

# Oxygen isotope fractionation between synthetic aragonite and water: Influence of temperature and $Mg^{2+}$ concentration

Sang-Tae Kim <sup>a,c,\*</sup>, James R. O'Neil <sup>b</sup>, Claude Hillaire-Marcel <sup>c</sup>, Alfonso Mucci <sup>a,c</sup>

<sup>a</sup> Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal, QC H3A 2A7, Canada

<sup>b</sup> Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, USA

<sup>c</sup> GEOTOP-UQAM & McGill, C.P. 8888, Montréal, QC H3C 3P8, Canada

Received 8 August 2006; accepted in revised form 26 April 2007; available online 3 May 2007

## Abstract

Aragonite was precipitated in the laboratory at 0, 5, 10, 25, and 40 °C to determine the temperature dependence of the equilibrium oxygen isotope fractionation between aragonite and water. Forced CO<sub>2</sub> degassing, passive CO<sub>2</sub> degassing, and constant addition methods were employed to precipitate aragonite from supersaturated solutions, but the resulting aragonite–water oxygen isotope fractionation was independent of the precipitation method. In addition, under the experimental conditions of this study, the effect of precipitation rate on the oxygen isotope fractionation between aragonite and water was almost within the analytical error of  $\pm\sim 0.13\%$  and thus insignificant. Because the presence of  $Mg^{2+}$  ions is required to nucleate and precipitate aragonite from Na–Ca–Cl–HCO<sub>3</sub> solutions under these experimental conditions, the influence of the total  $Mg^{2+}$  concentration (up to  $\sim 0.9$  molal) on the aragonite–water oxygen isotope fractionation was examined at 25 °C. No significant  $Mg^{2+}$  ion effect, or oxygen isotope salt effect, was detected up to 100 mmolal total  $Mg^{2+}$  but a noticeable isotope salt effect was observed at  $\sim 0.9$  molal total  $Mg^{2+}$ .

On the basis of results of the laboratory synthesis experiments, a new expression for the aragonite–water fractionation is proposed over the temperature range of 0–40 °C:

$$1000\ln\alpha_{\text{aragonite-water}} = 17.88 \pm 0.13(10^3/T) - 31.14 \pm 0.46$$

where  $\alpha_{\text{aragonite-water}}$  is the fractionation factor between aragonite and water, and  $T$  is in kelvins. Given the analytical and statistical errors associated with this and previous determinations, the new relation reveals that many biogenic aragonites are precipitated at and or very near oxygen isotope equilibrium with their ambient water. When the new aragonite–water expression is combined with the calcite–water calibration published by Kim and O'Neil [Kim S.-T., and O'Neil J. R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta* **61**, 3461–3475], a positive aragonite–calcite fractionation ( $\sim 0.8\%$  at 25 °C) is obtained over the temperature range investigated.

© 2007 Elsevier Ltd. All rights reserved.

## 1. INTRODUCTION

Aragonite is one of the most abundant carbonate minerals on Earth, and comprises the bulk of the skeletal material of many marine organisms, including various species of corals, calcareous algae, and bivalve shells. Oxygen isotope analyses of natural aragonite, of both biogenic and

abiogenic origin, are frequently used in studies of paleoclimatology, oceanography and carbonate diagenesis, and yet only two experimental determinations of the oxygen isotope fractionation factor between inorganic aragonite and water have been carried out to date. Tarutani et al. (1969) measured the aragonite–water oxygen isotopic fractionation factor at 25 °C and concluded that inorganically-precipitated aragonite was enriched in <sup>18</sup>O by 0.6‰ relative to calcite at this temperature. More recently, Zhou and Zheng (2003) measured the temperature dependence of the aragonite–water oxygen fractionation factor from isotopic

\* Corresponding author. Fax: +1 301 405 3597.

E-mail address: [sangtae@eps.mcgill.ca](mailto:sangtae@eps.mcgill.ca) (S.-T. Kim).

analyses of aragonite synthesized from 0 to 70 °C and reported that the aragonite–water fractionation was smaller than the theoretical calcite–water fractionation. Because calcite and aragonite are polymorphs of CaCO<sub>3</sub>, the direction and magnitude of the equilibrium oxygen isotope fractionation between these two minerals are of considerable theoretical interest and possibly of practical interest (e.g., to estimate formation temperature or provide proof of cogenicity of coexisting aragonite and calcite).

