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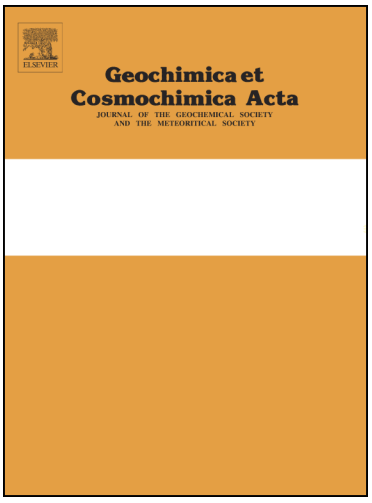

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Mechanism of Solid-State Clumped Isotope Reordering in Carbonate Minerals from Aragonite Heating Experiments

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Abstract

The clumped isotope compositions of carbonate minerals are subject to alteration at elevated temperatures. Understanding the mechanism of solid-state reordering in carbonate minerals is important in our interpretations of past climates and the thermal history of rocks. The kinetics of solid-state isotope reordering has been previously studied through controlled heating experiments of calcite, dolomite and apatite. Here we further explore this issue through controlled heating experiments on aragonite. We find that Δ_{47} values generally decrease during heating of aragonite, but increase by 0.05–0.15‰ as aragonite starts to transform into calcite. We argue that this finding is consistent with the presence of an intermediate pool of immediately adjacent singly-substituted carbonate ion isotopologues ('pairs'), which back-react to form clumped isotopologues during aragonite to calcite transformation, revealing the existence of kinetically preferred isotope exchange pathways. Our results reinforce the 'reaction-diffusion' model as the mechanism for solid-state clumped isotope reordering in carbonate minerals. Our experiments also reveal that the reordering kinetics in aragonite is faster than in calcite and

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dolomite, making its clumped isotope composition highly susceptible to alteration during early diagenesis, even before conversion to calcite.

Key Words: aragonite, calcite, clumped isotopes, phase transition, solid-state reordering, reaction-diffusion model

1. Introduction

The carbonate 'clumped isotope thermometer' is based on the preferential bonding of ^{13}C and ^{18}O atoms within the same carbonate ion group at low temperatures, which transitions toward a more random isotope distribution among carbonate ions at high temperatures (Wang et al., 2004; Ghosh et al., 2006; Schauble et al., 2006; Eiler, 2011). Carbonate clumped isotope abundances are reported using the Δ_{47} notation, which is the ratio of the mass 47 isotopologue of CO_2 ($^{13}C^{18}O^{16}O$) to the mass 44 isotopologue ($^{12}C^{16}O_2$) in CO_2 released from a carbonate mineral by acid digestion, normalized to the ratio expected for a stochastic isotope distribution (Wang et al., 2004). The thermometer is interpreted to reflect homogeneous isotope exchange equilibrium between isotopic forms of carbonate ions in the mineral:

$$^{13}C^{18}O^{16}O^{2}_{2}{}^{-} + {}^{12}C^{16}O^{2}_{3}{}^{-} \Leftrightarrow {}^{12}C^{18}O^{16}O^{2}_{2}{}^{-} + {}^{13}C^{16}O^{2}_{3}{}^{-} \quad (Rxn\ 1)$$

The temperature dependent equilibrium constant for this reaction can constrain the temperature of mineral formation or equilibration, independent of the carbon and/or oxygen isotope composition of the fluid from which the mineral grew, and of the mineral itself (Eiler, 2007; Eiler, 2011). This quality makes this proxy useful for reconstructing Earth-surface temperatures for geological times and locations where the ^{18}O content of the water is not well known (e.g., Thiagarajan et al., 2014; Tripati et al., 2014; Rodriguez-Sanz et al., 2017; Henkes et al., 2018). Carbonate clumped isotope thermometry has also been used to infer temperatures of processes

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that occur in the shallow crust such as diagenesis (Dennis & Schrag, 2010; Huntington et al., 2011; Cummins et al., 2014; Winkelstern & Lohman, 2016; Ryb & Eiler, 2018) and metamorphism (Ferry et al., 2011; Ryb et al., 2017; Lloyd et al. 2017).

The application of carbonate clumped isotope thermometry to the reconstruction of climate, water $\delta^{18}O$ values, or the thermal histories of rocks is complicated by the alteration of Δ_{47} values at elevated burial temperatures through solid-state reordering of C–O bonds (Passey & Henkes, 2012; Henkes et al., 2014; Stolper & Eiler 2015; Lloyd et al., 2017; Shenton et al., 2015; Gallagher et al., 2017; Lacroix & Niemi, 2019; Ryb et al., 2017; Ingalls, 2019). Previous studies have used controlled heating experiments to constrain the kinetics of solid-state isotope reordering of calcite (Passey & Henkes, 2012; Henkes, et al., 2014; Stolper & Eiler, 2015; Brenner et al., 2018), apatite (Stolper & Eiler, 2015) and dolomite (Lloyd et al., 2018). In these experiments, aliquots of the mineral of interest were held at a constant temperature for different amounts of time to create a time series over which the mineral Δ_{47} values could be observed to gradually approach equilibrium appropriate for that temperature. The rate of change of Δ_{47} values observed in such experiments constrains the kinetics of isotopic re-distribution among carbonate ions in the mineral lattice.

A key finding of these previous experiments is that solid-state alteration of Δ_{47} values in calcite, apatite, and dolomite all follow non-first-order kinetics. This finding has been interpreted as evidence that isotopic reordering is a two-stage process involving two mechanisms with different rate laws. Early in each set of time-series experiments, the rate of change of Δ_{47} values is dominated by a relatively fast process, which sharply transitions to a slower process that controls the remainder of the time series. Passey & Henkes (2012) attributed the initial rapid decrease in Δ_{47} in calcite to rapid diffusion facilitated by initially abundant lattice defects, and

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suggested the transition to slower kinetics reflects annealing of those defects, reducing their abundance and therefore the overall rate of isotopic re-equilibration. Stolper & Eiler (2015) proposed an alternative reaction-diffusion model to explain the two stages of calcite reordering. This model introduced the concept of 'pairs' and 'singletons'. Whereas a 'clump' is a carbonate group that contains both ^{13}C and ^{18}O, a 'pair' is a set of two adjacent carbonate groups, one of which contains ^{13}C and the other of which contains ^{18}O, while a 'singleton' is any carbonate group that contains either a single ^{13}C or a single ^{18}O, and has as immediate neighbors only carbonate ion units that lack ^{13}C and ^{18}O (i.e., they are all $^{12}C^{16}O_3^{2-}$). Stolper and Eiler (2015) suggested that clumped isotope evolution reflects rapid exchange between 'clumps' and 'pairs' coupled with slow diffusion-controlled separation of 'pairs' into isolated 'singletons' (Figure 1a). In this case, the reordering reaction is described by the equation:

$$^{13}C^{18}O^{16}O^{2}_{2}{}^{-} + {}^{12}C^{16}O^{2}_{3}{}^{-} \overset{k_f/k_b}{\Leftrightarrow} pair \overset{k_d/k_s}{\Leftrightarrow} {}^{12}C^{18}O^{16}O_{2,single}^{2-} + {}^{13}C^{16}O_{3,single}^{2-} \quad (Rxn\ 2)$$

where k_f is the forward rate of transformation of a clump and neighboring unsubstituted carbonate ion into a pair, k_b is the rate of back reaction of a pair to form a clump, k_d is the diffusion-controlled rate of separation of pairs to form singletons, and k_s is the rate of diffusion for singletons to remake pairs.

The presence of the intermediate pool of pairs can explain the two stages of clumped isotope reordering as follows (Stolper and Eiler, 2015): The first stage of rapid reaction is dominated by the formation of pairs from clumps through isotope exchange of immediately adjacent neighbors, while the second stage is dominated by diffusion in the crystal lattice. Because the second stage is slower than the first, the region surrounding initial clumps become saturated with pairs of singly-substituted carbonate ion units that have not yet diffused away from each other; back reaction of this saturated pool of pairs is what buffers the decrease in the

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Δ_{47} value during the slower, diffusion-limited stage of the time series. Stolper and Eiler (2015) did not offer an atomistic explanation for why the transition from clump to pair is faster than the separation of pairs — intuition might predict these should have the same rate, as both types of reactions involve migration of ^{18}O (and perhaps ^{13}C) from one carbonate ion unit to another. This unresolved aspect of the reaction-diffusion model is one of the inspirations for the present study.

While both the defect-annealing and reaction-diffusion models have been successfully applied to natural samples (Henkes et al., 2014; Shenton et al., 2015; Lloyd et al., 2017; Ryb et al., 2017, Ingalls, 2019), it has been argued that the reaction-diffusion model is favored by the observation that the kinetics of isotopic reordering in optical calcite, brachiopods, and deformed and undeformed natural marbles are indistinguishable from one another (the idea being that these diverse materials might be expected to differ in their initial defect populations; Stolper & Eiler, 2015; Ryb et al., 2017; Lloyd et al., 2018). Nevertheless, there is a strong motivation to establish which of these two interpretations (or perhaps some other not yet proposed) is correct. And, if the reaction-diffusion model is correct, we still must understand why it is that an initial exchange between two adjacent carbonate ion groups is significantly faster than subsequent, but otherwise generally similar exchanges. The answers to these questions will dictate how carbonate clumped isotope measurements are used to reconstruct temperature-time histories of rocks that have been heated during protracted burial in sedimentary basins, and may inspire new tools based on the physical processes that control this phenomenon.

In this study, we re-examine this problem through observations of the kinetics of Δ_{47} changes when aragonite is exposed to elevated temperatures, at either high pressure where aragonite remains stable during heating, or at low pressure where it transforms into calcite over the time scales of our heating experiments. This work was initiated to obtain constraints on the

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susceptibility of aragonite to clumped-isotope reordering at shallow crustal conditions. However, our initial experimental results made it clear that this process provided an unexpected window on the atomistic mechanisms of the general phenomenon of clumped isotope reordering.

Aragonite is a polymorph of calcium carbonate that is common in nature, despite the fact that it is thermodynamically unstable at Earth surface conditions and readily transforms into calcite through heating or dissolution-reprecipitation reactions (Jamieson, 1953; Bischoff, 1969; Carlson, 1980; Budd, 1988). Clumped isotope compositions of aragonite follow the same temperature vs. Δ_{47} calibration curve as other carbonate minerals (Ghosh et al., 2006; Thiagarajan et al., 2011; Bonifacie et al., 2017). Clumped isotope compositions of fossil aragonite have been used in paleoclimate reconstructions of the recent ice age (Thiagarajan et al., 2014) and deeper times of the Phanerozoic (Dennis et al., 2013). Given its thermodynamic instability, it has generally been assumed that aragonite found in nature has been unaltered in its elemental and isotopic compositions. Recently, it has been shown in laboratory experiments and natural speleothems that the carbon, oxygen, and clumped isotope compositions can all be altered during the aragonite to calcite phase transition (Zhang et al., 2014; Staudigel & Swart, 2016). In particular, Staudigel & Swart (2016) observed complicated clumped isotope reordering patterns in aragonite heating experiments over a range of temperatures (125–425°C), including unexpected increases in Δ_{47} values during the heating process in certain experiments. These increases in Δ_{47} values are, however, not consistently observed in all their experiments, and are statistically indistinguishable from the previous time step in many cases. The authors noted these complexities but described aragonite reordering with a first order kinetic model. Staudigel & Swart (2016) also noticed that aragonite reordering initiates at lower temperatures than does calcite. However, a systematic decreasing trend in the bulk isotope composition (2.5‰ in $\delta^{18}O$

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and 1.5‰ in $\delta^{13}C$) with time was observed in these experiments, suggesting a possible influence of open system exchange that would complicate the interpretation of these data as simply reflecting the solid-state reordering process.

