. Candonids in Keatings et al., 2002, Fig. 3.3). Assuming that ostracods elevate the pH$_{cf}$ relative to the host water pH like marine calcifiers, then a significant proportion of the DIC$_{cf}$ should convert to carbonate ion following the pH increase, and DIC speciation should be different in the ostracod CF than in the host water. This leads to the counter intuitive hypothesis that the contribution of carbonate ions to the DIC$_{cf}$ pool is significant even when the $\delta^{18}$O of the resulting calcite reflects a DIC$_{cf}$ with no or little carbonate ions. This discrepancy can only be resolved if there is no or little isotopic equilibration between the DIC$_{cf}$ pool and water following the elevation of the pH$_{cf}$. In other words, for the $^{18}$O/$^{16}$O of bicarbonate ions to be recorded by ostracod calcite, fast
calcification must occur immediately following the pHcf elevation, otherwise ostracod δ¹⁸O would not record the bicarbonate ion ¹⁸O/¹⁶O. Overall, ostracod calcite may be considered as a biologic analogue to fast and quantitative inorganic carbonate precipitation experiments (McCrea, 1950; Beck et al., 2005; Kim et al., 2006) where the δ¹⁸O of the carbonate mineral reflects the δ¹⁸O value of the DIC pool from the precipitating solution. A quantitative DIC precipitation model for biogenic calcite was first suggested by Zeebe (1999) to explain the sensitivity of planktic foraminifer δ¹⁸O to the carbonate ion concentration in seawater (Spero et al., 1997) but the ostracod δ¹⁸O data presented in this chapter are closer in value to the host water DIC δ¹⁸O than the planktic foraminifer δ¹⁸O data.

Yet, δ¹⁸Oostr does not reflect the exact ¹⁸O/¹⁶O of the host water DIC, since δ¹⁸Oostr is insensitive to the host water [CO₂(aq)]/[DIC] ratio (Fig. 3.5). Fast precipitation of CO₂(aq) leads to lower CaCO₃ δ¹⁸O due to the CO₂ hydration and hydroxylation steps during the conversion of CO₂(aq) into HCO₃⁻ and CO₃²⁻ (McConnaughey, 1989b; Beck et al., 2005; Wang et al., 2013). Thus, the non-sensitivity of δ¹⁸Oostr to CO₂(aq) suggests that CO₂(aq) must be converted into HCO₃⁻ and CO₃²⁻ well before the onset of calcite precipitation, allowing sufficient time for the isotopic equilibrium between hydrated / hydroxylated CO₂ and water to be reached before the onset of calcification. This may be achieved by the isolation of host water DIC by the ostracod with subsequent storage of the DIC pool at a higher pH than the host water pH but at lower pH than during the calcification step.

In summary, we suggest that the transfer of DIC from the host water to the ostracod calcifying site occurs in two steps. Ostracods first isolate pockets of water from the environment. The DIC speciation of the isolated water is not significantly modified during the ‘storage’ phase, although the pH would have to be maintained above a threshold value of ~ 7.0-8.0 to retain low concentrations of carbon dioxide and carbonic acid. During storage, the DIC species reach full isotopic equilibrium with water perhaps due to the presence of carbonic anhydrase in the fluid. Then, the isolated solution undergoes a rapid increase in calcite saturation state and/or is transferred to a calcifying site with a high calcite saturation state, likely due to elevated pH and high Ca²⁺ concentration. Shortly after the increase in calcite saturation state, most of the DIC pool precipitates into amorphous calcium carbonate, which then recrystallises as calcite (Keyser and Walter, 2004). The fast consumption of the DICcf pool, prevents DIC-H₂O isotope equilibrium, and hence the bicarbonate ion ¹⁸O/¹⁶O is recorded in ostracod calcite.

3.5. Implications for previous and future studies

This chapter shows that δ¹⁸Oostr decreases by 4 to 6‰ across the 0-70% range in host water [CO₃²⁻]/[DIC]. Extrapolating the carbonate ion effect to a [CO₃²⁻]/[DIC] of 100% suggests a maximum carbonate ion effect on δ¹⁸Oostr in the order of 6 to 8‰. These results suggest that previous paleoclimatic interpretations of ostracod oxygen isotope records should be reassessed. Particular
attention should be paid to $\delta^{18}O_{ostr}$ records obtained from closed basins where salinity and pH are commonly high (e.g. Lister et al., 1991; Chivas et al., 1993; Hodell et al., 1995; Holmes et al., 1997; Smith et al., 1997; Curtis et al., 1999; Leng et al., 1999; Schwalb et al., 1999; Henderson et al., 2003; Hodell et al., 2005; Ortiz et al., 2006; Jin et al., 2009; Wrozya et al., 2010; Escobar et al., 2012; Stansell et al., 2013), or $\delta^{18}O_{ostr}$ records from lakes with evidence of past variations in salinity (e.g. Hodell et al., 1991; Bahr et al., 2006; Hodell et al., 2012). This is because higher salinity and pH leads to higher $[\text{CO}_3^{2-}]/[\text{DIC}]$ (Millero et al., 2006, Fig. 3.3), which in turn leads to more negative ostracod $\delta^{18}O$. Saline lakes are commonly associated with a high evaporation/precipitation ratio ($E/P$), which leads to high lake water $\delta^{18}O$, and hence a positive effect on $\delta^{18}O_{ostr}$. This reasoning suggests that ostracod $\delta^{18}O$ may not accurately record an increase in lake water $\delta^{18}O$ if the latter parameter covaries with salinity and/or pH, a situation that is expected. A decreasing trend in $\delta^{18}O_{ostr}$ (‘fresher’) originally interpreted as a decrease in lake $E/P$ (more precipitation) could potentially reflect the opposite situation: the low $\delta^{18}O_{ostr}$ reflects a higher lake salinity and $E/P$ (with higher $[\text{CO}_3^{2-}]/[\text{DIC}]$).

For example, Holocene $\delta^{18}O_{ostr}$ records from Lake Qinghai, China’s largest lake, were used to reconstruct past hydrologic changes on the Tibetan plateau (Lister et al., 1991b; Zhang et al., 1994; Liu et al., 2007; An et al., 2012; Li and Liu, 2014; Jin et al., 2015). These $\delta^{18}O_{ostr}$ records have been interpreted in terms of changing lake water $\delta^{18}O$ value, which in turn were interpreted as reflecting changes in the regional E/P and the Asian monsoon influence. However, a lake level reconstruction obtained from direct dating of Lake Qinghai palaeoshorelines (Fig. 3.11a, Liu et al., 2015) suggests that high stands in lake level are coincident with high $\delta^{18}O_{ostr}$ values while low lake levels are associated with low $\delta^{18}O_{ostr}$ (Li and Liu, 2014, Fig. 3.11d). For example, a major low stand in lake level during the early Holocene (11 to 9 thousand years ago) is coincident with $\delta^{18}O_{ostr}$ of $\sim -3$ to $-2\%o$. The lake’s highest levels occurred between 5 to 2 ka when the $\delta^{18}O_{ostr}$ was $\sim +3$ to $+4\%o$. The positive covariation between the lake level and $\delta^{18}O_{ostr}$ is counter intuitive because high lake levels correspond to low $E/P$, low rainfall $\delta^{18}O$ values, which in turn result in low lake water $\delta^{18}O$ (e.g. von Grafenstein et al., 1999a).

Ostracod $\delta^{18}O$ records from Lake Qinghai offer an opportunity to investigate the effect of DIC speciation on $\delta^{18}O_{ostr}$ and reconcile inconsistencies between proxies, because of the range of complementary data from the site. Lake Qinghai’s $\delta^{18}O_{ostr}$ record was constructed from the $\delta^{18}O$ of benthic ostracod species (Limnocythere inopinata and Eucypris mareotica) and thus the $\delta^{18}O_{ostr}$ record (partly) reflects variations in the bottom lake water $\delta^{18}O$ and temperature. Calibration work with modern L. inopinata and E. mareotica in Lake Qinghai suggests that the $\delta^{18}O_{ostr}$ of these ostracods increases with the lake water depth (Fig. 3.11h) due to the effect of water depth on the water temperature (Liu et al., 2009). Based on the lake level reconstruction of Liu et al. (2015) and the $\delta^{18}O_{ostr}$-‘water depth’ relationship of Liu et al. (2009), change in water depth during the Holocene can
explain a 2‰ positive increase in $\delta^{18}$O$_{ostr}$ during the early Holocene (Fig. 3.11e). Changes in the water depth of ostracod habitats therefore do not fully reconcile the discrepancy between the Holocene lake level and $\delta^{18}$O$_{ostr}$ records.

To investigate if variations in the lake $[\text{CO}_3^{2-}]/[\text{DIC}]$ contributed to the apparent discrepancy between the $\delta^{18}$O$_{ostr}$ record and the lake level reconstruction, past changes in the lake $[\text{CO}_3^{2-}]/[\text{DIC}]$ were estimated based on paleo-salinity estimates (Fig. 3.11b, Zhang et al., 1994) and the modern relationship between salinity and pH in Lake Qinghai and nearby lakes (Fig. 3.11h, Liu et al., 2009; Xu et al., 2010). The salinity record is based on the ostracod Sr/Ca ratio from Lake Qinghai and display similar variations than the lake level reconstruction of Liu et al. (2015). Ostracod calcite accurately records of the water Sr/Ca during valve formation, which in turn is reflective of the water salinity in closed basin saturated with respect to calcite (Chivas et al., 1985). Calcite and aragonite represent more than 60% of the Lake Qinghai’s sediment accumulation since 12 ka (Ji et al., 2005; An et al., 2012), suggesting a persistent calcite/aragonite saturation during the Holocene. The pH reconstruction in Figure 3.11c relies on the assumption that the modern pH vs salinity relationship (Fig. 3.10i, $r^2 = 0.86$, p-value < 0.01) remained similar during the Holocene. Using these salinity and pH time series (Fig. 3.10b and 3.10c), variations in lake water $[\text{CO}_3^{2-}]/[\text{DIC}]$ were calculated with the CO2sys software (Parkhurst and Appelo, 2005). Results from this computation suggest that the lake $[\text{CO}_3^{2-}]/[\text{DIC}]$ may have varied from ~ 0.5 to 50% during the Holocene while the modern $[\text{CO}_3^{2-}]/[\text{DIC}]$ is around 30-40% (Liu et al., 2009; Xu et al., 2010). Based on the estimated range in $[\text{CO}_3^{2-}]/[\text{DIC}]$ during the Holocene and applying Eq. (3.2) with the $\Delta$ and $\gamma$ values for Cyprids and Limnocytherids (Table 3.2), a maximum $[\text{CO}_3^{2-}]/[\text{DIC}]$-induced variation in $\delta^{18}$O$_{ostr}$ of ~ 2-3‰ was estimated (Fig. 3.11f). Combining the effect of $[\text{CO}_3^{2-}]/[\text{DIC}]$ with the effect of changing water depth on $\delta^{18}$O$_{ostr}$ (Fig. 3.11e) could potentially explain more than 4‰ variation in $\delta^{18}$O$_{ostr}$ (Fig. 3.11g) but do not fully resolve the discrepancy between the Holocene lake level (Fig. 11a, Liu et al., 2015) and the $\delta^{18}$O$_{ostr}$ records (Fig. 3.11d, Li and Liu, 2014). Importantly, the 4‰ increase in $\delta^{18}$O$_{ostr}$ between ~ 7 and ~ 1 ka cannot be explained in terms of a varying lake water $[\text{CO}_3^{2-}]/[\text{DIC}]$ and/or a water depth effect. Our analysis therefore suggests that the main cause of increase in $\delta^{18}$O$_{ostr}$ between ~ 7 and ~ 1 ka is a significant increase in lake water $\delta^{18}$O, which in turn indicates increasing evaporation/precipitation ratio and/or change in precipitation $\delta^{18}$O. This result is in consistent with many other terrestrial oxygen isotope records from the Asian region showing a progressive increase in carbonate $\delta^{18}$O during the Mid- and Late Holocene (e.g. Yuan et al., 2004, Wang et al., 2005, Hu et al., 2008, Jiang et al., 2010).
Figure 3.11 (previous page) Impacts of lake level, salinity and pH on Lake Qinghai’s estimated water δ\(^{18}\)O value during the Holocene. (a) Lake level variations relative to the present lake level (3194 m) estimated from AMS \(^{14}\)C and optically stimulated luminescence dating of shoreline deposits (black circles), nearshore sediment (grey squares), and ruppia seeds (green diamonds) (Liu et al., 2015). (b) Lake water salinity inferred from the ostracod Sr/Ca ratio (Zhang et al., 1994). (c) Lake water pH inferred from (b) and the modern correlation between pH and salinity in Lake Qinghai and surrounding lakes (panel i). (d) Ostracod δ\(^{18}\)O record showing a 6 ‰ increase between the early Holocene to the late Holocene (Li and Liu, 2014). (e) Bottom lake water δ\(^{18}\)O value inferred from (d) and corrected for the effect of carbonate ions on the ostracod δ\(^{18}\)O value (green curve). (f) Bottom lake water δ\(^{18}\)O value inferred from (d) and corrected for the effect of water depth on the ostracod δ\(^{18}\)O value (blue curve). (g) Bottom lake water δ\(^{18}\)O value inferred from (d) and corrected for the cumulative effect of carbonate ion and water depth on the ostracod δ\(^{18}\)O value (orange curve). The grey curves in (e), (f) and (g) represent the reconstructed bottom lake water δ\(^{18}\)O value from (d) assuming no water depth and carbonate ion effect on the ostracod δ\(^{18}\)O value. The estimated effect of ‘water depth’, ‘carbonate ion’ and ‘water depth + carbonate ion’ on the ostracod δ\(^{18}\)O value is shown as the difference in δ\(^{18}\)O value between the grey and coloured curves (Δδ\(^{18}\)Ouncor-cor) in (e), (f) and (g) respectively. Each time series except (a) is presented as a 1000 year running mean with steps of 50 years. In each panel, the thick line represents the mean value while the bracketing thin lines represent the mean value plus or minus 1 standard error. (h) The effect of ostracod calcification depth on the δ\(^{18}\)O of modern Limnocythere inopinata and Eucypris mareotica valves from Lake Qinghai (data from Liu et al., 2009). (i) Modern relationship between pH and salinity in Lake Qinghai and surrounding lakes from the NE Tibetan plateau (data from Liu et al., 2009 and Xu et al., 2010). These data suggest that a large fraction of the 6 ‰ increase in ostracod δ\(^{18}\)O between the early Holocene to the late Holocene could be attributed to the effect of decreasing salinity and pH associated with and an increasing water depth.

This example from Lake Qinghai shows that modern and past DIC speciation in the ostracod host water should be evaluated carefully prior to inferring past climatic changes from δ\(^{18}\)Oostr records. Overall, ostracod δ\(^{18}\)O records are expected to reflect past water δ\(^{18}\)O and temperature more accurately when obtained from freshwater lakes than from saline lake since in most freshwater lakes the contribution of carbonate ions to the DIC pool is negligible.