A few semi-empirical calculations of the aragonite–calcite fractionation factor at 25 °C have been made. Tarutani et al. (1969) estimated an aragonite–calcite fractionation of 0.79‰ and noted its good agreement with their experimentally determined value of 0.6‰. Golyshev et al. (1981), using a different model for the lattice vibrations, calculated a similar fractionation of 0.53‰. Using a modification of the increment method, Zheng (1999) derived a much larger but negative fractionation factor of –4.47‰. In addition to these experimental determinations and theoretical calculations, a number of calibrations have been proposed on the basis of the analysis of natural materials. González and Lohmann (1985) found that aragonite grains and cements in Holocene reefal carbonates were enriched in <sup>18</sup>O by 1.5–2.0‰ relative to calcite that would precipitate in isotopic equilibrium under the same conditions. Grossman and Ku (1986) analyzed coeval aragonitic and calcitic foraminifera as well as aragonitic gastropods believed to have formed in approximate isotopic equilibrium with the same environmental fluids and reported that aragonite is enriched in <sup>18</sup>O by 0.6 ± 0.3‰ relative to calcite between 3 and 18 °C. According to the aragonite–water fractionation factors determined from analyses of various biogenic aragonites (fish otoliths, freshwater bivalves, marine mollusks, and coralline sponges), it was shown that biogenic aragonite is enriched in <sup>18</sup>O by 0.4‰ to 1.4‰ relative to the equilibrium calcite (Patterson et al., 1993; Rahimpour-Bonab et al., 1997; Thorrold et al., 1997; White et al., 1999; Böhm et al., 2000). In contrast, Lécuyer et al. (2004) found no fractionation between calcite and aragonite layers collected from the same mollusk shells or from different species grown in the same environment. Horibe and Oba (1972) reported that aragonite was depleted in <sup>18</sup>O relative to calcite in mollusks.

Biologic (vital) effects on both the carbon and oxygen isotope compositions of biogenic aragonite were addressed by numerous researchers. In an early study, Weber and Woodhead (1970, 1972) found that the oxygen isotope composition of aragonitic reef corals varies with the genera because each genus uses a different proportion of metabolic CO<sub>2</sub> and inorganic HCO<sub>3</sub><sup>–</sup> in seawater during calcification. McConnaughey (1989a,b, 2003) provided additional details about kinetic (disequilibrium) isotope effects that accompany the formation of certain biogenic carbonates, particularly coralline aragonite. Metabolic processes employed by some organisms that precipitate aragonite in nature may obscure a reliable assessment of the equilibrium oxygen isotope properties of this CaCO<sub>3</sub> polymorph.

In an attempt to obtain precise and accurate equilibrium oxygen isotope fractionation factors for the aragonite–water system and to resolve some of the long-standing inconsistencies described above (e.g., size and direction of the aragonite–calcite fractionation), we developed novel methods to precipitate aragonite slowly under laboratory-controlled conditions. On the basis of principles established in previous work (Kim and O’Neil, 1997), precipitation was assumed (see Section 3) to occur at isotopic equilibrium and measurements were made of the aragonite–water fractionation factor as a function of temperature and solution chemistry.

## 2. EXPERIMENTAL METHODS

### 2.1. Synthesis of aragonite

#### 2.1.1. Forced CO<sub>2</sub> degassing method

Morse et al. (1997) reported that aragonite rather than calcite will precipitate from seawater when the [Mg<sup>2+</sup>]:[Ca<sup>2+</sup>] ratio of the solution is greater than 4:1 at 10 °C and 1:1 above 25 °C. In accordance with these findings, most of the aragonite precipitations carried out in this study were from a Na–Ca–Mg–Cl–HCO<sub>3</sub> solution with a [Mg<sup>2+</sup>]:[Ca<sup>2+</sup>] ratio of 4:1. A 5 mmolal NaHCO<sub>3</sub> solution was prepared gravimetrically in Nanopure (~18 MΩ cm), deionized water, stored in a closed container and allowed to equilibrate thermally and isotopically (between carbonic acid species and water) while immersed in a constant (±0.01 °C) temperature bath for 2–10 days depending on the temperature (Beck et al., 2005). Reagent grade magnesium and calcium chloride salts were then added to the solution to the following final concentrations: 5 mmolal Ca<sup>2+</sup> and 20 mmolal Mg<sup>2+</sup>. At 40 °C, pure CO<sub>2</sub> gas was bubbled through the NaHCO<sub>3</sub> solution for no more than 5 min prior to the addition of magnesium and calcium chloride to circumvent spontaneous precipitation. The addition of pure CO<sub>2</sub> gas did not affect the oxygen isotope fractionations reported in this study. To investigate the influence of Mg<sup>2+</sup> ions and its ion-pairs on the oxygen isotope fractionation between aragonite and water, solutions with final concentrations of 100 mmolal Mg<sup>2+</sup> and 5 mmolal Ca<sup>2+</sup> were also prepared at 25 °C. After preparation and equilibration of the Na–Ca–Mg–Cl–HCO<sub>3</sub> solutions, an aliquot of each solution was taken for δ<sup>18</sup>O analysis and the pH was measured with an Orion combination pH electrode. The electrode was calibrated using two NIST-traceable buffers (7.00 and 10.00) at 25 °C. Between 250 and 300 mL of the experimental solutions were transferred to a specially designed, reaction vessel immersed in a constant temperature bath (±0.01 °C). The solutions were allowed to equilibrate for one more hour before pre-purified nitrogen gas, saturated with water of the same oxygen isotope composition as the experimental solutions, was bubbled slowly through the solutions to remove CO<sub>2</sub> and, thus, promote supersaturation, spontaneous nucleation, and precipitation of aragonite. The initial saturation index ( $\log\{\{Ca^{2+}\} \times \{CO_3^{2-}\}\} / K_{sp}^{(aragonite)}$  where  $\{Ca^{2+}\}$  and  $\{CO_3^{2-}\}$  are the activity of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2–</sup>, respectively) of the least concentrated experimental solutions (5 mmolal

$\text{Ca}^{2+}$ , 5 mmolal  $\text{HCO}_3^-$ , and 20 mmolal  $\text{Mg}^{2+}$ ) with respect to aragonite was calculated using the Geochemist Workbench® (B-dot equation, an extended form of the Debye–Hückel equation described by Helgeson (1969)) and the resulting values at 5, 10, 25, and 40 °C were 0.67, 0.68, 0.71, and 0.84, respectively.