We present new aragonite reordering experiments that reproduce and extend the previously observed complex clumped isotope reordering patterns, and we explain these findings as natural consequences of the reaction-diffusion model in a system undergoing a phase transition. We then test this hypothesis further through experiments in which we manipulate the distributions of clumped, pair, and singleton carbonate groups by preliminary thermal treatments to aragonite and calcite, and then observe the effect of those treatments on the solid-state reordering kinetics of both phases in a second heating experiment (Figure 1b,c). We summarize our hypothesis and experimental tests in the reaction-diffusion framework with a fluid-flow analogy in Figure 1, which are detailed in the following sections. Our experimental results suggest the presence of an intermediate pool of pairs in both aragonite and calcite, re-enforcing the reaction-diffusion model of clumped isotope reordering.

2. Materials and Methods

2.1 Aragonite Samples

The aragonite used in our experiments was obtained from Tazouta, Sefrou Province, Fès-Boulemane, Morocco. It is a fist-sized aggregate of faceted intergrown crystals that are 0.5–1 cm in size. The sample was chosen due to its size, visual homogeneity and low-temperature origin. Replicate analysis (n = 21) of the bulk and clumped isotope composition of the aragonite yields a $\delta^{13}C$ value of 7.53±0.17‰ (VPDB), a $\delta^{18}O$ value of –7.49±0.19‰ (VPDB), and a Δ_{47} value of 0.757±0.028‰ (means and aliquot-to-aliquot standard deviations; all reported Δ_{47} values are

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given in the absolute reference frame following Dennis et al., 2011). The Δ_{47} value corresponds to a formation temperature of 16±5°C (Dennis et al., 2011). The reported standard deviations of bulk and clumped isotope compositions are higher than the long-term reproducibility of carbonate standards at Caltech (0.03‰ for $\delta^{13}C$, 0.08% for $\delta^{18}O$, 0.02‰ for Δ_{47}), and suggest some natural heterogeneity within our sample. In interpreting our experiment results, we consider a measured isotope composition of a sample significantly different from others only when these differences exceed the internal variabilities in the starting materials.

2.2 Aragonite Reordering Experiments

The aragonite crystals were coarsely crushed into ~10 mg fragments (each ~1–2 mm across). The crystals were not further reduced in grain size because we wished to minimize the surface area and therefore any effects of adsorbed water or other surface chemistry. Approximately 20 mg of aragonite fragments were sealed in ¼″ quartz or Pyrex® tubes with 6.6 kPa isotopically distinct CO_2 gas ($\delta^{13}C$ = –11‰, $\delta^{18}O$ = +16‰, VPDB) in the headspace. The CO_2 gas was cryogenically purified with a dry ice-ethanol mixture to remove water vapor. The experiments were carried out under CO_2 atmosphere to minimize decarbonation of the aragonite, as well as to detect whether open-system isotope exchange reactions had occurred. The tubes containing aragonite and CO_2 were put into a box furnace held at one of several prescribed temperatures (200–500°C). For each temperature, different aragonite samples were heated for different lengths of time to create a time series of clumped isotope reordering. After heating, we weighed each sample and determined the fractions of aragonite and calcite in the samples by X-ray diffraction (XRD) or Raman spectroscopy before isotope compositions were measured. For most samples, the weight loss is <0.3mg before and after heating, and the bulk isotope

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compositions are within the initial heterogeneities of the starting material, consistent with no decarbonation or open-system exchange (Table 1, Figure 2c,f). In three of the heating experiments, the aragonite was run in unsealed tubes and thus was exposed to the ambient atmosphere (Table 1). As with the sealed tube experiments, no significant decarbonation or open system exchange was observed for these three experiments. The aragonite to calcite phase transition was faster when exposed to the ambient atmosphere (Figure 2b,e), but the clumped isotope reordering pattern was similar to the experiments with sealed tubes.

2.3 High-Pressure Aragonite Experiment

For this experiment, we used a cylinder cored from a large crystal that comprised a portion of our aragonite sample. The core (260 mg) was loaded into a 0.2″ (outer diameter) Au capsule welded at both ends (for the second weld, the capsule was partially immersed in a water bath to minimize any heating of the aragonite). The capsule was run in a 1/2″ piston cylinder pressure vessel using an assembly that consisted of inner pieces of MgO (dried at 1000°C for ~8 hours), a straight-walled graphite furnace, and an outer sleeve of calcium fluoride. Temperature was monitored and controlled to within 1°C of the set point using a $W_3Re/W_{25}Re$ thermocouple (care was taken to avoid thermocouple oxidation by bleeding N_2 gas into the slot in the thermocouple plate). Run conditions were 1.7 GPa and 600°C and the sample was quenched after 10 days. Based on thermocouple output as a function of time, the sample cooled to room temperature in ~30 s. The experiment was designed to equilibrate the clumped isotope composition (and potentially the concentration of pairs) at high temperature while maintaining aragonite in its stability field. The *P-T* conditions of the experiment were well within the aragonite field based on the $CaCO_3$ *P-T* phase relations compiled by Carlson (1980), and Raman

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spectroscopy showed that the post-run material was, indeed, aragonite (Figure 3c). Next, an aliquot of this *P-T*-treated aragonite was measured for bulk and clumped isotope composition, while other fragments went through a reordering experiment at 350°C at ambient pressure in a CO_2 atmosphere (see Section 2.2) before isotopic analysis. A 350°C reordering experiment using untreated fragments of the aragonite was carried out in parallel for direct comparison.

2.4 Two-Step Calcite Heating Experiment

The two-step calcite heating experiment was designed to test if the complex clumped isotope reordering behavior in aragonite, in particular increases in Δ_{47} during heating, can occur in calcite. An optical calcite (catalog # N21-1) was selected from the Caltech mineral collection for its size, clarity, lack of visible defects or inclusions, and its relatively low-temperature origin. Bulk and clumped isotope analyses (n = 17) yield a $\delta^{13}C$ value of –1.55±0.45‰ (VPDB), a $\delta^{18}O$ value of –16.96±0.30‰ (VPDB) and a Δ_{47} value of 0.586±0.006‰, which corresponds to a temperature of 63±3°C (Bonifacie et al., 2017). While the bulk isotope compositions of this calcite show substantial heterogeneity, the clumped isotope composition is relatively homogeneous. The sample was crushed into 10–30 mg fragments and sealed in quartz tubes with 6.6 kPa purified CO_2 gas that is isotopically distinct ($\delta^{13}C$ = –11‰, $\delta^{18}O$ = +16‰, VPDB) in the headspace. The tubes were initially heated at 450°C for 5 hours, and cooled quickly to room temperature (within ~2 minutes) using a compressed air duster. In the second step of this experiment, the pretreated samples from the first step were heated at 500°C for different time intervals. We repeated this experiment twice to generate a replicate set of samples.

2.5 Mineralogy

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In order to determine the extent to which aragonite transformed to calcite during the low-pressure, high-temperature experiments, samples were analyzed post-run by XRD or Raman spectroscopy. XRD measurements were performed with a Bruker D2 Phaser benchtop instrument (Cu K_α source) at Caltech. Relative peak areas at specific 2θ angles (30° for calcite, 46° for aragonite) were compared to determine the proportions of aragonite and calcite in the samples, using an approach similar to Dickinson & McGrath (2001). Relative peak areas were converted to mass fractions with a calibration curve generated from powder mixtures of pure aragonite and calcite. The detection limit of the method is approximately 1% for calcite and 5% for aragonite.

The Raman measurements were performed on a Renishaw M1000 Micro Raman Spectrometer at Caltech. The system uses a solid-state 514.3 nm laser with 100 mW beam power, and the measurements were done with 10% power at 5x magnification (~2 mW on sample) to minimize sample damage and maximize the covered area. Multiple spots (n = 5–10) were measured for each sample to get an average spectrum. Following Dickinson & McGrath (2001), the relative proportions of aragonite and calcite were determined using the scattering peaks for the carbonate ion planar bending mode (704 cm^{-1} for aragonite, 713 cm^{-1} for calcite). Relative peak areas were converted to mass fractions with a calibration constructed from powder mixtures of pure aragonite and calcite (Figure 3). The peak areas scale close to 1:1 with mass fractions in the calibration standards. The Raman method was used for most samples because it requires less material than the XRD method we employed, and limited amounts of sample were recovered from each experiment (especially the high-pressure experiment described in Section 2.3). We also viewed the Raman measurement as more robust because of the greater linearity of its calibration trend.

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2.6 Stable Isotope Measurements

The bulk and clumped isotope compositions of the samples were measured using a Thermo MAT253 isotope ratio mass spectrometer at Caltech. Sample preparation and analysis procedures have been previously described in detail (Ghosh et al., 2006; Guo et al., 2009; Huntington et al., 2009; Passey et al., 2010). In brief, samples (~10 mg) were digested in phosphoric acid at 90°C. Evolved CO_2 gas was purified cryogenically and went through a Porapak Q (50/80 mesh) GC column held at –20°C, and then measured against a reference CO_2 gas. The measurements were standardized to heated (1000°C) and water-equilibrated (25°C) CO_2 gases, and in-house carbonate standards. In the calculation of bulk and clumped isotope compositions, we used the $^{17}O/^{16}O$, $^{18}O/^{16}O$ ratios for VSMOW and the $^{13}C/^{12}C$ ratio for VPDB suggested by Brand et al. (2010), which were found to minimize inter- and intra-laboratory discrepancies in reported Δ_{47} values (Schauer et al., 2016; Daëron et al., 2016). Measurements and uncertainties were calculated in the absolute reference frame (Dennis et al., 2011) following Daëron et al. (2016).