3.6. Conclusions

This chapter compiled a database of published ostracod δ\(^{18}\)O from field-based and culture studies, and associated host water parameters (temperature, water δ\(^{18}\)O, pH, salinity and DIC concentration). The data were used to construct a model of the major drivers of the oxygen isotope fractionation between ostracod calcite and water, and thereby improve palaeoenvironmental interpretations of δ\(^{18}\)Oostr variability. Based on our analysis, we conclude that:

1) The δ\(^{18}\)O of marine and non-marine ostracods is negatively correlated with the host water [CO\(_3^{2-}\)]/[DIC]. The \(^{18}\)O/\(^{16}\)O of non-marine ostracods is close to the \(^{18}\)O/\(^{16}\)O ratio of the sum of host water CO\(_3^{2-}\) and HCO\(_3^{-}\) ions (i.e. similar to the Zeebe (1999) model). For a given temperature, the δ\(^{18}\)O of non-marine ostracods decreases to between ~ 4 and ~ 6 ‰ across the 0-70% range in [CO\(_3^{2-}\)]/[DIC], depending on the ostracod species. Extrapolating to a [CO\(_3^{2-}\)]/[DIC] of 100% suggests a decrease in δ\(^{18}\)Oostr of between 6 and 8‰. In low [CO\(_3^{2-}\)]/[DIC] settings (i.e. high HCO\(_3^{-}\)/CO\(_3^{2-}\)), ostracod \(^{18}\)O/\(^{16}\)O
is close in value to the $^{18}\text{O}/^{16}\text{O}$ of HCO$_3$ ions (as measured in Beck et al., 2015), making $\delta^{18}\text{O}_{\text{ostr}}$ higher than the $\delta^{18}\text{O}$ of slowly precipitated inorganic calcite precipitated in the same conditions.

2) Taxonomic offsets in $\delta^{18}\text{O}_{\text{ostr}}$ vary with the host water [CO$_3^{2-}$/DIC]. In environments with [CO$_3^{2-}$/DIC] $<$ 2% (i.e. mostly freshwater with HCO$_3^{−}$ $>>$ CO$_3^{2-}$), the $^{18}\text{O}/^{16}\text{O}$ of Candonids is indistinguishable from the $^{18}\text{O}/^{16}\text{O}$ of HCO$_3$ ions (difference of 0.10 ± 0.16‰) while the $^{18}\text{O}/^{16}\text{O}$ of ostracods from other taxonomic groups is lower than the $^{18}\text{O}/^{16}\text{O}$ of HCO$_3$ ions by -0.32 to −0.77‰ for Cyprids, -0.88 ±0.29‰ for Cytherids and -1.12 ±0.05‰ for Limnoocytherids. The sensitivity of $\delta^{18}\text{O}_{\text{ostr}}$ to [CO$_3^{2-}$/DIC] also varies with taxonomy. For each percent increase in [CO$_3^{2-}$/DIC], $\delta^{18}\text{O}_{\text{ostr}}$ decreases by -0.098 ±0.024‰ for Candonids, -0.073 ±0.004‰ for Cyprids, -0.057 ±0.012‰ for Cytherids and -0.058 ±0.005‰ for Limnoocytherids. Our model suggests that the taxonomic differences in $\delta^{18}\text{O}_{\text{ostr}}$ are due to different levels of isotopic equilibration between the DIC pool and H$_2$O in the ostracod calcifying fluid. In our model, ostracods isolate a parcel of host water, and then increase the pH of the isolated fluid. The higher pH changes the DIC speciation towards higher [CO$_3^{2-}$/DIC], which in turn lowers the $^{18}\text{O}/^{16}\text{O}$ of the DIC in the calcifying fluid. Although a change in the DIC speciation to higher [CO$_3^{2-}$/DIC] is near-instantaneous, there is a lag in the calcifying fluid reaching DIC-H$_2$O isotopic equilibrium. It is postulated that the $^{18}\text{O}$ ‘enrichment’ of ostracod calcite is due to the precipitation of a DIC pool that is not isotopically equilibrated with H$_2$O, for example, Candonids, with $^{18}\text{O}/^{16}\text{O}$ similar to host water HCO$_3$-, likely calcify fast and have the lowest degree of DIC-H$_2$O isotopic equilibrium in the calcifying fluid relative to the other ostracod taxa. The more negative the $^{18}\text{O}/^{16}\text{O}$ of a given species relative to HCO$_3$-, the greater the degree of isotopic equilibrium in the ostracod calcifying fluid.

3) Host water salinity and pH affect $\delta^{18}\text{O}_{\text{ostr}}$ by affecting the DIC speciation of the host water. Higher salinities and pH induce higher [CO$_3^{2-}$/DIC], resulting in lower $\delta^{18}\text{O}_{\text{ostr}}$. This explanation resolves conflicting observations of variable salinity effects on $\delta^{18}\text{O}_{\text{ostr}}$.

4) The modest oxygen isotope fractionation between ostracod calcite and the sum of host water CO$_3^{2-}$ and HCO$_3$- ions, relative to the fractionations of other biocalcifiers, implies that the calcite building blocks of the ostracod shell must form at very high rates, preventing DIC-H$_2$O isotopic equilibration in the alkaline calcifying fluid. The similarity in $^{18}\text{O}/^{16}\text{O}$ between ostracod calcite and host water DIC also indicates that the DIC pool in the calcifying fluid is almost fully consumed. Ostracod calcification therefore occurs within a closed system.

5) Ostracod $\delta^{18}\text{O}$ records from environments with high or variable [CO$_3^{2-}$/DIC] (e.g. closed basins) should be checked for carbonate ion effects. In particular, the effect of lake water evaporation on $\delta^{18}\text{O}_{\text{ostr}}$ may be complex since evaporation typically increases the lake water $\delta^{18}\text{O}$, salinity and pH.
Higher salinity and pH increase the \([\text{CO}_3^{2-}] /\text{DIC}\) and thus decrease the \(\delta^{18}\text{O}_{\text{ostr}}\), offsetting the effect of increasing lake water \(\delta^{18}\text{O}\) on the ostracod \(\delta^{18}\text{O}\) record. A case study with a \(\delta^{18}\text{O}_{\text{ostr}}\) record from Lake Qinghai (China) suggests potential \(\delta^{18}\text{O}_{\text{ostr}}\) variations of \(~3-4\)‰ induced by changes in \([\text{CO}_3^{2-}] /\text{DIC}\) during the Holocene.

References


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Chapter IV: KINETIC OXYGEN ISOTOPE FRACTIONATION DURING CORAL ARAGONITE PRECIPITATION

4.1. Introduction

The $\delta^{18}O$ of tropical corals is a valuable proxy for sea surface temperature (SST) and seawater $\delta^{18}O$ ($\delta^{18}O_{sw}$) variations (for reviews see Gagan et al., 2000; Corrège, 2006), and are used to reconstruct past interannual climate variability, including the El Niño Southern Oscillation (ENSO; e.g. Cole et al., 1993; Dunbar et al., 1994; Tudhope et al., 2001; Cobb et al., 2003; McGregor and Gagan, 2004; Cobb et al., 2013; McGregor et al., 2013).

The reliability of coral climate reconstructions depends on understanding of the oxygen isotope fractionation between coralline aragonite and seawater. A longstanding observation is that coral skeletons are significantly depleted in $^{18}O$ relative to other marine calcifiers (Grossman and Ku, 1986), and relative slowly precipitated inorganic aragonite (Kim et al., 2007) precipitated under the same temperature and $\delta^{18}O_{sw}$. Importantly, intercolony variations in mean coral aragonite $\delta^{18}O$ and in the temperature sensitivity of coral $\delta^{18}O$ can complicate paleoclimate reconstructions (Weber and Woodhead, 1970; de Villiers et al., 1995; Linsley et al., 1999). For Porites sp. corals, varying coral extension rates explain a significant fraction of the variance in mean $\delta^{18}O$ between contemporaneous colonies from the same location (Allison, 1996; Felis et al., 2003; Maier et al., 2004; Suzuki et al., 2005). However, the effect of coral extension rate on Porites sp. $\delta^{18}O$ ($\delta^{18}O_{P}$) varies between studies with some corals showing little variation (McGregor et al., 2011; Hayashi et al., 2013) and the cause of these differences is unresolved. Another puzzling observation is that the $\delta^{18}O$ of shallow and deep-sea corals display several per mil variations at the microscale that cannot be explained by variations in temperature and $\delta^{18}O_{sw}$ (Adkins et al., 2003; Rollion-Bard et al., 2003; Allison and Finch, 2010; Rollion-Bard et al., 2011).

These oxygen isotope ‘vital effects’ in coral aragonite have been explained by kinetic isotope fractionations during the hydration and hydroxylation of metabolic CO$_2$ in the coral calcifying fluid (CF) (McConnaughey, 1989a; Rollion-Bard et al., 2003; Allison and Finch, 2010). According to the McConnaughey (1989) model, metabolic CO$_2$ is the dominant source of DIC for calcification. Once in the coral CF, metabolic CO$_2$ is converted into HCO$_3^-$ via the hydration and/or hydroxylation pathway (Johnson, 1982). These conversions result in a DIC $^{18}O/^{16}O$ that is initially lower than the $^{18}O/^{16}O$ of an isotopically equilibrated DIC pool. If coral calcification is faster than the rate of DIC-H$_2$O equilibration in the CF, the low $^{18}O/^{16}O$ of hydrated/hydroxylated CO$_2$ is recorded in coralline aragonite. This model is qualitatively consistent with (1) the low $\delta^{18}O$ of corals relative to inorganic
aragonite precipitated in the same conditions, (2) the growth rate dependence of coral $\delta^{18}O$ and (3) the microscale variations in coral $\delta^{18}O$.

However, the kinetic isotope model of McConnaughey (1989a) could not be tested quantitatively until recently because the rate of oxygen isotope equilibration between DIC and H$_2$O in the coral tissues and calcifying fluid was not known. Recent quantification of CO$_2$ hydration rates in coral tissues (via measurement of coral carbonic anhydrase activities, Hopkinson et al., 2015) as well as new estimates of kinetic oxygen isotope fractionation during CO$_2$ hydration (Zeebe, 2014) and CO$_2$ hydroxylation (Chapter 2) allow quantitative predictions for the $^{18}O/^{16}O$ of the calcifying fluid DIC (DIC$_{cf}$).

Here we investigate the link between coral extension rate and kinetic oxygen isotope effects in *Porites* sp. aragonite. A comparison of four new and three previously published $\delta^{18}O$ records from fast growing *Porites* sp. microatolls retrieved from Kiritimati Is., Kiribati in the central Pacific Ocean shows that the mean $\delta^{18}O$ of *Porites* sp. microatolls is reproduced between neighbouring colonies ($\pm$ 0.09‰, 1$\sigma$) and appears independent of the coral extension rate over the range 12 to 28 mm/yr. Comparison of these data with previous work from other locations shows that the oxygen isotope fractionation between *Porites* sp. aragonite and seawater ($\alpha_{V/w}$) decreases with coral extension rate down to a “kinetic limit” in $\alpha_{p/w}$ of $\sim$ 1.0256 ± 0.0002 at 25°C. The effect of coral growth rate on $\alpha_{p/w}$ is reproduced by a model of kinetic oxygen isotope fractionation for inorganic CaCO$_3$ that includes the catalytic effect of carbonic anhydrase (CA) on the rate of CO$_2$ hydration in the CF. In contrast, model simulations without CA cannot reproduce the growth rate effect on $\alpha_{p/w}$. These results suggest that variable CA activity in the CF is likely to be a main cause of intra- and inter-colony variations in $\delta^{18}O_p$.

4.2. Methods

4.2.1. Coral samples

Four *Porites* sp. microatolls were collected from Kiritimati Island between 2009 and 2011 (Figure 4.1). Kiritimati Island lies within the dry equatorial zone of the central Pacific, with interannual variability in SST and rainfall dominated by ENSO (Bjerknes, 1969). Sea surface temperature for the open ocean near Kiritimati Is. averaged 27.2 ± 1.2 (1$\sigma$) for 1982-2011 (OI SST for the 1° x 1° grid centred on 157°30’W, 1°30’N, Reynolds, 2002), with the SST minima occurring in early February, and the maxima occurring in June. El Niño events produce marked positive SST anomalies of up to 3°C in the boreal winter. La Niña events result in negative SST anomalies of 1–2°C. Kiritimati Island is considered an “optimal” location for reconstructing past ENSO variability (Evans et al., 1999).
Sections across the diameter of two modern Porites microatolls (XM22 and CH38) were collected in 2011 from Cecile Peninsula (a reef flat located on the south coast of Kiritimati Is.; Figure 4.1). Coral XM22 was originally sampled in 2007 and several parts of this coral were analysed for δ¹⁸O to determine intracolony variability (McGregor et al., 2011).

Figure 4.1. Composite satellite photographs (Google Earth) of Kiritimati Island in the central Pacific Ocean. Also shown are the locations of coral sampling (A: Northeast Point (157°19' W, 1°59' N); B: Cecile Peninsula (157°30' W, 1°51' N)), in situ water temperature recording and the G1 SST (Chao et al., 2009) 1 km grid squares closest to the Porites microatoll sampling locations. Porites microatolls were sampled in 1992 (Woodroffe and Gagan, 2000: CW3), 1999 (Woodroffe et al., 2003: XM0), 2007 (McGregor et al., 2011: XM22), and between 2009 and 2011 (this study: NEP1, NEP3, CH10, CH38 and a second section of XM22). The dome Porites was sampled in 1994 (Evans et al., 1999).

Sections were also taken from three fossil Porites microatolls (NEP1, NEP3, CH10) collected in 2009 and 2011 from the reef flat at Northeast Point, Kiritimati Is. The fossil microatolls were sampled in their original growth positions.

All modern and fossil corals sampled grew between ~ 50 to ~ 300 m from the present day reef crest (Figure 4.1). The corals are well flushed with open ocean waters between mid to high tide, while the water depth is generally less than 40 cm at low tide. HOBO temperature loggers were deployed for 5 days near sampled corals to assess potential differences in SST between the reef flats and open ocean waters and to refine the δ¹⁸O-SST relationships of living microatolls from these reef flats. Results
from these microatolls are compared to previously published results from living microatolls CW3 (Woodroffe and Gagan, 2000), XM0 (Woodroffe et al., 2003) and XM22 (McGregor et al., 2011) sampled on the same reef flats as the fossil microatolls analysed in this study.

Fossil corals were screened for diagenesis using X-ray diffraction (XRD) and petrographic analysis. Samples for XRD were crushed to a fine powder under ethanol with a mortar and pestle. XRD samples were measured on a Phillips Goniometer with a Spellman DR3 Copper X-ray generator run at 1 kV, and scanned at 2° per minute for a 20 range of 4-70°. The aragonite and calcite content of each sample was estimated using SIROQUANT version 3 software utilising the Rietvelt method for analysing diffraction peaks. Samples for thin sections were taken along the sampling transects for δ¹⁸O analysis, allowing screening for calcite, secondary aragonite, dissolution, and other post-depositional textures (McGregor and Gagan, 2003; McGregor and Abram, 2008). Both the samples for XRD and thin sections were cleaned using RiOS water and a Branson 450 ultrasonic probe. All samples contained < 1 % calcite, and all corals were rated as excellent preservation (Appendix A4.1 for thin sections), based on thin section analysis and the criteria of McGregor and Abram (2008).