Upon completion of each experiment, a 20 mL aliquot of the final solution was recovered from the reaction vessel for subsequent determinations of  $\delta^{18}\text{O}$  and pH. The oxygen isotope compositions of the final solutions were statistically indistinguishable from those of the initial solutions. The solid carbonate, precipitated on the walls and at the bottom of the vessel, was removed using a rubber policeman, vacuum filtered through a Gelman Supor® 0.45  $\mu\text{m}$  membrane disc filter, and rinsed several times, first with deionized water and then with methyl alcohol. The precipitates were dried on filter paper for at least 15 h at 70–80 °C prior to storage for isotopic analysis. The amount of aragonite precipitates harvested varied from 5 to 45 mg depending on the precipitation conditions. All precipitates were identified as pure aragonite by X-ray diffraction (XRD) analysis as well as scanning electron microscopy (SEM). Analyses of a few representative samples by ICP-MS, following their dissolution in a dilute HCl solution, revealed that magnesium impurities were negligible ( $\text{Mg}/\text{Ca} < 10^{-3}$ ). Experimental conditions and chemical characteristics of the experimental solutions are given in Table 1.

### 2.1.2. Passive $\text{CO}_2$ degassing method

Aragonite samples were also synthesized by passive  $\text{CO}_2$  degassing of a Na–Ca–Mg–Cl– $\text{HCO}_3$  solution stored in a sealed glass bottle at set temperatures of 0 or 25 °C. In contrast to the previous set of experiments,  $\text{N}_2$  was not bubbled through the solution but  $\text{CO}_2$  was allowed to degas freely to the headspace, thus increasing the supersaturation and inducing spontaneous aragonite precipitation. Precipitation occurred within 1–4 days at 25 °C and 6–9 days at 0 °C and continued for 6–189 days (Table 2). Because the solution was kept in a sealed bottle during the course of aragonite precipitation, the oxygen isotope compositions of the initial and final solutions were practically identical. The Na–Ca–Mg–Cl– $\text{HCO}_3$  solutions were prepared as described in the previous section. Aragonite was also precipitated from solutions containing 902.5 mmolal  $\text{Mg}^{2+}$  to investigate the influence of the  $\text{Mg}^{2+}$  ion and its ion pairs (salt effects) on the oxygen isotope fractionation between aragonite and water. Detailed initial experimental conditions and equilibration times can be found in Table 2.

### 2.1.3. Constant addition method

A modified version (Kim et al., 2006) of the constant addition method described by Hartley and Mucci (1996) was used to precipitate aragonite at two different pH values (~8.2 and ~10.8). Briefly, two titrants, a  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3$  solution and a  $\text{CaCl}_2$  solution with or without  $\text{Mg}^{2+}$  (depending on the pH of the solution) were simultaneously and continuously injected at selected rates of from 0.05 to 1.0 mL/h by a dual syringe pump into a water-jacketed and closed Teflon® reaction vessel containing thermally ( $25 \pm 0.03$  °C) and isotopically equilibrated Na–Ca–

Mg–Cl– $\text{HCO}_3$  solutions. The titrant and experimental solutions were prepared several days prior to each experiment to ensure oxygen isotope equilibrium between dissolved carbonate species and water. The chemical composition of the two titrants and the starting solutions were adjusted so that the pH of the reacting solution remained nearly invariant during the course of the precipitation for a given injection rate of the titrants. The addition of the two titrants to the experimental solution led to a supersaturation and spontaneous nucleation of aragonite onto which crystal growth proceeded thereafter. A more detailed description of the experimental design and procedures employed in this study can be found in Kim et al. (2006). The mineralogy of every run product was examined by SEM to determine if mineral phases other than aragonite were present. Experimental details and corresponding results are presented in Table 3.

## 2.2. Oxygen isotope analysis

All oxygen isotope measurements were carried out on  $\text{CO}_2$  gas using an isotope ratio mass spectrometer. During the course of this study, aragonite and water samples were analyzed at three facilities (University of Michigan, USA/Finnigan Delta S, Korea University, Republic of Korea/Finnigan MAT 252, and GEOTOP-UQAM-McGill, Canada/GV IsoPrime).  $\delta^{18}\text{O}$  values were normalized to the recommended values for the international reference standards NBS-18, NBS-19, SMOW, and SLAP. Oxygen isotope compositions of both aragonite and water are reported in the familiar  $\delta^{18}\text{O}$  notation relative to the SMOW standard.

