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To cite this version:
Anna Harrison, Jacques Schott, Eric Oelkers, Katharine Maher, Vasileios Mavromatis. Rates of carbon and oxygen isotope exchange between calcite and fluid at chemical equilibrium. Geochimica et Cosmochimica Acta, 2022, 335, pp.369-382. 10.1016/j.gca.2022.06.041. hal-03811110

HAL Id: hal-03811110
https://hal.science/hal-03811110
Submitted on 11 Oct 2022

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Rates of carbon and oxygen isotope exchange between calcite and fluid at chemical equilibrium

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Abstract

The isotopic composition of carbonate minerals provides a record of historical geochemical and environmental conditions, but the ability to interpret these compositions as paleo-proxies hinges on their preservation over thousand to million year timescales. At chemical equilibrium, alteration of initial isotopic compositions of calcite can occur in the presence of a fluid without visible changes in morphology at the submicron scale, complicating the interpretation of stable isotope compositions of carbonates. However, the rates and mechanisms of isotope exchange at chemical equilibrium are poorly understood. To evaluate the rates and processes by which C and O isotopes are exchanged between calcite and fluid, batch reactor experiments were conducted at chemical equilibrium between calcite and a fluid enriched in $^{13}$C and $^{18}$O relative to the solid at 25°C. Both natural and synthetic calcite of different grain sizes were investigated to evaluate the impact of mineral surface area and size on C and O isotope exchange rates. Our experimental results indicate that rapid exchange of both C and O isotopes occurs within 72 h for all calcite grain sizes studied, likely indicative of exchange of surface species in combination with a backward reaction during dissolution and Ostwald ripening of high energy surface sites. After 72 h, C and O isotope exchange rates were slower but near constant for timescales of thousands of hours. Surface-area normalized C and O isotope exchange rates were similar for all calcite grain sizes studied, and O and C were exchanged in a ~3:1 ratio consistent with exchange of CO$_3^{2-}$. The rates of C and O exchange were ~4 orders of magnitude lower than far-from-equilibrium calcite dissolution rates, suggesting exchange was controlled either by dissolution-precipitation of pre-existing reactive sites alone, or a combination of dissolution-precipitation and solid state/aqueous mediated diffusion. Overall, the results of this study suggest alteration of O and C isotope compositions of calcite at ambient temperatures can
proceed readily over short time scales, though the extent to which this process continues to operate over geologic time scales is difficult to predict at present. The results of this study further highlight the importance of generating a mechanistic understanding of the process of isotope exchange at chemical equilibrium, and represent a step towards this understanding.

**Keywords:**
C isotopes, O isotopes, diffusion, dissolution-reprecipitation, isotopic alteration
1. Introduction

The isotopic composition of carbonate minerals provides a record of historical geochemical and environmental conditions, generating a window into Earth’s past. Calcium carbonate minerals are abundant at Earth’s surface and form by both biotic and abiogenic processes, making them ideal archives of Earth’s past environmental conditions. Trace metal, major element, and isotopic compositions of carbonate minerals can be used to infer conditions occurring at the time of mineral formation (Bernard et al., 2017; Coggon et al., 2010; Dekens et al., 2002; Friedrich et al., 2012; Hoefs, 1997; Ravelo and Hillaire-Marcel, 2007; Urey et al., 1951). Carbon, oxygen, and calcium isotopes in carbonates can be used to provide insights into geochemical processes ranging from marine to groundwater environments including acting as proxies for temperature, carbon cycle dynamics, and pH (Avrahamov et al., 2013; Bernard et al., 2017; Fantle and Tipper, 2014; Friedrich et al., 2012; Füger et al., 2019; Garnier, 1985; Gussone et al., 2016; Hoefs, 1997; Katz et al., 2010; Marriott et al., 2004; Mavromatis et al., 2013, 2015, 2019; Mozeto et al., 1984; Ravelo and Hillaire-Marcel, 2007; Riechelmann et al., 2018; Spero et al., 1997; Urey et al., 1951). To use any of these proxies effectively requires first that isotopic and trace element compositions are preserved over timescales up to millions of years, and second that the mechanisms of isotope fractionation are known. Samples that have undergone recrystallization evidenced by observable morphological, chemical, or mineralogic features detected by tools such as light or electron microscopy can be excluded from paleo-reconstruction studies as the likelihood of poor preservation of isotopic compositions is obvious. For example, calcitic foraminifera tests can be excluded from analysis when they appear “frosty” under light microscopy due to recrystallization (Sexton et al., 2006). However, experimental studies have revealed that isotopic compositions of calcite [CaCO$_3$] can be altered substantially without visual
evidence of recrystallization if isotopic disequilibrium between fluids and calcite occurs (Bernard et al., 2017; Chanda et al., 2019; Cisneros-Lazaro et al., 2022; Géhin et al., 2021). The mechanism and rate of this isotopic alteration will determine whether and under what conditions carbonate archives preserve their isotopic compositions. Although a number of studies have reported isotopic alteration of calcium carbonate and a variety of other minerals at chemical equilibrium without morphological alteration observed at the scale of electron microscope analysis, the mechanism of alteration of isotopic composition is yet to be fully understood (Beard et al., 2010; Beard and Johnson, 2009; Curti et al., 2010; Frierdich et al., 2014; Géhin et al., 2021; Gorski and Fantle, 2017; Oelkers et al., 2019).

There exist several mechanisms that can lead to alteration of isotopic compositions at chemical equilibrium: exchange of surface species, solid state diffusion, and dissolution-precipitation processes such as Ostwald ripening. In this study, these different processes are defined as described below.

*Surface isotope exchange* involves the change in the isotopic ratio of the solid surface sites (surface CO₃ groups in the present study) without bulk dissolution/precipitation impacting deeper layers of the crystal. Exchange of surface species has often been invoked in isotope exchange studies to explain the commonly observed initial rapid exchange of isotopes upon interaction of isotopically different fluids and solids (Avrahamov et al., 2013; Géhin et al., 2021; Mozeto et al., 1984; Stamm et al., 2019)

*Ostwald ripening* is a dissolution/precipitation process that occurs at (or near) bulk chemical equilibrium to minimize the interfacial energy of a crystal or an ensemble of small crystals. It drives the growth of the largest crystals at the expense of the smallest ones, and, for a given crystal, the transfer of matter from the surfaces of excess surface free energy (affected by
defects, heterogeneities, etc.) to zones of lower surface free energy. Ostwald ripening has been
proposed as a mechanism for the exchange of isotopes between solutions and solids, especially
where diffusion in the solid is slow and crystals are small (Cole and Chakraborty, 2001; Dubnina
and Lakshtanov, 1997; Géhin et al., 2021).

Dynamic equilibrium is a dissolution/precipitation process that occurs at chemical
equilibrium and relates to the principle of detailed balancing, from which transition state theory
(TST) rate laws are constructed. In this process, it is assumed that the net reaction rate at
equilibrium is zero, yet continued transfer of mass may occur between solid and fluid with equal
forward (dissolution) and backward (precipitation) rates (Che et al. 2021, Oelkers et al., 2019;
Liu et al., 2016; Pearce et al., 2012; Mavromatis et al., 2015). Recent experimental studies have
utilized the principle of simultaneous forward and backward reactions (though not necessarily
TST) to estimate near-to-equilibrium reaction rates of a variety of minerals including calcite
(Subhas et al., 2017; Zhu et al., 2016), to account for equilibration of isotopic compositions
between fluid and solid after initial precipitation (Fernandez et al., 2019; Mavromatis et al.,
2016; Pearce et al., 2012) and to explain isotope exchange at or near chemical equilibrium
(Chanda et al., 2019; Grimm et al., 2021; Oelkers et al., 2019, 2018). However, the driving force
for dynamic equilibrium as a mechanism for isotope exchange is not clear, but could be related
to isotopic disequilibrium.

