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Triple oxygen isotope fractionation between CaCO_3 and H_2O in
inorganically precipitated calcite and aragonite

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Highlights:

The ^{17}O fractionation between CaCO_3 and its parent water is examined experimentally

The triple oxygen isotope fractionation slope, $(\ln^{17}\alpha/\ln^{18}\alpha)$, is similar in calcite and aragonite

The fractionation slope is independent of temperature at 10, 27°C but somewhat lower at 35°C

ABSTRACT

Carbonate bearing materials, such as foraminifera, mollusks shells, or speleothems, have the potential to preserve geochemical and isotopic signatures reflecting the environmental conditions at the time they formed. Beyond the conventional $\delta^{18}\text{O}$, information from triple oxygen isotopes (reported as $^{17}\text{O}_{\text{excess}}$, which is defined as $(\ln (\delta^{17}\text{O}/1000+1) - \lambda_{\text{ref}} \ln (\delta^{18}\text{O}/1000+1)) \times 10^6$) in these archives promises to be a valuable tool to reconstruct past hydrological processes. The goal of this study is to determine the triple oxygen isotope fractionation between CaCO_3 and H_2O under well-constrained laboratory conditions. We performed laboratory experiments to precipitate CaCO_3 polymorphs, either calcite or aragonite, at temperatures between 10 and 35°C. We then evaluated the effect of polymorphism, temperature, and solution concentration on the $^{17}\text{O}_{\text{excess}}$ of CO_2 extracted from these carbonates and the ^{17}O isotopic fractionation ($^{17}\alpha$) between water and CaCO_3 . The obtained values of $^{18}\alpha$ and $^{17}\alpha$ between CO_2 extracted from CaCO_3 and parent water allow us to calculate the fractionation slope $\theta (= \ln^{17}\alpha / \ln^{18}\alpha)$. Our observations suggest that θ is indistinguishable at temperatures of 10 and 27°C, but is slightly lower at 35°C. The lower value at 35°C may be related to disequilibrium during these experiments. We found that θ is independent of polymorph and of solution concentration, indicating that $^{17}\text{O}_{\text{excess}}$ is less sensitive than $\delta^{18}\text{O}$ to these geochemical parameters and can thus be a robust proxy for reconstructing $^{17}\text{O}_{\text{excess}}$ of parent water.

Keywords: Triple oxygen isotope fractionation; Calcite–Aragonite; $^{17}\text{O}_{\text{excess}}$; Paleo-hydrology proxy.

1. INTRODUCTION

Calcium carbonate is well-known to have the potential to preserve various geochemical signals, reflecting the environmental conditions at the time in which the carbonate mineral formed. Since the pioneering works of Urey (1947) and Emiliani (1966), the isotopic composition, specifically $\delta^{18}\text{O}$, of marine and terrestrial carbonates has been used as a paleoclimate proxy that records a combination of temperature and water isotopic composition. Additional carbonate-based proxies, such as Mg/Ca and clumped isotopes, are often used as geochemical thermometers (e.g., Eiler, 2011; Elderfield et al., 2006), complementing information from $\delta^{18}\text{O}$. In terrestrial carbonates, such as speleothems, $\delta^{18}\text{O}$ is interpreted as a recorder of the weighted mean rainfall $\delta^{18}\text{O}$, often reflecting the amount of rainfall in low latitude records (e.g., McDermott, 2004). This, however, does not capture the full hydrological complexity, such as the variability in moisture sources and the effect of local evaporation (although a few studies were able to link speleothem $\delta^{18}\text{O}$ changes with changes in moisture sources during specific time intervals in the past, such as the 8.2 ka event; e.g., Dominguez-Villar et al., 2009; Voarintsoa et al., 2019). These gaps can be filled by information from $^{17}\text{O}_{\text{excess}}$ in water that may be archived in a variety of carbonates.

The parameter $^{17}\text{O}_{\text{excess}}$ is expressed as $(\ln(\delta^{17}\text{O}/1000+1) - \lambda_{\text{ref}} \ln(\delta^{18}\text{O}/1000+1)) \times 10^6$, or simply $^{17}\text{O}_{\text{excess}} = (\delta^{17}\text{O} - \lambda_{\text{ref}} \times \delta^{18}\text{O}) \times 10^3$, and is reported in per meg (e.g., Barkan and Luz, 2012; Luz and Barkan, 2010). The slope λ_{ref} is a mass dependent reference, with the value 0.528 used in water, CO_2 , and CaCO_3 .

Meteoric water $^{17}\text{O}_{\text{excess}}$ is largely dependent on the atmospheric conditions, such as relative humidity, in the region where water vapor form (e.g., Angert et al., 2004; Luz and Barkan, 2010). However, there are indications for the influence of additional processes during

precipitation, associated with local conditions. The $^{17}\text{O}_{\text{excess}}$ data of Li et al. (2015) from U.S tap waters suggest a potential influence of mixing of moisture sources and re-evaporation during precipitation. In high latitude regions, $^{17}\text{O}_{\text{excess}}$ is mainly influenced by kinetic processes related to super-saturation during vapor condensation at cold climate (e.g. Landais et al., 2012; Schoenemann et al., 2014). In mid to low latitude regions, $^{17}\text{O}_{\text{excess}}$ is mainly affected by evaporation of rain droplets, especially during warm climatic conditions (Landais et al., 2010; Risi et al., 2013; Li et al., 2015; Passey and Ji, 2019).