Most of the carbonate run-products were analyzed at 25 °C using the classical procedure of McCrea (1950). Some aragonite samples, as well as NBS-18 and NBS-19 standards, were analyzed either at 90 °C on a VG MultiCarb™ system at GEOTOP-UQAM-McGill or at 75 °C on a Kiel device at the University of Michigan and these samples are identified in Tables 2 and 3. The acid fractionation factor at 25 °C for aragonite used for this study was 1.01063 (Kim et al., in press). For samples run at higher temperatures, the oxygen isotope composition of the  $\text{CO}_2$  evolved by reaction of phosphoric acid with the aragonite was first normalized to the published  $\delta^{18}\text{O}$  values of the acid-liberated  $\text{CO}_2$  at 25 °C from the two international standards. The new acid fractionation factor for aragonite,  $\alpha = 1.01063$ , was then applied to the normalized  $\delta^{18}\text{O}$  values of acid-liberated  $\text{CO}_2$ . The overall reproducibility ( $1\sigma$ ) of the  $\delta^{18}\text{O}$  measurements, based on replicate analyses of the carbonate samples, was  $\pm 0.07\text{‰}$ , and the isotopic compositions were reported to the nearest hundredth per mil.

Water samples were analyzed at the University of Michigan by the  $\text{CO}_2$ – $\text{H}_2\text{O}$  equilibration method (Cohn and Urey, 1938) using a modification of the vacutainer® method of Socki et al. (1992). A  $\text{CO}_2$ – $\text{H}_2\text{O}$  fractionation factor of 1.0412 (O'Neil et al., 1975) was applied to obtain the isotopic composition of the water itself. At Korea University, water samples were analyzed by an automated  $\text{CO}_2$ – $\text{H}_2\text{O}$  equilibration device, and  $\delta^{18}\text{O}$  values were normalized to the oxygen isotope ratios of two laboratory standards calibrated against SMOW and SLAP. The precision ( $1\sigma$ ) of the

Table 1  
 Experimental conditions and oxygen isotope data for aragonite precipitation experiments carried out at 5, 10, 25, and 40 °C

