



# Isotopic behavior during the aragonite-calcite transition: Implications for sample preparation and proxy interpretation



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## ARTICLE INFO

### Article history:

Received 12 April 2016

Received in revised form 12 September 2016

Accepted 13 September 2016

Available online 14 September 2016

### Keywords:

Paleothermometry

Clumped isotopes

Stable isotopes

Aragonite

## ABSTRACT

At the Earth's surface, aragonite, a polymorph of calcium carbonate, is thermodynamically unstable, and readily converts to calcite, a process accelerated by heating and mechanical stress. This study has investigated the behavior of the  $^{13}\text{C}/^{12}\text{C}$ ,  $^{18}\text{O}/^{16}\text{O}$  ratios, and the clumped isotope temperature proxy ( $\Delta_{47}$ ) during this mineral transition. Aragonite samples were partially or completely converted to calcite in an oven (normal atmospheric composition and pressure) or in a sealed tube in the presence of a vacuum or pure  $\text{CO}_2$  of varying isotopic compositions. Other samples were converted from aragonite to calcite using a drill. These experiments demonstrate a relationship between the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values and percent transition from aragonite to calcite. The  $\Delta_{47}$  value of the aragonite changed independently from the mineral transition at temperatures as low as 125 °C and was accompanied by a 0.5‰ decrease in the  $\delta^{18}\text{O}$  value. This change occurred irrespective of the presence of  $\text{CO}_2$  suggesting that water trapped in the mineral may facilitate some of this alteration. Results show that sampling techniques, such as drilling, produce sufficient heat to convert aragonite to calcite and can considerably alter  $\Delta_{47}$ . Even small degrees of conversion (~10%) can increase clumped isotope derived paleotemperature estimates by nearly 10 °C.

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## 1. Introduction

Aragonite, a polymorph of calcium carbonate, is unstable under most conditions on the earth's surface (Johnston et al., 1916; Bäckström, 1925; Jamieson, 1953). The transition from aragonite to calcite is most commonly facilitated by the dissolution of one mineral and reprecipitation of another, a process known as neomorphism (Folk, 1965). The conversion of aragonite to calcite can also occur without the influence of water, the rate of which is sensitive to temperature, requiring heating >250 °C (Kunzler, 1969; Yoshioka and Kitano, 1985). At increased pressure, aragonite is the more stable polymorph of  $\text{CaCO}_3$  (Jamieson, 1953; Hacker et al., 2005), making it an accessory mineral in low-temperature high pressure metamorphic rocks (e.g. blueschist) (Coleman and Lee, 1962; Taylor and Coleman, 1968). The pressures produced in laboratory grinders can also be sufficient to convert calcite to aragonite (Burns and Bredig, 1956; Zorkovská and Baláž, 2011). Aside from those circumstances wherein it forms at high pressure, most aragonite forms under conditions wherein it is thermodynamically unstable. As most forms of chemical alteration result in the transition from aragonite to calcite, the presence of primary aragonite is suggestive that the mineral is original and therefore favorable to provide primary paleoenvironmental information through chemical and isotopic analyses (Stahl and Jordan, 1969).

While the transformation from aragonite to calcite occurs under normal surface conditions at a very slow rate, the transition can be accelerated significantly even with moderate heating (>200 °C) (Kunzler, 1969; Lécuyer, 1996). The change in mineralogy is accompanied by up to a 3% decrease in mass and by the release of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  (Yoshioka and Kitano, 1985). At higher temperatures (600–650 °C), additional  $\text{CO}_2$  is released as a result of the thermal decrepitation of carbonate ions (Milodowski and Morgan, 1980; Swart et al., 1982). The mineral transition is accompanied by a change in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values during the heating of carbonate at temperatures in excess of 300 °C (Epstein et al., 1951; Land et al., 1975; Gaffey et al., 1991). This procedure was commonly used during the early history of C and O isotopic analyses in order to remove organic contamination (Weber et al., 1976), but has now been largely abandoned. In biogenic aragonite, temperatures >100 °C can facilitate changes in crystal lattice d-spacing as determined using X-ray diffractometry, this process does not affect mineralogy (Pokroy et al., 2006; Pokroy et al., 2007).