4.2.2. U/Th dating

U-series age estimates were made on fossil microatoll NEP1, NEP3 and CH10. For each U-series age estimate, a small coral piece was thoroughly cleaned in MilliQ water and by ultrasonic probe. A 50–100 mg aliquot was weighed out, prepared and measured at the Radiogenic Isotope Laboratory, University of Queensland, following the procedures outlined in Zhou et al. (2011). In summary, the aliquots were dissolved in nitric acid and spiked with a ²²⁹Th-²³³U mixed tracer. Following chemical separation, a mixed U–Th solution was made such that the final 3 ml solution had a U concentration of ~10 ppb or less.

U–Th isotopic ratio measurement was performed on a Nu Plasma multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) following the analytical protocol described by Hellstrom (2003), with minor modifications (Zhou et al. 2011). The ²³⁸U/²³⁵U value of 137.88 was used for mass fractionation correction for both U and Th isotopic ratio measurements. Monitoring of carryover memories showed that ²³⁰Th memory was consistently less than 0.1 count s⁻¹, and was negligible for all other isotopes. U–Th ages were calculated using the Isoplot/EX 3.0 program (Ludwig, 2003). δ²³⁴U_initial values for all dates are within the acceptance criteria of 145.5 ± 2.3 ‰ based on values for seawater (Cheng et al., 2000). The U-Th ages were calculated from the date of U-Th chemistry and are quoted in CE (Table A3.2).

For each coral, two small coral pieces, separated by a known number of years (NEP1: ~ 4 years, NEP3: ~ 4 years, CH10 ~ 26 years) using the coral’s growth-band internal chronologies, were...
collected for dating. The U-series results for these corals preserved the relative age difference between the samples (NEP1: 1923-1929 AD, NEP3: 1931-1935 AD, CH10: 1910-1942 AD) and dated all three corals to the first half of the 20th century. However, using U/Th ages and plotting the $\delta^{18}$O results along with the instrumental SST record (ERSSTv3b for the $2^\circ \times 2^\circ$ grid square centred on 158°W, 2°N; Smith et al., 2008) indicate that U-series ages are offset by 10 to 16 years. This is likely due to the very high seawater $^{230}$Th/$^{232}$Th in the central Pacific (2.5 ×10-5 to 2.6 ×10-4 Roy-Barman et al., 1996) relative to the bulk Earth $^{230}$Th/$^{232}$Th (4–5 ×10-6, Richards and Dorale, 2003), which was assumed for the U-Th age calculations. A high initial $^{230}$Th/$^{232}$Th increases the U-Th age relative to the real age of the sample (Edwards et al., 2003). The assigned ages of coral samples (NEP1: 1936-1939, NEP3: 1943-1947, CH10: 1927-1953) were adjusted to maximise the correlation coefficients between the coral $\delta^{18}$O records and instrumental SST.

4.2.3. $\delta^{18}$O analyses

A ~ 7 mm slice was taken from each coral section and X-rayed to reveal the coral density bands (Appendix A4.2). The X-radiographs were used to identify the maximum growth axis from which transects were defined for $\delta^{18}$O analysis. Each coral transect was reduced to 2 mm thickness, thoroughly cleaned using RiOS water and a Branson 450 ultrasonic probe, and left in an oven at 40°C until dried. The transects were then continuously sampled at 1.0–1.6 mm resolution, equivalent to monthly sampling, using a low-speed milling system (Gagan et al., 1994).

Coral $\delta^{18}$O was measured at approximately bi-monthly resolution on a Finnigan MAT 251 mass spectrometer at the Research School of Earth Sciences, Australian National University. For each sample aliquot, 200 ± 20 µg of powder was initially dissolved in 105% H$_3$PO$_4$ at 90°C in an automated carbonate Kiel device. Isotope results were calibrated relative to Vienna PeeDee Belemnite (VPDB) using the NBS19 ($\delta^{18}$O = -2.20‰) and NBS18 ($\delta^{18}$O = -23.0‰) standards. The standard deviation for in-run $\delta^{18}$O measurements on NBS19 (n = 279) was 0.04‰ during the course of the analysis.

Coral $\delta^{18}$O time-series were established based on the average coral growth rate and by assigning $\delta^{18}$O maxima to the climatological SST minima (early February), using the Analyseries software package (Paillard et al., 1996) and were cross-checked against annual growth bands seen in the coral X-rays (A4.3). Where a $\delta^{18}$O maximum was poorly resolved in the coral no tie-point was assigned. The $\delta^{18}$O data were then interpolated using ARAND software (Howell et al., 2006) to give 6 values per year. Coral mean annual extension rates were determined from the annual growth bands in the coral by X-rays and the seasonal component of the coral $\delta^{18}$O time series.
4.3. Results

4.3.1. Seawater temperature

*In-situ* recording of the water temperature at Cecile Peninsula and Northeast Point show daily cycles of 1-2°C between 03/08/2013 and 08/08/2013 (Figure 4.2A). At Northeast Point, seawater warmed between ~7 am and ~4 pm and cooled between ~5 pm and 6 am. At Cecile Peninsula, the warming phase was shorter and mostly occurred between ~7 am and midday while cooling took place from midday to midnight. The daily seawater temperature cycle appears less regular at Cecile Peninsula than at Northeast Point. The different patterns in the daily water temperature cycle between the two sites are attributed to tidal effects on the water temperature at Cecile Peninsula (data not shown).

Mean daily water temperature was warmer on the northern reef by ~0.4°C relative to the southern reef over the 5 days of in-situ temperature recording. The good agreement of the mean daily water temperature on the reefs with nearby open ocean SST (G1 SST satellite product, 1 km grid square centred on 157°16’ W, 2°01’ N and 157°31’ W, 1°49’ N; Chao et al., 2009; Figure 4.3B) suggests that the difference in water temperature between the two reefs is due to the thermal signature of different water masses around the island.

Mean monthly SST records of open ocean waters nearby the coral sampling locations (Figure 4.3C) where obtained from the G1 SST satellite product (Chao et al., 2009). These data confirm that seawater is consistently warmer on the north coast than on the south coast, with maximum differences in SST of 0.6°C during cold events (e.g. La Niña events of 2008 and 2011). Modelling of Island oceanography suggests that tropical instability waves in the central Pacific and upwelling of cold water on the southern side of Kiritimati Island lead to a North-South SST gradient across Kiritimati Island (Stevenson et al., 2015).

Although G1 SST data appear to be a good indicator of the water temperature on Kiritimati Island reef flats, this product is only available from 2002 onwards, which is not optimal for calibrating the coral δ¹⁸O with SST. We compared the G1 SST data with Optimum Interpolated (OI) SST (a satellite SST product of lower spatial resolution but available for 1980-2011, Reynolds et al., 2002) centred on Kiritimati Island. North coast G1 SST appears consistently warmer by up to 0.5°C relative to the OI SST for OI SSTs of 24-26°C while south coast G1 SST and OI SST are very similar. Since the north and south coast G1 SST data are strongly correlated with the OI SST data at these sites (Figure 4.2D, N. coast G1 vs OI SST: $r^2 = 0.94$, S. coast G1 vs OI SST: $r^2 = 0.97$), we used the OI SST relations to obtain monthly SST time series for Kiritimati Island’s North and South coasts back to 1982.
Figure 4.2. SST for coastal waters of Kiritimati Island. (A) *In situ* SST recorded every 20 minutes during 5 days at the locations of coral sampling (Northeast Point and Cecile Peninsula). At both sites, the water temperature increased by ~ 1-2°C during day time relative to night time (grey shaded areas). During day time, the water temperature at Northeast Point can be warmer by up to 1°C relative to Cecile Peninsula. (B) Comparison of mean daily water temperature between the *in situ* data presented in (A) and the G1 SST satellite product (1 km grid square centred on 157°16' W, 2°01' N and 157°31' W, 1°49’ N; Chao et al., 2009). In situ temperature and G1 SST are in good agreement with each other and show a difference in mean daily water temperature of 0 to 0.5°C between the northern and southern locations. (C) Comparison of monthly G1 SST between the north and south coasts between 2002 and 2013. Seawater is systematically warmer on the north coast relative to the south coast, although the difference is more pronounced during cold events. (D) Relationship between mean monthly G1 SST and mean monthly OI SST (Reynolds et al., 2002) centred on Kiritimati Island (157°30’ W, 1°30’ N) for the north coast (left) and the south coast (right). The difference in SST between the two satellite products is depicted by the difference between the 1:1 line (black) and the regression lines (reduced major axis method, pink dashed line).
These adjusted OI SST records (Figure 4.3B) were used for calibrating the effect of seawater temperature on the microatoll δ¹⁸O records.

4.3.2. *Porites* microatoll δ¹⁸O records

The δ¹⁸O records of *Porites* microatolls analysed in this study (NEP1, NEP3, CH10, CH38 and XM22) are presented in Figure 4.3A along with previously published *Porites* δ¹⁸O records from Kiritimati Island (*Porites* microatolls: Woodroffe and Gagan, 2000, Woodroffe et al., 2003, McGregor et al., 2011; domed *Porites*: Evans et al., 1999). Differences in mean δ¹⁸O between individual corals for temporally overlapping sections are reported in Table 4.1. Intercolony variations in δ¹⁸O (i.e. not climate driven) between corals that do not overlap temporally were also inferred by comparing differences in mean δ¹⁸O between pairs of contemporaneous coral records that include a common coral record. For example, an intercolony difference in δ¹⁸O between coral CH10 and XM0 of -0.13 ‰ was inferred from the δ¹⁸O differences between corals CH10 and Evans99 (-0.22 ‰) and between corals XM0 and Evans99 (-0.35 ‰). These inferences assume that the oxygen isotope disequilibrium effect of a *Porites* colony is constant on a decadal scale (Linsley et al., 1999) and that local differences in seawater temperature and δ¹⁸O around Kiritimati Island remained similar throughout the 20th century. Considering all seven *Porites* microatoll colonies, the maximum intercolony difference in mean δ¹⁸O value is 0.25 ‰. Removing colony CH10, which is most offset in δ¹⁸O value relative to the other colonies, reduces the maximum intercolony offset to 0.12 ‰.

**Table 4.1** Intercolony differences in δ¹⁸O between *Porites* corals from Kiritimati Island

<table>
<thead>
<tr>
<th></th>
<th>CW3a</th>
<th>XM0b</th>
<th>NEP1</th>
<th>NEP3</th>
<th>CH10</th>
<th>XM22c</th>
<th>CH38</th>
<th>Evans99d</th>
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<td>CW3a</td>
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<td>-0.08</td>
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<tr>
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<td>0.07</td>
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<td>0.05</td>
<td>0.30</td>
</tr>
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<td>0.02</td>
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</tr>
<tr>
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<tr>
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<td>-0.30</td>
<td>-0.44</td>
<td>-0.22</td>
<td>-0.34</td>
<td>-0.39</td>
<td></td>
</tr>
</tbody>
</table>

Differences in δ¹⁸O between coral records that overlap temporally are in black. Inferred differences in δ¹⁸O between coral records that do not overlap temporally are in grey.

a δ¹⁸O record from Woodroffe and Gagan (2000)
b δ¹⁸O record from Woodroffe et al., (2003)
c A shorter δ¹⁸O record of coral XM22 was first published in McGregor et al. (2011)
d δ¹⁸O record from Evans et al. (1999). This record is from a dome shaped *Porites* and shows positive and irregular spikes in δ¹⁸O during spawning events. No correction was applied for removing the effect of spawning spikes on the δ¹⁸O record. Removing δ¹⁸O data associated to spawning spikes do not change the calculated differences in δ¹⁸O between coral colonies by more than 0.01‰.
Figure 4.3. *Porites* microatoll $\delta^{18}O$ records from Kiritimati Is. compared to SST and estimated sea surface $\delta^{18}O$ ($\delta^{18}O_{sw}$). (a) Microatoll $\delta^{18}O$ records between 1928 and 1953 and between 1982 and 2011. NEP1, NEP3, CH10 and CH38 are bimonthly $\delta^{18}O$ records while CW3, XM0 and XM22 are monthly $\delta^{18}O$ records. Variations in coral $\delta^{18}O$ are well reproduced between different colonies from the Northeast Point (light to dark red) and from Cecile Peninsula (light to dark blue). The microatoll $\delta^{18}O$ records are also compared to the dome shaped *Porites* $\delta^{18}O$ record of Evans et al. (1999). (b) Monthly extended reconstructed sea surface temperature version 3b (ERSSTv3b) for the 2° x 2° grid square centred on 158° W, 2° N (black line; Smith et al., 2008) and OI SST for the 1° x 1° grid square centred on 157°30' W, 1°30' N (Reynolds et al., 2002) adjusted for local SST effect at Northeast Point (red line) and Cecile Peninsula (blue line). The OI SST time series was corrected for local warming and cooling effects by applying linear regression equations between G1 SST and OI SST for the period 2002-2013 (see Figure 4.2D). (c) Estimated seawater $\delta^{18}O$ ($\delta^{18}O_{sw}$) time series for open ocean waters near Kiritimati Island. The $\delta^{18}O$ time series was inferred from the EN4 sea surface salinity product (Good et al., 2013) for the 1° x 1° grid square centred on 157°30' W, 1°30' N and the (d) $\delta^{18}O_{sw}$-salinity relationship obtained from a compilation of central Pacific $\delta^{18}O_{sw}$ and salinity data (Fairbanks et al., 1997: data from Kiritimati Is.; McGregor et al., 2011: open ocean data; Conroy et al., 2014: data from 0-75 m band; GISS Global Seawater Oxygen-18 Database (Schmidt et al., 1999): data from the 0-75 m band).
The relationship between previously published modern microatoll $\delta^{18}O$ records and seawater temperature was re-examined in light of the in situ temperature data and the newly available high resolution satellite SST product. Seasonal maxima and minima in coral $\delta^{18}O$ and SST were used to obtain $\delta^{18}O_p$-SST relationships for coral XM22 and XM0 for the period 1989-2011 (Figure 4.4A). Anomalously low $\delta^{18}O_p$ during the El Niño events of 91/92 and 97/98 were caused by high rainfall in the central Pacific during these years (McGregor et al., 2011). Excluding these El Niño events from the regression increases the correlation coefficients between $\delta^{18}O_p$ and SST from 0.85 to 0.89 for coral XM22 and from 0.77 to 0.78 for coral XM0. The resulting $\delta^{18}O_p$ vs SST linear regressions (reduced major axis method) for coral XM22 and XM0 without the data related to the 91/92 and 97/98 El Niño events are:

XM22: $\delta^{18}O_p = -0.15(\pm0.01)SST -1.0(\pm0.2)$ (4.1)

XM0: $\delta^{18}O_p = -0.14(\pm0.02)SST -1.4(\pm0.4)$ (4.2)

The above relations do not take into account potential effects of variable $\delta^{18}O_{sw}$ on $\delta^{18}O_p$. Variation in $\delta^{18}O_{sw}$ between 1982 and 2011 (Figure 4.3C) were estimated from the EN4 sea surface salinity product (Good et al., 2013) for the 1° x 1° grid square centred on 157°30’ W, 1°30’ N and a $\delta^{18}O_{sw}$-salinity relationship obtained from a compilation of $\delta^{18}O_{sw}$ measurements in the central Pacific Ocean (Figure 4.4). Using this $\delta^{18}O_{sw}$ time series and excluding $\delta^{18}O_p$ data related to the 97/98 and 91/92 El Niño events from the regressions, the following ‘$\delta^{18}O_p - \delta^{18}O_{sw}$’ vs SST relations were obtained for coral XM22 and XM0 (Figure 4.5B):

XM22: $\delta^{18}O_p - \delta^{18}O_{sw} = -0.16(\pm0.01)SST -1.2(\pm0.3)$ (4.3)

XM0: $\delta^{18}O_p - \delta^{18}O_{sw} = -0.15(\pm0.02)SST -1.4(\pm0.4)$ (4.4)

These latter calibrations suggest a slightly stronger temperature effect on $\delta^{18}O_p$ than equations (4.1) and (4.2), although the differences are within error of the regression slopes. Very similar correlation coefficients were obtained for the $\delta^{18}O_p$ vs SST and $\delta^{18}O_p$-$\delta^{18}O_{sw}$ vs SST regressions. This confirms previous findings that $\delta^{18}O_{sw}$ variability in the central Pacific does not significantly contribute to the $\delta^{18}O_p$ signal, except during strong El Niño events (Evans et al., 1999, McGregor et al., 2011). Regardless of the calibration method employed, the $\delta^{18}O_p$ of coral XM22 and XM0 have a very similar temperature sensitivity of -0.15(±0.01)‰/°C and a $\delta^{18}O$ offset relative to slowly precipitated
inorganic aragonite (Kim et al., 2007) of -3.5‰ at 25°C. A temperature dependence of -0.15(±0.01)‰/°C is assumed for the δ¹⁸O record of the coral microatolls CH38, NEP1, NEP3 and CH10.