Whereas fossil water $^{17}\text{O}_{\text{excess}}$ can be obtained from ice cores, fluid inclusions, or gypsum hydration water (Affolter et al., 2015; Gázquez et al., 2018; Landais et al., 2008), these archives are limited in their geographical distribution. A broader coverage can be obtained by measuring $^{17}\text{O}_{\text{excess}}$ in carbonates. Recent analytical developments (Passey et al., 2014; Barkan et al., 2015; Mahata et al., 2016) enable high precisions measurements of $^{17}\text{O}_{\text{excess}}$ in CO_2 released from CaCO_3 , which in turn may serve as a recorder of $^{17}\text{O}_{\text{excess}}$ of the water in which the mineral grows (Passey et al., 2014; Levin et al., 2014; Passey and Ji, 2019). Despite the recent advancement in measuring triple oxygen isotopes in carbonate materials, the fractionation involved in this proxy has not yet been characterized by laboratory experiments, to provide a framework necessary to quantitatively interpret past records. Here, we examine the triple oxygen isotope fractionation in the $\text{CaCO}_3\text{--H}_2\text{O}$ system focusing on the effect of mineralogy, using laboratory precipitation experiments of calcite, aragonite, and their mixtures at temperatures of 10, 27, and 35°C. We also examine the role of initial solution concentrations, as a simple way to assess the role of dissolved inorganic carbon (DIC) concentration on the triple oxygen isotope fractionation in the same system. The data allows us to calculate the fractionation slope, θ (=

$\ln^{17}\alpha / \ln^{18}\alpha$), in order to interpret $^{17}\text{O}_{\text{excess}}$ in natural carbonates as a geochemical archive for paleo-hydrological processes.

2. METHODS

2.1. Precipitation experiment

Precipitation experiments were performed by mixing solutions containing NaHCO_3 (Baker Analyzed Reagent, J.T. Baker ref. 1-3506) and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich CAS no. 10035-04-8) to reach an initial DIC concentration of 25 mM (at 10, 27, and 35°C) and 5mM (at 27°C, to test the effect of initial DIC). $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich CAS no. 7791-18-6) was added to obtain a total Mg–Ca concentration of 25mM or 5mM, respectively. The Mg:Ca ratio for either the 5mM or 25mM solution was defined following Morse et al. (1997), which we used as a guide for the Mg:Ca–Temperature combination to precipitate either calcite, aragonite, or a mixture of both (Table 1, Figure 1). It varied between 0 and 5. The composition of CO_2 extracted from the NaHCO_3 is 26.88 ‰ versus VSMOW for $\delta^{18}\text{O}$ and -260 per meg for $^{17}\text{O}_{\text{excess}}$. All samples were prepared without initial CO_2 bubbling. Starting (pre-mixing) solutions were allowed to reach isotopic equilibrium at room temperature overnight (>15 h), so that the starting solution is the same in all experiments. This equilibration time was based on estimated equilibration times of Beck et al. (2005) and Affek (2013) for $\delta^{18}\text{O}$ and Δ_{47} . We assume that $\delta^{17}\text{O}$ would have a similar equilibration time. This assumption is consistent with model simulations of Guo and Zhou (2019), where the time to reach equilibrium is similar for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$. This model predicts that isotopic exchange between dissolved inorganic carbon and water should reach equilibrium after about 20 hours at pH=10.4 and 25°C; equilibration at the lower pH of our experiments is expected to be faster. The solutions were then thermally equilibrated at their

corresponding experimental temperature for at least 1 hour prior to mixing (following Kim and O'Neil., 1997). A 200 ml aliquot of the solution mixture was placed in a 250 ml Erlenmeyer flask that was covered with two layers of Parafilm and a glass plate. The pH of the starting and ending solution varied between 5.85 and 7.67, indicating a HCO_3^- dominated solution (Table 1).

CaCO_3 precipitation occurred via passive CO_2 degassing. Experiments were performed at 10, 27, and 35°C. Temperature was maintained by placing the precipitating solutions in an incubator (10°C) or in a circulating water bath (27 and 35°C). The time of appearance of the first precipitates varied depending on the temperature and on the initial solution concentration. In the 35°C experiments, precipitates were observed 15-30 minutes after mixing the solutions, and the experiment lasted ~3 days. In the 27°C experiment, precipitates were observed after few hours at 25mM or after ~24hrs at 5mM, and the precipitation experiment lasted ~7 days and ~29 days for the 25 mM and 5 mM, respectively. In the 10°C experiment, the appearance of first precipitates took 1–2 days, and the precipitation experiment lasted ~50 days. We note that the ending date for each experiment was determined by assessing when no more precipitates were being produced.

Water evaporation during the experiment was negligible, as seen by the lack of change in solution volume through the experiment and by the similar $\delta^{18}\text{O}$ values of the water at the beginning and at the end of the experiment. The mineralogical composition and proportion of calcite and aragonite in the CaCO_3 precipitates was determined by X-ray diffractometer (Bruker AXS D8 Advance at the Harvey M. Krueger Family Center for Nanoscience and Nanotechnology at The Hebrew University of Jerusalem).

2.2. Analytical procedures and isotopic measurements

The analytical procedures for determining the triple oxygen isotope composition in carbonates and water were previously described by Barkan et al. (2015; 2019) and Affek and Barkan (2018), respectively. Briefly, CaCO_3 samples were digested by phosphoric acid at 25°C following McCrea (1950), and water samples were equilibrated with CO_2 following the technique of Epstein and Mayeda (1953) and O’Neil and Truesdell (1991). In both cases, the resulting CO_2 underwent isotopic exchange over hot platinum with pure O_2 of known isotopic composition, followed by O_2 being analyzed for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values. The O_2 samples were measured by dual-inlet mass spectrometry versus an O_2 working reference gas that was calibrated with respect to VSMOW. Each sample was analyzed in duplicates or triplicates. All measurements were performed alongside an in-house CO_2 standard that was analyzed daily to check the performance of the CO_2 - O_2 isotope exchange line and the mass spectrometer. The typical reproducibility of $^{17}\text{O}_{\text{excess}}$ is approximately ± 6 per meg (Barkan et al., 2019).