Solid-phase diffusion occurs within the crystal lattice by either interstitial or
substitutional mechanisms. In isotope diffusion (self-diffusion), controlled by substitutional
mechanisms, diffusion often depends on the availability of point vacancies throughout the crystal
lattice (Cole and Chakraborty, 2001). Solid-state diffusion has been invoked to explain both C
and O isotope alteration of biogenic calcite in the form of foraminifera tests in experiments at
90°C and above, and abiotic nano-crystalline calcite at 25°C (Bernard et al., 2017; Cisneros-Lazarø et al., 2022; Géhin et al., 2021).

The term *stable mineral recrystallization* is defined by Gorski and Fantle (2017) as “a reaction in which a stable mineral undergoes extensive exchange of atoms with ions in solution with no overt changes in mineral structure, morphology or grain size.” Where “extensive” refers to exchange of more than the atoms initially present at the solid-fluid interface (Gorski and Fantle, 2017) and thus does not include solely surface isotope exchange. “Overt” refers to changes not evident with macroscopic or microscopic tools, but is dependent on the observation scale (Gorski and Fantle, 2017). In the present study, we consider changes observable at the scale of electron microscopy to be overt. Stable mineral recrystallization does not explicitly define a mechanism of exchange and could therefore include a combination of diffusion and dissolution-precipitation processes that do not result in overt alteration of the mineral surface.

Identifying the mechanism of alteration of isotope composition in calcite is valuable, as the mechanism will strongly influence both the overall extent of exchange and its time-dependence. Diffusion and recrystallization could lead to significant alteration of isotopic compositions and little preservation of the original mineral isotopic composition, whereas the exchange of surface species would not have a substantial impact on bulk isotopic composition of the mineral. Ostwald ripening is likely an important control on isotopic exchange in early stages of mineral precipitation and growth for poorly crystalline materials and/or materials with surface textures of excess surface energy. However, this mechanism is likely less important for well-crystallized and aged materials. The objective of this study is to evaluate the rates of alteration of C and O isotope compositions of calcite at 25°C and chemical equilibrium, and generate insights into the possible mechanism. Chemical equilibrium is here defined as the equivalency of the ion
activity product of Ca and CO$_3^{2-}$ and the solubility product of pure calcite. A series of batch reactor experiments were conducted in which both natural and synthetic calcite of different grain sizes were exposed to a fluid enriched in $^{18}$O and $^{13}$C relative to calcite at chemical calcite-fluid equilibrium. This is the first study to our knowledge to evaluate O and C exchange simultaneously, and at bulk calcite-fluid equilibrium with high purity calcite, allowing new insights into the mechanisms and rates of isotope exchange.

2. Methods

2.1. Experimental methods

A series of batch reactor experiments was used to evaluate the rate of exchange of C and O isotopes between calcite and co-existing fluid at chemical equilibrium and 25°C. A mass of 0.06 g of calcite was placed in each of 52 borosilicate glass vials in two experimental series. Three different calcite grain sizes were used: a “large” and “small” grain size of a natural Siberian spar, and a fine-grained synthetic calcite purchased from Merck. The natural calcite was pulverized using an agate mortar and pestle and sieved to the desired grain size. The natural calcite was rinsed and ultrasonically cleaned with ethanol after being sieved to remove fine particulates. The first experimental series used only “large” natural calcite grains of 200-400 µm. The second experimental series examined reproducibility of the large calcite results, by using large natural calcite grains of 250-500 µm, and investigated the impacts of surface area on rates of exchange using small natural calcite grains between 150-200 µm, and synthetic calcite (Table 1). Duplicate reactors of the large calcite were collected at a number of timepoints. The
properties of the initial calcite are described in Table 1. Three reactors contained solution only
with no calcite to serve as control experiments without fluid-solid interaction.

Experimental conditions of each series are summarized in Table 2. An initial solution that
was slightly undersaturated with respect to calcite was prepared for each of the two experimental
series (saturation index between -0.47 and -0.63). The initial solution was prepared using $^{18}$O-
enriched water ($97\%^{18}$O) and $^{13}$C-enriched NaHCO$_3$ ($98\%^{13}$C). The fluid for the first
experimental series was prepared using 23.84 g of the $^{18}$O-enriched water diluted to 1159.09 g of
total fluid by mixing with non-enriched de-ionized water. A mass of 0.0671 g of $^{15}$C-enriched
NaHCO$_3$ and 0.3245 g of non-$^{13}$C-enriched NaHCO$_3$ was added to this fluid to obtain the desired
$\delta^{13}$C and initial NaHCO$_3$ concentration. The initial solution for the second experimental series
was prepared by mixing 24.02 g of $^{18}$O-enriched water diluted to 1024.49 g of total fluid by
mixing with non-enriched de-ionized water. A mass of 0.0672 g of $^{13}$C-enriched NaHCO$_3$ with
0.3203 g of non-$^{13}$C-enriched NaHCO$_3$ was added to this fluid. The calculated $\delta^{18}$O and $\delta^{13}$C of
the initial reactive solution for the first experimental series was 9861‰ VPDB (expressed as
VPDB for ease of comparison with solid compositions) and 18037‰ VPDB, respectively. The
calculated $\delta^{18}$O and $\delta^{13}$C of the initial reactive solution for the second experimental series was
9851‰ VPDB and 18301‰ VPDB, respectively. Although the initial isotopic composition of
the fluid could not be measured owing to the extreme values, the uncertainty based on weighing
error (balance repeatability) is less than 0.15% of the value. The initial solution composition was
adjusted to achieve close to equilibrium conditions with respect to calcite by adding CaCl$_2 \cdot 2$H$_2$O
to each initial reactive solution prior to putting it in contact with the calcite. The initial solutions
had concentrations of $4.0 \times 10^{-3}$ M NaHCO$_3$ and $2.5 \times 10^{-4}$ M CaCl$_2$ in the first experimental
series and $4.5 \times 10^{-3}$ M NaHCO$_3$ and $2.8 \times 10^{-4}$ M CaCl$_2$ in the second experimental series. The
initial saturation index of calcite in the solutions was -0.63 and -0.47 in the first and second experimental series, respectively (calculated using PHREEQC as described below, with pH fixed by charge balance). The borosilicate reactors were filled leaving no headspace using ~25 mL of the initial solutions. The reactors were then sealed with screw tops, wrapped in parafilm, and placed into a 25°C shaking water bath for the duration of each experiment.

Individual reactors were sampled in their entirety at selected times over 125 days for the small and synthetic calcite and 592 and 219 days for the large calcite in the first and second experimental series, respectively. Fluids were removed from each reactor using a 30 mL syringe and filtered through a 0.22 µm polyethersulfone syringe filter. One aliquot was acidified to 2% bi-distilled HNO₃ for subsequent analyses of Ca concentration and another aliquot remained unacidified for pH and alkalinity measurement. Fluid pH was measured immediately following sampling using a Metrohm 913 pH-meter and a Metrohm combined electrode (6.0234.1000) for the first experimental series. The fluid pH was measured using a WTW pH 3310 portable meter equipped with a SenTix 41 electrode for the second experimental series. The pH probes were calibrated prior to each measurement period using pH 4.01, 7.00, and 9.18 (25 °C) buffer solutions, with an uncertainty of approximately ±0.03 pH units. Care was taken to minimize exposure to the atmosphere during sampling. The resulting solids from each reactor were vacuum filtered onto a 0.45 µm filter. Solids were rinsed thoroughly with de-ionized water and ethanol and dried at room temperature.

2.2 Analytical methods

2.2.1 Fluid chemical composition
Calcium concentration of the fluids collected from each experiment was analyzed by atomic absorption spectroscopy (AAS) using a Perkin Elmer AAnalyst 400. Based on triplicate analysis of samples, this method had an analytical error better than $\pm 2.55 \times 10^{-5}$ mol/L and detection limit of $2.03 \times 10^{-7}$ mol/L. Alkalinity was determined using an automated Schott Titroline AlphaPlus titrator by HCl titration. Measurement uncertainty was determined by repeated analysis of triplicate samples and an in-house NaHCO$_3$ standard and was better than $\pm 9.54 \times 10^{-5}$ mol/L as HCO$_3^-$. Dissolved inorganic carbon (DIC) concentrations were calculated using the measured fluid composition and PHREEQC V3 (Parkhurst and Appelo, 2013) with the minteqv4 database. The uncertainty introduced by calculation of DIC from alkalinity is unknown, therefore the same uncertainty as alkalinity measurements of $\pm 9.54 \times 10^{-5}$ mol/L was applied to calculated DIC concentrations. Saturation indices of calcite and fluid speciation were determined using the same PHREEQC V.3 calculations.