**Figure 4.4.** Regressions (RMA method) between δ¹⁸O Porites and SST (OI SST, Reynolds et al., 2002, SST was adjusted for local temperature effect, cf. Figure 4.2) (A) and between δ¹⁸O Porites-δ¹⁸O sw and SST (B) for the modern Porites microtolls XM0 and XM22. Each data point corresponds to a seasonal monthly maxima or minima in δ¹⁸O Porites and SST. In (A), the calculated δ¹⁸O Porites temperature sensitivities are 0.14‰ and 0.15‰ for coral XM0 and XM22 respectively. In (B), δ¹⁸Osw values were obtained from the δ¹⁸Osw time series presented in Figure 4.3c. The calculated δ¹⁸O Porites temperature sensitivities are 0.15‰ and 0.16‰ for coral XM0 and XM22, respectively.

### 4.4. Discussion

#### 4.4.1. Intercolony variations in *Porites* microatoll δ¹⁸O at Kiritimati Island

The differences in mean δ¹⁸O P between *Porites* microatoll colonies growing on Kiritimati Island reef flats (< 0.25‰) are similar in magnitude to the *Porites* microatoll intracolony variations in δ¹⁸O P (maximum difference ~ 0.1‰, McGregor et al., 2011). This intercolony variability in mean δ¹⁸O P is significantly smaller than previously reported variations in mean δ¹⁸O between *Porites* colonies that grew in the same environment (e.g. Linsey et al., 1999: 0.40‰, Felis et al., 2003: 1.28‰, Maier et al., 2004: 0.92‰, Hayashi et al., 2013: 0.30‰). The small intercolony variability in microatoll δ¹⁸O P at Kiritimati Is. is attributed to the combination of analytical uncertainties (~ 0.04‰), local differences in SST (up to ~ 0.5°C equivalent to ~ 0.08‰) and variable oxygen isotope fractionations between coral aragonite and seawater (i.e. vital effects). We rule out diagenesis as a cause of δ¹⁸O P offset between *Porites* microatolls colonies since all corals analysed in this study showed no sign of alteration (Section 4.2.1, Appendix A4.1). The largest difference in δ¹⁸O P between two *Porites* microatoll colonies was obtained from corals that grew over the same time period and on the same
reef flat (CH10 and NEP1, Noth-East Point), suggesting that coral biology is likely to be the major factor behind the intercolony variations in $\delta^{18}$O$_P$.

4.4.2. Growth rate effect on Porites $\delta^{18}$O

Intercolony differences in mean $\delta^{18}$O$_P$ have been explained in part by variations in coral extension rates (Allison, 1996; Felis et al., 2003; Maier et al., 2004; Suzuki et al., 2005). To investigate the potential effect of coral extension rate on the microatoll $\delta^{18}$O$_P$, the average oxygen isotope fractionations between Porites sp. aragonite and seawater at 25°C (reported in ‰ with the $\varepsilon_{P/w25}$ notation) were calculated for the different Porites sp. microatolls colonies from Kiritimati Is. For each coral sampled at Cecile Peninsula (XM22 and CH38), the $\varepsilon_{P/w25}$ was calculated from the ‘$\delta^{18}$O$_P$ - $\delta^{18}$O$_{sw}$’ vs SST relationship of coral XM22 (equation 4.3; Figure 4.4B) and by adding the mean $\delta^{18}$O$_P$ offsets relative to the $\delta^{18}$O$_P$ of coral XM22 (Table 4.1). For each coral sampled at Northeast Point (XM0, CW3, NEP1, NEP3 and CH10), the $\varepsilon_{P/w25}$ was calculated from the ‘$\delta^{18}$O$_P$ - $\delta^{18}$O$_{sw}$’ vs SST relationship of coral XM0 (equation 4.4) and by adding the mean $\delta^{18}$O$_P$ offsets relative to the $\delta^{18}$O$_P$ of coral XM0 (Table 4.1).

The microatoll $\varepsilon_{P/w25}$ values range from 25.4 ±0.1 ‰ to 25.7 ±0.1 ‰ and are not significantly correlated to the coral’s extension rates over the 12 to 28 mm/y range (Figure 4.5, $r^2 = 0.22$, p-value = 0.29). This result contrasts with some previous studies reporting a significant growth rate dependence on coral $\delta^{18}$O (McConnaughey, 1989a; de Villier et al., 1995; Felis et al., 2003; Maier et al., 2004; Suzuki et al., 2005). There are suggestions that coral $\delta^{18}$O is independent of the coral extension rate above a threshold value in extension rate (McConnaughey, 1989b; Felis et al., 2003). According to the McConnaughey (1989) kinetic isotope model, the growth rate effect is caused by a variable level of isotopic equilibration between the DIC in the CF (DIC$_{cf}$) and seawater. Slow aragonite growth rates should promote DIC$_{cf}$-H$_2$O isotopic equilibrium while a fast aragonite growth rate should result in DIC$_{cf}$-H$_2$O isotopic disequilibrium. An absence of a growth rate effect on coral $\delta^{18}$O therefore suggests that DIC$_{cf}$-H$_2$O isotopic equilibration remained minimal, regardless of the coral extension rate. In other words, a lack of growth rate effect on coral $\delta^{18}$O suggest that a “kinetic limit” in $\varepsilon_{P/w}$ has been attained. The calculated $\varepsilon_{P/w25}$ values of Kiritimati Island’s Porites sp. microatolls suggests a kinetic limit in $\varepsilon_{P/w25}$ of 25.6 ± 0.2‰ (2σ).
Figure 4.5. Oxygen isotope fractionation between *Porites* microatoll aragonite and seawater ($\varepsilon^{18}O_{P/w}$) at 25°C as a function of coral extension rate. Vertical error bars integrate the uncertainties (1σ) in $\delta^{18}O_P$ and $\delta^{18}O_{sw}$. The horizontal bar for the McGregor et al. (2011) data point indicates the range of outcome for six $\delta^{18}O$ transects in a single coral. $\varepsilon^{18}O_{P/w}$ is not significantly correlated to coral extension rate between the 12 and 28 mm/yr rates ($r^2 = 0.22$, p-value = 0.29). The average $\varepsilon^{18}O_{P/w}$ for the seven colonies (grey line) is 25.56 ± 0.18 ‰ (2σ, grey shaded area).

A comparison of the microatoll’s $\varepsilon_{P/w25}$ values with calculated $\varepsilon_{P/w25}$ from other studies (Figure 4.6, Table 4.2) shows that $\varepsilon_{P/w25}$ is rarely lower than 25.6 ±0.2 ‰, suggesting that the kinetic limit defined with the *Porites* sp. microatolls may be relevant to other morphologies of *Porites* corals. An overall dependence of $\varepsilon_{P/w25}$ on the *Porites* sp. extension rate can be approximated by a logarithmic function for extension rates varying between 2 and 28 mm/yr ($r^2 = 0.52$, p-value < 0.01):

$$\varepsilon_{P/w25} = 27.0(\pm 0.1) - 1.0(\pm 0.1)\log(\text{extension rate})$$

(4.5)

However, the predictive power of this relation is poor, especially for slow extension rates (Figure 4.6). This could be in part due to uncertainties in the calculated the $\varepsilon_{P/w25}$ values (typical uncertainty of ~0.1 ‰) and to uncertainties in coral extension rates (most likely > 10 %). However, some of the differences in ‘$\varepsilon_{P/w25}$ vs extension rate’ observed between studies are in the order of 1 ‰ (e.g. Felis et al., 2003 or Maier et al., 2004 compared to Hayashi et al., 2013), which is significantly higher than the data uncertainty. This suggests that the effect of coral growth rate on $\varepsilon_{P/w}$ varies between coral colonies and/or environmental settings. One or more additional biological factor other than coral extension rate therefore affects $\delta^{18}O_P$. 
Figure 4.6 Calculated $\varepsilon^{18}$O$_{P/w}$ (25°C) vs Porites extension rate obtained from published modern Porites $\delta^{18}$O records. Each data point indicates a single Porites colony. The average $\varepsilon^{18}$O$_{P/w}$ and 2σ variations for Porites microatolls (this study, Woodroffe and Gagan, 2000, Woodroffe et al., 2003, McGregor et al., 2011) are indicated by the dark grey line and light grey shaded area respectively. Bars on the data point for McGregor et al. (2011) indicate the range of outcomes for six $\delta^{18}$O transects within a single coral colony. The relationship between $\varepsilon^{18}$O$_{P/w}$ and coral extension rate appears to be logarithmic (black line, equation (4.5), $r^2 = 0.52$, p-value < 0.01).

4.5. Model for kinetic isotope fractionation during coral aragonite precipitation

4.5.1. Background on coral calcification

Symbiotic corals precipitate aragonite in a semi-isolated calcifying fluid (CF) located between the skeleton and a tissue layer composed of calicoblastic cells (CC) (Al-Horani et al., 2003). Pathways of DIC and Ca$^{2+}$ transport towards the CF are illustrated on Figure 4.7. The CF is a thin space with a thickness of a few µm (Venn et al., 2011; Cai et al., 2016) and the growing aragonite crystals occupy a significant fraction of the CF volume (Venn et al., 2011). A calcium pump (Ca$^{2+}$ ATPase), increases the Ca$^{2+}$ concentration of the CF relative to that of seawater and exports protons out of the CF, resulting in an alkaline environment suitable for calcification (Al-Horani et al., 2003). The pH of the CF ($pH_{cf}$) is always higher than seawater and direct measurement with micro electrodes indicate higher $pH_{cf}$ values during day time relative to night time for symbiotic corals (Al-Horani et al., 2003). Higher $pH_{cf}$ values during the day are consistent with faster calcification rates during day time rather than night time (Furla et al., 2000). A compilation of estimated $pH_{cf}$ for Porites based on the $\delta^{11}$B pH proxy (Table 4.2) suggests an average $pH_{cf}$ of ~ 8.5 during calcification with no significant differences in $pH_{cf}$ between different coral colonies, species and environmental settings.
Figure 4.7 Pathways of DIC and Ca\textsuperscript{2+} transport towards the coral calcification fluid (modified from Bertucci et al., 2013). The enzyme Calcium ATPase pumps Ca\textsuperscript{2+} toward the calcifying fluid while removing H\textsuperscript{+}. The low pH of cellular cytoplasm (~ 7.4, Venn et al., 2015) relative to the calcifying fluid (~ 8.5) favours the diffusion of metabolic CO\textsubscript{2} across the boundary membranes. In the calcifying fluid, CO\textsubscript{2} is rapidly converted to HCO\textsubscript{3}\textsuperscript{-} and CO\textsubscript{3}\textsuperscript{2-} via the hydration pathway. Passive transport of seawater from the polyp coelenteron to the calcifying fluid may provide an additional source of DIC and Ca\textsuperscript{2+}. In the calicoblastic cells and the calcifying fluid the enzyme carbonic anhydrase (CA) catalyses the reversible reaction of CO\textsubscript{2} hydration/dehydration.

**Table 4.2** Compilation of *Porites* calcifying fluid pH estimates based on the δ\textsuperscript{11}B pH proxy

<table>
<thead>
<tr>
<th>Reference</th>
<th><em>Porites</em> species</th>
<th>sampling location</th>
<th>mean pH\textsubscript{cf}</th>
<th>within coral pH\textsubscript{cf} variability (1σ)</th>
<th>within coral pH\textsubscript{cf} range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allison et al. (2014)</td>
<td><em>Porites spp.</em></td>
<td>Hawaii</td>
<td>8.53</td>
<td>0.14</td>
<td>-</td>
</tr>
<tr>
<td>Allison et al. (2014)</td>
<td><em>Porites spp.</em></td>
<td>Hawaii</td>
<td>8.48</td>
<td>0.17</td>
<td>-</td>
</tr>
<tr>
<td>Allison et al. (2014)</td>
<td><em>Porites spp.</em></td>
<td>Jarvis Island</td>
<td>8.51</td>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>Allison et al. (2011a)</td>
<td><em>Porites lobata</em></td>
<td>Hawaii New</td>
<td>8.57</td>
<td>0.12</td>
<td>8.30 to 8.85</td>
</tr>
<tr>
<td>Rollion-Bard et al. (2011)</td>
<td><em>Porites lutea</em></td>
<td>Caledonia</td>
<td>8.53</td>
<td>0.16</td>
<td>8.08 to 8.92</td>
</tr>
<tr>
<td>McCulloch et al. (2012)</td>
<td><em>Porites cylindrica</em> (pH\textsubscript{sw} = 8.17)</td>
<td>culture experiment</td>
<td>8.48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>McCulloch et al. (2012)</td>
<td><em>Porites spp.</em> (pH\textsubscript{sw} = 8.10)</td>
<td>culture experiment</td>
<td>8.54</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>mean</strong></td>
<td></td>
<td></td>
<td><strong>8.52</strong></td>
<td><strong>0.15</strong></td>
<td>-</td>
</tr>
<tr>
<td><strong>σ</strong></td>
<td></td>
<td></td>
<td><strong>0.03</strong></td>
<td><strong>0.02</strong></td>
<td>-</td>
</tr>
</tbody>
</table>
The high pH of the calcifying fluid contrasts with the low pH of the overlying CC (~ 7.4, Venn et al., 2011; Venn et al., 2013), creating a negative gradient in pCO₂ between the CF and the CC, and thus a positive flux of metabolic CO₂ towards the CF (McConnaughey, 1989b). Metabolic CO₂ (i.e. the CO₂ contained within the coral tissue) is thought to be the primary source of DIC for coral calcification (McConnaughey, 1989b; Furla et al., 2000). However, the relative contributions of respired CO₂, passive environmental CO₂ diffusion and active HCO₃⁻ transport to the metabolic CO₂ pool for calcification remain poorly constrained for symbiotic corals (Allison et al., 2012). In addition, small amount of DIC may also enter the CF via passive transport of seawater from the coelenteron (Gagnon et al., 2012). The DIC concentration in the CF ([DIC cf]) was estimated at ~ 3 mM for Porites sp. (Allison et al., 2014), which is higher than in seawater (~ 2 mM). DIC turnover time in the CF is very short due to fast coral calcification rates and the small volume of the CF (seconds to minutes, Furla et al., 2000). Rapid inputs of metabolic CO₂ to the CF are promoted by the enzyme carbonic anhydrase (CA), which catalyses the conversion of CO₂ to HCO₃⁻. CA is thought to be present in the CF, since it was localised in the overlying CC (Hayes and Goreau, 1977; Moya et al., 2008) as well as in the organic matrix linked to the skeleton (Tambutté et al., 2007). The importance of the metabolic CO₂ source for calcification also strongly depends on CA activity (Goreau, 1959). Recent work suggests a CA activity in Porites tissues between ~ 5 and ~ 100 s⁻¹ (Hopkinson et al., 2015).