3. RESULTS

The results from this study are presented in Figures 1–4, and details are given in Tables 1–3.

3.1. Mineralogy and molarity

Figure 1 depicts the distribution of the carbonate mineralogy as a function of temperature and the Mg:Ca ratio of the starting solution. The results are in good agreement with the mineralogical distribution obtained by Morse et al. (1997) and Balthasar and Cusack (2015). Briefly, in the absence of magnesium (Mg:Ca=0) the dominant calcium carbonate phase is calcite. At higher Mg:Ca ratios or high temperatures, aragonite is the dominant phase.

Our results show that in precipitation temperatures between 10 and 35°C, $^{17}\text{O}_{\text{excess}}$ is independent of mineralogy and of the molarity of the starting solution (Table 2). Values of $^{17}\text{O}_{\text{excess}}$ of CO_2 extracted from carbonate (denoted $\text{CO}_{2\text{-carb}}$) overlap between calcite (−185 to −202 per meg) and aragonite (−185 to −215 per meg). The mean difference in $^{17}\text{O}_{\text{excess}}$ between water and $\text{CO}_{2\text{-carb}}$ is 215 ± 17 (1SD) per meg for samples that are mostly calcite and 220 ± 12 per meg for samples that are mostly aragonite. When considering the molarity of the starting solution, the difference in $^{17}\text{O}_{\text{excess}}$ between $\text{CO}_{2\text{-carb}}$ and water is 204 ± 16 (1SD) per meg for the 5mM experiments and 212 ± 4 per meg for the 25mM experiments at 27°C.

Figure 1: Scatter plot showing the distribution of CaCO_3 polymorphs precipitated in this study, as a function of Mg:Ca ratio and temperature (°C), compared to the data of Morse et al. (1997). The proportion of each mineral in each sample was determined via XRD, and is depicted in the blue / green partitioning of the symbol. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3.2. ^{18}O fractionation factors

Table 1 summarizes the experimental conditions and the $\delta^{18}\text{O}$ data for carbonates and their parent water, along with the resulting ^{18}O fractionation factors ($^{18}\alpha_{\text{CaCO}_3-\text{H}_2\text{O}}$). The expected difference of $\sim 0.8\text{‰}$ (e.g., Kim et al., 2007b) between calcite and aragonite is observed in our 5mM experiments. At 25mM, no significant difference is observed between the two polymorphs. The reason for this may be related to kinetic isotopic fractionation that is often observed in laboratory precipitation. The precipitation rates are significantly higher at 25mM relative to 5mM (calculated using kinetic parameters for calcite and aragonite precipitation from Burton and Walter (1987) with saturation state (Ω) calculated from the concentrations at the beginning of our experiments and the solubility product of calcite or aragonite from Mucci (1983), and compared at 27°C). The higher concentration experiments are therefore more sensitive to kinetic isotope effects, that may affect the difference in $^{18}\alpha_{\text{CaCO}_3-\text{H}_2\text{O}}$ between the two polymorphs. Burton and Walter (1987) observed higher precipitation rates in aragonite relative to calcite when compared at the same saturation state (at relatively low Ω , $\log(\Omega-1) < 1$). In our experiments Ω is significantly higher, but is lower for aragonite ($\log(\Omega-1)=4.2-4.7$) than for calcite ($\log(\Omega-1)=5.2-5.3$) due to aragonite being more soluble, leading to faster precipitation in the calcite experiments. Therefore, a combination of kinetic isotope effects would likely influence $\delta^{18}\text{O}$ of calcite and aragonite to a different extent, and may thus affect the difference between them.

Figure 2 shows the ^{18}O fractionation curve between CaCO_3 and H_2O determined from our experimental study, in comparison to previous studies, including biogenic carbonates and laboratory precipitation of both calcite and aragonite. The fractionation curve for all our 25mM samples precipitated at 10, 27, and 35°C , is expressed as $1000\ln^{18}\alpha_{\text{CaCO}_3-\text{H}_2\text{O}} = 17.743 \pm 0.493 * 1000/T - 30.316 \pm 1.675$ (with T in degrees K). It is higher than the aragonite fractionation curve

of Kim et al. (2007b) and Patterson et al. (1993), slightly lower than the biogenic aragonite fractionation curve of Grossman and Ku (1986), and is similar to the curve from slowly grown calcite of Gabitov et al. (2012). Despite the wide range of the $^{18}\alpha$ fractionation curves (Figure 2) and the potential kinetic effects associated with this range, the overall consistency of our $\delta^{18}\text{O}$ data with these expected fractionation factors suggest that our ^{17}O fractionation factors are broadly relevant for calcite and aragonite of both biogenic and abiogenic sources.