3. Results

3.1 Aragonite-Calcite Phase Transition

Given its instability under ambient pressure, aragonite is expected to transform into calcite during our low pressure heating experiments. XRD and Raman spectroscopy measurements confirm this general prediction, although there is significant variation in the reaction progress as a function of time (Figure 2b,e). Similar variations in reaction progress were observed in the XRD powder patterns in the aragonite heating experiments of Staudigel & Swart (2016). This is likely related to the phase transition progressing inhomogeneously through the

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crystal lattice. Nevertheless, the overall pattern of the time and temperature evolution of the reaction is clear: At 200 and 300°C, we observed negligible production of calcite over the course of our experiments. Significant amounts of newly grown calcite were observed at temperatures of 350°C and above. When the samples were exposed to the ambient air (rather than being heated in a pure CO_2 atmosphere), 80% of the aragonite was converted to calcite in 72 hours at 350°C (Experiment SC-C). However, such rapid conversion at this relatively low temperature was atypical; the experiments conducted at 350°C in a CO_2 atmosphere underwent 5–25% conversion after 72 hours (Experiment SC-D, SC-E and SC-H). We conclude that when the reaction proceeds in air the phase transformation is accelerated, perhaps due to the presence of water vapor. At 400°C and 450°C, aragonite was mostly converted to calcite within 10 hours. At 500°C, nearly complete conversion to calcite was achieved in 40 minutes (Figure 2e). Previous studies that conducted in-situ XRD and FTIR characterizations of the aragonite to calcite phase transition show a more rapid conversion over a period of ~10 minutes as the temperature is raised to 400–450°C (Antao & Hassan, 2010; Koga et al., 2013). Other experimental studies have found timescales for the phase transition more similar to what we observe, from minutes to hours above 400°C, depending on the sample origin, grain sizes and the experimental method (Davis & Adams, 1965; Madon & Gillet, 1984; Koga et al., 2013; Staudigel & Swart, 2016). Thus, we find a threshold temperature for significant phase transition similar to that observed in previous studies, and rates of conversion that lie at the slower end of the spectrum of values reported in previous work. We suspect that the relatively slow rate of the phase transition measured in our experiments is related to the length scale of the techniques we used to characterize crystal structure for most of our experimental products. XRD (used for only a few of our samples) observes structures that are coherent over hundreds to thousands of unit

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cells (10^{-8}–10^{-7} m), whereas Raman spectroscopy (used for most of our samples) observes structural properties at length scales corresponding to the wavelengths of infrared light (10^{-6} m). As a result, phase transitions detected by Raman spectroscopy might be seen to occur later than those detected by XRD (i.e., assuming phase transformation is structurally coherent over longer length scales as time progresses). This suspicion is supported by the observation that our XRD characterization of the phase transition at 400°C indicated that it was completed in two hours, faster than the 450°C experiment measured by Raman spectroscopy.

3.2 Clumped Isotope Reordering of Low-Temperature Aragonite

Given the thermodynamic basis for the carbonate clumped isotope thermometer, it is expected that the Δ_{47} value of a carbonate mineral that initially grows at low-temperature and then is subjected to a higher temperature will monotonically decrease in Δ_{47} until it approaches the new, higher temperature equilibrium state of a lower Δ_{47} value (Figure 1a). This behavior was previously observed in calcite, apatite, and dolomite reordering experiments (Passey & Henkes, 2012; Henkes et al., 2014; Stolper & Eiler, 2015; Lloyd et al., 2018; Brenner et al., 2018). The reaction progress of solid-state isotopic reordering we observe in aragonite violates this expectation. Following an initial rapid decrease in Δ_{47}, we observe abrupt increases in Δ_{47}, with amplitudes in the range of 0.05–0.15 ‰, followed by a more gradual decrease in Δ_{47} values toward the thermodynamic equilibrium values (Figure 2a,d, Figure 4). This complex pattern has amplitudes of initial fall and subsequent rise that are large multiples of our analytical precision, and was observed to be significant and generally homologous in form in all of the experiments in which there was significant contrast between the initial and final equilibrium Δ_{47} values.

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In our 350°C experiments conducted in both air (SC-C) and CO_2 (SC-D and SC-E), it is clear that there are two separate increases in Δ_{47} in the first 24 hours, separated by an intermediate 'dip', and that both of the increases and all three periods of decrease are statistically well resolved (Figure 2a, 4). There is a suggestion that the 450°C experiment conducted in air could also have two separate periods of increasing Δ_{47}, but the first of them is not clearly resolved from the surrounding pattern of decreasing Δ_{47}. Experiments conducted at higher and lower temperatures have only one increase in Δ_{47} during the reordering process.

For most series of experiments conducted at one temperature, the first (or only) increase in Δ_{47} observed mid-way through the heating period occurred at the initial stage of the phase transition, i.e., the sample contained less than 20% calcite as determined by XRD or Raman spectroscopy (Figure 4). However, as the proportion of calcite increases (i.e., >20%), the Δ_{47} values decrease again with further heating. Because the timing of the first appearance of calcite and time-evolution in the calcite/aragonite ratio are somewhat irregular in detail, it is not always clear how the rate and direction of change in Δ_{47} relates to the progress of the aragonite to calcite phase transition. However, when we plot the percentage of calcite vs. the Δ_{47} value (a bulk measurement of both aragonite and calcite), it is clear that increases in Δ_{47} occur early in the progress of the aragonite to calcite transition (Figure 4). In summary, the reorganization of ^{13}C and ^{18}O (i.e., changes in Δ_{47} value) that occurs when aragonite is heated can be described as a (at least) three-stage process: initial destruction of ^{13}C–^{18}O bonds (decrease in Δ_{47}), followed by a re-formation of ^{13}C–^{18}O bonds (increase in Δ_{47}), followed by a monotonic decay in ^{13}C–^{18}O bonds until the high temperature equilibrium Δ_{47} value is reached. As noted above, in some experiments, a second cycle of increase and subsequent decrease in Δ_{47} is observed. The stage or stages of heating during which ^{13}C-^{18}O bonds re-form is both a strong departure from

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thermodynamic equilibrium at the conditions of the experiment, and clearly first occurs during the early stage of aragonite to calcite transition. This pattern is reproducible across a temperature range of more than 100°C. We also note that the Δ_{47} values approach equilibrium at rates that are statistically indistinguishable from the calcite reordering experiments (Passey & Henkes, 2012; Henkes et al., 2014; Stolper & Eiler, 2015) after most of the aragonite has been converted to calcite.

3.3 Clumped Isotope Reordering of High-Temperature-Equilibrated Aragonite

The aragonite heated at 600°C at high-pressure for 10 days achieved a clumped isotope composition (Δ_{47} = 0.283±0.016‰) that is within error of the expected equilibrium at 600°C (Δ_{47_eqm} = 0.273±0.021‰, Bonifacie et al., 2017) (Note that $\delta^{13}C$ and $\delta^{18}O$ of this material are similar to other samples of the starting material: 7.43‰ and –7.12‰, VPDB, respectively; Figure 2f). When this pretreated aragonite was subsequently subjected to a second stage of heating at 350°C in a CO_2 atmosphere, the Δ_{47} increased slightly over the course of 72 hours to the somewhat higher Δ_{47} value expected for equilibrium at 350°C, accompanied by 22% conversion of aragonite to calcite (Figure 2d,e, Figure 4a,d). The amount of phase transition is similar to the untreated low-temperature aragonite going through the same reordering experiment, but we see no evidence for a sharp rise in Δ_{47} in the middle of the second heating period, as occurred when non-pre-treated aragonite was subjected to this same low-pressure heating schedule (Figure 4a,d). A key feature of the high P-T treatment performed on this sample is that it involved a time-at-temperature sufficiently prolonged such that the reaction-diffusion model would predict complete mutual equilibration of all three populations of isotopic species: clumps, pairs and singletons (Figure 1c). This series of experiments demonstrates that the anomalous rise

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in Δ_{47} associated with conversion of aragonite to calcite does not occur in materials that have already attained a fully equilibrated high-temperature isotopic structure due to a long, high-temperature 'soak'; that is, this phenomenon requires that the aragonite to calcite transition takes place in a material that has experienced a sharp drop in Δ_{47} within the previous few hours. This finding also indicates that the increase in Δ_{47} does not arise through a kinetic isotope effect associated with the aragonite to calcite transition (i.e., a dependence of the rate of phase transition on the isotopic composition of the carbonate groups).

3.4 Clumped Isotope Reordering in a Two-Step Calcite Experiment

After we subjected two samples of calcite to a first heating treatment of 450°C for 5 hours, their Δ_{47} values dropped from 0.586‰ to 0.474‰ and 0.426‰, respectively, without significant changes in their bulk $\delta^{13}C$ or $\delta^{18}O$ (Table 1, Figure 5). When each of these pre-heated calcites were subjected to a second heat treatment at 500˚C, their Δ_{47} values increased by 0.03–0.06‰ in the first 15 minutes of the second heating treatment, before decreasing again afterwards. Interpretation of this experiment must be equivocal as the variations in Δ_{47} that we observe are near the 2 standard error limit of significance. Nevertheless, both experimental series suggest that it is possible to subject calcite to a heating schedule that creates subtle but resolvable increases in Δ_{47} in the absence of a phase transition. The specific heating schedule we selected to create this effect was based on a prediction of the reaction-diffusion model, and this experiment is important to our efforts below to interpret and generalize the more pronounced Δ_{47} increases we observe during the aragonite to calcite transition.

4. Discussion

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The formation of excess $^{13}C–^{18}O$ bonds (producing an increase in Δ_{47}) during high-temperature transformation of aragonite to calcite is a significant, reproducible observation of this study and appears to act opposite to thermodynamic driving forces. Yet it also is not a kinetic isotope effect associated with some elementary step of the phase transformation, as no such isotopic reordering is observed when aragonite is allowed to achieve a fully equilibrated high-temperature isotopic structure prior to transformation to calcite. This phenomenon has not only been reproduced in our experiments, but also resembles the similar (though less regular) findings of previous heating experiments performed on aragonites of different origins (Staudigel & Swart, 2016). Moreover, we see suggestive evidence that the same phenomenon can be made to occur in calcite, absent any phase transformation, provided the calcite is subjected to a specific heating schedule. We find no evidence that any of these effects are accompanied by changes in bulk isotopic content ($\delta^{13}C$ and $\delta^{18}O$) that might provide evidence for open system reactions. We suggest that this behavior is an integral feature of solid-state isotopic reordering in carbonate minerals that needs to be incorporated in future reordering models.

In the following discussion, we describe how this behavior can be conceptually explained by the reaction-diffusion model of Stolper & Eiler (2015). We also discuss the new insights these findings provide regarding the kinetics of atomic mobility within carbonates and the kinetics of the aragonite to calcite transition. Finally, we use these results to support the presence and significance of pairs in carbonate minerals, and to generalize the reaction-diffusion mechanism across carbonate minerals

4.1 The Reaction-Diffusion Model and High-Temperature Formation of Excess $^{13}C–^{18}O$ Bonds

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418 Increases in Δ_{47} during a high-temperature heating step are a previously unrecognized
419 prediction of the reaction-diffusion model of Stolper and Eiler (2015). Specifically, we now
420 recognize that this phenomenon is a natural consequence of the fact that disproportionation of
421 clumps to form pairs leads to a brief period of time (typically hours at the temperatures of our
422 experiments) when the pairs have not yet diffused apart to form singletons and have the potential
423 to back-react to re-form clumps (Figure 1b).

424 Stolper and Eiler (2015) proposed the reaction-diffusion model as a way of explaining the
425 kink in the time evolution of decreasing Δ_{47} values; specifically, they suggested that this feature
426 marks the time when the rate of net formation of pairs by breakdown of clumps is nearly
427 balanced by the rate of diffusive separation of pairs to form singletons.

428 We observe several low-pressure time-series where Δ_{47} values rise sharply during the
429 aragonite to calcite transition, with amplitudes of 0.13–0.18‰, or roughly 30–40% of the
430 contrast between the initial Δ_{47} value and the Δ_{47} value the carbonate would have after fully
431 equilibrating at the temperature of the experiment. Interpreted in the context of the reaction-
432 diffusion model, this implies that the reaction of a clump to form a pair largely reverses at the
433 onset of the aragonite to calcite transition (i.e., 50–80% of clumps destroyed during the earliest
434 stage of heating temporarily re-form). For experiments with two separate Δ_{47} increases at 350°C,
435 the second increase is almost a quantitative reversal of the previous drop in Δ_{47}.