4.5.2. Kinetic oxygen isotope model

Overview

To investigate the processes of isotopic fractionation that cause the extension rate effect on Porites δ¹⁸O, the model of oxygen isotope fractionation for inorganic carbonate minerals presented in Chapter 2 is adapted. For coral aragonite, kinetic isotope fractionations arise from the conversion of metabolic CO₂ to HCO₃⁻ and CO₃²⁻ in the CF, resulting in a DIC pool initially depleted in ¹⁸O (McConnaughey, 1989b). Subsequent isotopic equilibration between DIC and H₂O in the CF elevate the ¹⁸O/¹⁶O of the DIC to equilibrium values (Beck et al., 2005). Accordingly, the oxygen isotope fractionation between the DIC cf and seawater in the model is calculated from (1) an initial kinetic isotope fractionation during the conversion of CO₂ to HCO₃⁻, (2) the equilibrium fractionations between the DIC species and water (Beck et al., 2005) and (3) the average level of isotopic equilibration between DIC and water (E_DIC) during aragonite precipitation. A similar approach was previously adopted by Rollion-Bard et al. (2003, 2011) and Allison et al. (2011) to explain wide variations in Porites δ¹⁸O at the microscale. In our model, the main addition relative to previous models is the quantification of the effect of CA on kinetic isotope fractionations and of the rate of DIC-H₂O isotopic equilibration in the coral CF. This was not previously possible as the activity of CA in Porites tissues was only recently quantified (Hopkinson et al., 2015). We show that the level of measured CA activity is sufficient to
induce significant DIC-H₂O isotopic equilibration in the CF of slow growing *Porites* (less than ~ 5 mm/yr) and can explain the observed growth rate effect on δ¹⁸Oₚ.

**Closed system assumption**

The oxygen isotopic fractionation between a precipitating carbonate mineral and water is the result of a sum of fractionations between the mineral and the precipitating DIC species and between DIC and water (Watkins et al., 2013; Watkins et al., 2014, Chapter 2). Since coral aragonite precipitation occurs rapidly in a thin isolated space and under a high Ω, a quantitative precipitation of the DIC_{cf} pool (i.e. full DIC consumption) is expected and we assume no fractionation between aragonite and the DIC_{cf} pool (c.f. McCrea, 1950; Beck et al., 2005; Kim et al., 2006). Note that a quantitative precipitation of the DIC_{cf} pool can occur even if CO₃²⁻ is the only precipitating DIC_{cf} species (as per Chapter 2), since the CO₃²⁻ ions consumed during aragonite precipitation would be constantly replaced by deprotonated HCO₃⁻ in a pH regulated environment. This is because DIC speciation must remain constant where there is a constant pH. Herein, it is assumed that the oxygen isotope fractionation between *Porites* aragonite and water (α_{DIC/w}) reflects the fractionation between the DIC and water (α_{DIC/w}):

\[
\alpha_{P/w} \equiv \alpha_{DIC/w} \quad (4.6)
\]

**CO₂ hydration and hydroxylation**

The main source of DIC for coral calcification is thought to be metabolic CO₂ (McConnaughey, 1989b, Furla et al., 2000). In the CF, CO₂ is rapidly converted to HCO₃⁻ due to the high pH_{cf} and the enzyme carbonic anhydrase. The conversion of CO₂ to HCO₃⁻ occurs via the hydration and hydroxylation reactions (Johnson, 1982):

\[
CO₂ + H₂O \underset{k_{-2}^+}{\overset{k_{+2}^-}{\rightleftharpoons}} H₂CO₃ \leftrightarrow HCO₃⁻ + H^+ \quad \text{(hydration)}
\]

and

\[
CO₂ + OH⁻ \overset{k_{-4}^+}{\underset{k_{+4}^-}{\rightleftharpoons}} HCO₃⁻ \quad \text{(hydroxylation)}
\]

where \(k_{+2}^+, k_{-2}^-\) are the forward and backward reaction rate constants for CO₂ hydration (* denote the inclusion of the catalytic effect of CA on the CO₂ hydration-dehydration rate constants, cf. Uchikawa and Zeebe, 2012) and \(k_{+4}, k_{-4}\) are the forward and backward reaction rate constants for CO₂
hydroxylation. The rate of CO\textsubscript{2} hydration increases with CA activity while the rate of CO\textsubscript{2} hydroxylation increases with the solution pH (Chapter 2, Figure 2.5A).

A CA activity between 5 and 100 s\textsuperscript{-1} in \textit{Porites} tissues at 28°\textdegree C (Hopkinson et al., 2015) corresponds to a \(k^*_{+2}\) of between 5 and 100 s\textsuperscript{-1}. In comparison the uncatalysed CO\textsubscript{2} hydration rate constant \((k_{+2})\) is \(\sim 4.7\times10^{-2}\) s\textsuperscript{-1} at 28°\textdegree C (Johnson, 1982), thus CA increases the rate of CO\textsubscript{2} hydration in \textit{Porites} tissues by 2 to 3 order of magnitudes (i.e. \(k^*_{+2}/k_{+2} = 106\) to 2128). Over this range of CA activity and a pH\textsubscript{cf} between 8.1 and 8.9 (Allison et al., 2011; Rollion-Bard et al., 2011), the interconversion between CO\textsubscript{2} and HCO\textsubscript{3}\textsuperscript{-} mostly occurs via the hydration pathway (Figure 4.8). Thus, kinetic isotope fractionation between DIC and H\textsubscript{2}O in the CF should mostly originate from CO\textsubscript{2} hydration rather than CO\textsubscript{2} hydroxylation. Previous kinetic isotope models for corals (McConnaughey, 1989b; Rollion-Bard et al., 2003, 2011; Allison et al., 2011) assumed a significant contribution from CO\textsubscript{2} hydroxylation because these models did not include the effect of CA. The inclusion of CA activity constrains the overall kinetic isotope fractionation between newly formed HCO\textsubscript{3}\textsuperscript{-} (i.e. mostly via CO\textsubscript{2} hydration) and H\textsubscript{2}O to \(+26.9 \pm 1.0\) \textperthousand at 25°C (Zeebe, 2014, Chapter 2, Figure 2.5B).

![Figure 4.8](image)

**Figure 4.8** Relative importance of CO\textsubscript{2} hydroxylation \((k_{+4}([\text{OH}^-])\) over CO\textsubscript{2} hydration \((k^*_{+2})\) in seawater at 25°C as a function of pH and the \(k_{+2}^*/k_{+2}\) (i.e. the increase in CO\textsubscript{2} hydration rate induced by the enzyme carbonic anhydrase, blue lines). The range of outcomes for \(k_{+2}^*/k_{+2}\) ratios measured in the tissue of a \textit{Porites} (106 to 2128, Hopkinson et al., 2015) is indicated by the grey shaded area. The mean and range of pH values in the calcifying fluid is indicated by the continuous and dotted red lines. The pH in the calicoblastic cells is indicated by the black line. This diagram suggests that CO\textsubscript{2} hydration is likely to be the dominant pathway for CO\textsubscript{2} interconversion with HCO\textsubscript{3}\textsuperscript{-} in a \textit{Porites} calcifying fluid and calicoblastic cells.
DIC-H$_2$O oxygen isotope equilibration

The value of $\alpha_{DIC/w}$ in the CF depends on the initial value of $\alpha_{DIC/w}$ following CO$_2$ hydration ($\alpha_{DIC/w}^0$), the equilibrium $\alpha_{DIC/w}$ value ($\alpha_{DIC/w}^{eq}$) and the level of isotopic equilibrium between the DIC and water ($E_{DIC}$) (Usdowski et al., 1991):

$$\alpha_{DIC/w} = (1 - E_{DIC}) (\alpha_{DIC/w}^0 - \alpha_{DIC/w}^{eq}) + \alpha_{DIC/w}^{eq}$$  \hspace{1cm} (4.9)

The value of $E_{DIC}$ is calculated from the residence time of DIC in solution ($RT_{DIC}$) and the time constant $\tau$ (Chapter 2):

$$E_{DIC} = 1 - e^{(-RT_{DIC}/\tau)}$$  \hspace{1cm} (4.10)

The time constant $\tau$ mostly depends on pH and CA activity (Usdowski et al., 1991; Uchikawa and Zeebe, 2012; Chapter 2, Equation 2.34). Figure 4.9 shows calculated $E_{DIC}$ values in the coral CF (pH 8.5) and CC (pH 7.4) as a function of $RT_{DIC}$ and in the presence or absence of CA.

Figure 4.9. Simulated level of oxygen isotopic equilibrium between DIC and a seawater-like solution ($E_{DIC}$) as a function of DIC residence time ($RT_{DIC}$) in the coral calcifying fluid (pH = 8.5, blue curves) and in the cytoplasm of the calicoblastic cells (pH = 7.4, red curves). Continuous curves show $E_{DIC}$ assuming no carbonic anhydrase (CA) in solution while dashed curves show $E_{DIC}$ assuming a $k^*/k_2$ (i.e. the increase in CO$_2$ hydration induced by the enzyme carbonic anhydrase) of 1100 in Porites tissues and fluids (Hopkinson et al., 2015). This level of CA activity would reduce the DIC-H$_2$O isotopic equilibration time from ~ one day to ~ 10 min in the calcifying fluid and from ~ 5 h to ~ 10 s in the calicoblastic cells. For the calicoblastic cells, the equilibration time would be even lower than shown if salinity is lower than in seawater. This diagram shows that CA reduces the isotopic equilibration between DIC and H$_2$O in coral tissues and in the calcifying fluid by 3 orders of magnitude relative to seawater at equivalent pH but without CA.
Without CA, it would take ~ 24 h for the DIC to reach isotopic equilibrium in the CF and ~ 2 h in the CC. At the average CA activity measured in *Porites asteroides* tissues \((k_{+2}/k_{+2} \sim 50\), Hopkinson et al., 2015), full isotopic equilibrium would only take ~ 2 min in the CF and ~ 10 s in the CC. For the CC, the equilibration time would be even shorter than 10 s if salinity is lower than in seawater. Since DIC residence time in coral tissues is in the order of minutes to hours (Furla, 2000), the very short oxygen isotopic equilibration time in the CC suggests that the metabolic CO₂ source is at isotopic equilibrium with H₂O. Hence, the \(^{18}\text{O}/^{16}\text{O}\) of the DIC\(_{cf}\) is likely to be independent of the metabolic CO₂ sources (e.g. biologic vs environmental) and metabolic processes. This can explain why \(\delta^{18}\text{O}_P\) is mostly insensitive to the symbiont photosynthesis activity while \(\delta^{13}\text{C}_P\) is not (e.g. Gagan et al., 2015).

Although the light isotopes \(^{16}\text{O}\) and \(^{12}\text{C}\) should be preferentially consumed by the symbiont, oxygen atoms are subsequently exchanged with H₂O in the CC while the carbon atoms maintain their photosynthesis imprint. These observations suggest that the metabolic CO₂ source for coral calcification enters the CF at isotopic equilibrium with H₂O. Subsequent conversions of CO₂ into HCO₃⁻ and CO₃²⁻ in the CF due to the high pH\(_cf\) however lead to DIC-H₂O isotopic disequilibrium effects.

**DIC residence time in the calcifying fluid**

At steady state conditions (i.e. DIC\(_{cf}\) inputs = DIC\(_{cf}\) outputs), the DIC residence time in the calcifying fluid \((R_{T,DIC})\) is obtained from the molar quantity of DIC in the CF \((n_{DIC})\) divided by the calcification rate \((R_c)\):

\[
R_{T,DIC} = \frac{n_{DIC}}{R_c}
\]  

(4.11)

For *Porites* corals, the calcification rate is mostly proportional to the *Porites* extension rate (Lough and Barnes, 2000):

\[
R_c(\text{mol/s/m}^2) \approx \text{extension rate (mm/yr)} \times 3.65 \cdot 10^{-7}
\]  

(4.12)

A massive *Porites* with a typical extension rate of 10 mm/yr would therefore have a \(R_c\) of ~ 3.6 \(\mu\)mol/m²/s. Using an average [DIC\(_{cf}\)] of ~ 3 mM (Allison et al., 2014) and a CF thickness of ~ 5 µm (Venn et al., 2011; Cai et al., 2016), the molar quantity of DIC in the CF over one square metre of coral would be ~ 15 µM. This calculation suggests that the residence time of DIC in the calcifying fluid of a fast growing *Porites* is in the order of a few seconds only. Note that changing the CF thickness to values between 1 µm and 10 µm would still result in a DIC residence time in the order of
seconds. Such a short residence time suggests a low level of isotopic equilibration between DIC and H₂O in the CF of a fast growing *Porites*, even in the presence of CA (\(E_{DIC} < 0.2\), Figure 4.10).

**Effect of Porites extension rate on \(E_{DIC}\)**

The effect of *Porites* extension rate on \(E_{DIC}\) was estimated for variable CA activities (\(1 < k'_{+2}/k_{+2} < 10^4\), Figure 4.10) by using the same parameters as in the previous Sections (\(T = 25^\circ\text{C}\), \(\text{pH}_{cf} = 8.5\), \([\text{DIC}_{cf}] = 3 \text{ mM}\), CF thickness = 5 µm). This simulation shows that \(E_{DIC}\) only increases significantly where \(k'_{+2}/k_{+2}\) is \(\sim 10^2\) or more. Importantly, a significant growth rate dependence on \(E_{DIC}\) is expected for levels of CA activity measured in *Porites* tissues (\(10^6 < k'_{+2}/k_{+2} < 2100\), grey shaded area). Without any CA in the CF, \(E_{DIC}\) would remain near 0 even for extremely slow *Porites* extension rates of \(\sim 1 \text{ mm/yr}\). The presence of CA in the CF is therefore necessary to explain the effect of growth rate on \(\delta^{18}\text{O}\) in terms of DIC-H₂O kinetic effects. Figure 4.10 also shows that \(E_{DIC}\) is likely to approach 0 where *Porites* extension rate is \(> 20 \text{ mm/yr}\) for \(k'_{+2}/k_{+2} < 2100\).