Figure 2: The $^{18}\text{O}/^{16}\text{O}$ isotopic fractionation curve between CaCO_3 and H_2O calculated in this study (thick pink curve) compared with published fractionation curves for CaCO_3 –water. A and C denote aragonite and calcite, respectively. Bio and Inorg denote biogenic carbonates and inorganic precipitation experiments. Our $^{18}\text{O}/^{16}\text{O}$ isotope fractionation curve is consistent with other studies. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

4. DISCUSSION

4.1. Mineralogy and molarity

Calcite and aragonite are two common carbonate minerals that are used in paleoclimate and paleo-environment reconstruction (e.g., in speleothems, foraminifera, mollusk shells, and lake deposits). Often, calcite and aragonite co-occur in one sample (e.g., in speleothems;

Holmgren et al., 2003; Voarintsoa et al., 2017). In such cases, the difference in $^{18}\alpha$ between the two polymorphs (Kim et al., 2007b) has to be accounted for in the aragonite $\delta^{18}\text{O}$ to conform with the calcite values and to avoid bias in the interpretation of the data. The polymorph independence of the fractionation slope θ observed in this study (Table 3, Figure 4c) suggest that regardless of whether a sample is composed of pure calcite (e.g., foraminifera), aragonite (e.g., many mollusk shells), or a mixture of both (e.g., some speleothems or lake deposits), it should not pose further complications when calculating $^{17}\text{O}_{\text{excess}}$ as part of the interpretation of carbonate triple oxygen isotopes data to reconstruct $^{17}\text{O}_{\text{excess}}$ in their parent water. This polymorph independence of θ has been observed also in theoretical models (Guo and Zhou, 2019). The modeled absolute values of $\theta_{\text{CaCO}_3\text{--H}_2\text{O}}$ (0.5256 and 0.5257, respectively, for calcite and aragonite at 25°C) are higher than our experimental $\theta_{\text{CO}_2\text{carb--H}_2\text{O}}$ values (0.5228 and 0.5226, respectively for calcite and aragonite at 27°C), with the difference likely reflecting, at least in part, the fractionation between CaCO_3 and CO_2 extracted from it (see below).

We also found that initial Mg:Ca ratio and DIC concentration (5mM and 25mM, at 27°C) do not significantly affect θ and the $^{17}\text{O}_{\text{excess}}$ values (Figures 4a; Table 3). The initial solution concentration and the Mg:Ca ratio used in this study are not far from those in natural systems, such as cave drip water (between 0 and 1.5; e.g., Matthey et al., 2010; Oster et al., 2012) and seawater (around 5; e.g., Ligi et al., 2013, and references therein). Our results are therefore relevant for natural samples, but as discussed below, caution should be taken as to the higher temperature data, as these may be influenced by various kinetic isotopic effects such as fast degassing and fast precipitation rates. It appears, therefore, that $^{17}\text{O}_{\text{excess}}$ in carbonates is less sensitive than $\delta^{18}\text{O}$ to geochemical parameters, simplifying its interpretation as a proxy for reconstructing paleo-hydrological conditions.

4.2. Temperature dependence of $^{17}\alpha$

It has been long known, and also observed in this current study, that the ^{18}O isotopic fractionation factor between carbonate and water is temperature dependent; it decreases while temperature increases. Although there are variations among ^{18}O thermometer calibrations (e.g., Figure 2), this relationship has enabled carbonate $\delta^{18}\text{O}$ to be used as a tool for reconstructing paleo-temperatures (e.g., Urey, 1947; Emiliani, 1966). The general consistency of the $^{18}\alpha$ obtained from our samples with common ^{18}O thermometer calibrations allows us to examine $^{17}\alpha$ between carbonate and its parent water, and what controls $^{17}\text{O}_{\text{excess}}$ in CaCO_3 .

The difference in $^{17}\text{O}_{\text{excess}}$ between $\text{CO}_{2\text{-carb}}$ and water in our experiments is similar at 10°C and 35°C (-222 ± 14 and -227 ± 9 per meg), and is somewhat higher at 27°C (-207 ± 12 per meg). Figure 3 compares these observed values (as well the corresponding values for carbonate-water) to those predicted by model simulations (Hayles et al., 2018; Guo and Zhou, 2019). The observed 15 per meg difference between 10 and 27°C is consistent with the results of the models, and it approximately reflects the temperature dependence of $^{18}\alpha$, as the change in θ is small. The value at 35°C , however, deviates from the modeled trend. There is no analytical reason to reject the set of experiments at 35°C , but it is possible that kinetic isotope effects have played a significant role. Laboratory precipitation experiments are inherently fast, leading to potential kinetic isotope effect due to fast CO_2 degassing and fast mineral growth (e.g., Gabitov et al., 2012), which are likely to be more pronounced in our high temperature experiments. In these experiments, first precipitates were observed after 15–30 minutes. This time is shorter than needed to reach equilibrium between DIC and CO_2 in air (about 2 hours; Guo and Zhou, 2019) and also for the DIC to reach isotopic equilibrium at the experimental temperature, through

exchange with water, which is expected to be even slower (Guo and Zhou, 2019). The non-equilibrium conditions, stemming from a combination of processes, may lead to the observed deviations at 35°C.

Figure 3: The difference in $^{17}\text{O}_{\text{excess}}$ between X (= $\text{CO}_{2\text{-carb}}$ or CaCO_3) and water in our experiments (data points) compared to the theoretical models (lines) of Hayles et al. (2018) and Guo and Zhou (2019). CaCO_3 observed values are calculated from the measured $\text{CO}_{2\text{-carb}}$ using the acid digestion fractionation derived from either Wostbrock et al. (2020) or Guo et al. (2009), as in Table 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