436 Perhaps the strongest argument that an intermediate pool of pairs is required to drive Δ_{47}
437 increases at high temperature comes from the lack of a Δ_{47} rise when aragonite is given a long,
438 very high temperature, high pressure 'soak' before the aragonite to calcite transition (see section
439 3.3 above). This experiment indicates that the sharp increases in Δ_{47} are only a feature of

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aragonite that undergoes transformation to calcite immediately (within minutes to hours) after its Δ_{47} has decreased in response to heating.

This can be understood as a consequence of the pair mechanism: For all of our experiments involving a single, low-pressure stage of heating, clumps are transformed to pairs early in the experiment, but those pairs have not had enough time to diffusively separate to form singletons, so they are present as a potentially reactive pool of excess pairs when the phase transformation occurs (Figure 1b). In aragonite that has undergone long, high-temperature, high-pressure heating, the pool of pairs has been depleted through diffusion to form singletons, removing that pool of excess pairs (Figure 1c).

We hypothesize that the reformation of clumps from an over-abundant pool of pairs is associated with the rearrangement of carbonate ions in the crystal lattice on the unit-cell scale. Several models have been proposed to describe the atomistic mechanism of the aragonite-calcite phase transition. Previous studies agree that this solid-state transition involves displacement of calcium layers relative to carbonate layers, and 30° rotations of carbonate groups (Madon & Gillet, 1984; Antao & Hassan, 2010; Miyake & Kawano, 2010). The rotation of carbonate groups converts the 9-coordinated aragonite structure to the 6-coordinated calcite structure, and clearly involves reorganization of Ca–O bonds (Madon & Gillet, 1984; Miyake & Kawano, 2010). However, prior studies did not specify whether this reorganization of the geometries of carbonate ions is accomplished by the breaking and re-forming of C–O bonds or simply involves motions of carbonate ions with respect to one another. Our findings that the aragonite-to-calcite reaction is accompanied by a large change in ^{13}C–^{18}O ordering suggests that the first possibility is the case.

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Each O atom in the aragonite lattice has up to eight nearest neighbor O atoms (i.e., those that can be reached in a straight line, omitting those that share the moving atom's own carbonate ion unit, and noting that some sites that are 'adjacent' by this definition are much closer than others; Figure 6a). Thus, if the clump-to-pair transition involved purely random movement of O atoms from one carbonate ion unit to a randomly-selected neighbor, and that the aragonite to calcite transition was accompanied by a second random exchange of an O atom with one of its set of possible 'straight line' nearest neighbors, it should only be possible to recover a small fraction of the original clumped isotope signature (i.e., most ^{18}O atoms that make the first jump away from a clump will not return to their original carbonate ion unit on their second jump; nor are they likely to reach another ^{13}C atom on making a second jump). The fact that most of the Δ_{47} signature that was initially lost is recovered suggests that the transition from clumps to pairs preferentially involves O exchange between only one (or perhaps two) of the possible nearest neighbor pairs, and that the aragonite to calcite transformation is accompanied by an O exchange that takes advantage of that same preferred oxygen site or sites. This might be expected if one of the possible pathways for exchanging an O atom between two carbonate groups has a lower activation energy than any of the other possible exchange mechanisms, and so occurs at a higher rate. In the 9-coordiated aragonite structure, there are five different Ca–O bonds and two non-equivalent oxygen sites, O1 and O2 (Figure 6a; Antao & Hassan, 2010; Ye et al., 2012). The strengths of the Ca–O and C–O bonds for these two oxygen sites are different, which we anticipate could give rise to different activation energies of the various possible oxygen exchange pathways. In particular, the three exchange pathways labeled in Figure 6a involve breaking the weakest bonds in the aragonite structure and, we suggest, could be energetically favorable. Two of these three pathways involve an O1–O2 exchange (pathways 2 and 3 in Figure

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485 6a). After exchange through these two pathways, the aragonite-calcite phase transition would
486 keep the singly-substituted carbonate groups in neighboring positions (i.e., remaining as pairs) as
487 shown in Figure 6b. We suggest that quantitative conversion of pairs to clumps can be explained
488 as a two-step mechanism: 1) initial preferential conversion of clumps to pairs along the O1–O2
489 exchange pathway, followed by 2) forced exchange of O1–O2 oxygen atoms during the
490 aragonite to calcite phase transition. This hypothesis is an attractive target for future molecular
491 dynamic models of the kinetics of the $CaCO_3$ phase transition and solid-state clumped isotope
492 reordering.

493 We also draw attention to the fact that the rise in Δ_{47} that accompanies the aragonite to
494 calcite transition is observed at approximately the time when XRD or Raman evidence for calcite
495 formation is first observed, but well before complete conversion of aragonite to calcite (by which
496 time Δ_{47} has fallen again). It would be rational to argue that this is just the behavior expected if
497 the rise in Δ_{47} reflects a kinetic isotope effect associated with the transition (i.e., a dependence of
498 its rate on the isotopic content of the reacting carbonate ions). However, our experiment
499 performed on aragonite that had been isotopically equilibrated at high pressure shows this is not
500 the case. Isotope exchange between adjacent carbonate ion units happens over atomic length
501 scales (10^{-10} m), whereas XRD and Raman observe structures that are coherent over much longer
502 length scales (10^{-8}–10^{-6} m). A comparison of the apparent rates of these three measurements of
503 the aragonite to calcite transition at different spatial scales is shown in an Arrhenius plot (Figure
504 7). We see that over our experimental temperature range the rate of initial clump-to-pair
505 conversion in aragonite is faster by an order of magnitude than the rate of XRD determined
506 phase transition, which is in turn an order of magnitude faster than the rate of phase transition
507 estimated by Raman spectroscopy over our experimental temperature range. We suggest that the

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508 structural rearrangements involved in the aragonite to calcite transition begin at short length
509 scales and only gradually does the calcite structure become coherent to longer length scales;
510 furthermore, we argue that the clumped isotope composition is sensitive to the earliest, shortest
511 length scale re-arrangements, while XRD and Raman are sensitive to structural re-organization
512 on increasingly longer length scales.

513 The trend in Figure 7 for the rate of clumped isotope reordering in aragonite is not a
514 straight line. This observation suggests that clumped isotope reordering may occur through two
515 or more separate steps that differ in activation energies. This finding may offer insight into why
516 we sometimes see two separate rises in Δ_{47} over the course of the aragonite to calcite transition.
517 The two separate increases in Δ_{47} at 350°C may reflect the fact that we can see two separate steps
518 in a complex bond reordering process because the phase transition is slow, letting us observe
519 isotopic evolution over a gradually spreading conversion of aragonite to calcite; by this
520 interpretation, no clear evidence for two Δ_{47} rises is seen at higher temperatures simply because
521 the phase transition progresses too quickly relative to our sampling interval.

522 In summary, we explain the complex evolution in Δ_{47} values observed when an aragonite
523 that formed at low temperature converts to calcite at high temperature as an interplay between
524 the mechanisms of isotope exchange between clumps, pairs and singletons on one hand and the
525 dynamics of the aragonite-calcite phase transition on the other. The initial reduction in Δ_{47} that
526 occurs when aragonite is first heated but has not yet reacted to form detectable calcite is an
527 exchange between the clumped and unsubstituted carbonate ions to build up pairs in the
528 aragonite lattice. This initial exchange preferentially occurs by an exchange of oxygen between
529 only one (or perhaps two) of the several possible pairs of nearest-neighbor O sites. The
530 subsequent rise in Δ_{47} marks the first detectable stage of conversion of aragonite to calcite, which

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is associated not only with re-alignment of carbonate ion units but also with the breaking and re-forming of C–O bonds. The first of these bond breaking and re-forming events take advantage of the same low activation energy pathway that is the preferred mechanism of clumped isotope reordering. Thus, the O atom exchange that is forced by the phase transition effectively reverses any immediately preceding conversion of clumps to pairs. The only exception to this pattern is seen when aragonite is allowed to isotopically equilibrate at high temperatures before conversion to calcite, which we take as evidence for slower diffusion-limited separation of pairs to form randomly distributed singletons. We suggest that the observation of two separate periods of increasing Δ_{47} when low-temperature aragonite is converted to calcite at 350°C indicates that this structural re-organization occurs through two or more steps that differ in their rates, but that are only clearly observed when phase transformation is slow yet goes to completion (conditions that are not both met at significantly higher or lower temperatures).

4.1.2 Back-reaction of pairs during sharp temperature changes

Our two-step calcite heating experiments were designed to generate pair excesses and drive back-reactions to re-form clumps in the absence of a phase transformation (Figure 1b). During the first stage of the experiments, the samples were heated at 450°C for 5 hours. According to the kinetic parameters derived in Stolper & Eiler (2015), these temperature-time conditions should have allowed the clumps to pairs reaction to go nearly to completion. In contrast, the diffusion-limited separation of pairs to form singletons should not yet have progressed to a significant extent. Thus, a pair excess should have existed at this point. The samples were then exposed to a higher temperature of 500°C, which lowers the equilibrium pair

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553 concentration, increasing the driving force for pairs to either separate or back-react to form
554 clumps.

555 The magnitude of the change in Δ_{47} predicted by the reaction-diffusion model for this
556 heating history depends on the excesses above a random distribution for both clumps and pairs
557 prior to any heating (i.e., when the studied sample first crystallized), and the temperature
558 dependence of the equilibrium concentrations for clumps and pairs. These quantities are
559 relatively well known for the clumped isotope species, but are essentially unverified assumptions
560 in the case of pairs. If we adopt the assumed values by Stolper and Eiler (2015) for pairs, and
561 adjust their estimated values for the rate constants, k_f, k_d in Rxn 2 within their stated
562 uncertainties, the model can predict a rise in Δ_{47} during the second stage of this heating
563 experiment (Model-1 in Figure 5) that is similar in timing to the rises we observe, but so muted
564 in amplitude it could not be measured with current analytical methods (whereas we reproducibly
565 observe an effect several times analytical precision). We constructed several alternative model
566 predictions of the consequences of our experimental heating schedule by increasing the
567 temperature sensitivity of the pair excess by a factor of 6 relative to the value assumed by Stolper
568 and Eiler (2015) (Model-4 in Figure 5). A model that closely matches the rate of Δ_{47} decrease in
569 this experiment also requires adjustment of the initial pair concentration, by a few parts in 10^4
570 (see Table 2 and Figure 5). These modifications demonstrate the capacity of the reaction-
571 diffusion model to generate temporary increases in Δ_{47}, but show that quantitatively fitting
572 experimental data requires tuning the parameters that define the abundances and behavior of
573 pairs—parameters that are, at present, poorly constrained. For this reason we consider this set of
574 experiments and the calculations discussed above to provide only suggestive evidence regarding

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575 the underlying mechanism that produces the anomalous Δ_{47} rises in calcite during the two-stage
576 heating process.

577 Despite the complexities in and assumptions of the model required to explain the
578 significant Δ_{47} increases, the experimental observations are important for two reasons: 1) they
579 show that anomalous increases in Δ_{47} can occur during heating in the absence of a phase
580 transformation; and 2) they confirm a peculiar prediction of the reaction-diffusion model that
581 arises from the hypothesized existence and properties of pairs. It remains true that we have no
582 direct observations of pairs (nor can we think of a way in which they could be observed with
583 meaningful precision). However, these results suggest that the dynamics of interconversion of
584 clumps, pairs and singletons could be universal to the solid-state isotopic reordering of carbonate
585 minerals (and perhaps other molecular salts).