Sample	Temp. (°C)	HCO <sub>3</sub> /Ca/Mg <sup>a</sup> (mmolal)	Initial pH	Final pH	Ppt. rate (mg/kg/day)	$\delta^{18}\text{O}_{\text{aragonite}}$ (‰)	$\delta^{18}\text{O}_{\text{water}}$ <sup>b</sup> (‰)	$\alpha_{(\text{aragonite-water})}$	1000ln $\alpha_{(\text{aragonite-water})}$
<i>Experiment 1</i>									
UMICH-8-a	10.0	5/5/20 <sup>c</sup>	N/A	N/A	N/A	23.93	−8.4	1.03260	32.08
UMICH-8-b	10.0	5/5/20	N/A	N/A	N/A	23.70	−8.4	1.03237	31.86
UMICH-9-a	10.0	5/5/20	N/A	8.22	N/A	23.70	−8.4	1.03237	31.86
UMICH-9-b	10.0	5/5/20	N/A	8.27	N/A	23.60	−8.4	1.03227	31.76
UMICH-12-a	25.0	5/5/20	7.97	8.09	N/A	20.33	−8.4	1.02897	28.56
UMICH-12-b	25.0	5/5/20	7.97	8.20	N/A	20.27	−8.4	1.02891	28.50
UMICH-13-a	25.0	5/5/20	7.94	8.43	N/A	20.52	−8.4	1.02916	28.75
UMICH-13-b	25.0	5/5/20	7.94	8.23	N/A	20.36	−8.4	1.02900	28.59
UMICH-14-a	25.0	5/5/20	7.92	8.22	N/A	20.59	−8.4	1.02924	28.82
UMICH-14-b	25.0	5/5/20	7.92	8.15	N/A	20.51	−8.4	1.02915	28.74
UMICH-15-a	25.0	5/5/20	7.85	8.13	N/A	20.54	−8.4	1.02919	28.77
UMICH-15-b	25.0	5/5/20	7.85	8.26	N/A	20.41	−8.4	1.02905	28.64
UMICH-16-a	25.0	5/5/20	7.94	8.49	N/A	20.40	−8.4	1.02904	28.63
UMICH-16-b	25.0	5/5/20	7.94	8.37	N/A	20.23	−8.4	1.02887	28.46
UMICH-17-b	40.0	5/5/20	N/A	8.72	N/A	17.48	−8.4	1.02610	25.76
UMICH-18-a	40.0	5/5/20	8.06	8.95	N/A	17.57	−8.4	1.02619	25.85
UMICH-18-b	40.0	5/5/20	8.06	8.75	N/A	17.58	−8.4	1.02620	25.86
UMICH-21-a	40.0	5/5/20	7.95	8.46	N/A	17.58	−8.4	1.02620	25.86
UMICH-21-b	40.0	5/5/20	7.95	8.39	N/A	17.72	−8.4	1.02634	26.00
<i>Experiment 2</i>									
#4-A-Nov8-A	5.0	5/5/20	N/A	8.11	N/A	22.69	−10.46	1.03350	32.95
#4-A-Nov8-B	5.0	5/5/20	N/A	8.17	N/A	22.68	−10.51	1.03354	32.99
#4-A-Nov8-C	5.0	5/5/20	N/A	8.27	1.9	22.75	−10.48	1.03358	33.03
#4-Ara-May26-A	10.0	5/5/20	N/A	N/A	3.3	23.48	−8.54	1.03230	31.79
#4-Ara-May26-C	10.0	5/5/20	N/A	N/A	3.4	23.49	−8.53	1.03230	31.78
#4-Ara-June7-A	10.0	5/5/20	N/A	N/A	3.2	23.70	−8.60	1.03258	32.06
#4-Ara-June7-C	10.0	5/5/20	N/A	N/A	5.1	23.77	−8.56	1.03261	32.09
#4-Ara-Sep8-A	10.0	5/5/20	N/A	N/A	3.6	21.66	−10.52	1.03252	32.00
#4-Ara-Sep8-B	10.0	5/5/20	N/A	N/A	4.0	21.53	−10.49	1.03236	31.85
#4-Ara-Sep8-C	10.0	5/5/20	N/A	N/A	2.1	21.67	−10.50	1.03251	31.99
#4-A-Jan1503-A	10.0	5/5/20	7.95	8.13	1.1	21.51	−10.52	1.03237	31.86
#4-Ara-May11-A	25.0	5/5/20	N/A	N/A	3.2	20.44	−8.72	1.02942	28.99
#4-Ara-May11-B	25.0	5/5/20	N/A	N/A	5.2	20.35	−8.71	1.02932	28.89
#4-Ara-May17-A	25.0	5/5/20	N/A	N/A	3.0	20.53	−8.69	1.02948	29.05
#4-Ara-May17-B	25.0	5/5/20	N/A	N/A	6.7	20.37	−8.68	1.02930	28.88
#4-A-Oct6-A	25.0	5/5/20	N/A	7.88	1.3	18.60	−10.41	1.02932	28.89
#4-A-Oct6-B	25.0	5/5/20	N/A	7.99	4.4	18.56	−10.46	1.02933	28.90
#4-A-Oct6-C	25.0	5/5/20	N/A	8.22	3.7	18.60	−10.42	1.02933	28.90
#4-A-Dec12-A	25.0	5/5/20	N/A	8.14	4.5	18.45	−10.46	1.02922	28.80
#4-A-Dec12-B	25.0	5/5/20	N/A	8.13	5.4	18.40	−10.47	1.02918	28.76
#4-A-Dec12-C	25.0	5/5/20	N/A	8.15	3.8	18.47	−10.47	1.02925	28.83
#4-A-Jan303-A	25.0	5/5/20	7.95	7.95	6.6	18.39	−10.53	1.02923	28.81
#4-A-Jan303-B	25.0	5/5/20	7.95	7.84	4.3	18.34	−10.47	1.02911	28.70
#4-A-Jan303-C	25.0	5/5/20	7.95	8.14	6.0	18.36	−10.47	1.02914	28.72
#4-A-Oct903-A	25.0	5/5/100	7.52	8.49	5.9	18.56	−10.31	1.02917	28.75
#4-A-Oct903-B	25.0	5/5/100	7.52	8.77	7.0	18.67	−10.34	1.02931	28.89
#4-A-Oct903-C	25.0	5/5/100	7.52	8.21	3.3	18.63	−10.34	1.02927	28.85
#4-Nov1403-A	25.0	5/5/100	7.55	8.26	8.1	18.52	−10.32	1.02914	28.72
#4-Nov1403-B	25.0	5/5/100	7.55	8.43	14.0	18.77	−10.30	1.02937	28.95
#4-Nov1403-C	25.0	5/5/100	7.55	8.31	4.9	18.51	−10.34	1.02915	28.73
#4-Ara-July4-A	40.0	5/5/20	N/A	N/A	12.3	17.65	−8.56	1.02644	26.09
#4-Ara-July4-B	40.0	5/5/20	N/A	N/A	13.5	17.60	−8.55	1.02638	26.03
#4-Ara-July4-C	40.0	5/5/20	N/A	N/A	12.0	17.62	−8.53	1.02637	26.03
#4-A-Feb20	40.0	5/5/20 <sup>(passive)</sup>	6.45	7.64	1.3	15.77	−10.51	1.02656	26.21

Table 1 (continued)

Sample	Temp. (°C)	HCO <sub>3</sub> /Ca/Mg <sup>a</sup> (mmolal)	Initial pH	Final pH	Ppt. rate (mg/kg/day)	δ <sup>18</sup> O <sub>aragonite</sub> (‰)	δ <sup>18</sup> O <sub>water</sub> <sup>b</sup> (‰)	α <sub>(aragonite–water)</sub>	1000ln α <sub>(aragonite–water)</sub>
#4-A-Mar12-A	40.0	5/5/20	6.72	8.12	7.1	15.80	−10.46	1.02654	26.19
#4-A-Mar12-B	40.0	5/5/20	6.72	8.10	7.6	15.83	−10.50	1.02661	26.26

Aragonite was precipitated by the forced CO<sub>2</sub> degassing method.

Temp., temperature; Ppt., precipitation.

<sup>a</sup> HCO<sub>3</sub>/Ca/Mg denotes NaHCO<sub>3</sub>/CaCl<sub>2</sub> or CaCl<sub>2</sub>·2H<sub>2</sub>O/MgCl<sub>2</sub> or MgCl<sub>2</sub>·6H<sub>2</sub>O.

<sup>b</sup> Oxygen isotope composition of the experimental solution at the end of the precipitation experiment.

<sup>c</sup> 5/5/20 denotes 5 mmolal NaHCO<sub>3</sub> + 5 mmolal CaCl<sub>2</sub> or CaCl<sub>2</sub>·2H<sub>2</sub>O + 20 mmolal MgCl<sub>2</sub> or MgCl<sub>2</sub>·6H<sub>2</sub>O.