![Figure 4.10](image_url)

**Figure 4.10.** Calculated level of oxygen isotope equilibration between DIC and water (\(E_{DIC}\)) in the calcifying fluid as a function of the *Porites* extension rate and \(k'_{-2}/k_{-2}\) (i.e. the increase in CO₂ hydration induced by the enzyme carbonic anhydrase; blue lines). The range of outcomes for measured \(k'_{-2}/k_{-2}\) in the tissue of a *Porites asteroideas* (106 to 2128, Hopkinson et al., 2015) is indicated by the grey shaded area. A growth rate dependence on the level of oxygen isotope equilibration between DIC and water in the calcifying fluid is expected for the level of carbonic anhydrase activity measured in *Porites* tissues.
The kinetic limit of $\alpha_{P/w}$

In the case where DIC is consumed by aragonite precipitation before any significant DIC-H$_2$O isotopic equilibration takes place, $\alpha_{P/w}$ is expected to reach a ‘kinetic limit’. At a given temperature, the kinetic limit of $\alpha_{P/w}$ should depend on the relative importance of CO$_2$ hydration versus CO$_2$ hydroxylation in the CF and on the potential contribution of seawater DIC in addition to metabolic CO$_2$. To constrain the above parameters, we compare the kinetic limit of $\alpha_{P/w25}$ inferred from the measured $\alpha_{P/w25}$ of fast growing *Porites* ($\varepsilon_{P/w25} = 25.6 \pm 0.2$, Figure 4.6) with model results for varying $k^*_+2/k+2$ and varying contribution of metabolic CO$_2$ relative to seawater DIC (DIC$_{sw}$) (Figure 4.11). For the model simulations, we used kinetic oxygen isotope fractionation factors between CO$_2$ and HCO$_3^-$ of -15.4 ‰ for the hydration pathway (Zeebe, 2014) and -30.7 ‰ for the hydroxylation pathway (Chapter 2) and assumed an isotopically equilibrated DIC pool at pH 8.5 for the seawater source in the coelenteron. Note that applying lower seawater pH would not change the results discussed below. Modelled and measured $\alpha_{P/w25}$ values are in agreement for several combinations of CO$_2$/DIC$_{sw}$ ratio and $k^*_+2/k+2$. However, within the range of $k^*_+2/k+2$ measured in *Porites*, the measured kinetic limit of $\alpha_{P/w}$ is best explained by a DIC pool originating exclusively from metabolic CO$_2$.

![Figure 4.11 Simulated kinetic limit for the oxygen isotope fractionation between *Porites* aragonite and seawater ($\varepsilon^{18}O_{P/w}$) at 25°C as a function of $k^*_+2/k+2$ (i.e. the increase in CO$_2$ hydration induced by the enzyme carbonic anhydrase) and for different contributions of DIC derived from metabolic CO$_2$ versus seawater DIC (blue lines). The 0% CO$_2$ line shows $\varepsilon^{18}O_{P/w}$ for aragonite precipitating from an isotopically equilibrated DIC pool at pH 8.5. A DIC pool derived from 100 % metabolic CO$_2$ is consistent with the measured kinetic limit of $\varepsilon^{18}O_{P/w}$ (grey line) and $k^*_+2/k+2$ in *Porites* tissues (106 to 2128, Hopkinson et al., 2015).](image)
4.5.3. Data-model comparison

We model the effect of *Porites* extension rate on $\varepsilon_{P/w25}$ for a $k^*_{+2}/k_{+2}$ varying from 1 to $10^5$ (Figure 4.12A and B). Modelled and measured $\varepsilon_{P/w25}$ values (Table 4.2) agree best where the $k^*_{+2}/k_{+2}$ is between 60 and 1600 (Figure 4.12B), in reasonable agreement with measured $k^*_{+2}/k_{+2}$ in *Porites* tissues. Interestingly, varying $k^*_{+2}/k_{+2}$ from 60 and 1600 has a little effect on $\varepsilon_{P/w25}$ (e.g. ~1 %o for an extension rate of 10 mm/yr) relative to the ~14 %o maximum range in modelled $\varepsilon_{P/w25}$ (15.6 to 29.7 %o, Figure 4.12A). In fact, over the 60-1600 range in $k^*_{+2}/k_{+2}$, $E_{DIC}$ is near 0 for fast growing *Porites* (Figure 4.10) and the kinetic limit of $\varepsilon_{P/w25}$ is not significantly affected by $k^*_{+2}/k_{+2}$ (Figure 4.11). A large range of $k^*_{+2}/k_{+2}$ can therefore produce very similar $\varepsilon_{P/w}$.

The small ~1 %o variation in $\varepsilon_{P/w25}$ between most *Porites* colonies contrast with the ~3 to 10 %o variations in $\delta^{18}O_P$ measured within single *Porites* colonies at the microscale (Rollion-Bard et al., 2003; Allison et al., 2010). Assuming constant $\delta^{18}O_{sw}$ values for the environments in which these coral grew, we can estimate and compare the range of (temperature independent) microscale variations in $\varepsilon_{P/w25}$ with model outputs (Figure 4.12A, coloured vertical bars). The lowest microscale $\varepsilon_{P/w25}$ calculated for the Rollion-Bard et al. (2003) study can be explained by full isotopic disequilibrium between DIC and H$_2$O ($E_{DIC} = 0$) and a very low CA activity ($k^*_{+2}/k_{+2}$ ~ 2). The highest $\varepsilon_{P/w25}$ values (up to 30.0 %o) are reasonably consistent with a DIC$_{cf}$ pool at isotopic equilibrium with seawater. Full isotopic equilibrium between the DIC$_{cf}$ and seawater may be attained by a high CA activity ($k^*_{+2}/k_{+2}$ > $10^5$), a very slow aragonite growth rate (i.e. a long DIC$_{cf}$ residence time) and/or the precipitation of DIC derived from seawater. Note that these conditions would not reflect the average conditions of *Porites* aragonite precipitation but rather a small fraction of the overall mass of aragonite precipitated. Overall, the model presented in this study explains both bulk and microscale temperature-independent variations in coral-seawater oxygen isotope fractionation.

4.6. Implications

4.6.1. The effect of carbonic anhydrase on $\delta^{18}O_P$

The kinetic oxygen isotope model presented in this chapter explains intercolony differences in $\varepsilon_{P/w}$ in terms of variable isotopic composition of the precipitating DIC pool, like previously published models (McConnaughey, 1989b; Rollion-Bard et al., 2003, 2011; Allison et al, 2010). However, in contrast with past studies, our model predicts that where CA is present in the coral CF (as seem to be the case for *Porites*), the pH$_{cf}$ is not the dominant driver of DIC$_{cf}^{18}O/^{16}O$. Instead, we suggest that for a given temperature, CA activity in the CF is likely to be the dominant factor controlling the oxygen isotope
Figure 4.12. Simulated oxygen isotope fractionation between *Porites* aragonite and seawater ($\varepsilon_{18O_{P/w}}$) at 25°C as a function of $k^*_{+2}/k_{+2}$ (i.e. the increase in CO$_2$ hydration induced by the enzyme carbonic anhydrase, blue lines). (A) Model outputs for a $k^*_{+2}/k_{+2}$ ranging from 1 to $10^5$. The oxygen isotope fractionation between slowly precipitated inorganic aragonite and water at 25°C (Kim et al., 2007) is indicated by the dotted line. (B) Same as (A) but for a $k^*_{+2}/k_{+2}$ ranging from 50 to 3200. The range of model outcomes for measured $k^*_{+2}/k_{+2}$ in the tissue of a *Porites* (106 to 2128, Hopkinson et al., 2015) is indicated by the grey shaded area. Model outputs are compared to measured mean $\varepsilon_{18O_{P/w}}$ at 25°C for individual *Porites* colonies (black points). The mean and range of $\varepsilon_{18O_{P/w}}$ values derived from SIMS analysis of two *Porites* are indicated by the coloured symbols and bars respectively (Allison et al., 2010b: red rectangle, Rollion-Bard et al., 2003: pink square).
fractionation between the precipitating DIC pool and H₂O. The presence of CA in the CF has two major effects on the ¹⁸O/¹⁶O of the precipitating DIC pool. First, it affects the ratio between the CO₂ hydration and CO₂ hydroxylation pathways for the conversion of metabolic CO₂ into HCO₃⁻. This dictates the initial fractionation between HCO₃⁻ and H₂O following CO₂ conversion to HCO₃⁻. Over the pHₐ range (~ 8 to 9), CO₂ hydroxylation is outpaced by the catalysed CO₂ hydration reaction (Fig. 4.8). This results in a reduced pH sensitivity of the kinetic isotope fractionation and in turns of the DICcf ¹⁸O/¹⁶O. Second, CA increases the rate of isotopic equilibration between DIC and water, causing higher δ¹⁸Oᵢ in slow growing colonies.

4.6.2. The cause of variable coral extension rate effects on δ¹⁸Oᵢ

As can be seen in Figure 4.6, the sensitivity of εᵥ/ᵢw₂₅ to the Porites sp. extension rate differ significantly between studies. For Porites australiensis, εᵥ/ᵢw₂₅ is negatively correlated to coral extension rate over the 8 to 15 mm/yr range in the study of Maier et al. (2004) but εᵥ/ᵢw₂₅ is mostly constant over the 2 to 10 mm/yr in coral extension rate in the study of Hayashi et al. (2013). Our model results suggest that the discrepancy between these studies can be explained by distinct CA activities between coral colonies. A high CA activity in the CF results in a strong growth rate effect on δ¹⁸Oᵢ while a low CA activity dampens the growth rate effect (Figure 4.12). Since both studies analysed colonies of the same species but growing in distinct environments, we suggest that CA activity in the CF is affected by environmental factors. In fact, the expression of the gene linked to CA activity in corals is known to decrease with light exposure (Moya et al., 2008). The corals analysed by Hayashi et al. (2013) grew in outdoor tanks (< 1 m water depth) while Maier et al. (2004) collected corals at a depth of ~ 6 m depth. Difference in light exposure between the two environments may therefore explain the different δ¹⁸Oᵢ-extension rates relationship between the two studies. A dampening of the δ¹⁸Oᵢ-extension rate by high light intensities is also consistent with the lack of a growth rate effect on the δ¹⁸Oᵢ of shallow growing coral microatolls (this study). Further investigation of the relationship between CA activity in coral tissues, light intensity and δ¹⁸Oᵢ is needed to test this hypothesis.

4.6.3. The temperature sensitivity of δ¹⁸Oᵢ

Since kinetic oxygen isotope fractionation dominates over equilibrium fractionation in the CF of Porites, the temperature dependence of δ¹⁸Oᵢ is expected to deviate from the value of 0.20 (±0.01) ‰/°C determined for slow growing inorganic aragonite (Kim et al., 2007) and isotopically equilibrated DIC species (Beck et al., 2005). Recent work suggests that the δ¹⁸Oᵢ–SST sensitivity mostly varies between 0.13 to 0.20 ‰/°C depending on coral colonies and environmental settings
Our modelling results suggest that the reduced temperature sensitivity of $\delta^{18}O_P$ relative to inorganic aragonite can be explained by the association of oxygen atoms from CO$_2$ and H$_2$O to form HCO$_3^-$ during the CO$_2$ hydration reaction. Since the $^{18}O/^{16}O$ of H$_2$O is independent of temperature, the mixing of oxygen atoms from CO$_2$ and H$_2$O should reduce the temperature dependence on the $^{18}O/^{16}O$ of HCO$_3^-$ by 1/3 relative to the isotopically equilibrated CO$_2$ (i.e. 0.20 to 0.13 ‰/°C). Although this calculation ignores potential temperature effects on the kinetic oxygen fractionation between CO$_2$ and hydrated CO$_2$ (i.e. HCO$_3^-$), theoretical work suggests that the $^{18}O/^{16}O$ of hydrated CO$_2$ is very close to an isotopic mass between CO$_2$ and H$_2$O (Zeebe, 2014). Finally, $\delta^{18}O_P$ –SST sensitivities higher than 0.13 ‰/°C may be the result of partial isotopic equilibration between the DIC and water. Slower aragonite growth rate during seasonal SST minima (Lough, 2008) would also promote DIC-H$_2$O isotope equilibrium and therefore a higher $\delta^{18}O_P$–SST sensitivity. Another factor that should be investigated in future studies is the relationship between coralline CA activity and temperature.

4.6.4. Expected model outcomes for carbon isotope fractionation during coral calcification

Although this chapter focuses on the oxygen isotope systematic of Porites aragonite, there are direct implications for the carbon isotope fractionation between the coral skeleton and the cellular DIC source. The model suggests that most of the DIC used for calcification enters the CF in form of CO$_2$, which then quickly hydrates and converts into HCO$_3^-$ and CO$_3^{2-}$ within the CF due to the high pH$_{cf}$ and presence of carbonic anhydrase (Goreau, 1959; Hayes and Goreau, 1977; Tambutté et al., 2007; Moya et al., 2008). At 25°C, the CO$_2$ hydration step induces a maximum carbon isotope fractionation of ~ -7‰ relative to the CO$_2$ reactant (Marlier and O’Leary, 1984), although the presence of carbonic anhydrase may reduce carbon kinetic fractionation (Paneth and O’Leary, 1985). Assuming that the CO$_2$ source is isotopically equilibrated before entering the CF, the CO$_2$ source $\delta^{13}C$ should be lower than that of cellular DIC by 9‰ (i.e. the isotopic equilibrium fractionation between CO$_2$(aq) and HCO$_3^-$, Mook et al., 1974). This implies a maximum expected carbon isotope fractionation between the DIC$_{cf}$ and the DIC$_{cell}$ of ~ -16‰ (-9 -7). However, this calculation only applies to a small proportion of DIC being transferred from the CC to the CF without back reaction. Hence, if our model is correct, the initial carbon isotope fractionation between the DIC$_{cf}$ and the DIC$_{cell}$ would be expected to vary between 16‰ (small fraction of DIC transferred to the CF) and 0‰ (quantitative DIC transfer) depending on the carbon supply/demand ratio. Subsequent carbon exchange between the DIC$_{cf}$ and the DIC$_{cell}$ would then increase the $\delta^{13}C$ of the DIC$_{cf}$ towards the DIC$_{cell}$ $\delta^{13}C$ value.