To calculate $^{17}\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ we must convert our measured $\text{CO}_{2\text{-carb}}$ data to that of carbonate. This requires knowing the ^{17}O fractionation factor for the acid digestion of CaCO_3 to CO_2 ($^{17}\alpha_{\text{acid}}$). There are currently no accepted values for $^{17}\alpha_{\text{acid}}$ for either calcite or aragonite, as opposed to $^{18}\alpha_{\text{acid}}$ of 1.01025 (Kim et al., 2015) and 1.01063 (Kim et al., 2007a) for these minerals, respectively. Wostbrock et al. (2020) suggest an experimental value for $^{17}\alpha_{\text{acid}}$ in

calcite reacted at 25°C. However, knowing that there is a significant difference in $^{18}\alpha_{\text{acid}}$ between calcite and aragonite, it is likely that $^{17}\alpha_{\text{acid}}$ values also differ between the two polymorphs. As our samples are composed of calcite, aragonite, and mixtures of both (Figure 1), we cannot use the calcite $^{17}\alpha_{\text{acid}}$ of Wostbrock et al. (2020) to directly convert our $\text{CO}_2\text{-carb}$ data to carbonate values. Instead, we assume that the fractionation slope for the phosphoric acid digestion at 25°C, $\theta_{\text{acid}} (= \ln^{17}\alpha_{\text{acid}} / \ln^{18}\alpha_{\text{acid}})$, is the same for both calcite and aragonite, so that $^{18}\alpha_{\text{acid}}$ and $^{17}\alpha_{\text{acid}}$ vary together with polymorph. Based on this assumption, we derive the ^{17}O fractionation factor for the acid digestion ($^{17}\alpha_{\text{acid}}$) for both minerals using the accepted $^{18}\alpha_{\text{acid}}$ and θ_{acid} (see below).

There are two suggested values for the relationship between $^{18}\alpha_{\text{acid}}$ and $^{17}\alpha_{\text{acid}}$ for calcite reacted at 25°C. A θ_{acid} value of 0.5230 was obtained via fluorination of CaCO_3 (Wostbrock et al., 2020), and a value of 0.5281 was determined by transition state theory modeling (Guo et al., 2009). As we do not know *a priori* which of these θ_{acid} values (if any) is correct, we examine our data in the context of both θ_{acid} values. We use θ_{acid} together with the accepted ^{18}O acid fractionations factors for calcite and aragonite (Kim et al., 2007a; 2015), to calculate $^{17}\alpha_{\text{acid}}$ (Table 2). Using the θ_{acid} of 0.5230 from Wostbrock et al. (2020), we obtained $^{17}\alpha_{\text{acid}}$ values of 1.00535 and 1.00555 for calcite and aragonite, respectively. Using the θ_{acid} of 0.5281 of Guo et al. (2009), we obtained respective $^{17}\alpha_{\text{acid}}$ values of 1.00540 and 1.00560. Samples of mixed polymorphs were then calculated as: $^{17}\alpha_{\text{acid}} = \% \text{calcite} \times ^{17}\alpha_{\text{acid-calcite}} + \% \text{aragonite} \times ^{17}\alpha_{\text{acid-aragonite}}$. The resulting CaCO_3 $\delta^{17}\text{O}$ values are given in Table 2, from which we can calculate the fractionation between CaCO_3 and H_2O using both θ_{acid} values (Table 3).

4.3. The fractionation slope $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$

Using the $^{17}\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ and $^{18}\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ above, we calculated $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ (Table 3, Figure 4). The advantage of using $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ rather than directly $^{17}\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ is that it normalizes differences that are known to occur in $^{18}\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ among different types of carbonates (e.g., biogenic versus laboratory precipitated carbonates; Figure 2). Using $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$, it is possible to rely on the vast literature data of $^{18}\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ to calculate $^{17}\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ for different cases. Table 3 gives values of $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ using the two different θ_{acid} values noted above, as well as the $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ which is based directly on the measured CO_2 extracted from carbonate, without accounting for the acid digestion fractionation.

Figure 4: Fractionation slope in the $\text{CaCO}_3\text{-H}_2\text{O}$ system presented in box-and-whisker plots that show outlier points (little dot) as a function of (a) molarity (initial concentration of the solution for the 27°C experiments), (b) temperature, and (c) mineralogy. Values calculated using θ_{acid} of 0.5230 or 0.5281 are shown in grey and orange, respectively. Calculated $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ values using the model of Hayles et al. (2018) at 10, 27, and 35°C are shown in blue in Figure 4b. Details are given in Table 3. The boxes show the interquartile range, calculated including the samples' median (horizontal line inside the box). The horizontal lines that mark off the box at the lower and upper hinge are the 25th and the 75th percentiles, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

The results indicate that under laboratory precipitation conditions between 10 and 35°C, $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ does not vary with polymorph, meaning that it is the same for our calcite and

aragonite samples (Figure 4c), consistent with model predictions (Guo and Zhou, 2019). In terms of the effect of temperature, for both polymorphs $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ obtained at 10°C and 27°C are indistinguishable (0.5228 and 0.5225, respectively, using θ_{acid} of 0.5230), but those at 35°C are lower (0.5215; Table 3).

Modeling studies predict a positive temperature dependence of ~ 0.00001 change in $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ for a change in 1°C (Cao and Liu, 2011; Hayles et al., 2018; Guo and Zhou, 2019). For the temperature range of 25°C in our experiments this would result in a range of 0.0002-0.0003 around the mean $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ value, which is within our analytical uncertainty. We found a similarly negligible trend between 10 and 27°C, but our lower $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ value at 35°C show a relatively steep negative shift (a decrease of ~ 0.001 between 27 and 35°C) which is inconsistent with the models (Figure 4b). As discussed above for the $^{17}\text{O}_{\text{excess}}$ difference between $\text{CO}_2\text{-carb}$ and water (see Section 4.2), this lower $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ value in the 35°C experiments could result from a combination of kinetic effects that require further investigation.