2.2.2 Analysis of solids

The initial synthetic and natural calcite used were analyzed by X-ray diffraction to confirm the presence of calcite and identify trace phases, if present. A Bruker D8 Advance X-ray diffractometer with Cu radiation was used. A scan speed of 76.8 s/step and 0.01°/step was utilized. The morphology of the initial calcite and select reacted samples was evaluated using an FEI Quanta 650 field emission environmental scanning electron microscope (SEM) and a JEOL JSM 7100F TTLS LV field emission SEM. The initial surface area of each initial calcite material was determined using BET analysis with Kr gas with a Micromeritics Tristar II Plus (reported in Table 1). The chemical composition of the initial calcite was measured by digesting the calcite in
bi-distilled HNO₃ and analyzing using inductively coupled plasma mass spectrometry (ICP-MS) with a Thermoscientific iCap TQ (reported in Table 1).

2.2.3 Isotopic analyses

Carbon and oxygen isotope analyses of the initial and reacted calcite were conducted with a GasBench II coupled to a ThermoFinnigan MAT 253 mass spectrometer at the Ruhr-University Bochum in continuous-flow mode following the methodology of Breitenbach and Bernasconi (2011). Solids were ground with an agate mortar and pestle and homogenized prior to analysis. Between 90 and 120 µg of ground solid was weighed into borosilicate glass vials and these samples were acid-digested at 70°C and analyzed together with international standards NBS19, IAEA603, and CO-8. Results are reported as δ¹³C and δ¹⁸O solid with respect to the Vienna PeeDee belemnite (VPDB) standard. The external standard deviation for oxygen and carbon isotope ratios was ≤0.07 and ≤0.06 ‰, respectively (n = 17). The isotopic composition of the fluids were not measured as the isotopic composition was too enriched relative to natural values and calibration standards.

Delta notation is defined by equation (1):

\[ \delta^x A = \left( \frac{\frac{x_A}{y_A}}{\frac{x_A}{y_A}}_{\text{sample}} - 1 \right) \times 1000 \]  \hspace{1cm} (Eq. 1)

where \( A \) refers to the element (C or O) and \( x \) and \( y \) refer to the mass of the heavier and lighter isotope, respectively.

2.2.4 Isotope exchange rate calculations
The extent of isotope exchange was calculated as follows for carbon (eq. 2-4):

\[ X_{13}^{calcite,t} = (1 - F_{calcite,i})X_{13}^{calcite,i} + F_{calcite,i}X_{13}^{calcite,t} \]  

(Eq. 2)

\[ F_{calcite,i} + F_{spike} = 1 \]  

(Eq. 3)

\[ C_m = F_{spike}m_{C,calcite} \]  

(Eq. 4)

where \( X_{13}^{calcite,i} \) and \( X_{13}^{calcite,t} \) are the mole fraction of \( ^{13}\text{C} \) in the calcite initially and at time \( t \), \( X_{13}^{calcite} \) refers to the mole fraction of \( ^{13}\text{C} \) of the initial reactive fluid which is assumed not to change substantially throughout the experiment, \( F_{spike} \) represents the fraction of C in the calcite that originated from the initial reactive fluid, \( m_{C,calcite} \) denotes the total moles of C in the initial calcite, \( C_m \) refers to the total moles of C exchanged between calcite and fluid at the sampling time, and \( F_{calcite,i} \) represents the fraction of C in the calcite that has not exchanged with the fluid (i.e., maintains its original isotopic composition). The same approach is used for calculating the fraction of oxygen exchanged between fluid and solid but considers the mole fraction of \( ^{18}\text{O} \) in the solid and fluid. When applied to the bulk system (the total moles of C and O), this mass balance approach is termed a “homogeneous model,” and it assumes that the exchanged solid has the same isotopic composition as the initial fluid at all times (Gorski and Fantle, 2017). This assumption is justified due to the very large enrichment of the fluid in both \( ^{18}\text{O} \) and \( ^{13}\text{C} \), which means that 1) the fluid isotopic composition can be treated as effectively constant and 2) fractionation during exchange can be neglected. Using the homogeneous model, it is estimated that the maximum change in the mole fraction of \( ^{13}\text{C} \) in solution would be 1.95\% and the maximum change in the mole fraction of \( ^{18}\text{O} \) in solution would be \( \sim 4 \times 10^{-4} \% \). The use of the homogeneous model to estimate the extent of C and O exchange is therefore justified.

The rate of C or O isotope exchange was calculated as follows (eq. 5):
rate = \frac{C_{m,t}}{t \cdot S \cdot M} \quad \text{(eq. 5)}

where $C_{m,t}$ refers to the moles of C or O exchanged at time $t$ as calculated using equations 2-4, $t$ is time of sampling of a given experiment (s), $S$ refers to the specific surface area ($m^2/g$), and $M$ refers to the total mass of calcite in each reactor (g).

3. Results

3.1 Calcite composition and morphology

Both the initial synthetic and natural calcite did not contain any other phases detectable by XRD (Figure 1). The trace metal composition and BET surface area of the initial natural and synthetic calcite is reported in Table 1. The natural calcite had higher concentrations of most measured trace elements compared to the synthetic calcite, with the exception of Sr, which was present above the quantification limit in the synthetic but not natural calcite (Table 1). However, in both cases, the initial calcite was of high chemical and mineralogical purity. The majority of calcite surfaces imaged were not visibly altered in any of the experiments, nor were there noticeable changes in calcite grain size before and after the experiment as observed using SEM (Figure 2). The surfaces of the natural calcite remained rough, with small surface particles, fractures, and sharp boundaries retained at the end of each experimental series (Supplementary Information Figure S1a). At the surface of a low number of large calcite grains (~3 in one sample only), small 2D rhombohedrons were observed consistent with minor precipitation, though it could not be determined if these were truly new features post reaction or were initially present but unobserved in the initial calcite (Supplementary Information Figure S1b). Synthetic calcite
grains remained smooth before and after the experiment at the scale of observation and no visible alteration was observed (Figure 2).

3.2 Temporal evolution of fluid composition

The pH of the reactive fluid increased slightly during the first ~1056 h of the experiments, from ~7.5 to ~8.0, consistent with minor dissolution of calcite to achieve equilibrium (Figure 3). After this time, the reactive fluid pH remained relatively stable, between 7.97 and 8.20 in all experimental series. The pH of control experiments run in the absence of calcite ranged between 7.83 and 7.97. The Ca concentration of the reactive fluid increased rapidly during the first 72 h of each experimental series as calcite dissolved towards equilibrium, after which it remained relatively stable throughout the experiments. The Ca concentration of the reactive fluid after 72 h was an average (n = 7) of $3.71 \times 10^{-4} \pm 3.54 \times 10^{-5}$ M in the first large calcite experimental series, and $3.53 \times 10^{-4} \pm 1.60 \times 10^{-5}$ M (n = 14) in the second experimental series. The Ca concentration of the reactive fluid in the small natural calcite experimental series was an average of $3.65 \times 10^{-4} \pm 1.60 \times 10^{-5}$ M after 72 h. The Ca concentration of the reactive fluid was slightly lower in the experimental series containing synthetic calcite with an average after 72 h of $3.35 \times 10^{-4} \pm 2.73 \times 10^{-5}$ M. The Ca concentration of the reactive fluid in the control experiments conducted in the absence of calcite remained the same as initial concentrations within error, indicating no measurable interaction between Ca in the fluid and the reactor walls, and no significant calcite precipitation or evaporation. Dissolved inorganic carbon concentrations remained relatively constant in all experiments between $4.0 \times 10^{-3}$ and $5.1 \times 10^{-3}$ M (Figure 3).
The initial solutions were slightly undersaturated with respect to calcite (saturation index (SI) = -0.63 and -0.47). As Ca concentrations increased, the SI of calcite approached equilibrium and remained effectively at equilibrium for the remainder of all experiments (Figure 3).