586 We could not think of a way that the defect-annealing mechanism would be predicted to
587 drive a Δ_{47} increase during heating, against the thermodynamic driving force. Our expectation is
588 that the defect density in a crystal changes the rate of diffusion and thus the time it takes to reach
589 equilibrium, but not the direction of clumped isotope evolution. We observed Δ_{47} reversals
590 against thermodynamic trends in both the aragonite-calcite phase transition and the two-stage
591 calcite heating experiments. While the former may involve creation of new defects as the crystal
592 structure is rearranged, we do not expect significant changes in the number of defects in the same
593 calcite over a short period of time (15 minutes) as the temperature is raised by 50°C. Only the
594 presence of an intermediate pool of pairs can possibly cause the observed clumped isotope
595 reversals.

596 We also note that the observed Δ_{47} increases in calcite are expected only for specific
597 heating pathways, have been observed only for the experiments discussed here, and are of

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598 secondary importance to the overall reordering trend. The original pair-diffusion model
599 parameters in Stolper & Eiler (2015) still predict the general trend of our calcite data better than
600 the variety of other parameters that generate Δ_{47} increases (Figure 5), as well as for calcite under
601 a wide range of experimental and geological thermal histories.
602
603 *4.2 Differences Between Aragonite and Calcite in Reordering Kinetics*
604 While the reaction-diffusion reordering mechanism can conceptually explain the
605 complicated clumped isotope reordering pattern in aragonite, it should be noted that the kinetics
606 of clumped isotope reordering in aragonite are distinct from calcite, even in the absence of the
607 aragonite to calcite phase transformation. In our experiments, aragonite clumped isotope
608 reordering is triggered at temperatures much lower than those for calcite. No clumped isotope
609 reordering was observed for calcite up to temperatures of 380°C (Passey & Henkes, 2012;
610 Stolper & Eiler, 2015). In contrast, we see aragonite reordering take place at temperatures as low
611 as 200°C in our experiments, and significant reordering has been observed at even lower
612 temperatures (125°C–175°C) by others (Staudigel & Swart, 2016). Given the complicated
613 reordering pathways and the interplay with the phase transformation, it is challenging to estimate
614 accurate rate constants for clumped isotope reordering in aragonite with the existing data. Using
615 the reaction-diffusion model to fit the data, the initial stage of rapid Δ_{47} decrease by clump-pair
616 conversion in aragonite requires a rate constant (k_f in Rxn 2) that is 1–2 orders of magnitude
617 larger than that in calcite (Figure 7). Large uncertainties remain with these estimates due to the
618 scarcity of data points before the phase transition is triggered to cause a reversal in Δ_{47}. We
619 expect time series experiments of aragonite reordering at high pressure (in its stability field) to
620 provide better estimates of the rate constants. However, it is a robust observation in our

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experiments that when an aragonite-calcite phase transition is involved, the time it takes for the mineral to reach clumped isotope equilibrium is much shorter than for calcite (Figure 4). For example, it took 500 hours for calcite to reach equilibrium at 430°C (Stolper & Eiler, 2015), while the equilibrium composition was reached in 42 hours in our 450°C experiment as aragonite was converted to calcite (Figure 4). As a result, aragonite's initial clumped isotope composition is predicted to alter at much lower temperatures than that of calcite and dolomite (Stolper & Eiler, 2015; Lloyd et al., 2018), making it highly susceptible to moderate heating during early diagenesis. The Δ_{47} increases during heating and phase transition may further complicate the interpretation of clumped isotope compositions of aragonite and aragonite-derived calcite in sedimentary basin settings. Because unit-cell-scale transformations of aragonite to calcite can artificially raise Δ_{47} values, carbonate materials with 'cold' clumped isotope temperatures that appear to be pristine, unmodified aragonite (based on XRD and Raman spectroscopy) may be indistinguishable from aragonite that experienced moderate heating, partially-reordered in the solid-state, and partially transformed to calcite at a scale finer than the above conventional techniques can detect. However, our reordering experiments make it possible to better constrain a quantitative model of clumped isotope reordering in carbonate minerals in general, and potentially will allow a more complete understanding of the temperature history of natural carbonates measured using clumped isotopes.

Because aragonite and calcite have the same chemical composition, the difference in reordering kinetics is likely a result of structural differences between the two minerals. We surmise that the rate of isotope exchange in the solid-state is determined by the bonding environment of atoms in the crystal lattice. Aragonite has a more tightly compacted structure compared to calcite, and the shortest pathway between oxygen atoms in neighboring carbonate

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644 groups is smaller in aragonite than in calcite. Nevertheless, certain Ca–O and C–O bonds in
645 aragonite are longer and thus weaker in aragonite than in calcite (Antao & Hassan, 2010; Ye et
646 al., 2012). As a result, the pairs in aragonite that originate from disproportionation of a clump
647 may have a lower energetic barrier to form (and to exchange back to the clumped species, in the
648 event that a phase transformation forces an oxygen exchange between neighboring pairs). The
649 bonding environment of oxygen atoms is also less symmetric in aragonite than calcite (Figure 6),
650 which may create multiple pools of pairs at the non-equivalent oxygen sites; we speculate that
651 this diversity of O bonding environments may be related to the fact that we observe two separate
652 Δ_{47} increases when the aragonite to calcite transformation occurs at 350 ˚C. The factors
653 controlling these elementary kinetic steps could be further investigated by performing reordering
654 experiments of other carbonate minerals of both calcite-type (e.g., siderite, rhodochrosite) and
655 aragonite-type (e.g., strontianite, witherite) structures, as well as developing molecular dynamic
656 models of solid-state isotope exchange.
657
658 **5. Conclusions**
659 We conducted a series of isotopic reordering experiments in aragonite at different
660 temperatures and observed complicated patterns of decreasing and increasing Δ_{47} values. In
661 general, the reordering pathway can be described as a series of steps in which Δ_{47} initially drops
662 sharply, then rises sharply at the onset of conversion of aragonite to calcite, and finally falls
663 asymptotically toward the high-temperature equilibrium value. We propose that this pattern can
664 be explained with the reaction-diffusion reordering mechanism associated with the aragonite-
665 calcite phase transition. We tested the hypothesis with a reordering experiment on an aragonite
666 sample whose isotopic structure (clumps, pairs and singletons) was equilibrated at high

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667 temperature and pressure. The lack of an abrupt rise in Δ_{47} when this sample was subsequently
668 converted to calcite suggests that such Δ_{47} increases require pools of excess pairs. We further
669 tested the presence of pairs in carbonates in general by conducting a two-step calcite heating
670 experiment. After a pretreatment aimed at increasing pair concentrations in calcite, a small but
671 statistically significant rise in Δ_{47} was reproduced during the second stage of the experiment.
672 These experiments suggest a general mechanism of clumped isotope reordering based on the
673 reaction-diffusion model that can be applied to different carbonate minerals.

674 Although the mechanism of clumped isotope reordering in aragonite and calcite may be
675 similar, the kinetics of the reordering reactions is different for the two minerals. Clumped isotope
676 compositions of aragonite are highly susceptible to reordering at moderate heating, and the
677 reordering kinetics is much faster than in calcite and dolomite. This must be taken into account
678 when applying the clumped isotope thermometer to natural aragonite that has gone through early
679 diagenesis. The lower activation energy of clumped isotope reordering in aragonite as compared
680 to calcite may be related to the bonding environment of the oxygen atoms in the crystal lattice
681 associated with its structure. Factors determining the kinetics of isotope exchange in carbonate
682 minerals could be further investigated by reordering experiments of other carbonate minerals, as
683 well as molecular dynamic models of the mobility of different isotopes through crystal structures.
684

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692 **Table 1 Data from Aragonite and Calcite Clumped Isotope Reordering Experiments**

Sample	Temp (°C)	Heat Time (hrs)	$\delta^{13}C$ (‰,VPDB)[e]	$\delta^{18}O$ (‰,VPDB)[e]	Calcite%[f]	Δ_{47} (‰,ARF)[g]
SC-A2[a]	500	0.71	7.055±0.005	–7.665±0.014	97	0.429±0.015
SC-A3	500	0.33	7.548±0.002	–7.022±0.017	32	0.496±0.016
SC-A4	500	0.17	7.308±0.003	–7.518±0.010	12	0.584±0.020
SC-A5	500	0.50	7.668±0.004	–7.050±0.016	85	0.441±0.019
SC-A6	500	0.20	7.014±0.004	–7.283±0.010	17	0.539±0.010
SC-A7	500	1.05	6.996±0.004	–7.674±0.007	98	0.407±0.018
SC-A8	500	0.08	7.016±0.005	–7.583±0.008	8	0.502±0.017
SC-B1	450	1	7.250±0.003	–7.568±0.004	13	0.564±0.015
SC-B2	450	19	7.706±0.002	–7.193±0.009	70	0.473±0.017
SC-B4	450	8.5	7.564±0.003	–7.285±0.009	75	0.499±0.021
SC-B5	450	2	7.316±0.002	–7.527±0.009	24	0.528±0.020
SC-B6	450	3.1	8.110±0.002	–6.917±0.006	7	0.551±0.014
SC-B7	450	6.5	7.241±0.004	–7.634±0.008	92	0.340±0.015
SC-B9	450	13.5	7.572±0.004	–7.448±0.009	91	0.485±0.011
SC-B10	450	42	7.075±0.005	–7.771±0.004	100	0.317±0.017
SC-B11	450	4	7.531±0.003	–7.952±0.008	13	0.504±0.015
SC-B12	450	0.5	7.919±0.003	–7.145±0.006	11	0.655±0.015
SC-B13	450	5	7.440±0.003	–7.865±0.010	64	0.385±0.021
SC-B14	450	62	7.364±0.003	–7.722±0.007	100	0.334±0.023
SC-B15	450	5.5	7.269±0.003	–7.527±0.013	85	0.366±0.022
SC-C2[b]	350	5	7.585±0.002	–7.370±0.010	14	0.669±0.023
SC-C3	350	13	7.494±0.003	–7.655±0.006	16	0.459±0.013
SC-C4	350	1.02	7.268±0.003	–7.453±0.006	6	0.638±0.013
SC-C5	350	3	6.985±0.003	–7.727±0.004	4	0.490±0.018
SC-C6	350	18.5	7.728±0.005	–7.341±0.017	13	0.537±0.018
SC-C7	350	37	7.696±0.003	–7.268±0.006	17	0.489±0.016
SC-C8	350	45	7.153±0.002	–7.616±0.010	44	0.469±0.017
SC-C9	350	24	7.389±0.002	–6.976±0.010	8	0.566±0.014
SC-C10	350	72	7.150±0.003	–7.696±0.014	54	0.418±0.022
SC-C11	350	9.5	7.105±0.003	–7.397±0.011	11	0.457±0.019
SC-C12	350	100	7.707±0.004	–7.220±0.016	79	0.432±0.019
SC-D1[b]	350	9	7.142±0.008	–7.464±0.012	6	0.559±0.019
SC-D2	350	1	6.880±0.007	–7.681±0.011	3	0.563±0.024
SC-D3	350	3	7.436±0.010	–7.323±0.014	4	0.696±0.026
SC-D4b	350	18	7.697±0.006	–6.942±0.007	5	0.691±0.020
SC-D5	350	0.5	7.400±0.008	–7.449±0.011	3	0.677±0.030
SC-D6	350	48	7.613±0.004	–6.845±0.008	11	0.602±0.016
SC-D7	350	72	7.064±0.008	–7.202±0.013	26	0.517±0.025
SC-D8	350	6	7.306±0.007	–7.489±0.011	4	0.660±0.028
SC-D8b	350	6	7.483±0.006	–7.257±0.008	4	0.643±0.023
SC-D9	350	24	7.632±0.007	–7.112±0.011	8	0.681±0.021