The extent of carbon kinetic effects during Porites calcification is difficult to quantify solely from the skeletal $\delta^{13}C$ of these corals because the DIC source $\delta^{13}C$ is unknown and photosynthesis significantly increase the DIC$_{cell}$ $\delta^{13}C$ (McConnaughey, 1989a). However, the skeletal $\delta^{13}C$ of asymbiotic corals
with highly variable growth rates suggests a maximum carbon kinetic isotope effect of -11 ±1‰ (McConnaughey, 1989a). A maximum aragonite-seawater carbon fractionation of ~ -12‰ was also reported for deep sea corals (Adkins et al., 2003), which is fairly close to a full expression of the carbon kinetic effect predicted by our model (-16‰) and a significantly lower fractionation than the -27‰ expected for the CO₂ hydroxylation step (Siegenthaler and Munnich, 1981) if the enzyme carbonic anhydrase was not present in the CF. Given that symbiotic and asymbiotic coral skeletons show similar expression of the kinetic oxygen isotope effect (McConnaughey, 1989a, Adkins et al., 2003), these corals should also display similar carbon kinetic isotope effects. Assuming a carbon fractionation of -11 ±1‰ for symbiotic corals (including Porites), we can use Porites aragonite δ¹³C values to estimate the δ¹³C value of the cellular DIC pool used for calcification. The Porites microatolls analysed in this study have δ¹³C varying from ~ -3.5 to -0.5‰ with an average value of ~ -2‰ (data not shown), which fits within the range of skeletal δ¹³C values of other modern Porites morphologies and other symbiotic corals (e.g. McConnaughey, 1989a; Omata et al., 2008). For the Porites corals analysed in this study, the expected DIC_{cell} δ¹³C would then be between +6.5 to +11.5‰. Knowing that preferential ¹²C uptake by zooxanthellae enriches coral aragonite by a maximum of ~ +7‰ (McConnaughey, 1997), the initial δ¹³C of the DIC source for photosynthesis and calcification should be no lower than ~ -0.5‰. This latter value can be compared with the δ¹³C of potential DIC sources for coral calcification and photosynthesis. Respired CO₂ has a δ¹³C ranging between -9‰ to -17‰ (Swart et al., 2005), indicating that respiration is not a significant carbon source for calcification. This is in agreement with radiocarbon labelling results suggesting a contribution of respired CO₂ to calcification of less than 8% for deep sea corals (Adkins et al., 2003) and less than 5% for bamboo corals (Saenger and Watkins, 2016). Seawater DIC (mostly HCO₃⁻) in the open ocean has a δ¹³C of ~ 0 to +3‰ while the δ¹³C of seawater CO₂(aq) is lower, being ~ -9 to -6‰ (Mook et al., 1974). The δ¹³C of seawater DIC is therefore consistent with the calculated δ¹³C of the DIC source for Porites calcification and photosynthesis while seawater CO₂(aq) is not. This result support a previous suggestion that active seawater HCO₃⁻ pumping by coral cells provides a large fraction the coral cellular DIC pool (Carvalho et al., 2015). Although the above calculation and discussion relies on several assumptions that require further testing, it shows that our model of oxygen isotope fractionation is broadly consistent with our current knowledge of carbon isotope fractionation during coral calcification and photosynthesis.

4.7. Conclusions

This study presented four new Porites sp. microatoll δ¹⁸O records from Kiritimati Is., central Pacific spanning parts of the 1928-2011 period. The data were used with a model of kinetic oxygen isotope fractionation between DIC and H₂O to in investigate the effect of coral extension rate and carbonic
anhydrase activity on Porites sp. $\delta^{18}$O. Analysis of this data and comparison with previous studies lead to the following conclusions:

1. The oxygen isotope fractionation between Porites sp. coral aragonite and seawater ($\alpha_{P/w}$) decreases with coral extension rate down to a “kinetic limit” in $\alpha_{P/w}$ of $\sim 1.0256 \pm 0.0002$ at 25°C. Where the $\alpha_{P/w}$ is close in value to the kinetic limit, it is insensitive to the coral extension rate. This appears to be true for different Porites morphologies, species and for Porites sp. that grow in different settings. According to our model and the inferred $\alpha_{P/w25}$ from the compilation of measured Porites sp. $\delta^{18}$O, Porites sp. with extension rate $> 15$ mm/yr will have reduced intercolony differences in mean Porites sp. $\delta^{18}$O.

2. The effect of coral extension rate on $\alpha_{P/w}$ varies between studies but appears consistent at a given site. Because coral taxonomy does not seem to affect $\alpha_{P/w}$, it is postulated that the variable ‘extension rate’-$\alpha_{P/w}$ relationships between studies are environmentally induced.

3. A carbonic anhydrase activity of $\sim 2$ to $50$ s$^{-1}$ in the coral calcifying fluid is necessary to explain the growth rate dependence of Porites sp. $\delta^{18}$O in terms of kinetic isotope effects between the coral’s internal DIC and H$_2$O (i.e. the McCaunaughey (1989b) hypothesis). This range of enzymatic activity in the coral calcifying fluid is consistent with published estimates of carbonic anhydrase activities in the tissues of Porites asteroides, thus a DIC-H$_2$O kinetic isotope control of coral $\delta^{18}$O is supported. The presence of carbonic anhydrase in coral calcifying fluids also greatly reduces the effect of pH on Porites sp. $\delta^{18}$O.

4. Porites sp. $\delta^{18}$O is not sensitive to the symbiont photosynthesis activity because the metabolic carbon source for calcification becomes isotopically equilibrated with H$_2$O in coral tissues prior to its diffusion in the coral’s calcifying fluid. This is in contrast with the Porites sp. $\delta^{13}$C which retains the isotopic enrichment caused by symbiotic photosynthesis.

5. The commonly lower temperature sensitivity of Porites sp. $\delta^{18}$O (0.13 to 0.20 ‰/°C) relative to that of slowly precipitated inorganic aragonite $\delta^{18}$O (0.20 to 0.23 ‰/°C) is explained by the contribution of oxygen atoms from CO$_2$ and H$_2$O to form HCO$_3^-$ during the CO$_2$ hydration reaction. This reaction step initially results in a temperature sensitivity of $\sim 0.13$ ‰/°C for HCO$_3^-$.$^{18}$O/18O.
Table A4.1. Results from U-series dating of corals NEP1, NEP3 and CH10.

| Lab code | Sample name | Time of chemistry | U (ppm) | $^{235}$Th (ppt) | ($^{235}$Th/$^{232}$Th) x10$^6$ | $^{238}$Th/$^{234}$U | $\delta^{234}$U (‰) | Uncorr. Age (AD) | corr. Age (AD) | corr. Initial $\delta^{234}$U (‰) |
|----------|-------------|-------------------|---------|------------------|--------------------------|----------------|----------------|----------------|----------------|----------------|------------------|
| AN09_24  | NEP1-5      | 2012.88           | 2.621   | ± 0.001          | 4.44 ± 0.14              | 1681 ± 60     | 939 ± 16    | 143.8 ± 1.2   | 1923.2 ± 1.5 | 1923.3 ± 1.5 | 143.8 ± 1.2       |
| AN09_25  | NEP1-7      | 2012.88           | 2.761   | ± 0.001          | 4.42 ± 0.06              | 1672 ± 35     | 881 ± 14   | 145.9 ± 1.2   | 1928.9 ± 1.3 | 1928.9 ± 1.3 | 146.0 ± 1.2       |
| AN09_26  | NEP3-14     | 2012.88           | 2.733   | ± 0.002          | 3.78 ± 0.10              | 1883 ± 55     | 859 ± 10   | 144.2 ± 1.1   | 1930.9 ± 1.0 | 1930.9 ± 1.0 | 144.2 ± 1.1       |
| AN09_27  | NEP3-16     | 2012.88           | 2.682   | ± 0.002          | 11.15 ± 0.16             | 598 ± 13      | 819 ± 14   | 144.6 ± 1.0   | 1934.7 ± 1.3 | 1934.8 ± 1.3 | 144.6 ± 1.0       |
| ET3-43   | CH10-F1     | 2013.17           | 2.578   | ± 0.001          | 12.87 ± 0.26             | 452 ± 12      | 743 ± 13   | 147.3 ± 1.0   | 1942.4 ± 1.2 | 1942.5 ± 1.2 | 147.4 ± 1.0       |
| ET3-44   | CH10-A2     | 2013.17           | 2.565   | ± 0.001          | 17.92 ± 0.53             | 468 ± 16      | 1076 ± 20  | 147.0 ± 1.1   | 1910.7 ± 1.9 | 1910.9 ± 1.9 | 147.0 ± 1.1       |
Table A4.2 Calculated Oxygen isotope fractionation between *Porites* aragonite and seawater at 25°C from published studies

<table>
<thead>
<tr>
<th>Reference</th>
<th>Species</th>
<th>Average extension (mm/yr)</th>
<th>rate</th>
<th>$\Delta^{18}O_{P}$ at 25°C (VPDB)</th>
<th>$\delta^{18}O_{w}$ (%)</th>
<th>$\epsilon_{Pw}$ at 25°C</th>
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<td>Woodroffe et al. (2003)</td>
<td><em>Porites</em> spp.</td>
<td>23.3</td>
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<td>Woodroffe and Gagan (2000)</td>
<td><em>Porites</em> spp.</td>
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<td>18.45</td>
<td>$-5.15^a$</td>
<td>0^a</td>
<td>25.60</td>
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<td><em>P. lutea</em></td>
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<td></td>
<td>$-4.67$</td>
<td>0.52</td>
<td>25.56</td>
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<td>Asami et al. (2004)</td>
<td><em>P. lobata</em></td>
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<td></td>
<td>$-5.06^a$</td>
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<td><em>P. lutea</em></td>
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a $\delta^{18}$O$_P$ was calculated from the published $\delta^{18}$O$_P$ vs SST relationship using $\delta^{18}$O$_w = 0\%$

b from Munksgaard et al. (2012)

c from Oba (1988)

d Recalculated value (Suzuki, pers. comm.) as the published average $\delta^{18}$O$_w$ value of -0.96 ‰ for the 25°C tank in Suzuki et al. (2005) is incorrect.
References


Chapter V: SYNTHESIS

The δ\textsuperscript{18}O of inorganic and biogenic carbonates are used extensively to reconstruct past temperatures and/or water δ\textsuperscript{18}O values. However, there are temperature independent variations in carbonate-water oxygen isotope fractionation (\(\alpha_{c/w}\)) that complicate paleoclimate reconstructions. This thesis investigates the factors controlling \(\alpha_{c/w}\) for inorganic and biogenic carbonates (Figure 5.1), and derives new models for \(\alpha_{c/w}\) in inorganic, ostracod and coral during carbonate precipitation. This synthesis summarises the three models presented in Chapters 2-4 and discusses their similarities and differences. The chapter discusses the origins of biogenic ‘vital effects’, including for foraminifera carbonate precipitation, a biocalcifier not covered in detail in this thesis. Finally, the implications for paleoclimate reconstructions based on carbonate δ\textsuperscript{18}O are discussed, and possible future research directions are presented.

5.1 Oxygen isotope fractionation in the CaCO\textsubscript{3}-DIC-H\textsubscript{2}O system

The starting point for the models presented in this thesis is to view carbonate-water oxygen isotope fractionation as being the result of fractionations between H\textsubscript{2}O and DIC, and fractionation between DIC and CaCO\textsubscript{3}. Previous work on inorganic carbonate oxygen isotope fractionation investigated DIC-CaCO\textsubscript{3} fractionations (Watkins et al., 2013, 2014) and this thesis goes one step further to include DIC-H\textsubscript{2}O fractionations. The oxygen isotope data from recent and well-controlled inorganic calcite growth experiments (Dietzel et al., 2009; Baker, 2015) were used to quantify fractionations arising from oxygen isotope exchanges between CaCO\textsubscript{3} and CO\textsubscript{3}\textsuperscript{2-} and between CO\textsubscript{3}\textsuperscript{2-} and H\textsubscript{2}O. In the model, CO\textsubscript{3}\textsuperscript{2-} is the only precipitating DIC species while the other DIC species can affect \(\alpha_{c/w}\) via conversion into CO\textsubscript{3}\textsuperscript{2-}. The model gives a more complete picture of isotope fractionation, explains seemingly contradictory results, and provides a framework to adapt the model to oxygen isotope fractionation to biogenic calcifying organisms.

5.1.1 Equilibrium versus kinetic fractionation in inorganic carbonate

Equilibrium isotope fractionation between two or more phases is approached where the system in near chemical equilibrium (Urey, 1947). Where the phases are far from chemical equilibrium, isotopic fractionation is influenced by kinetic processes (DePaolo, 2011). Equilibrium oxygen isotope fractionation between carbonate and occurs where all components of the carbonate-water system are in isotopic equilibrium (Watkins et al., 2013). Where one component is out of isotopic equilibrium, fractionation is referred as ‘kinetic fractionation’. Model results indicate that equilibrium isotopic fractionation between CaCO\textsubscript{3} and H\textsubscript{2}O is only attained in rare conditions, where the solution calcite saturation state (Ω) approaches 1 and the ionic strength is low (e.g. freshwater). These are the
conditions of calcite precipitation in Devil’s Hole, Nevada (Coplen, 2007) and thus the $\alpha_{c/w}$ of calcite from this cave should reflect (near) isotopic equilibrium conditions. However, for most other natural inorganic and biogenic CaCO$_3$, the $\alpha_{c/w}$ reflects kinetic isotope fractionation between CaCO$_3$ and CO$_3^{2-}$ and/or between CO$_3^{2-}$ and H$_2$O.

Figure 5.1. Flow chart summary of the controls on the oxygen isotope fractionation between carbonates and water, as investigated in this thesis. Symbols and abbreviations have the following meaning: $\alpha_{c/w}$: carbonate-water fractionation; $\alpha_{c/CO3}$: carbonate-CO$_3^{2-}$ fractionation; $\alpha_{CO3/w}$: CO$_3^{2-}$-water fractionation; $T$: temperature; $\Omega$: calcite or aragonite saturation state; $pH(t_0)$ and salinity($t_0$): solution pH and salinity prior to a change in DIC speciation; $pH(t)$ and salinity($t$): solution pH and salinity following the change in DIC speciation; $E_{DIC}$: level of isotopic equilibration between DIC and H$_2$O; $X_{DIC}$: Fraction of the DIC pool consumed; ($^{18}O/^{16}O$)$_{CO2}$: $^{18}O/^ {16}O$ of the CO$_2$ input or output. Published studies that specifically investigated the different processes of equilibrium and kinetic isotope fractionation are indicated for each process. The thesis chapters in which these processes are quantified and/or discussed are also indicated.

5.1.2 Kinetic isotope fractionations in the CaCO$_3$-DIC-H$_2$O system

Model results and the analysis of published $\alpha_{c/w}$ values (Kim et al., 2006; Coplen, 2007; Dietzel et al., 2009; Baker, 2015) show that for low ionic strength solutions ($I < 0.05$), the oxygen isotope fractionation between calcite and CO$_3^{2-}$ ($\alpha_{c/CO3^{2-}}$) decreases from $\sim$1.0054 to $\sim$1.0030 ($\sim$ 2.4‰ decrease) where the solution $\Omega$ increases from below $\sim$1.6 to $\sim$12 (Figure 2.7). Quasi-instantaneous
precipitation of barium carbonate (BaCO$_3$) in highly saturated solution ($\Omega > 100$) indicates that the carbonate-CO$_3^{2-}$ fractionation can be as low as ~0.999. This value taken with the near equilibrium $\alpha_{c/CO_3^{2-}}$ value of ~1.0054 inferred from the published $\alpha_{c/w}$ of Devil’s Hole calcite (Coplen, 2007) indicates a maximum kinetic isotope effect (KIE) of ~6.4‰ during CO$_3^{2-}$ transport to and incorporation within the carbonate mineral lattice. The experimental data suggest that $\alpha_{c/CO_3^{2-}}$ is insensitive to the solution temperature and pH. Furthermore, the model predicts lower $\alpha_{c/CO_3^{2-}}$ values with increasing solution ionic strength due to a positive correlation between ionic strength and the CO$_3^{2-}$ partial reaction order during CaCO$_3$ precipitation (cf. Zhong and Mucci, 1993; Chapter 2). This latter model prediction has yet to be verified with experimental data.

The oxygen isotope fractionation between CO$_3^{2-}$ and H$_2$O ($\alpha_{CO_3^{2-}/H_2O}$) deviates from equilibrium values where a change in DIC speciation or an input/output of inorganic carbon with a different $^{18}$O/$^{16}$O than the DIC in solution occur at a faster rate than the rate of oxygen isotope equilibration between DIC and H$_2$O. Three types of KIE between CO$_3^{2-}$ and H$_2$O have been postulated in this thesis to account for the oxygen isotope vital effects of ostracods and shallow corals.