3.3 Temporal evolution of calcite isotopic composition

The initial δ¹³C composition of the natural Siberian calcite spar used for the large and small calcite experimental series was -0.23±0.06‰ (n = 13) and its initial δ¹⁸O composition was -16.11±0.37‰ (n = 13) (Table 3). The analysis of 13 different aliquots in total demonstrates only minor heterogeneity in initial composition. The initial δ¹³C and δ¹⁸O composition of the synthetic calcite was -9.09±0.04‰ (n = 3) and -19.10±0.04‰ (n = 3), respectively (Table 3). The δ¹³C and δ¹⁸O compositions of the calcite in all experimental series increased over time although the chemical composition of the fluid remained relatively constant (Figure 4). In all experiments, a rapid increase in both δ¹³C and δ¹⁸O of calcite was observed by the first sampling point (either 44 or 72 h). This rapid increase was followed by a slower but consistent increase in δ¹³C and δ¹⁸O of the solid throughout the remainder of the small and synthetic calcite experiments (Figure 4). In the large calcite experiments, the δ¹³C and δ¹⁸O composition of the calcite slowly increased between 72 and ~2112 h, after which no clear trend in composition was observed, but significant enrichment of the solids in ¹⁸O and ¹³C was sporadically recorded (Figure 4).

The extent of alteration of the δ¹³C and δ¹⁸O values of calcite was strongly dependent on grain size. The change in calcite isotopic composition was greatest in the synthetic calcite experiments, which had the finest grain size, followed by the small natural calcite, and the large natural calcite. A similar change in calcite isotopic composition over time was observed for both
sets of large calcite experimental series, despite their slightly different grain sizes (200-400 µm vs. 250-500 µm). In the large calcite experiments, δ¹³C increased from -0.23±0.06‰ to 0.55±0.06‰ within 1679 h and 1.12±0.06‰ within 2112 h in the first and second experimental series, respectively. The δ¹⁸O values of the large calcite increased from -16.11±0.37‰ to -15.81±0.07‰ within 1679 h and -15.12±0.07‰ within 2112 h in the first and second experimental series, respectively. In the small calcite experiments, δ¹³C values of the calcite increased from -0.24±0.06‰ to 37.05±0.06‰ in 3000 h and δ¹⁸O values of the calcite increased from -16.11±0.37‰ to 7.06±0.07‰. In the synthetic calcite experiments, δ¹³C values of the calcite increased to the greatest extent from -9.09±0.04‰ to 48.30±0.06‰ in 3000 h, and δ¹⁸O values of the calcite increased from -19.10±0.04‰ to 16.49±0.07‰.

The small and synthetic calcite generally exhibited a continuous increase in δ¹³C and δ¹⁸O values over time, albeit with some variability (Figure 4). The large calcite in both experimental series exhibited a low but positive change in δ¹³C and δ¹⁸O values over time during the first ~2112 h of the experiments (Figure 4). However, over longer time periods, large variability in isotopic composition was observed in both large calcite experimental series. For example, after 3000 h in the second large calcite series, the calcite in duplicate reactors had δ¹³C values of 1.06±0.06‰ and 9.18±0.06‰ and δ¹⁸O compositions of -15.41±0.07‰ and -10.13±0.06‰. Similarly, in the first large calcite experimental series after 9437 h, the calcite in duplicate reactors had δ¹³C values of 4.73±0.06‰ and 0.61±0.06‰ and δ¹⁸O compositions of -13.37±0.07‰ and -15.56±0.06‰. Repeated analysis of different aliquots of large calcite samples from the same reactor indicated the measurements were reproducible and likely not an artefact of measurement error or substantial heterogeneity in initial or reacted calcite composition. For example, the sample collected at 4656 h in the first large calcite experimental series was
measured three times, with a δ\textsuperscript{13}C composition of 26.69±1.06‰ (n = 3) and δ\textsuperscript{18}O composition of -1.22±0.75‰ (n = 3). The large enrichment in \textsuperscript{13}C and \textsuperscript{18}O in some large calcite reactors exhibited no discernible trend though anomalously high δ\textsuperscript{13}C were generally coincident with high δ\textsuperscript{18}O values. The lack of a temporal trend for the isotopic enrichment at longer timescales in the large calcite experimental series is evidenced by the large differences between duplicate reactors described, however it is noted that these sporadic high δ\textsuperscript{13}C and δ\textsuperscript{18}O values occurred in both large calcite experimental series at times greater than ~3 months only and not in the small or synthetic calcite experimental series.

The C and O exchange rate was calculated using equation 5, which indicated a similar surface area normalized rate of exchange for both the small and synthetic calcite, and a somewhat lower rate of exchange for the large calcite (Figure 5). Bulk rates, not normalized to surface area, indicate the highest rate of exchange for the synthetic calcite, followed by the small calcite, and finally the large calcite. After the initially rapid exchange during the first 72 h in all experimental series, the C and O exchange rates were relatively constant throughout the experimental series of the small and synthetic calcite and up to 2112 h in the large calcite experimental series. Due to the highly variable δ\textsuperscript{13}C and δ\textsuperscript{18}O compositions of the large calcite after 2112 h, only the data up to this time point are used to estimate exchange rates. The average rate of C exchange after 72 h was 1.98 (± 0.57) × 10\textsuperscript{-11} mol C/m\textsuperscript{2}/s, 2.93 (± 0.83) × 10\textsuperscript{-11} mol C/m\textsuperscript{2}/s, and 5.85 (± 1.42) × 10\textsuperscript{-12} mol C/m\textsuperscript{2}/s in the synthetic, small, and large calcite experimental series, respectively. The average rate of O exchange after 72 h was 5.83 (± 1.65) × 10\textsuperscript{-11} mol O/m\textsuperscript{2}/s, 8.69 (± 2.52) × 10\textsuperscript{-11} mol O/m\textsuperscript{2}/s, and 1.72 ± (0.60) × 10\textsuperscript{-11} mol O/m\textsuperscript{2}/s in the synthetic, small, and large calcite experimental series, respectively (Table 3). The average C and O exchange rate of the large calcite experiments was determined using an average of both
experimental series between either 44 and 2112 h or 72 and 1678 h before the occurrence of sporadic enrichment behaviour of $^{13}$C and $^{18}$O in both experimental series.

The molar ratio of O:C exchanged between calcite and fluid was an average of 2.93±0.02, 2.97±0.04, 1.92±0.56, and 3.56±0.64 in the synthetic, small, first large, and second large calcite experimental series, respectively (Table 3, Figure 6). The O:C exchange ratio was relatively constant in the synthetic and small calcite experimental series, increased over time in the first large calcite experimental series, and decreased over time in the second large calcite experimental series.