Irrespective of the temperature trend, the absolute $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ values in recent models (Hayles et al., 2018; Guo and Zhou, 2019) are higher than our experimental data. The choice of θ_{acid} , however, can strongly influence the resulting experimental $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ values. Given the large uncertainty in θ_{acid} , we examine $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ using both available values. The $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ values calculated using the θ_{acid} of Wostbrock et al. (2020) are close to our $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ (e.g., 0.5227 ± 0.0003 for samples grown at 27°C), due to the similar value of θ_{acid} (0.5230). This is lower than the values predicted by the theoretical models (0.5256-0.5258 for calcite grown at 25°C; Hayles et al., 2018; Guo and Zhou., 2019) and a preliminary experimental $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ of 0.5252 for calcite grown at 30°C (Gibbons et al., 2017). However, when using the θ_{acid} of Guo et al. (2009) the $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ values obtained are even lower, 0.5207 ± 0.0003 (for the 27°C samples).

Although the model of Guo and Zhou (2019) predicts no significant difference between $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ for calcite and aragonite, as we observed (Table 3), the absolute $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ values suggested by this model are inconsistent with our experimental results, for either one of the available values of θ_{acid} . The consistency between the modeled $\theta_{\text{CaCO}_3\text{-H}_2\text{O}}$ values and those directly measured by Gibbons et al. (2017), together with the inconsistency with our data that is based on measuring $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$, suggest that both available values for θ_{acid} are likely wrong.

Passey et al. (2014) measured $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ in biogenic calcite and aragonite, comprising of an oyster shell, a coral, and eggshells that grew at temperatures of 24, 26 and 39°C. (Note that they report the fractionation slope as λ , rather than θ , to indicate that the fractionations are associated with a combination of several processes. For simplicity, we use the symbol θ for the fractionation slope either in the case of a single equilibrium process or for a combination of processes). They observed a mean $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ value of 0.5245 ± 0.0002 that is higher than our observed value. The coral sample deviated in both $^{17}\alpha$ and $^{18}\alpha$, likely reflecting the vital effect that is often observed in corals, but the fractionation slope of the coral was the same as that for oyster and eggshells, showing lack of trend with either temperature or polymorph.

The observed inter-laboratory difference in the mean $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ value may be associated with systematic errors related to the different sample preparation method used in both laboratories. It is important to note that there is also a difference of ~50 per meg in $^{17}\text{O}_{\text{excess}}$ of standards measured in both laboratories (Barkan et al., 2019). If this difference in standards is accounted for in the data of Passey et al. (2014), the $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ obtained from these data is 0.5231, much closer to the value we obtain here. Preliminary data from aragonitic freshwater mollusks measured in our laboratory also yield a $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ value of 0.5231 ± 0.0003 (Affek et al., 2019). This value is consistent with the scaled value of Passey et al. (2014) and is also within

error from the values obtained here from laboratory precipitation at 10 and 27°C (where we do not suspect dis-equilibrium).

The different analytical procedure and the uncertainty in θ_{acid} discussed above may explain discrepancies in the absolute $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ values among laboratories, or a difference between measured $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ and modeled of $\theta_{\text{carb-H}_2\text{O}}$. These cannot explain, however, a different trend with temperature. Although models also include uncertainty, the lack of temperature trend in the Passey et al. data set is consistent with the very weak trend predicted by the models. Whereas our 10 and 27°C data also shows no trend, the 35°C data is offset in both $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ and $^{17}\text{O}_{\text{excess}}$. The eggshell calcite in Passey et al. grew at 39°C but their $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ is similar to the lower temperature samples, suggesting that it is probably not the temperature itself that leads to our lower $\theta_{\text{CO}_2\text{carb-H}_2\text{O}}$ value at 35°C. Instead, the offset may be related to differences between laboratory precipitation and biogenic mineral growth or to specific differences between our high temperature experiments and the lower temperatures, such as the kinetic effects noted above. Further measurements at a range of temperatures for both biogenic carbonates and laboratory precipitation using a variety of methods, as well as experiments focusing specifically on the effect of growth rates and of degassing, may help resolve these discrepancies.

5. CONCLUSIONS

Results from this experimental study allow us to determine the triple oxygen isotope fractionations in the $\text{CaCO}_3\text{--H}_2\text{O}$ system. We found that the fractionation slope $\theta_{\text{CaCO}_3\text{--H}_2\text{O}}$ is: (1) polymorph independent, i.e., we observe no significant difference between calcite, aragonite, and their mixture; (2) indistinguishable at temperatures of 10 and 27°C but possibly slightly lower at

35°C (the lower value may be associated with kinetic effects related to the fast precipitation observed in these experiments); and (3) independent of the molarity of the precipitating solution. These are also reflected in the $^{17}\text{O}_{\text{excess}}$ values of the carbonates, that seem to be insensitive to a range of geochemical parameters. The triple oxygen isotopes in carbonates could therefore be a robust novel proxy for $^{17}\text{O}_{\text{excess}}$ in parent water and thus used to understand past hydrological processes.

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Table 1: Summary of the experimental conditions and ^{18}O data for the inorganically precipitated calcite and aragonite and their corresponding water at 10, 27, and 35°C.