It has been noted that sample preparation techniques such as mechanical mixing (Dachille and Roy, 1960; Zorkovská and Baláž, 2011) or milling techniques (Aharon, 1991; Gill et al., 1995; Foster et al., 2008; Waite and Swart, 2015) can alter the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of aragonite. Even the modest temperatures in a Kiel III Autocarb device oven (70 °C) have been suggested to facilitate a decrease in the  $\delta^{18}\text{O}$  value of very fine ground aragonite over time (−0.125‰ per day) (Tobin et al., 2011). A study of fish otoliths recorded changes in chemistry and  $\delta^{18}\text{O}$  when fish were cooked at high temperatures for extensive periods of

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time, although thermal shielding from organic material minimized this effect at lower temperatures (Andrus and Crowe, 2002). These effects invariably produce carbonate with lower  $\delta^{18}\text{O}$  values, and bias paleotemperature estimates toward warmer values.

Advances in the measurement of multiply substituted isotopologues of  $\text{CO}_2$  (Eiler and Schauble, 2004) over the past decade have enabled the development of a new method of determining paleotemperature (Ghosh et al., 2006). This approach involves measuring the abundance of mass 47 of  $\text{CO}_2$  (~95% composed of the species  $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ ) released from carbonate during the dissolution by phosphoric acid and comparison to the predicted “stochastic” abundance. This value, expressed as  $\Delta_{47}$ , is directly related to the carbonate formation temperature and is independent of both the  $\delta^{13}\text{C}$  and the  $\delta^{18}\text{O}$  value of the fluid from which the carbonate precipitated (Eiler, 2011; Ghosh et al. 2006) making it an extremely powerful tool for studying systems where temperature and the  $\delta^{18}\text{O}$  value of the fluid cannot be independently verified. After the formation of the carbonate mineral, the carbon and oxygen atoms are able to exchange within the crystalline lattice either with adjacent carbonate ions or via solid state diffusion (Farver, 1994; Dennis and Schrag, 2010), which, at elevated temperatures, such as those relevant to the transition from aragonite to calcite, have the potential to change the  $\Delta_{47}$  value (Passey and Henkes, 2012; Henkes et al., 2014). This solid-state reordering does not exclusively follow a first-order rate law, as two distinct trends are observed during heating experiments, an initial rapid decrease (dubbed annealing) followed by a slower exponential change. The  $\Delta_{47}$  value of heated carbonate materials will rapidly decrease at the onset of heating, a process initially described as an annealing of crystalline defects (Passey and Henkes, 2012). Later modeling showed that changes in the  $\Delta_{47}$  value could also be a result of isotope exchange between adjacent carbonate ions in the crystal lattice (Stolper and Eiler, 2015). The clumped isotopes will approach an equilibrium distribution over time, as atoms are able to diffuse through the crystal lattice.

Clumped isotopes studies that have been carried out on aragonitic corals and otoliths have used a range of sampling techniques including a file, mortar and pestle (Ghosh et al., 2006; Ghosh et al., 2007; Spooner et al., 2016), a rotary tool and manual crushing (Thiagarajan et al., 2011), as well as an automated Micromill™ (Saenger et al., 2012).

In this study, a series of experiments have been conducted in order to facilitate this annealing process in aragonite. In addition, the effect of sampling methods have been evaluated upon the mineralogy and clumped isotope composition of aragonite materials.

## 2. Materials and methods

### 2.1. Materials selected for study

The samples for this study have been taken from materials analyzed in previous investigations, a Bahamian sclerosponge (*Ceratoporella nicholsoni*) (Rosenheim et al., 2006), a scleractinian coral (*Siderastrea siderea*) from the island of Tobago (Moses and Swart, 2006), and an aragonite speleothem from Desoto Caverns Alabama (Lambert and Aharon, 2010).

### 2.2. Direct heating experiments

Two sets of direct heating experiments were conducted between 2014 and 2016. The first experiments investigated the behavior of aragonite between 300 and 425 °C, the second set of experiments was conducted between 125 and 250 °C. Two subsamples (hereafter referred to as Batch A and B) were taken from the same Sclerosponge specimen (~2 g each), these were ground and sieved (<63  $\mu\text{m}$ ) and stored in glass vial in a desiccator when not in use. Isotopically these two samples had similar  $\delta^{18}\text{O}$  and  $\Delta_{47}$  values, however the  $\delta^{13}\text{C}$  value of Batch B was approximately 0.3‰ more positive (Tables 1a, 1b).