4. Discussion

4.1 C and O exchange processes

4.1.1 Initial C and O isotope exchange

In all experimental series, a rapid increase in $\delta^{13}$C and $\delta^{18}$O values was followed by a lower, but fairly constant rate of increase for the remainder of the small and synthetic calcite experimental series, and for up to ~2112 h in the large calcite experimental series. The change in the O and C isotope exchange rates after 72 h may indicate a change in the isotope exchange mechanism, or a change in reactivity of the solid over time or with depth as the reaction front infiltrates further into the calcite particles. The initial rapid increase of the solid $\delta^{13}$C and $\delta^{18}$O values may be attributable to exchange of surface species (e.g., Avrahamov et al., 2013; Géhin et al., 2021; Mozeto et al., 1984; Stamm et al., 2019). Assuming a density of calcite CO$_3$ surface sites of 8.22 × 10^{-6} mol/m$^2$ (Pokrovsky et al., 2000), the complete exchange of surface sites would result in 1 ×10^{-7}, 3 ×10^{-8}, 1 ×10^{-8} and 7 ×10^{-9} mols of C being transferred from the fluid to
the solid surface in the synthetic, small, first large and second large calcite experimental series, respectively based on the BET surface area of each material. This would generate $\delta^{13}\text{C}_{\text{calcite}}$ values of -6.46, 0.48, -0.12, and -0.06 ‰, respectively. These values are significantly lower than the measured $\delta^{13}\text{C}_{\text{calcite}}$ values (Table 3), which are consistent with up to 6.5-fold more C exchanged than can be attributed to surface sites alone. Calculated $\delta^{18}\text{O}$ values are similarly underestimated if exchange with the ideal surface site density is assumed. The implication is either that the site density is greater than predicted or that the mineral-fluid interaction extended beyond the surface layer. Calcite monolayers are ~0.5 nm thick (Subhas et al., 2017), indicating approximately 7, 6, 3, and 2 surface layers of calcite would need to completely exchange with the reactive fluid to produce the measured $\delta^{13}\text{C}$ values in the synthetic, small, and first and second large calcite experimental series, respectively (assuming each layer is comprised of $8.22 \times 10^{-6}$ mol CO$_3$/m$^2$). Similarly, approximately 6, 6, 1, and 2 surface layers of calcite would need to completely exchange with the reactive fluid to produce the measured $\delta^{18}\text{O}$ values in the synthetic, small, and first and second large calcite experiments, respectively. This extent of exchange is consistent with previous observations of C exchange between calcite and seawater in slightly undersaturated solutions, wherein 2 to 6 monolayers of calcite were observed to exchange within 48 h of reaction as determined by Secondary Ion Mass Spectrometry (SIMS) profiles (Subhas et al., 2017). In the present study, the fluids were initially slightly undersaturated with respect to calcite and dissolved to reach equilibrium within ~72 h. Thus, a similar process as documented by Subhas et al. (2017) may have operated in our experiments, whereby a backward (precipitation) reaction during calcite dissolution at close-to-equilibrium conditions results in isotopic alteration of the solid. In addition, Ostwald ripening involving the dissolution of calcite surface domains of excess free energy followed by precipitation on surface
domains of lower free energy could have contributed to isotopic exchange during the initial stages of the experiment, as these sites would exhibit greater reactivity than the bulk of the calcite surface. In the present study, we estimate the extent of C and O exchange between fluid and solid from the measured bulk isotopic compositions of the solids by mass balance. This assumes that the exchanged solid has the same isotopic composition as the fluid. The use of this approach may result in the underestimation of the number of monolayers impacted by isotopic exchange. Nevertheless, the good agreement of the results of this study with those of Subhas et al. (2017) suggests the observed rapid rate of exchange within the first 72 h of the experiment is likely attributable to isotopic exchange between the first 2-6 monolayers of calcite and the fluid, rather than a significant difference between the estimated and actual surface site density. The interaction with 2-6 monolayers of calcite implies that the Ca and O isotope exchange may occur by the combination of surface exchange, “backward” reaction, and Ostwald ripening (Géhin et al., 2021; Subhas et al., 2017). The loss of some, but not all, fine particulates at the small calcite surface over the course of the experiment is consistent with minor dissolution of the bulk crystals over the first 72 h and Ostwald ripening of higher energy surface sites (Figure 2). Ostwald ripening affecting approximately 0.3% of the surface of synthetic and small natural calcite grains could account for the observed early C and O isotope exchange with a calcite dissolution rate constant equal to $\sim 2 \times 10^{-7}$ mol/m²/s (Cubillas et al., 2005). In the case of large, well crystallized natural calcite crystals, it seems likely that the contribution of Ostwald ripening to the early isotope exchange should be less significant in accord with only approximately two surface layers affected by complete exchange.

4.1.2 Long-term C and O isotope exchange
After the initial rapid exchange, the rate of C and O exchange between fluid and calcite remained close to constant in the experimental series with small and synthetic calcite (Figure 5). The C and O rates of exchange were also fairly constant between 72 and ~2112 h of the large calcite experimental series before the sporadic behavior observed between ~ 2112 h and the end of the ~14 208 h and 5256 h first and second large calcite experimental series, respectively (Figure 5, Table 3). The extent of isotopic exchange during this slower exchange reaction using the homogeneous model would result in an approximate depth of reaction of a further ~7, 20, 2, and 1 nm, beyond that of the first 72 h in the synthetic, small, and first and second large calcite experimental series, respectively. This approximate depth of interaction suggests surface processes alone are not solely responsible for the continued isotopic alteration of the solid phase over time. Here, we assess the potential contribution of solid state diffusion and dissolution-precipitation processes to the continuous change in isotopic compositions of the solid phase.

4.1.2 Evaluation of diffusive processes

“Solid state” diffusion coefficients were estimated using the calculated moles of O or C exchanged by mass balance (eq. 2-4) during the second, slower stage of solid isotopic enrichment and equation 6 (Crank, 1975). As the extent of reaction is small compared to the crystal size, the particle shape was neglected and diffusion equations relative to a semi-infinite medium whose surface is maintained at a constant concentration were applied (Crank, 1975). The assumption of constant concentration at the calcite surface is justified by the very large $^{18}$O
and $^{13}$C enrichment of the spike relative to the solid. The following equation was used to estimate the diffusion coefficients (eq. 6):

$$\frac{M(t)}{a} = 2C_0 \left(\frac{Dt}{\pi}\right)^{0.5}$$  \hspace{1cm} \text{(eq. 6)}$$

where $M(t)$ is the moles of $^{18}$O or $^{13}$C transferred to the solid at a given time, $D$ is the diffusion coefficient ($m^2/s$), $t$ designates time elapsed between the first sample and a later sample time (s), $a$ represents the total calcite surface area ($m^2$), and $C_0$ is the $^{13}$C or $^{18}$O concentration in the fluid expressed as a mole fraction. $D$ was calculated for the final time point in the synthetic and small calcite experiments and at 1679 h and 2112 h in the first and second large calcite experiments, respectively. The values of $^{13}$C diffusion coefficients derived from Equation 6 for the long-term exchange in all experiments are $1.3 \times 10^{-24}$, $1.1 \times 10^{-23}$, $4.2 \times 10^{-26}$, and $1.2 \times 10^{-25} \text{ m}^2/\text{s}$ in the synthetic, small, and first and second large calcite experiments, respectively. The corresponding values derived for $^{18}$O diffusion coefficients are $1.3 \times 10^{-24}$, $1.0 \times 10^{-23}$, $2.0 \times 10^{-26}$, and $1.1 \times 10^{-25} \text{ m}^2/\text{s}$ in the synthetic, small, and first and second large calcite experiments, respectively. These diffusion coefficients are subject to substantial uncertainty as they are based on mass balance calculations only. Thus, the reported diffusion coefficients should be considered order-of-magnitude estimates at best.

The values of C and O isotope diffusion coefficients determined in the present study are comparable to the values reported in literature for ambient temperature experiments that investigated isotopic diffusion in calcite. Lahav and Bolt (1964) reported a diffusion coefficient of Ca in calcite of $8 \times 10^{-24} \text{ m}^2/\text{s}$, and Géhin et al. (2021) reported an effective diffusion coefficient for C in calcite on the order of $10^{-25} \text{ m}^2/\text{s}$, both in experiments conducted at 25°C. Notably, these experiments were conducted in the presence of a fluid phase, and the observed isotope exchange may be influenced by dissolution-precipitation, or aqueous diffusion in water-
filled pores in addition to true solid-state diffusion (Anderson, 1969; Géhin et al., 2021).

Interestingly, Géhin et al. (2021) report that calcite stored in dry conditions did not show evidence of isotopic exchange over similar timescales of their C aqueous isotope exchange experiments, implying that the presence of a fluid has a strong impact on the apparent diffusion coefficient of C in calcite. Fractures and higher porosity near the calcite surface, as observed in the natural calcite (Figure 2), would facilitate aqueous-mediated diffusion, which is many orders-of-magnitude faster compared to solid state diffusion (e.g., the diffusion coefficient of aqueous species at 25°C is \( \sim 8.00 \times 10^{-10} \, \text{m}^2/\text{s} \) (Mayer et al., 2002)).