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SC-D10	350	12	7.446±0.004	–7.260±0.007	4	0.596±0.022
SC-E1	350	6	7.549±0.004	–7.123±0.005	3	0.628±0.018
SC-E2	350	9	7.691±0.010	–7.271±0.004	2	0.665±0.015
SC-E3	350	1	7.604±0.002	–7.290±0.004	2	0.698±0.012
SC-E4	350	3	7.320±0.002	–7.289±0.005	2	0.718±0.014
SC-E5	350	18	7.375±0.002	–7.307±0.006	5	0.711±0.017
SC-E6	350	0.5	7.364±0.003	–7.509±0.006	1	0.688±0.012
SC-E7	350	48	7.493±0.005	–7.106±0.004	4	0.618±0.019
SC-E8	350	72	7.246±0.002	–7.333±0.003	5	0.593±0.019
SC-E9	350	24	7.610±0.004	–7.332±0.007	5	0.647±0.013
SC-E10	350	12	7.588±0.004	–7.213±0.003	4	0.680±0.013
SC-H0[c]	350	0	7.428±0.046	–7.122±0.049	0	0.283±0.016
SC-H1b	350	9	7.361±0.004	–7.196±0.005	6	0.317±0.015
SC-H2b	350	72	7.445±0.004	–7.201±0.009	22	0.316±0.022
SC-H3	350	48	7.639±0.004	–7.029±0.008	9	0.287±0.019
SC-H4	350	1	7.477±0.006	–7.062±0.009	3	0.307±0.020
SC-H5	350	18	7.459±0.005	–7.077±0.008	5	0.279±0.019
SC-H6	350	0.5	7.495±0.005	–6.981±0.008	3	0.294±0.020
SC-H7	350	12	7.388±0.008	–7.153±0.012	5	0.322±0.020
SC-H8	350	3	7.551±0.005	–7.077±0.009	6	0.280±0.019
SC-H9	350	6	7.499±0.005	–7.023±0.008	5	0.281±0.019
SC-H10	350	24	7.440±0.006	–7.006±0.008	13	0.313±0.010
AP-1	200	1	7.707±0.004	–7.428±0.012		0.656±0.027
AP-7	200	18	7.461±0.005	–6.834±0.010		0.649±0.027
AP-15	200	29	7.410±0.004	–7.642±0.008	0	0.661±0.039
AP-C3	200	90	7.374±0.002	–8.002±0.005		0.709±0.027
AP-C1	200	144	6.859±0.003	–8.166±0.004		0.723±0.024
AP-4	300	1	7.233±0.006	–7.928±0.011	0	0.673±0.033
AP-L	300	2	7.327±0.004	–7.700±0.010		0.635±0.031
AP-2	300	13	7.392±0.005	–7.240±0.010	0	0.619±0.041
AP-10	300	41	7.813±0.004	–7.167±0.010		0.720±0.031
AP-D6	300	216	7.001±0.003	–8.037±0.006		0.693±0.028
AP-G	400	1	7.096±0.004	–7.568±0.009	0	0.473±0.009
AP-B4	400	2	6.135±0.005	–7.055±0.010	99	0.503±0.033
AP-E	400	17	7.386±0.004	–7.599±0.006		0.608±0.030
AP-B2	400	24.6	7.292±0.005	–7.793±0.011	1	0.586±0.032
AP-B11	400	48	7.724±0.007	–7.547±0.015	94	0.549±0.029
N21-1a1[d]	500	0	–1.381±0.028	–16.788±0.080	100	0.474±0.015
N21-1a2	500	0	–1.168±0.068	–16.894±0.030	100	0.426±0.017
N21-1b1	500	0.25	–1.658±0.026	–17.205±0.101	100	0.503±0.018
N21-1b2	500	0.25	–2.296±0.025	–16.641±0.030	100	0.498±0.008
N21-1c1	500	0.5	–1.592±0.048	–17.049±0.134	100	0.424±0.014
N21-1c2	500	0.5	–1.802±0.008	–16.705±0.030	100	0.468±0.007
N21-1d1	500	0.75	–1.879±0.025	–16.936±0.081	100	0.443±0.019

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N21-1d2	500	0.75	–1.391±0.036	–17.176±0.030	100	0.439±0.001
N21-1e1	500	3	–1.549±0.026	–16.860±0.124	100	0.361±0.012
N21-1e2	500	3	–2.394±0.020	–16.803±0.030	100	0.406±0.011

a. Shaded rows represent heating experiments in ambient atmosphere without CO_2 in the headspace.
b. Both SC-C and SC-D experiments were conducted at 350°C, and are labeled C-350°C and D-350°C in the figures.
c. The SC-H series are reordering experiments with the clumped isotope randomized aragonite, H0 represents the composition after the 10-day high-pressure equilibration at 600°C (average of 2 aliquots). The SC-H series and SC-D series were done at the same time under the same conditions.
d. The N21-1 series are data from the two-step calcite reordering experiment. The experiment was replicated on two sets of samples. Samples N21-1a1 and N21-1a2 represent the composition after the first step of heating at 450°C for 5 hours.
e. Reported as internal standard errors (1σ).
f. Mass fraction of calcite was determined with XRD for AP samples, and with Raman spectroscopy for SC samples
g. The Δ_{47} errors are total standard errors (1 SE) calculated following Daëron et al. (2016).

Table 2 A Summary of Two-Stage Calcite Reordering Models in Figure 4

Model	Tuned Variable[a]	Variable Value Relative to Original Model[b]	Timing of 2nd-Stage Δ_{47} Increase (min)	Magnitude of Δ_{47} Increase (‰)
0	None	Original	N/A	None
1	(k_f, k_d)	(2, 0.5)	5	0.001
2	A	1.6	3	0.0003
3	(A, d_i)	(1.6, 0.99985)	6	0.0005
4	(A, d_i, k_f, k_d)	(6, 0.99918, 2, 2)	13	0.03

a. For the tuned variables, k_f and k_d represent the rate constants for isotope exchange in Rxn 2. 'A' represents the temperature sensitivity of the equilibrium pair concentration presented in the reaction-diffusion model of Stolper & Eiler (2015), following the equation:

$$\ln [pair]_{eqm}(T)/[pair]_{random} = A/T.$$

The variable 'd_i' represents an additional variable introduced to account for potential differences in initial pair concentration of different calcite minerals, and to better fit the data of the first-stage of reordering in our experiment. In Model-3 and Model-4, $[pair]_{initial} = d_i[pair]_{eqm}$.
b. Values represent a multiplication factor applied to the original reaction-diffusion model parameters.

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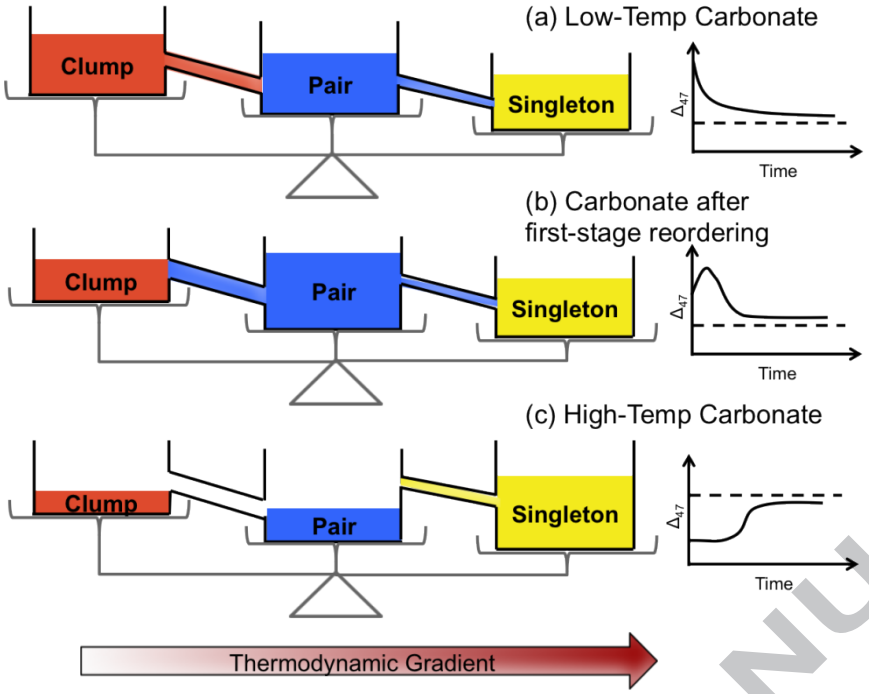

Figure 1 A fluid flow analogy to the reaction-diffusion model as applied to different reordering experiments in this study. In the model, there are three pools of isotopically substituted carbonate groups in carbonate minerals: clumps, pairs and singletons, shown as fluids of different colors. The directions of the reactions (fluid flow) depend on two things: the fluid levels and the vertical positions of the tanks. The fluid level corresponds to actual concentrations of these carbonate groups, and the relative base height of the tanks corresponds to the thermodynamic trend. The plots on the right column show expected clumped isotope reordering patterns in a controlled heating experiment based on the abundance of clumps, pairs and singletons in each case. **(a)** This scenario represents a low-temperature carbonate, like the untreated starting material in the experiment. When exposed to high temperatures, the thermodynamic gradient drives the reaction from clumps to pairs and pairs diffuse away to form singletons, with a decrease in Δ_{47} over time. **(b)** This scenario represents a mineral that has been heated for a relatively short amount of time. In this case, pairs build up in the mineral at the expense of clumps. The pairs may diffuse to fill the singleton tank, but this process has a higher kinetic limit (thinner tube between blue and yellow), so that the build-up of pairs exceeds the formation of singletons. The pretreated calcite in our experiment may represent this scenario, with pairs building up in excess of equilibrium, and could remake clumps when a higher temperature is imposed. A similar scenario may explain Δ_{47} increases in aragonite as phase transition is triggered. The multi-stage reordering in aragonite is a likely combination of (a) and (b). An analogy for pair-excess created by phase transition may be a shrink in the size of the tank for pairs due to a rearrangement of carbonate ions in the lattices. The difference between the two minerals may also be related to different reaction rates (size of connection rubes), or different responses of the equilibrium pair concentration (vertical position of tanks) to the thermodynamic gradient. **(c)** This scenario represents the aragonite equilibrated at high temperatures. The equilibration process destroys most clumps and separates pairs into singletons, and the reordering reaction only goes in the reverse direction afterwards at a lower temperature. Clump formation can only happen when excess pairs build up, and a buffering time is expected for an increase in Δ_{47} to be observed.