Table 2

Experimental conditions and oxygen isotope data for aragonite precipitation experiments conducted at 0 and 25 °C

Sample	Temp. (°C)	HCO <sub>3</sub> /Ca/Mg <sup>a</sup> (mmolal)	S.I.	ΣCO <sub>2</sub> Equil. Time (D) <sup>b</sup>	Precipitation (D) <sup>c</sup>	δ <sup>18</sup> O <sub>aragonite</sub> (‰)	δ <sup>18</sup> O <sub>prep. water</sub> (‰) <sup>d</sup>	δ <sup>18</sup> O <sub>water</sub> (‰) <sup>e</sup>	α <sub>(aragonite–water)</sub>	1000ln α <sub>(aragonite–water)</sub>
#4-Jan1405-a-1	0.0	10/5/20	0.95	3.81	74.1	25.22 <sup>f</sup>	−9.40	−9.39	1.03494	34.34
#4-Jan1405-a-2	0.0	10/5/20	0.95	3.84	104.0	25.20	−9.40	−9.40	1.03493	34.33
#4-Jan2605	0.0	30/5/35	1.22	10.85	51.3	25.50	−9.40	−9.42	1.03525	34.64
#4-Apr0105	0.0	15/5/20	1.11	20.18	39.2	24.52	−10.24	−10.19	1.03507	34.47
#4-Apr0405	0.0	30/5/20	1.37	16.98	39.2	24.60	−10.24	−10.19	1.03515	34.54
#5-May3005-a	0.0	15/15/60	1.15	21.75	24.8	24.46	−10.24	−10.15	1.03496	34.37
#5-July2305-a	0.0	5/10/40	0.69	6.95	189.0	27.48 <sup>f</sup>	−7.51	−7.58	1.03533	34.72
#5-Nov0605	0.0	10/5/20	0.95	10.02	80.0	27.10 <sup>f</sup>	−7.51	−7.56	1.03492	34.33
#4-Aug0904	25.0	5/5/20	0.71	4.06	93.9	19.80 <sup>g</sup>	−9.40	−9.34	1.02941	28.99
#4-Aug1204	25.0	10/5/20	1.00	7.90	91.0	19.80 <sup>g</sup>	−9.40	−9.41	1.02949	29.06
#5-Apr1505-b	25.0	10/5/20	1.00	5.99	80.9	18.94	−10.24	−10.14	1.02938	28.95
#5-Apr1505-a-1	25.0	30/50/902.5	0.46	13.90	6.0	18.79	−9.78 <sup>h</sup>	−10.78	1.02989	29.45
#5-Apr1505-a-2	25.0	30/50/902.5	0.46	13.92	20.9	18.92	−9.67 <sup>h</sup>	−10.67	1.02991	29.47
#5-Apr2805-A	25.0	30/50/902.5	0.46	1.97	11.0	18.91	−9.68 <sup>h</sup>	−10.68	1.02991	29.47
#5-Apr2805-B	25.0	30/50/902.5	0.46	1.97	10.9	18.74	−9.67 <sup>h</sup>	−10.67	1.02973	29.29

Aragonite was precipitated by the passive CO<sub>2</sub> degassing method.

Temp., temperature; S.I., saturation index; prep., preparation.

<sup>a</sup> HCO<sub>3</sub>/Ca/Mg denotes NaHCO<sub>3</sub>/CaCl<sub>2</sub>·2H<sub>2</sub>O/MgCl<sub>2</sub>·6H<sub>2</sub>O.

<sup>b</sup> ΣCO<sub>2</sub> Equil. Time (D) represents the equilibration time of the carbonic acid species in days.

<sup>c</sup> Precipitation (D) represents the time allowed for the precipitation of aragonite in days.

<sup>d</sup> Oxygen isotope composition of preparation water before adding any salts.

<sup>e</sup> Oxygen isotope composition of the experimental solution at the end of the precipitation experiment.

<sup>f</sup> Denotes a value obtained from an acid digestion reaction at 75 °C.

<sup>g</sup> Denotes a value obtained from an acid digestion reaction at 90 °C.

<sup>h</sup> Estimated oxygen isotope composition of preparation water before adding any salts based upon a salt effect of −1.0 ‰.

water δ<sup>18</sup>O analyses carried out at the University of Michigan and Korea University, on the basis of replicate analyses of the laboratory standards, was estimated at ±0.1‰ and ±0.05‰, respectively. As a result, the oxygen isotope ratios of the water samples were reported in this study to the nearest tenth and hundredth per mil, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Influence of synthesis method on aragonite–water fractionation