Despite good agreement of the calculated diffusion coefficients in the present work with those previously reported for experiments conducted at 25°C, the estimated diffusion coefficients in the present study are many orders of magnitude higher than those determined by extrapolation from experiments conducted at high temperature. The majority of reported solid state diffusion coefficients for O and C in calcite are from studies conducted at temperatures of >200°C and range from \( 3 \times 10^{-32} \) and \( 2 \times 10^{-65} \, \text{m}^2/\text{s} \) when extrapolated to 25°C using the Arrhenius equation (Anderson, 1969; Bernard et al., 2017; Haul and Stein, 1955; Kronenberg et al., 1984).

Compared to solid-state diffusion in single crystals, grain boundary diffusion of O is described by a diffusion coefficient that is \( \sim 20 \) orders of magnitude larger at 25°C (Farver and Yund, 1998), similar to those measured in low temperature studies. Similarly, the complex, interconnected porosity in foraminifera tests facilitate greater diffusive exchange between \(^{18}\text{O}-\)enriched fluid and the solid compared to abiotic single calcite crystals (Cisneros-Lazaro et al., 2022). The lack of agreement between diffusion coefficients from experiments conducted at 25°C versus those at high temperatures for single crystals suggests that the higher diffusion coefficients at low temperatures may be attributable to the presence of fractures and
microporosity in the calcite and aqueous-mediated diffusion, possibly with some contribution of
dissolution-precipitation, rather than a solid-state process alone.

In the present study, the calculated ratio of O:C exchange is relatively close to the
expected stoichiometry of exchange of CO$_3^{2-}$ for most of the experiments (Figure 6). This O:C
ratio is consistent with a dissolution-precipitation process as the carbonate ion (CO$_3^{2-}$) would be
incorporated or lost from the calcite solid. The stoichiometry that would be generated by a
diffusive process would also be 3:1 if diffusion occurred as CO$_3^{2-}$ ions. Generally, C and O
diffusion coefficients in calcite have been documented to be of similar order of magnitude,
particularly at low pressure (Cherniak, 2010). At 100 MPA, O diffusion could be double that of
C due to a change in diffusion mechanism, with diffusion of CO$_3$ occurring primarily at lower
pressure (Cherniak, 2010). The rate of O diffusion in calcite is however, more sensitive than the
rate of C diffusion to factors such as Mn content of the calcite, $p$CO$_2$, and $p$H$_2$O, suggesting
some divergence in behavior could occur between C and O (Anderson, 1969; Kronenberg et al.,
1984; Labotka et al., 2011). The measured stoichiometry in the present study is consistent with
diffusion of the carbonate ion, as may be expected for solid state diffusion under certain
conditions, or diffusion of aqueous DIC (CO$_3^{2-}$, HCO$_3^-$).

The relative agreement between the estimated diffusion coefficients of our study and
those determined at similar temperatures implies that diffusion cannot be excluded as a potential
mechanism of C and O isotope exchange in our experiments. However, the trend of $^{13}$C and $^{18}$O
enrichment of the solid phase over time is not consistent with a pure diffusive mechanism, which
would tend to produce a parabolic temporal trend as implied by Eq. 6 (Figure 7). This suggests
that solid state diffusion is unlikely to be the only mechanism responsible for the isotopic
changes measured in the solid, regardless of the value of the diffusion coefficient.
4.1.2.2 Evaluation of dissolution-precipitation processes

Carbon and O isotope exchange over the longer timescales could also be attributed in part to a dissolution-precipitation process such as Ostwald ripening. Although Ostwald ripening likely contributed to the initial rapid isotope exchange within the first 72 h of the experiment, it is less clear whether it could account for the longer-term isotopic alteration of the solid phase. Apart from a loss of some fine grains at the surface of the small calcite, and a small number of instances of possibly newly formed calcite islands on select large calcite grains, no pervasive or consistent change in size or morphology of the calcite grains was documented during the experiments at the submicron-scale resolution of SEM (Figure 2; Figure S1). The surface roughness of both the small and large natural calcite was maintained throughout the experiments, as was the dominance of aggregates of >10 µm scale crystals in the synthetic calcite; indicating only minor, if any, surface restructuring occurred (i.e., below the resolution of SEM or occurring in few enough locations to not be observed). The lack of observable alteration of the surface and size of the calcite crystals suggests that dissolution-precipitation did not occur extensively. In addition, the C and O isotope exchange rate is ~4 orders of magnitude lower than the predicted dissolution rate of calcite at a pH of ~8 (Cubillas et al., 2005; Figure 5). It is not unexpected that dissolution-precipitation rates are lower near-to-chemical equilibrium due to differences in reaction mechanisms, for example, etch pits are not readily formed near-to-equilibrium (Arvidson and Luttge, 2010; Hellmann and Tisserand, 2006; Schott et al., 2012, 1989; Subhas et al., 2017). For instance, Subhas et al. (2017) observed a ~4 order-of-magnitude decrease in calcite dissolution rates in seawater as equilibrium was approached. It is therefore possible that
the low rate of C and O exchange relative to dissolution of calcite at far-from equilibrium conditions reflects dissolution-precipitation reactions only occurring at pre-existing reactive sites, such as defects, that results in a much lower surface area-normalized dissolution and precipitation rate compared to far-from-equilibrium conditions. This is consistent with the lack of observable alteration of surface morphology, as only a limited portion of the reactive surface would participate in the reaction. Reaction occurring only at pre-existing reactive sites implies that the isotope exchange front is likely not homogeneous, and that $^{18}$O and $^{13}$C enrichment may be concentrated only near defects and step edges; a hypothesis that requires imaging of C and O isotope distribution to confirm. If sufficient highly reactive sites were available, a constant rate of exchange of O and C would be expected, consistent with the relatively linear trends observed in our experiments. Such a process is consistent with a type of Ostwald ripening of reactive surfaces, as dissolution-precipitation at a small number of sites may not result in observable surface alteration.

The measured C and O exchange rates in all experiments in the present study are in good agreement with those reported by Chanda et al. (2019) for Ca isotope exchange between natural abiotic calcite and fluid at 25°C (Figure 5). The good agreement between the exchange rate of C measured in this study and the Ca exchange rate for abiotic calcite measured by Chanda et al. (2019) suggests Ca and CO$_3^{2-}$ are exchanged at similar rates, and thus potentially by similar mechanisms. A similar rate of Ca and C exchange is consistent with a dissolution-precipitation mechanism controlling isotopic exchange, as stoichiometric calcite dissolution and precipitation would result in the same molar rate of Ca and C transfer between calcite and fluid. Alternatively, similar solid state Ca and C diffusion coefficients and similar isotopic gradients would also result in similar exchange rates. In contrast, the rates measured in the present experiments were at least
two orders of magnitude higher than C exchange rates between natural abiotic calcite and fresh
groundwater at 25°C reported by Avrahamov et al. (2013) (Figure 5). The reason for this
discrepancy may be due to the use of natural waters in the experiments of Avrahamov et al.
(2013), rather than the synthetic NaHCO$_3$-CaCl$_2$ solution used in this study. Fluid composition,
such as salinity and Mg concentration, has been observed to impact C isotope exchange rates,
with C isotopic exchange occurring at a slower rate in saline water compared to low salinity
water (Avrahamov et al., 2013; Mozeto et al., 1984). Moreover, the calcite solid used in the
Avrahamov et al. (2013) study contained impurities such as quartz, dolomite, and clays, which
may have additionally impacted isotopic exchange.