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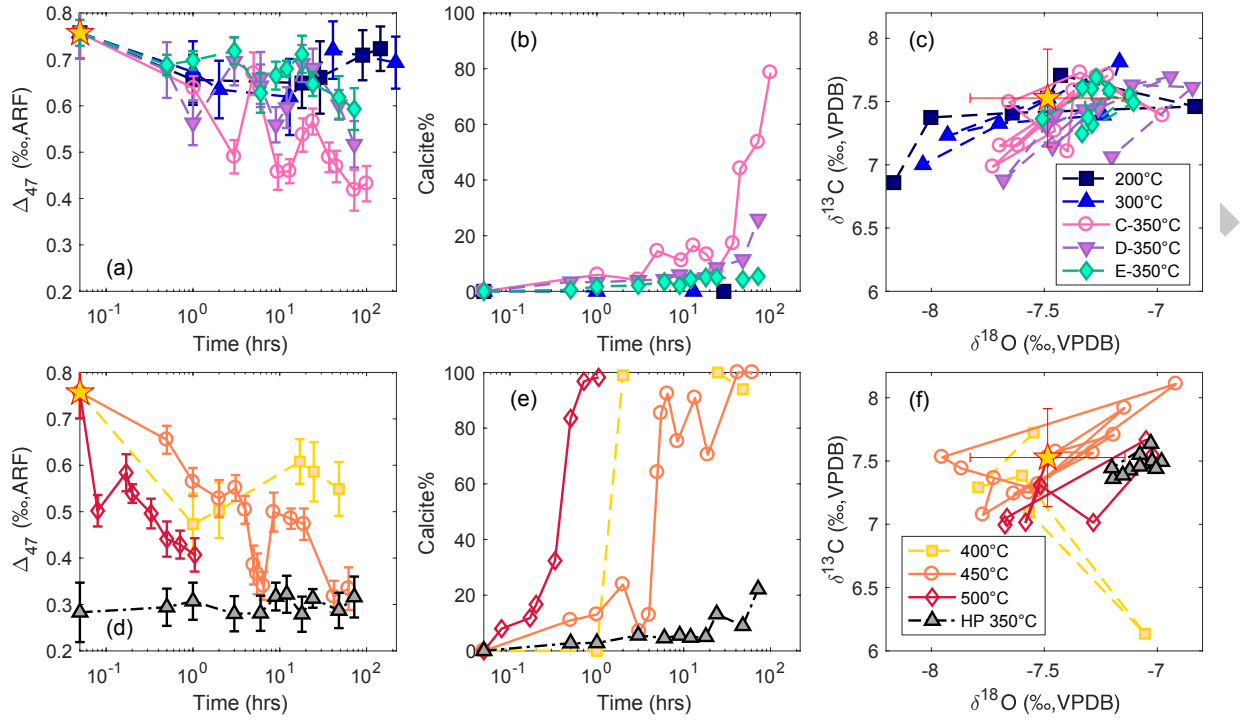

Figure 2 Isotope and mineralogy data of the aragonite reordering experiments. Panels (a)-(c) show results of the ambient pressure experiments between 200°C and 350°C, while panels (d)-(f) show results of the ambient pressure experiments between 400°C and 500°C together with the 350°C reordering experiment on the high pressure high temperature (600°C) equilibrated aragonite. (a, d) Clumped isotope composition evolution with time (2σ error bars). The star represents the starting composition of the aragonite. At each temperature, increases in Δ_{47} values of 0.05–0.15‰ during the heating process are observed in the ambient pressure experiments. The black triangles represent the reordering experiment starting with clumped isotope randomized aragonite. Three heating experiments (C-350°C, 450°C, 500°C) were conducted in air (open symbols) while others were conducted in CO_2 atmosphere (filled symbols). (b, e) Percentage of calcite in the samples determined by XRD (200°C, 300°C, 400°C) or Raman spectroscopy (other experiments). There is scatter in the proportions of calcite from the XRD and Raman measurements, but in general there is an increase in calcite% with time in all experiments above 300°C. (c, f) $\delta^{13}C$ and $\delta^{18}O$ values of the reordering experiments. The stars show the initial composition of the aragonite with 2σ standard deviations. The data points are connected in the order of heating time. Most data points scatter within the 2σ range of the initial composition of the aragonite ($\delta^{13}C$ = 7.53±0.17‰ and $\delta^{18}O$ = –7.49±0.19‰), and no systematic trend is observed, suggesting closed system behavior during the reordering experiments.

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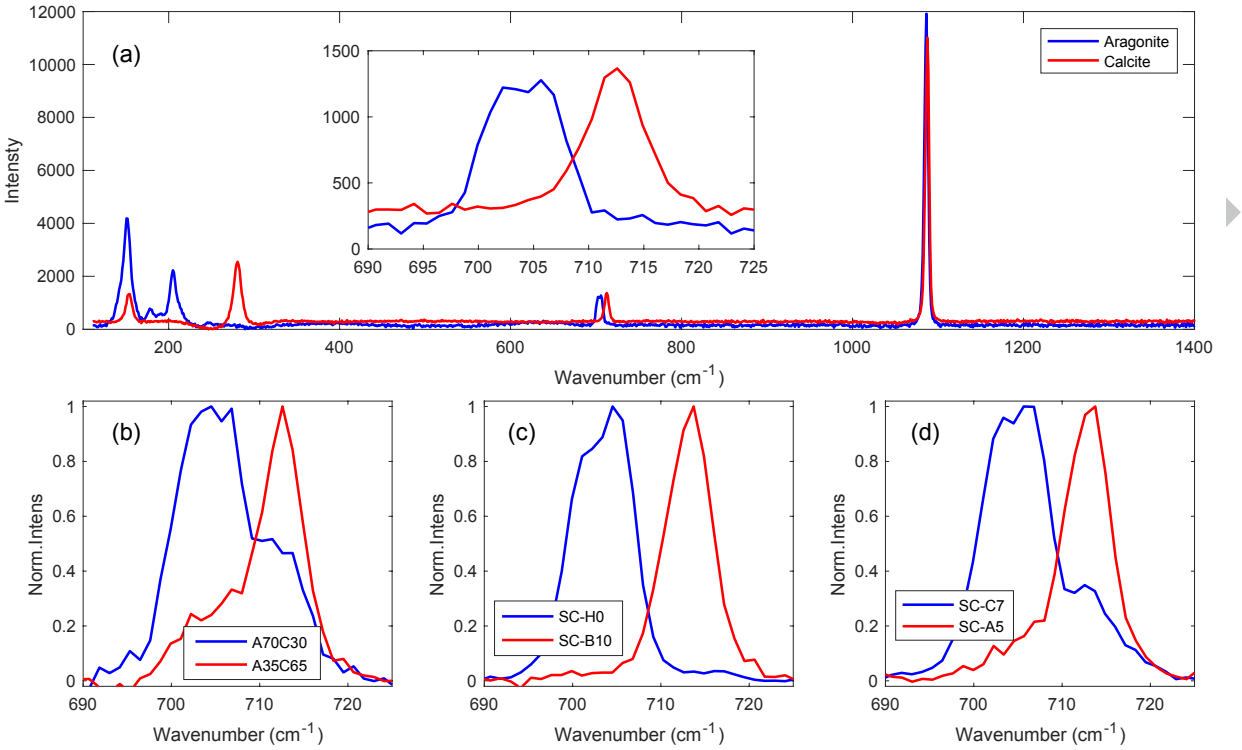

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767 **Figure 3** Examples of Raman spectra used to determine fractions of aragonite and calcite in the
768 samples. (a) Full spectra of pure aragonite (blue) and calcite (red), with the inset zooming in to
769 the wavenumber range of carbonate ion planar bending mode, used to determine relative
770 abundance of aragonite (704 cm^{-1}) and calcite (713 cm^{-1}) in the samples. (b) Spectra of powder
771 mixtures of aragonite and calcite used as calibration standards. Examples shown here are a 70:30
772 aragonite:calcite mixture (blue) and a 35:65 aragonite:calcite mixture. (c) Spectra of samples
773 from two experiments. SC-H0 is an aragonite sample whose clumped isotope composition was
774 equilibrated at high temperature (600°C) and high pressure (1.7 GPa). These P-T conditions
775 preserved its aragonite structure. SC-B10 is a sample that has been completely converted to
776 calcite after heating at 450°C for 42 hours. (d) Spectra of samples from two other experiments.
777 SC-C7 was heated at 350°C for 37 hours, and was determined to have 17% calcite by peak area.
778 SC-A5 was heated at 500°C for 30 minutes, and has 85% calcite.
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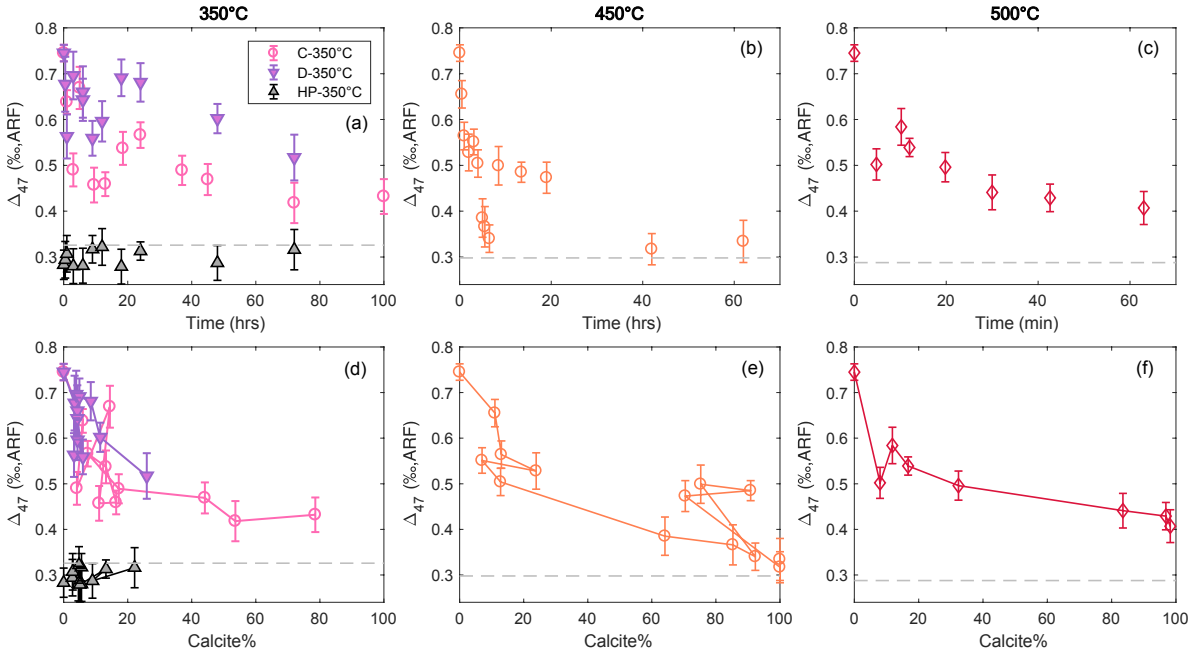

Figure 4 Clumped isotope reordering paths with time (a-c) and percentage of calcite (d-f) in the sample for the experiments at 350°C, 450°C, and 500°C. The lines in panels (d-f) connect points in the order of increasing running time. There are apparent reversals in calcite% with time in panels (d) and (e), which represent noise in the phase transition data at 350°C and 450°C. These reversals are more pronounced for experiments conducted in air (C-350°C and 450°C). Increases in Δ_{47} of 0.05–0.15‰ can be observed during each of the experiments, generally in the range of 0–20% phase transition. The experiments at 350°C (C with ambient atmosphere, D and HP with CO_2 atmosphere) have slightly different magnitudes of Δ_{47} reordering with time, but the reordering paths are similar when calcite% is used as the x-axis, suggesting the reordering kinetics is related to the rate of phase transition. The gray triangles are reordering experiments at 350°C with the clumped isotope randomized aragonite. The dashed lines mark the equilibrium Δ_{47} values at 350°C, 450°C ad 500°C respectively (Bonifacie et al., 2017). Note that the x-axis for the 500°C experiment in panel (c) is in minutes.