The first KIE is related to changes in DIC speciation prior or during CaCO$_3$ precipitation. For example, where the solution pH increases, the chemical equilibrium is shifted towards more CO$_3^{2-}$ and less HCO$_3^{-}$. The newly formed CO$_3^{2-}$ ions initially inherit the $^{18}$O/$^{16}$O of the parent HCO$_3^{-}$ ions because isotopic exchanges between CO$_3^{2-}$ and H$_2$O are indirect and slow. This can be understood by a lag between chemical equilibrium and isotopic equilibrium. If the newly formed CO$_3^{2-}$ ions precipitate before these ions reach isotopic equilibrium with H$_2$O, the $^{18}$O/$^{16}$O of CaCO$_3$ can retain the isotopic signature of HCO$_3^{-}$ ions. Because isotopically equilibrated HCO$_3^{-}$ are enriched in $^{18}$O relative to CO$_3^{2-}$ (difference of ~ 7‰, Beck et al., 2005), this KIE result in higher carbonate $\delta^{18}$O.

The second KIE is related to isotopic distillation effects between the DIC species (Rayleigh fractionation) during full or partial consumption of the DIC pool. This KIE can occur where a finite DIC pool is being consumed by CaCO$_3$ precipitation in a pH regulated environment (i.e. DIC speciation remain constant). As CO$_3^{2-}$ ions precipitate to form CaCO$_3$, the consumed CO$_3^{2-}$ ions are being replaced by deprotonated HCO$_3^{-}$ to maintain the chemical equilibrium imposed by the solution pH. The newly formed CO$_3^{2-}$ ions initially inherit the $^{18}$O/$^{16}$O of the parents HCO$_3^{-}$ ions and this $^{18}$O/$^{16}$O is recorded in CaCO$_3$ if calcification is faster than DIC-H$_2$O isotope exchanges. This KIE also result in higher carbonate $\delta^{18}$O.

The third KIE is caused by the (de)hydration and (de)hydroxylation of CO$_2$ (McConnaughey, 1989). The dissolution of an external CO$_2$ source affects the $^{18}$O/$^{16}$O of the DIC (including CO$_3^{2-}$) because
CO₂ carries its own isotopic signature \((\delta^{18}O/\delta^{16}O)_{CO₂}\) and because CO₂ bonds with H₂O and/or OH⁻, which also have distinct \(^{18}O/^{16}O\) ratios relative to isotopically equilibrated DIC species. In addition to these isotopic mixings between CO₂, H₂O and OH⁻, the \(^{18}O/^{16}O\) of hydrated/hydroxylated CO₂ (mainly HCO₃⁻ and CO₃²⁻) also depends on the kinetic isotope fractionations during CO₂ hydration and hydroxylation caused by differences in reaction rates between isotopically light and heavy molecules.

Comparisons of measured and modelled \(\alpha_{c/w}\) for calcite that precipitated from hydroxylated CO₂ (Chapter 2) indicate a kinetic isotope effect of \(-3 \pm 1\%\) during CO₂ hydroxylation. This fractionation factor does not appear to vary significantly with temperature between 5 and 40°C (Figure 2.8). Accounting for the isotopic mixing between CO₂ and OH⁻ and the KIE of \(-3 \pm 1\%\), an overall fractionation between hydroxylated CO₂ and H₂O of \(\sim 1.010 \pm 0.001\%\) at 25°C was calculated. Compared to the fractionation between hydrated CO₂ and H₂O (\(-1.027 \pm 0.001\%,\) Zeebe, 2014), hydroxylated CO₂ is \(\sim 17\%\) lower in \(^{18}O/^{16}O\) relative to hydrated CO₂. The \(^{18}O/^{16}O\) of the DIC that results from the dissolution of CO₂ strongly decreases with the solution pH because the rate of CO₂ hydroxylation increases with pH (Johnson, 1982). These KIE are recorded in carbonates if calcification is faster than DIC-H₂O isotopic equilibration (e.g. Dietzel et al., 2009). Overall, these KIE result in lower carbonate \(\delta^{18}O\) and make carbonate \(\delta^{18}O\) highly sensitive to the solution pH.

5.2. The origin of oxygen isotope vital effects in biogenic carbonates

Oxygen isotope values in biogenic carbonates are offset relative to slowly precipitated inorganic carbonate precipitated at the same water \(\delta^{18}O\) and temperature (Figure 1), and the origins of these so-called ‘vital effects’ are a matter of considerable debate. Chapters 3 and 4 take the inorganic CaCO₃-DIC-H₂O system, assume calcification occurs under closed system conditions, and explores the kinetic isotope fractionation processes that give rise to vital effects in corals and ostracods.

Ostracod calcite is enriched in \(^{18}O\) relative to slowly precipitated inorganic calcite in the same conditions (e.g. Kim and O'Neil, 1997), and has similar \(^{18}O/^{16}O\) to the sum of host water CO₃²⁻ and HCO₃⁻ from which the ostracod calcite is precipitated. Chapter 3 presents an explanation for these observations, which entails quasi-quantitative precipitation of host water DIC. The mechanism is reminiscent of the Zeebe (1999) oxygen isotope model where the host water DIC \(^{18}O/^{16}O\) controls foraminiferal \(\delta^{18}O\). However, ostracod calcite is closer in \(^{18}O/^{16}O\) to the host water DIC than is foraminiferal calcite (Figure 5.2), reflecting different oxygen isotope fractionation processes for ostracods compared to foraminiferal calcite.
The calcification-isotopic model proposed for ostracods is as follows: A pool of water is isolated from the environment. This pool is initially stored at a similar or slightly higher pH than the host water pH. Then, the isolated pool is transported and dumped into a high pH calcifying fluid or the pH of the pool itself is elevated. The pH increase provokes the deprotonation of HCO\textsubscript{3} ions, which then precipitate to form calcite. Calcification is faster than the rate of DIC-H\textsubscript{2}O isotopic equilibration and thus the isotopic signature of HCO\textsubscript{3} is (partially) retained in ostracod calcite. In other words, the precipitating CO\textsubscript{3} ions are enriched in \textsuperscript{18}O enriched relative to isotopically equilibrated CO\textsubscript{3} due to a change in DIC speciation as well as a near complete consumption of the DIC pool. Differences in \textsuperscript{\delta^{18}}O between ostracod taxa and between individual specimens from the same species precipitating in the same environment were explained by different level of DIC-H\textsubscript{2}O isotopic equilibration (\textit{EDIC}) in the ostracod calcifying fluid (CF). Ostracod \textsuperscript{\delta^{18}}O therefore depends on the host water DIC \textsuperscript{18}O/\textsuperscript{16}O and on \textit{EDIC} (Figure 5.3). At low \textit{EDIC}, ostracod \textsuperscript{\delta^{18}}O/\textsuperscript{16}O reflects the \textsuperscript{18}O/\textsuperscript{16}O of the host water DIC (e.g. some Candona ostracods) while a higher \textit{EDIC} decreases the ostracod \textsuperscript{\delta^{18}}O/\textsuperscript{16}O towards the \textsuperscript{18}O/\textsuperscript{16}O of an isotopically equilibrated DIC pool at high pH (e.g. Australocypris robusta). This hypothesis presented in Chapter 3 is consistent with the variable effect of host water [CO\textsubscript{3}]/DIC on ostracod \textsuperscript{\delta^{18}}O between ostracod taxa. Variable \textit{EDIC} between ostracod taxa may be due to different pH value and/or carbonic anhydrase activity in the CF.
Figure 5.3. Modelled and measured biogenic CaCO$_3$ $\delta^{18}$O at 25°C. The levels of DIC-H$_2$O isotopic equilibration in the biogenic calcifying fluid ($E_{DIC}$) were inferred from the relative differences between biogenic CaCO$_3$ $\delta^{18}$O and the theoretical kinetic ($E_{DIC} = 0$) and equilibrium ($E_{DIC} = 1$) end members for the $^{18}$O/$^{16}$O of the DIC. The inferred $E_{DIC}$ value are low for both symbiotic corals (see Table A4.2 for datapoints references) and ostracods (Candona: Xia et al., 1997; Australocypris: Chivas et al., 2002). For ostracods, the host water provides most of the DIC for calcification and thus the initial $^{18}$O/$^{16}$O of the DIC in the CF (DIC$_{cf}$) reflects that of the host water DIC (e.g. seawater or lake water). For corals, metabolic CO$_2$ provides most of the DIC for calcification and thus the initial DIC$_{cf}$ $^{18}$O/$^{16}$O mostly reflects hydrated CO$_2$ (and possibly small amounts of hydroxylated CO$_2$). Partial DIC$_{cf}$-H$_2$O isotopic equilibration ($E_{DIC} > 0$) due to slow growth rate and/or high carbonic anhydrase activity decreases the DIC $^{18}$O/$^{16}$O in the ostracod CF while it increases the DIC $^{18}$O/$^{16}$O in the coral CF. Modelled biogenic CaCO$_3$ $\delta^{18}$O at $E_{DIC} = 1$ were calculated using a mean CF pH of 8.5 for Porites (cf Table 4.2), 9 for Australocypris and 10 for Candona (these ostracod pH$_{cf}$ values are arbitrary). The calculated $\delta^{18}$O for an isotopically equilibrated DIC pool at the pH measured in the CF of the benthic foraminifer Amphistegina lobifera (8.7 ±0.1, Bentov et al., 2009, white diamond) is close in value to the $\delta^{18}$O of foraminiferal calcite (Orbulina: Bemis et al., 1998). Also shown on the right side of the plot are the $\delta^{18}$O of inorganic calcite (Kim and O’Neil, 1997) and aragonite (Kim et al., 2007) slowly precipitated in open system condition. Note that the inorganic calcite and aragonite $\delta^{18}$O overlap in value with the $\delta^{18}$O of an isotopically equilibrated DIC pool at pH ~ 8.6-8.8.

The $^{18}$O depletion of coralline aragonite relative to slowly precipitated inorganic aragonite (Kim et al., 2007; Figure 1), as well as the growth rate effect on coral $\delta^{18}$O are explained in Chapter 4 by a quasi-quantitative precipitation of DIC derived from metabolic CO$_2$. The main difference between the coral and the ostracod models is that the DIC in the coral CF originates from internal carbon pool rather than from a direct uptake of host water. The proposed coral model supports the McCaunaughey (1989b) hypothesis of a metabolic CO$_2$ control on coral $\delta^{18}$O. However, in contrast with previous coral models (McConnaughey, 1989; Rollion-Bard et al., 2003; Allison and Finch, 2010), the calcifying fluid pH is not a major driver of coral $\delta^{18}$O. A high carbonic anhydrase activity in the coral calcifying fluid (Tambutté et al., 2007; Hopkinson et al., 2015) makes CO$_2$ hydration the dominant
pathway for the conversion of metabolic CO$_2$ into HCO$_3^-$, irrespective to the CF pH. CO$_2$ hydration (and to a lesser extent CO$_2$ hydroxylation) in the coral CF results in a DIC pool that is initially depleted in $^{18}$O relative to an isotopically equilibrated DIC pool with identical DIC speciation. The presence of carbonic anhydrase in the coral CF also increases the rate of oxygen isotope exchanges between the DIC and H$_2$O, resulting in partial to full DIC-H$_2$O isotopic equilibrium in the CF of slow growing corals. For fast growing corals, there is rapid consumption of DIC, which prevents subsequent isotopic equilibration between the DIC species and H$_2$O, and the initial $^{18}$O/$^{16}$O of hydrated CO$_2$ is recorded in coral aragonite. The low $\delta^{18}$O of most Porites corals indicates that the level of isotopic equilibration between the CO$_3^{2-}$ pool and H$_2$O is low in the CF of Porites (Figure 5.3).

The ostracod and coral isotopic models summarised above may help to understand oxygen isotope fractionation in foraminiferal calcite since foraminiferal calcification also forms in an isolated biologic environment with an elevated pH relative to seawater pH (Bentov et al., 2009; de Nooijer et al., 2009). For example, at 25°C, the $\delta^{18}$O (VPDB) of the planktic foraminifer Orbulina universa is -2 to -2.5‰ lower than seawater $\delta^{18}$O (VSMOW; Bemis et al., 1998). These $\delta^{18}$O values would fit close to the DIC-H$_2$O equilibrium end member ($E_{DIC} > 0.6$) of both the ostracod and the coral isotopic model. In fact, the calculated $\delta^{18}$O for an isotopically equilibrated DIC pool at the pH measured in the CF of foraminifers (8.7 ±0.1, white diamond in Figure 5.3, Bentov et al., 2009) is close in value to the Orbulina universa $\delta^{18}$O values. Thus, the similarity in $\delta^{18}$O between foraminiferal calcite and slowly precipitated inorganic calcite in open system conditions (Kim and O’Neil, 1997) may be coincidental rather than reflecting a common mechanism of isotopic fractionation. This observation is important since the $\delta^{18}$O of foraminiferal calcite has been assumed to reflect near equilibrium fractionation (e.g. Bemis et al., 1998; Barras et al., 2010; Marchitto et al., 2014) based on its similarity with the $\delta^{18}$O expected from the expression of Kim and O’Neil (1997). It is postulated here that foraminiferal calcite is formed from the quantitative precipitation of an internal DIC pool that is near isotopic equilibrium with H$_2$O.

5.3. Recommendations for paleoclimate reconstructions

A strong carbonate ion effect on ostracod $^{18}$O/$^{16}$O is expected for environments where variations in salinity and/or pH are significant (e.g. closed basins, estuaries). Paleoclimate reconstructions based on ostracod $^{18}$O/$^{16}$O should therefore assess these potential effects carefully.

For seawater temperature and/or $^{18}$O/$^{16}$O reconstructions based on shallow corals, it is recommended to target fast growing corals (> 15 mm/yr) growing in shallow water to limit variations in mean coral
$^{18}$O/$^{16}$O between different coral colonies. The model predicts that the effect of temperature on coral $^{18}$O/$^{16}$O may be less variable for corals with low seasonal/interannual variations in coral growth rates.

References


Appendix A4.1: Coral thin sections

CH10_02 Plain polarised

CH10_02 cross polarised
CH10_03 Plain polarised

CH10_03 cross polarised
NEP1_01 Plain polarised

NEP1_01 cross polarised
NEP3_01 plain polarised

NEP3_01 cross polarised
NEP3_02 cross polarised

NEP3_02 cross polarised
Appendix A4.2: Coral X-rays

Coral CH38, the sampling transect for $\delta^{18}$O analysis is shown by the translucent white line

10 cm
Coral NEP1, the sampling transect for δ¹⁸O analysis is shown by the translucent white lines in the bottom panel. White rectangles indicate the sampling locations for U/Th dating (NEP1IV-7 and NEP1IV-5).
Coral NEP3, the sampling transect for $\delta^{18}O$ analysis is shown by the translucent white lines in the bottom panel. Rectangles (NEP3-16 and NEP3-14) indicate the sampling locations for U/Th dating.
Coral CH10, the sampling transect for $\delta^{18}O$ analysis is shown by the translucent white lines in the bottom panel.