T °C	Molarity	Samples ^a	Mg:Ca	%A ^b	pH _i	pH _f	$\delta^{18}_{\text{CaCO}_3}$	$\delta^{18}_{\text{H}_2\text{O}}$	$^{18}\alpha_{\text{CaCO}_3-\text{H}_2\text{O}}$	$1000\ln^{18}\alpha_{\text{CaCO}_3-\text{H}_2\text{O}}$
10 °C ^c	25mM	1	0	0	7.60	6.8	34.265	1.134	1.03309	32.55
	25mM	2	3	88	7.60	7.43	33.949	0.913	1.03301	32.47
	25mM	3	4	99	7.60	7.72	33.665	0.799	1.03284	32.31
	25mM	4	5	100	7.67	7.57	33.784	1.210	1.03254	32.02
27 °C ^d	25mM	5	0	0	7.14	6.31	31.009	1.493	1.02947	29.05
	25mM	6	4	97	7.14	6.89	30.612	1.456	1.02911	28.70
35 °C ^e	25mM	7	0	0	6.87	6.36	27.806	0.110	1.02769	27.32
	25mM	8	1	8	7.08	6.75	27.800	0.229	1.02756	27.19
	25mM	9	2	79	7.32	6.97	27.826	0.249	1.02757	27.20
27 °C ^d	5mM	10	0	4	5.89	5.85	28.453	0.400	1.02804	27.66
	5mM	11	1	37	6.02	6.01	28.990	0.380	1.02860	28.20
	5mM	12	2	100	6.42	6.64	29.270	0.493	1.02876	28.36

^a All samples were prepared without initial CO₂ bubbling, and they were precipitated via passive CO₂ degassing. $\delta^{18}\text{O}_{\text{CaCO}_3}$ was calculated using the acid fractionation of 1.01025 (Kim et al., 2015) and 1.01063 (Kim et al., 2007b) for calcite and aragonite, respectively, and using the following equation for samples of mixed polymorphs: $^{18}\alpha_{\text{acid}} = \% \text{calcite} \times ^{18}\alpha_{\text{acid-calcite}} + \% \text{aragonite} \times ^{18}\alpha_{\text{acid-aragonite}}$. $\delta^{18}\text{O}$ data is given versus VSMOW.

^b Percent aragonite, determined by XRD.

^c Covered flask placed in an incubator with shaking platform.

^d Covered flask placed in an incubator without shaking.

^e Covered flask placed in a thermally controlled water bath, without shaking.

Table 2: Summary of the triple oxygen isotopic composition of the CaCO_3 precipitates and their corresponding water. The units are ‰ for both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ and per meg for $^{17}\text{O}_{\text{excess}}$.

Sample	$\text{CO}_2\text{-carb}$			CO_2 eq. with H_2O		CaCO_3 (W&al) ^a			CaCO_3 (G&al) ^a			H_2O ^b		
	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$^{17}\text{O}_{\text{excess}}$	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$^{17}\text{O}_{\text{excess}}$	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$^{17}\text{O}_{\text{excess}}$	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$^{17}\text{O}_{\text{excess}}$
1	23.237	44.866	-202	21.886	42.217	17.794	34.265	-151	17.741	34.265	-203	0.618	1.134	20
2	23.238	44.892	-214	21.762	41.987	17.619	33.949	-162	17.565	33.949	-216	0.497	0.913	15
3	23.133	44.649	-194	21.693	41.867	17.492	33.665	-141	17.437	33.665	-195	0.430	0.799	9
4	23.176	44.774	-215	21.927	42.296	17.534	33.785	-162	17.479	33.785	-216	0.659	1.210	20
5	21.537	41.577	-200	22.074	42.591	16.104	31.009	-149	16.051	31.009	-201	0.803	1.493	15
6	21.517	41.555	-208	22.040	42.551	15.890	30.612	-156	15.835	30.612	-210	0.769	1.456	1
7	19.863	38.341	-197	21.336	41.151	14.438	27.806	-146	14.385	27.806	-198	0.080	0.110	22
8	19.879	38.367	-195	21.419	41.274	14.438	27.800	-144	14.385	27.800	-196	0.162	0.229	41
9	20.032	38.670	-198	21.416	41.296	14.449	27.826	-146	14.395	27.826	-200	0.158	0.249	27
10	20.223	39.012	-185	21.471	41.452	14.788	28.453	-134	14.735	28.453	-186	0.212	0.400	1
11	20.555	39.683	-201	21.467	41.432	15.051	28.990	-150	14.998	28.990	-202	0.209	0.380	8
12	20.845	40.211	-185	21.552	41.549	15.215	29.270	-133	15.160	29.270	-187	0.291	0.493	31

^a The $\delta^{18}\text{O}$ values of the carbonates were obtained after applying the phosphoric acid fractionation factors $^{18}\alpha=1.01025$ and $^{18}\alpha=1.01063$ (Kim et al., 2015; Kim et al., 2007a) for calcite and aragonite, respectively. The $\delta^{17}\text{O}$ values of the carbonates were calculated using the phosphoric acid fractionation slope ($\theta_{\text{acid}} = \ln^{17}\alpha/\ln^{18}\alpha$) of 0.5230 (Wostbrock et al. 2020; W&al), and 0.5281 (Guo et al., 2009; G&al), and the above phosphoric acid fractionation factors $^{18}\alpha$ for calcite and aragonite.

^b The $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of the water were derived by applying the $\text{CO}_2\text{-H}_2\text{O}$ equilibrium fractionation factors $^{18}\alpha_{\text{H}_2\text{O-CO}_2}=1.041036\pm0.00008$ and $^{17}\alpha_{\text{H}_2\text{O-CO}_2}=1.021254\pm0.00004$ (Barkan and Luz, 2012).