Samples were mounted on XRD slides and dried for 24 h (mounting procedure detailed in Section 2.5). The oven was set to the experimental temperature and allowed several hours to equilibrate. Samples were placed in the oven and heated for the duration of the experiment. When the oven was sealed, the temperature varied by no more than  $\pm 3$  °C after equilibration. Samples were removed and allowed to cool. An infra-red thermometer confirmed that samples cooled to within 5 °C of room temperature within 2 min of being removed from the oven. No changes in color were observed during the experiments, although in some instances the samples needed to be remounted. Samples were analyzed using X-Ray Diffractometry in order to quantify the degree of transformation from aragonite to calcite (detailed in Section 2.5), and were then analyzed for their isotopic composition (detailed in Section 2.6).

### 2.3. Sealed vessel heating experiments

Samples of the sclerosponge (Batch B) were either heated in a vacuum or in the presence  $\text{CO}_2$  gas with known  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. Either 22 or 11 mg (smaller samples denoted by an asterisk in Table 2) of aragonite powder was weighed and placed into a Pyrex™ tube, the tube was evacuated through a capillary (in order to prevent the powder being sucked into the vacuum line) before the tube was sealed using a gas torch. For a number of experiments an aliquot of  $\text{CO}_2$  gas was frozen into the tube with the carbonate prior to sealing. Three pure  $\text{CO}_2$  gasses, with differing  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, were used for this experiment; subsequently referred to as Tank A, B, and C. The tubes containing the samples were heated at 400 °C for 5 h, which was determined in previous

**Table 1a**

Direct Heating Results from heating experiments 300 °C–425 °C. Reported error: standard deviation for multiple analyses of same material (Batch A sclerosponge aragonite).

T (°C)	Time (s)	% Arag	$\delta^{13}\text{C}$ (‰ v-PDB)	$\delta^{18}\text{O}$ (‰ v-PDB)	$\Delta_{47}$ (‰)	N
initial	0	100%	4.481 ± 0.065	0.012 ± 0.020	0.670 ± 0.022	2
425	300	64%	4.228	-1.082	0.338	1
425	600	37%	4.194	-1.378	0.337	1
425	900	14%	4.008 ± 0.048	-2.290 ± 0.263	0.351 ± 0.015	2
425	1200	0%	3.780	-2.606	0.351	1
425	2700	0%	3.621	-3.090	0.349	1
400	300	100%	4.415	-0.363	0.471	1
400	600	92%	4.428	-0.462	0.394	1
400	900	71%	4.391	-0.685	0.360	1
400	1200	59%	4.212	-0.836	0.373	1
400	1920	70%	4.349	-0.821	0.381	1
400	2700	57%	4.242 ± 0.010	-1.002 ± 0.056	0.332 ± 0.004	2
400	3600	47%	4.073 ± 0.047	-1.299 ± 0.035	0.362 ± 0.018	2
400	5400	42%	3.776	-2.170	0.371	1
400	48,140	0%	3.215 ± 0.057	-3.892 ± 0.107	0.392 ± 0.014	3
400	86,400	0%	3.181 ± 0.023	-4.001 ± 0.094	0.382 ± 0.018	3
400	172,800	0%	3.325 ± 0.068	-3.262 ± 0.063	0.359 ± 0.017	2
375	300	78%	4.357	-0.699	0.334	1
375	600	66%	4.320	-0.936	0.337	1
375	900	75%	4.309	-0.968	0.335	1
375	10,980	69%	4.062	-1.623	0.334	1
350	300	90%	4.355 ± 0.081	-0.778 ± 0.014	0.399 ± 0.021	3
350	600	89%	4.468 ± 0.114	-0.743 ± 0.041	0.379 ± 0.020	2
350	900	87%	4.386	-0.461	0.441	1
350	11,280	62%	4.230	-0.927	0.391	1
350	3600	89%	4.414	-0.645	0.410	1
350	1200	87%	4.314	-0.777	0.384	1
350	1800	79%	4.395	-0.684	0.402	1
350	2700	79%	4.277	-0.891	0.342	1
350	5700	83%	4.242	-0.880	0.386	1
350	21,600	66%	4.135	-1.058	0.365	1
300	1020	95%	4.536 ± 0.093	-0.348 ± 0.133	0.502 ± 0.006	2
300	1800	100%	4.448	-0.550	0.402	1
300	2700	100%	4.442 ± 0.057	-0.670 ± 0.051	0.400 ± 0.007	3
300	3600	100%	4.467	-0.468	0.458	1
300	9300	96%	4.427 ± 0.016	-0.521 ± 0.111	0.410 ± 0.024	2
300	21,720	94%	4.383 ± 0.022	-0.734 ± 0.048	0.405 ± 0.000	2
300	839,100	83%	4.309	-0.874	0.357	1
300	1,441,500	87%	4.280	-0.951	0.392	1

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