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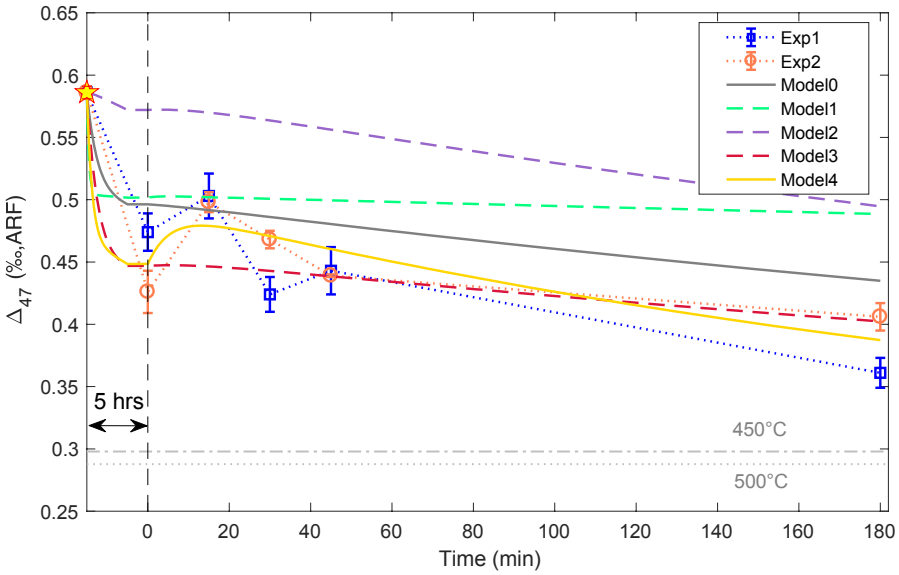

Figure 5 Clumped isotope reordering in the two-step calcite heating experiment compared to model calculations from the reaction-diffusion model (Stolper & Eiler, 2015). The squares and circles (connected by dotted lines) are replicate reordering experiments at 500°C (second step), to the calcite that was pretreated by heating at 450°C for 5 hours (first step). The star marks the initial composition of the calcite. The vertical line separates the two steps. To the left of the line is the Δ_{47} change with the pretreatment at 450°C for 5 hours (time is not to scale with the second step on the x-axis). The Δ_{47} value at time zero represents the composition after the pretreatment. The dash-dot and dotted horizontal lines mark the thermodynamic equilibrium values at 450°C and 500°C (Bonifacie et al., 2017). In both 500°C reordering experiments, the Δ_{47} values increased by 0.03–0.06‰ after 15 minutes of the second stage, before decreasing toward equilibrium. The solid and dashed curves are model outputs from the reaction-diffusion model with different parameter combinations. The model parameters for each case are listed in Table 2. Significant changes to the original model parameters in Stolper & Eiler (2015) are required to generate a curve that fits the data with a well-resolved Δ_{47} increase at the beginning of the second stage (solid gold curve).

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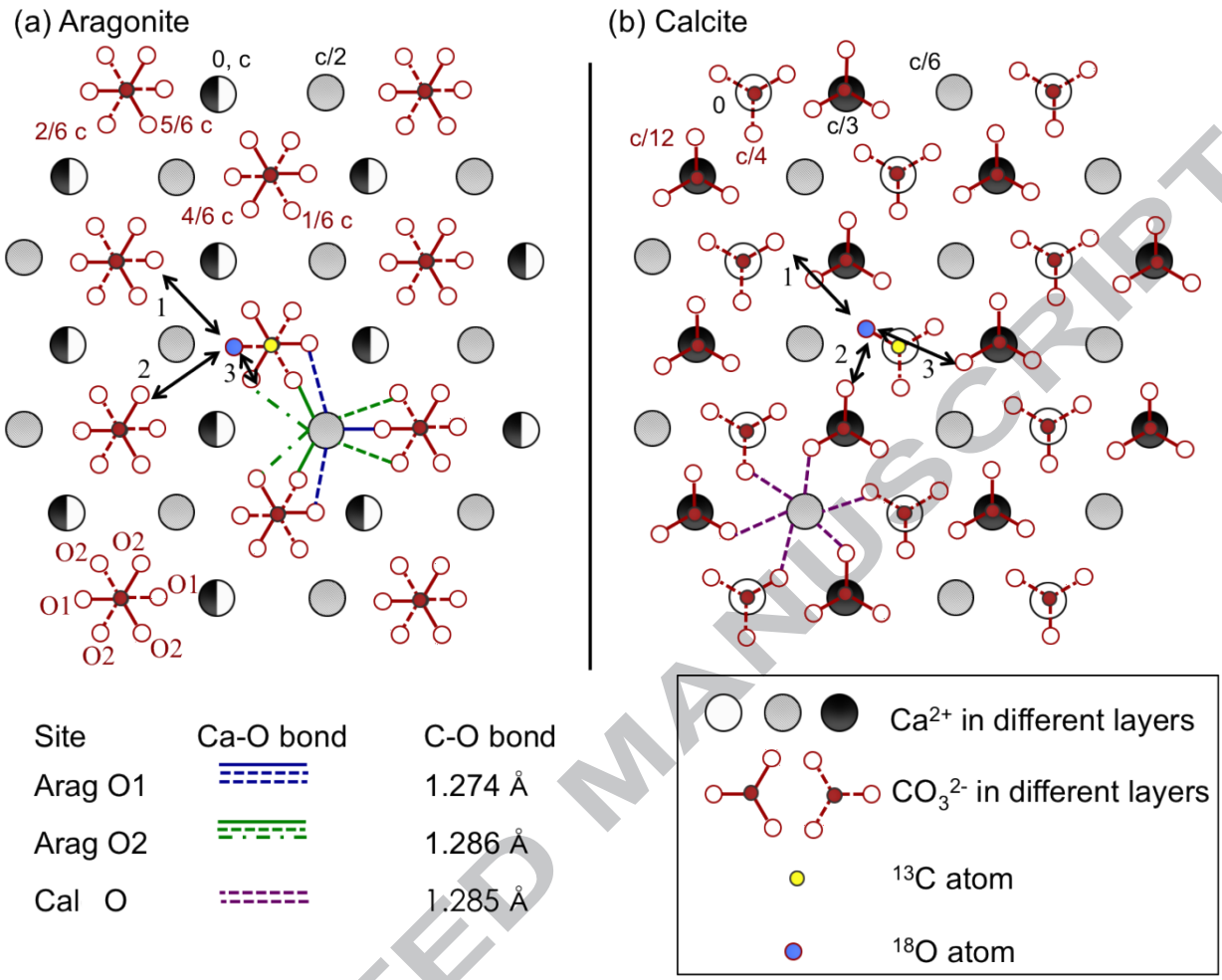

Figure 6 Comparison of aragonite and calcite mineral structures. The structures are presented as projections along the c-axis of the minerals, modified from Madon & Gillet (1984). The positions of Ca^{2+} and CO_3^{2-} along the c-axis are marked in the top two rows of the projected structures. The half filled Ca^{2+} ions in (a) represent overlapping layers at position 0 and c along the c-axis. The ^{18}O and ^{13}C atoms are marked by a different color, and are bonded here as a clumped isotopologue. The blue, green and purple lines show the Ca–O bond in the minerals. While all Ca–O bonds in calcite are equivalent, there are five different Ca–O bonds in the 9-coordinated aragonite structure, which gives rise to two non-equivalent oxygen sites O1 and O2. The length of the C–O bonds associated with O1 and O2 sites are listed in the lower left portion of the figure. O1 is more loosely bonded to Ca^{2+} with a slightly stronger C–O bond. In panel (a), the double headed arrows show 3 different pathways for possible preferential oxygen exchange pathways that involve breaking the fewest and weakest bonds. Pathway 1 is an O1-O1 exchange, while pathways 2 and 3 are O1-O2 exchange. In panel (b), the arrows show the same exchange pathways as in (a) after the mineral structure is rearranged. The O1-O2 exchange pathways in (a) have pairs remaining in neighboring positions after the phase transition in (b), and may cause the Δ_{47} increases observed during phase transition by a forced back-exchange.

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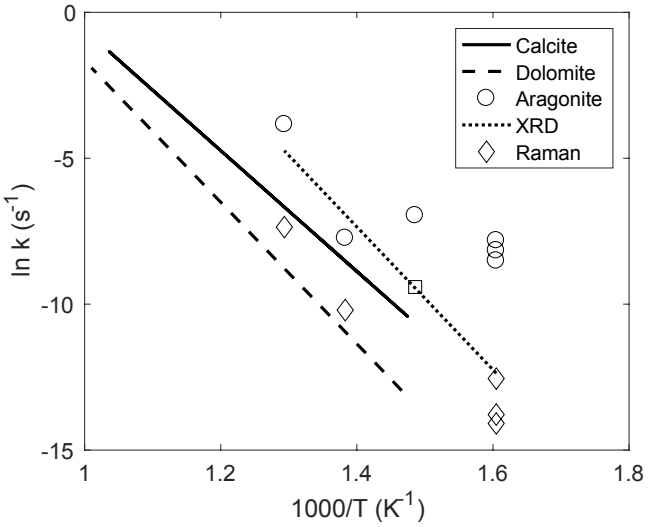

Figure 7 Arrhenius plot of clumped isotope reordering and $CaCO_3$ phase transition kinetics. The solid and dashed line represents the rate constants of clump to pair conversion (k_f in Rxn 2) calculated from calcite (Stolper & Eiler, 2015) and dolomite (Lloyd et al., 2018) reordering experiments. The circles represent rate constants (k_f) for aragonite estimated by fitting the first stage of Δ_{47} decrease (before the first Δ_{47} increase as phase transition in triggered) in the experimental data with the reaction-diffusion framework. Clumped isotope reordering in aragonite is faster than calcite and dolomite. The dotted line represents rates of aragonite-calcite phase transition at 1 atm calculated from XRD measurements by Davis & Adams (1965). The estimated rate of phase transition measured by XRD in our 400°C experiment (square) is consistent with the literature values. The diamonds represent rates of phase transition measured by Raman spectroscopy in our experiments. Detection of the phase transition by Raman spectroscopy postdates XRD measurements, and the rate of the aragonite to calcite transition as determined using either method is slower than the rate of the clumped isotope reordering reactions in aragonite. The rate constants for phase transition are estimated by $k = 1/\tau$, where τ is the e-folding time (63.2% reaction progress) of the transition. An exponential curve was fit to the noisy reaction progress data to estimate the rate of phase transition.

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