Table 3: Summary of the fractionation factors ($^{17}\alpha$ and $^{18}\alpha$) and their corresponding fractionation slope, calculated from (1) CO₂ extracted from CaCO₃ (CO_{2-carb}) and H₂O, (2) CaCO₃ and H₂O using $\theta_{\text{acid}} = 0.5230$ (Wostbrock et al. 2020), and (3) CaCO₃ and H₂O using $\theta_{\text{acid}} = 0.5281$ (Guo et al., 2009).

T °C	Sample ^a	%A ^c	1. CO _{2-carb} – water			2. Carbonate–water ($\theta=0.5230$)			3. Carbonate–water ($\theta=0.5281$)		
			$^{17}\alpha$	$^{18}\alpha$	θ	$^{17}\alpha$	$^{18}\alpha$	θ	$^{17}\alpha$	$^{18}\alpha$	θ
10 °C	1	0	1.02260	1.04368	0.5228	1.01717	1.03309	0.5228	1.01711	1.03309	0.5212
	2	88	1.02273	1.04394	0.5227	1.01711	1.03301	0.5226	1.01706	1.03301	0.5209
	3	99	1.02269	1.04382	0.5233	1.01705	1.03284	0.5234	1.01700	1.03284	0.5217
	4	100	1.02250	1.04351	0.5225	1.01686	1.03254	0.5223	1.01681	1.03254	0.5207
	Avg.		1.02263	1.04374	0.5228	1.01705	1.03287	0.5228	1.01700	1.03287	0.5211
	$\pm SE^*t$		0.00010	0.00018	0.0003	0.00013	0.00025	0.0005	0.00013	0.00025	0.0005
27 °C	5	0	1.02072	1.04002	0.5225	1.01529	1.02947	0.5224	1.01524	1.02947	0.5206
	6	97	1.02073	1.04004	0.5227	1.01511	1.02911	0.5225	1.01506	1.02911	0.5207
	Avg.		1.02072	1.04003	0.5226	1.01520	1.02929	0.5225	1.01515	1.02929	0.5207
	$\pm SE^*t$		0.00001	0.00001	0.0001	0.00013	0.00025	0.0001	0.00013	0.00025	0.0001
	10 ^b	4	1.02001	1.03860	0.5231	1.01457	1.02804	0.5231	1.01452	1.02804	0.5213
	11 ^b	37	1.02034	1.03929	0.5226	1.01484	1.02860	0.5224	1.01479	1.02860	0.5206
	12 ^b	100	1.02055	1.03970	0.5224	1.01492	1.02876	0.5222	1.01487	1.02876	0.5204
	Avg.		1.02030	1.03919	0.5227	1.01478	1.02847	0.5225	1.01472	1.02847	0.5207
	$\pm SE^*t$		0.00027	0.00056	0.0004	0.00018	0.00038	0.0005	0.00018	0.00038	0.0005
35 °C	7	0	1.01978	1.03823	0.5222	1.01436	1.02769	0.5218	1.01431	1.02769	0.5200
	8	8	1.01971	1.03813	0.5217	1.01427	1.02756	0.5212	1.01422	1.02756	0.5193
	9	79	1.01987	1.03841	0.5220	1.01429	1.02757	0.5216	1.01423	1.02757	0.5197
	Avg.		1.01979	1.03826	0.5220	1.01431	1.02761	0.5215	1.01425	1.02761	0.5197
	$\pm SE^*t$		0.00008	0.00014	0.0002	0.00005	0.00007	0.0003	0.00004	0.00007	0.0003

^a See details for each sample in Tables 1 and 2. ^b Samples precipitated at 27°C with a lower molarity (5mM). ^c Percent aragonite.

Figure captions:

Figure 1: Scatter plot showing the distribution of CaCO_3 polymorphs precipitated in this study, as a function of Mg:Ca ratio and temperature ($^{\circ}\text{C}$), compared to the data of Morse et al. (1997). The proportion of each mineral in each sample was determined via XRD, and is depicted in the blue / green partitioning of the symbol. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Figure 2: The $^{18}\text{O}/^{16}\text{O}$ isotopic fractionation curve between CaCO_3 and H_2O calculated in this study (thick pink curve) compared with published fractionation curves for CaCO_3 –water. A and C denote aragonite and calcite, respectively. Bio and Inorg denote biogenic carbonates and inorganic precipitation experiments. Our $^{18}\text{O}/^{16}\text{O}$ isotope fractionation curve is consistent with other studies. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Figure 3: The difference in $^{17}\text{O}_{\text{excess}}$ between X (= $\text{CO}_{2\text{-carb}}$ or CaCO_3) and water in our experiments (data points) compared to the theoretical models (lines) of Hayles et al. (2018) and Guo and Zhou (2019). In the data points, CaCO_3 values are calculated from the measured $\text{CO}_{2\text{-carb}}$ using the acid digestion fractionation derived from either Wostbrock et al. (2020) or Guo et al. (2009), as in Table 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Figure 4: Fractionation slope in the $\text{CaCO}_3\text{--H}_2\text{O}$ system presented in box-and-whisker plots that show outlier points (little dot) as a function of (a) molarity (initial concentration of the solution for the 27 °C experiments), (b) temperature, and (c) mineralogy. Values calculated using θ_{acid} of 0.5230 or 0.5281 are shown in grey and orange, respectively. Calculated $\theta_{\text{CaCO}_3\text{--H}_2\text{O}}$ values using the model of Hayles et al. (2018) at 10, 27, and 35°C are shown in blue in Figure 4b. Details are given in Table 3. The boxes show the interquartile range, calculated including the samples' median (horizontal line inside the box). The horizontal lines that mark off the box at the lower and upper hinge are the 25th and the 75th percentiles, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof

Figure 1

Figure 2

Figure 3

Figure 4