Aragonite was precipitated by three distinct methods, as described in the previous sections, and resulting aragonite–water fractionation factors are given in Tables 1–3. For comparison purposes, the aragonite–water oxygen isotope fractionation factors determined from aragonite synthe-

sized at 25 °C in the presence of 20 mmolal total Mg<sup>2+</sup> (hereafter Mg<sup>2+</sup>) or lower concentrations are plotted as four distinct groups in Fig. 1. Given that the maximum, cumulative analytical error (1σ) associated with the oxygen isotope analyses of water and aragonite is ±0.13‰ (see Section 2.2.), the last three groups, shown in Fig. 1, are statistically indistinguishable from each other. On the other hand, the average from the first group (*Experiment 1* conducted by the forced CO<sub>2</sub> degassing method) appears to be slightly lower than the other three. Given that the difference of ~0.2‰ between the averages of the first (28.65‰) and second (28.86‰) group of measurements is somewhat larger than the analytical precision (1σ ≈ ±0.13‰), we attribute this discrepancy to a systematic error among the isotopic analyses carried out at different institutions. It should be noted that all the oxygen isotope data of the *Experiment 1* group in Table 1 were determined at the University of Michigan whereas the others, in Tables 1–3, were

Table 3  
Summary of experimental conditions and revised oxygen isotope data for aragonite precipitation experiments performed at 25 °C taken from Kim et al. (2006)

Sample	Temp. (°C)	Ini. S.I.	Initial pH	Final pH	Ppt. rate (mg/kg/day)	$\delta^{18}\text{O}_{\text{aragonite}}$ (‰)	$\delta^{18}\text{O}_{\text{water}}$ (‰) <sup>a</sup>	$\alpha_{\text{aragonite-water}}$	$1000\ln \alpha_{\text{aragonite-water}}$
#4-Feb2504	25.0	1.5	10.75	10.59	1.7	19.80 <sup>b</sup>	-9.32	1.02939	28.97
#4-Mar0604	25.0	1.5	10.75	10.70	4.9	19.69 <sup>b</sup>	-9.36	1.02932	28.90
#4-Mar1304	25.0	1.5	10.74	10.63	3.6	19.61 <sup>b</sup>	-9.40	1.02929	28.86
#4-July1904	25.0	0.8	8.17	8.37	1.2	19.69 <sup>b</sup>	-9.33	1.02929	28.87
#4-Aug0404	25.0	0.8	8.28	8.15	15.5	19.65 <sup>b</sup>	-9.36	1.02928	28.86
#4-Aug1604	25.0	0.8	8.20	8.79	4.1	19.74	-9.33	1.02934	28.92
#4-Nov1604	25.0	1.5	10.78	10.78	2.4	19.40 <sup>b</sup>	-9.41	1.02908	28.67
#4-Nov2104	25.0	1.5	10.78	10.71	2.0	19.50 <sup>b</sup>	-9.37	1.02914	28.73
#4-Feb0405	25.0	1.5	10.77	10.72	1.6	18.84	-10.13	1.02927	28.85
#5-May0305	25.0	0.8	8.18	8.49	9.7	18.84	-10.17	1.02931	28.89
#5-Jun1805-A	25.0	0.2	8.25	8.44	6.2	18.80	-10.15	1.02925	28.83
#5-Jun1805-B	25.0	0.2	8.25	8.38	7.6	18.71	-10.08	1.02908	28.67

Aragonite was synthesized by the constant addition method and oxygen isotope data were obtained based upon the acid fractionation factor of 1.01063.

Temp., temperature; Ini. S.I., initial saturation index; Ppt., precipitation.

<sup>a</sup> Oxygen isotope composition of the experimental solution at the end of the precipitation experiment.

<sup>b</sup> Denotes a value obtained from an acid digestion reaction at 90 °C.

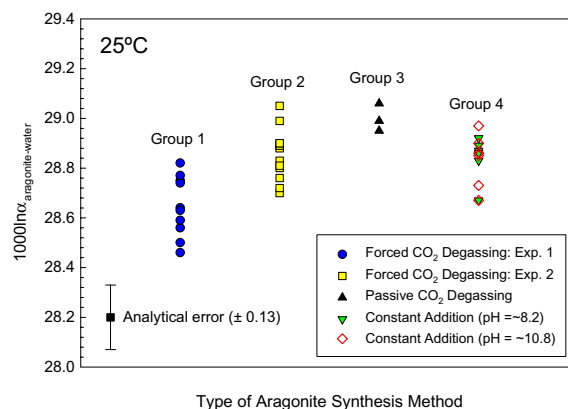


Fig. 1. Four groups of oxygen isotope data distinguished by aragonite synthesis protocols and the institution where the oxygen isotope analyses were conducted. Data from Tables 1–3 are plotted and an analytical error of  $\pm 0.13\%$  is indicated.

performed either at Korea University or at GEOTOP-UQAM-McGill. Given the similar variability of the  $1000\ln \alpha_{\text{aragonite-water}}$  values observed within each group of measurements in this study as well as those in previous studies (e.g., Kim and O’Neil, 1997; Zhou and Zheng, 2003), the experimental results from the first as well as the remaining three groups were combined to determine the temperature dependence of the equilibrium aragonite–water fractionation (see Section 3.4).

Finally, the  $1000\ln \alpha_{\text{aragonite-water}}$  values of group 4 were determined from precipitations carried out at two different pH values ( $\sim 8.2$  and  $\sim 10.8$ ) by the constant addition method (Kim et al., 2006). Nevertheless, the fractionations obtained are statistically identical to those of groups 2 and 3, which were obtained from precipitations conducted mostly over the pH range of 7.5–8.5. These results reaffirm that the equilibrium aragonite–water fractionation is independent of the pH of the parent solution (Kim et al., 2006).