The surface-area normalized isotopic exchange rates were consistent between
experiments with synthetic and natural calcite, and between different grain sizes, implying that
the observed absolute rates of C and O isotope exchange were mainly dependent on surface area.
The extent of isotopic exchange by both dissolution-precipitation and diffusion is expected to
depend on calcite surface area. However, the observation of similar surface-area-normalized
exchange rates between natural and synthetic calcite is inconsistent with previous studies that
have reported differences in isotope exchange rates due to chemical or crystallographic
differences between synthetic and natural calcite, and between abiotic and biogenic calcite
(Chanda et al., 2019; Cisneros-Lazaro et al., 2022; Kronenberg et al., 1984; Lahav and Bolt,
1964). A difference in Ca isotope exchange rates between biogenic versus abiotic calcite in the
study of Chanda et al. (2019) could be attributed to the higher amount of chemical impurities in
the biogenic calcite, facilitating greater dissolution and reprecipitation due to compositional
differences between solid and fluid. Cisneros-Lazaro et al. (2022) also observed a more rapid
alteration of δ$^{18}$O composition of biogenic calcite in foraminifera tests compared to abiotic
calcite, which the authors attributed to a diffusive process facilitated by connected porosity in the complex microstructure of the foraminifera. In the present study, both the natural and synthetic calcite contained only trace levels of metal impurities, which could explain their similar behavior. Moreover, the differences in morphology between natural and synthetic abiotic calcite are far less significant than between abiotic and biogenic calcite.

The relatively small mass of O and C estimated to have exchanged between fluid and solid based on bulk isotopic changes in the solids means that minor amounts of net precipitation cannot be absolutely excluded as an explanation of isotopic alteration. The number of moles of C incorporated in the solid to generate observed isotope changes is too small to generate a significant change in Ca concentration. Thus, the lack of change in Ca concentration in most experiments does not necessarily exclude a small amount of net precipitation. However, the lack of measurable change in DIC and relatively consistent fluid saturation state, coupled with the initial approach to equilibrium via dissolution, and the constant temperature of the experiments suggest there was unlikely a substantial driving force for precipitation to occur within the experiments, particularly at a constant rate over the entire duration of the experimental series. Thus, although it cannot be completely ruled out based on available data, net precipitation is unlikely the main process leading to isotopic alteration of calcite in the majority of reactors. The exception, however, may be the late time behavior of the large calcite experimental series.

The sporadic enrichment of the large calcite in both $^{18}$O and $^{13}$C over the longest experimental timescales has not been reported in previous studies, and the mechanism for its occurrence in the present study is unclear. Nevertheless, it is consistent with the isotope exchange rate being controlled by localized highly reactive sites rather than a homogeneous process, be it diffusion or dissolution-precipitation reactions at highly reactive sites. The
reproducibility of measurements on aliquots of samples from a single reactor, even over different analytical runs, suggests the observed changes are unlikely due to analytical issues with enriched samples. Similarly, the sporadic enrichment behavior was not observed in the small and synthetic calcite experiments which exhibited greater overall amounts of isotope exchange. We postulate that the continuous shaking of the reactors could have led to the generation of fractures in or roughening of the larger calcite crystals over time as they collided with each other and the reactor walls. This would facilitate greater access of the enriched fluid into the crystals as well as generate more highly reactive sites; the small islands of possible precipitates observed infrequently could be a result of this process (Figure S1). Thus, more rapid isotope exchange or incorporation of the enriched fluid could occur. The impact of this process would primarily be observed in the large calcite experiments partly because they were sampled over a longer time frame than the synthetic and small calcite experiments, and because the smaller particles with higher initial surface area would not be as significantly impacted by small changes in surface site availability.

4.1.3 Summary of proposed C and O isotope exchange processes at chemical equilibrium

Based on the observations of the present study, the following processes are proposed to explain the observed C and O isotope exchange operating over different time frames in our experiments. The first ~72 h of reaction is characterized by rapid exchange of surface species in combination with small amounts of precipitation during net dissolution within the first ~72 h, and Ostwald-ripening affecting surface areas of excess free energy on the calcite surfaces.
Between 72 h and ~2112 h during the large calcite experiments, and between 72 h and the end of the small and synthetic calcite experiments at 3000 h, the precise mechanism of isotope exchange remains ambiguous. However, the rates, time-dependent behavior, and stoichiometry of C and O exchange may reflect a combination of solid-state diffusion enhanced by aqueous diffusion in fractures and pores and dissolution-reprecipitation at existing steps or defects. The dissolution-precipitation process may represent a type of Ostwald ripening, whereby sites of higher surface energy are recrystallized to lower energy configurations. Finally, between ~2112 h and the end of the large calcite experiments, increased roughening of the calcite surface due to particle-particle and particle-wall collisions generates reactive sites that promote isotope exchange. The generation of reactive surface appears to be highly heterogeneous and does not occur for all calcite grains. The generation of surface area in the large calcite reactors is attributed to the experimental design, and is unlikely to be important for natural samples in quiescent sediments.

4.2 Implications

The use of the isotopic compositions of carbonate minerals as archives of past environmental conditions requires that the isotopic compositions imparted at the time of mineral formation are maintained for long time scales of hundreds of thousands to millions of years. When post-depositional recrystallization generates obvious chemical or morphological changes in carbonate archives, carbonate samples that have been visibly or chemically altered can be excluded from analysis. However, when isotopic compositions are altered without changes in the morphology or chemical composition of the carbonate at scales observable by typical tools such as light or scanning electron microscopy, it may not be possible to exclude isotopically altered
samples from analysis. Thus, it is necessary to understand the mechanisms and rates by which isotopic compositions of carbonate minerals may be altered to ensure samples can be selected and their compositions interpreted appropriately. Based on experiments conducted at 300°C, Bernard et al. (2017) suggested that diffusive processes operating over long timescales may alter $\delta^{18}$O values of foraminifera tests in sediment archives to such a significant extent that paleo-ocean temperature calculations may be altered by up to 15°C. Biogenic calcite tends to be altered more rapidly than abiotic calcite in experimental systems (Chanda et al., 2019; Cisneros-Lazaro et al., 2022), suggesting the abiotic carbonates like those used in our experiments may be less susceptible to post-depositional alteration. However, the present study demonstrates that distinct isotopic exchange between calcite and fluid can nevertheless occur at 25°C within short timescales of hours to months. Importantly, mass balance of C and O isotope exchange in our experiments demonstrates that the depth of isotopic alteration extends beyond the surface layer and is likely at least several nanometers below the calcite surface. If the exchange reaction continued to proceed at the same rate, it would take approximately 160 years to impact an entire crystal the size of the crystal edge of small calcite (~187 µm). However, it is possible that the rates may slow over time as the reaction front progresses further into the crystal so the extrapolation to longer timescales is likely to be overestimated, and it is unknown how the degree of isotopic equilibrium might impact exchange rates, if at all. If more realistic isotopic differences between solid and fluid are assumed compared to the experiments, substantial alteration of calcite isotopic compositions would occur if the experimental rates remained constant over time (Supporting Information Figure S2). For example, at the rate of O isotope exchange measured in the experiments with small natural calcite, it would take ~160 years for calcite with a surface area of 0.065 m²/g (equivalent to the small calcite) to reach isotopic
equilibrium with a fluid (Supporting Information Figure S2). Using the oxygen isotope
to fractionation factor of Daëron et al. (2019), assuming a fluid composition of 0.5‰ (VSMOW),
the calcite isotopic composition would change from its initial value of 14.3‰ (VSMOW) to
31.3‰ (VSMOW; Supporting Information Figure S2). Our experimental results imply that
significant alteration of the isotopic composition of carbonate minerals in sediments is possible
even under chemical equilibrium within decadal timescales. It should, however, be noted that
extensive alteration of the isotopic composition of calcite in natural systems would require
sustained isotopic disequilibrium between fluid and solid. In our experiments, the moles of C in
the solid and fluid were nearly equal. On the other hand, in a marine sediment, there is a far
greater mass of C in the solid than the fluid, suggesting that the fluid isotopic composition is
likely to be dictated by the composition of the solid post-deposition in the absence of substantial
fluid flow (Grimm et al., 2021). In the absence of fluid flow, however, the decomposition of
organic carbon, if present in the system, could maintain C isotope disequilibrium between calcite
and fluid. In the case of oxygen, there is approximately only twice the number of moles of O in
the solid than the fluid in a cubic meter of marine calcite sediment (40% porosity; Fantle and
DePaolo, 2007). This suggests the oxygen isotope composition of the solid may be more
sensitive to alteration than carbon isotopic compositions.

5. Conclusions

The results of this study suggest that the alteration of O and C isotope compositions of
calcite at Earth’s surface temperatures can proceed readily over short time scales, though the
extent to which this process continues to operate over geologic time scales is difficult to predict
at present. Rapid initial exchange between solid and fluid upon isotopic disequilibrium is attributed mainly to exchange of surface species. The process by which the observed slower rate of alteration of C and O isotope composition in calcite occurs over the longer time frames in or experiments remains uncertain. Carbon and O isotope alteration over longer time scales (>72 h) may proceed through a combination of dissolution-reprecipitation and solid state/aqueous mediated diffusion. The great utility of isotopic and trace element compositions of carbonates, however, highlights the necessity of a mechanistic understanding of solid-fluid exchange to allow robust interpretation of archives and sample selection. The present study represents a step towards this understanding, and demonstrates that abiotic calcite can undergo distinct C and O isotope exchange at low temperature over timescales of as little as weeks to months without morphologically visible evidence of alteration of the mineral.

Acknowledgements

The authors declare no competing interests. This study was supported by an NSERC Discovery grant (05324-2019), an NSERC Postdoctoral fellowship, an INSU Tellus Syster grant, and a Queen’s University Research Initiation grant to ALH. Meredith Watson is thanked for her assistance in the laboratory. We thank the AE, Mariette Wolthers, Hao Yan, and an anonymous reviewer for their constructive comments that helped improve this paper. We also appreciate the lab assistance and advice from Cristina Alvarez-Castillo and Andrea Perez-Fernandez, and helpful discussion with Martin Voigt, Christian Grimm, Franziska Stamm, and Giuseppe Saldi. We appreciate the AAS and alkalinity titration assistance from Carole Causserand. The Raimond Castaing MicroCharacterization centre, particularly Arnaud Proietti, are thanked for their
facilitation of SEM analyses, along with Agatha Dobosz at Queen’s University. Sylvia Reichelmann and Sebastian Breitenbach are thanked for conducting the C and O isotope analysis, and Ludovic Menjot (CNRS) for conducting the XRD analysis. We appreciate the donation of the calcite spar from Oleg Pokrovksy.
Table 1. Characterization of initial calcite

<table>
<thead>
<tr>
<th>Type</th>
<th>Size (µm)</th>
<th>BET surface area (m²/g)</th>
<th>Trace element composition*</th>
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<td></td>
<td></td>
<td></td>
<td>Mn (ppm) (±6.41)</td>
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<tr>
<td>large natural series 1</td>
<td>200-400</td>
<td>0.013</td>
<td>293.95</td>
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<td>large natural series 2</td>
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<td>0.019</td>
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<td>125-250</td>
<td>0.065</td>
<td>293.95</td>
</tr>
<tr>
<td>synthetic</td>
<td>~10</td>
<td>0.222</td>
<td>bq</td>
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</table>

\textsuperscript{a}elements present at > 1 ppm based on analysis of triplicate samples of initial natural and initial synthetic calcite

\textsuperscript{b}below quantification limit

Table 2. Initial experimental conditions

<table>
<thead>
<tr>
<th>Experimental series</th>
<th>Calcite type</th>
<th>Initial fluid δ¹³C (% VPDB)</th>
<th>Initial fluid δ¹⁸O (% VPDB)</th>
<th>Initial calcite saturation index</th>
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<tbody>
<tr>
<td>1</td>
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<td>18037</td>
<td>9861</td>
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<td>2</td>
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<tr>
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<td>18301</td>
<td>9851</td>
<td>-0.63</td>
</tr>
<tr>
<td>2</td>
<td>large natural</td>
<td>18301</td>
<td>9851</td>
<td>-0.63</td>
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<tr>
<td>Experiment</td>
<td>Sample time (h)</td>
<td>δ²⁹⁸C™</td>
<td>δ⁶⁰O™</td>
<td>Ca (× 10⁻⁹ mol/L)</td>
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<tr>
<td>---------------------</td>
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<tr>
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<td>-11.11</td>
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<td>2.98</td>
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<td>14208</td>
<td>25.21</td>
<td>-1.53</td>
<td>3.22</td>
</tr>
</tbody>
</table>

**Average:**

- Large natural calcite 1:
  - 0.23
  - 0.59
  - 0.99
  - 1.45
  - 2.31
  - 2.85
  - 3.00

- Average:
  - 0.99
  - 1.48
  - 2.36
  - 2.84
  - 3.00

- Small natural calcite:
  - 5.09
  - 6.24
  - 8.48
  - 10.56

- Average:
  - 5.09
  - 6.24
  - 8.48
  - 10.56

- Synthetic calcite:
  - -9.09
  - 8.78
  - 9.16
  - 28.35

- Average:
  - -9.09
  - 8.78
  - 9.16
  - 28.35

**Control 1:**

- 1.72
  - 3.71
  - 7.83

**Average:**

- 1.72
  - 3.71
  - 7.83
DIC = dissolved inorganic carbon, determined with PHREEQC from measured fluid composition. Average calculated for all time points after 72 h and less than 2112 h in the large calcite experimental series and all time points after 72 h in the small and synthetic calcite experimental series.

**Figure Captions**

**Figure 1.** X-ray diffraction patterns of initial calcite.

**Figure 2.** Scanning electron micrographs of initial large (a), small (b), and synthetic (c) calcite, and calcite at the end of the experiments for the large from the second experimental series (d; 5926 h), small (e; 3000 h), and synthetic (f; 3000 h) calcite.

**Figure 3.** Fluid composition versus time. a) Calcium concentrations versus time, b) Dissolved inorganic carbon concentrations versus time, c) pH versus time, and d) calcite saturation index versus time.

**Figure 4.** Isotopic composition of calcite over time in a) large natural calcite experimentsal series during the first 2112 h, b) small natural calcite experimental series, c) synthetic calcite experiments, and d) large natural calcite experiments for the total time series. Error bars are smaller than symbols employed if not otherwise visible.

**Figure 5.** Rate of isotope exchange versus time in all experiments. a) Carbon isotope exchange rates. b) Oxygen isotope exchange rates.
Figure 6. Stoichiometry of C and O isotope exchange.

Figure 7. Modeled versus measured extent of $^{13}$C exchanged with the fluid in a diffusion controlled reaction for small natural calcite. Experimental data are represented by circles, modelled data with dashed lines. Modelled lines are calculated using equation 6. The diffusion coefficients used for model calculations are indicated on the plot and were estimated from the experimental data either for the final data point ($D = 1.1 \times 10^{-23}$; this study 1) or for a visual best fit of the data ($D = 4.0 \times 10^{-24}$; this study 2), and from Gehin et al. (2021) ($D = 1 \times 10^{-25}$) and Lahav and Bolt (1964) ($8.0 \times 10^{-24}$).

Appendix A. Supplementary Material

The supplementary material includes two files, one with two figures, and the other a spreadsheet comprising raw XRD data. All other data are included in the manuscript.
References


Verlag.


a) initial large calcite

b) initial small calcite

c) initial synth calcite

d) final large calcite

e) final small calcite

f) final synth calcite
a) large calcite (<2112 h)

b) small calcite

c) synthetic calcite

d) large calcite complete time series
a) C isotope exchange rate

Chanda et al. (2019) Ca isotope exchange

Avrahamov et al. (2013) C isotope exchange

Cubillas et al. (2005) calcite dissolution rate

b) O isotope exchange rate

Cubillas et al. (2005) calcite dissolution rate
$^{13}\text{C}$ exchanged (mol)

Time (h)

- this study 1
- Lahav and Bolt (1964)
- this study 2
- Gehin et al. (2021)