### 3.2. Influence of total $\text{Mg}^{2+}$ concentration on aragonite–water fractionation

The adsorption of  $\text{Mg}^{2+}$  ions to the calcite surface and its incorporation into the crystal lattice are believed to inhibit its nucleation and precipitation by impingement at active growth sites (Reddy and Wang, 1980) and by a destabilization of the precipitate (Davis et al., 2000). In contrast, the presence of dissolved  $\text{Mg}^{2+}$  does not inhibit aragonite growth rates (Pytkowicz, 1973) because its crystal structure does not accommodate the adsorption and incorporation of  $\text{Mg}^{+2}$  ions (Lippmann, 1973; Mucci and Morse, 1983). Thus, aragonite, rather than calcite, precipitates from a Na–Ca–Cl– $\text{HCO}_3$  solution under the ambient temperature and pressure conditions in the presence of  $\text{Mg}^{2+}$ . Given that the presence of  $\text{Mg}^{2+}$  ions is required in the experimental solution in order to obtain aragonite precipitates exclusively, the influence of total  $\text{Mg}^{2+}$  concentration on the oxygen isotope fractionation between aragonite and water was investigated at 25 °C.

### 3.2.1. Forced CO<sub>2</sub> degassing method

Most aragonite precipitation experiments were carried out in the presence of 20 mmolal Mg<sup>2+</sup> at [Mg<sup>2+</sup>]/[Ca<sup>2+</sup>] = 4 whereas others were conducted at Mg<sup>2+</sup> concentrations of 100 and 200 mmolal at 25 °C. Speciation calculations by the Geochemist's Workbench® reveal that free HCO<sub>3</sub><sup>-</sup> remains the dominant carbonic acid species in the precipitating solution (Na–Ca–Mg–Cl–HCO<sub>3</sub>) but, as the total Mg<sup>2+</sup> concentration is increased, the mole fraction of MgHCO<sub>3</sub><sup>+</sup> and MgCO<sub>3</sub><sup>°</sup> ion-pairs gradually increases.

Aragonite was successfully precipitated and harvested from the 100 mmolal Mg<sup>2+</sup> solutions after 5 days of N<sub>2</sub> bubbling. In contrast, precipitation did not occur in solutions containing 200 mmolal Mg<sup>2+</sup> after 16 days of forced-CO<sub>2</sub> degassing. It appears that the abundance of Mg<sup>2+</sup> ion-pairs with bicarbonate/carbonate ions in the latter solution inhibited aragonite precipitation by lowering the activity coefficient of carbonate ions and, concomitantly, the saturation index with respect to aragonite, from 0.11 (in the presence of 100 mmolal Mg<sup>2+</sup>) to –0.26 (with 200 mmolal Mg<sup>2+</sup>) (Pytkowicz, 1973).

The aragonite–water oxygen isotope fractionations determined from analyses of aragonite precipitated at 25 °C in the presence of 20 and 100 mmolal Mg<sup>2+</sup> are given in Table 1; their averages and standard deviations (1σ), 28.86 ± 0.10‰ and 28.82 ± 0.09‰, respectively, are indistinguishable. Results presented in Fig. 2 for the forced

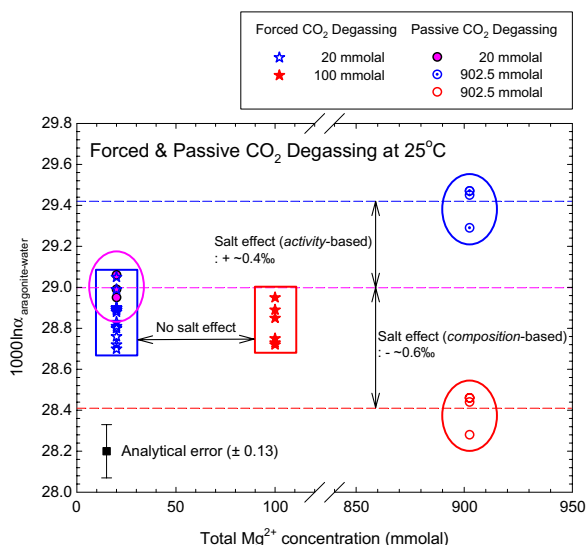


Fig. 2. Influence of total Mg<sup>2+</sup> concentration on 1000ln  $\alpha_{\text{aragonite-water}}$  determined at 25 °C. Aragonite was precipitated either from Na–Ca–Mg–Cl–HCO<sub>3</sub> solutions containing 20 and 100 mmolal Mg<sup>2+</sup> by the forced CO<sub>2</sub> degassing method or from similar solutions containing 20 or 902.5 mmolal Mg<sup>2+</sup> by the passive CO<sub>2</sub> degassing method. The averages of each group of experiments (20 and 100 mmolal Mg<sup>2+</sup>) from the forced CO<sub>2</sub> degassing method are statistically indistinguishable from each other under the experimental conditions investigated. Two types of oxygen isotope salt effects were identified based upon the oxygen isotope activity or composition ratio of the solutions in the presence of 902.5 mmolal Mg<sup>2+</sup> from the passive CO<sub>2</sub> degassing method. Each dashed line represents an average value for each group from the passive CO<sub>2</sub> degassing method.

CO<sub>2</sub> degassing method reveal that the presence and relative abundance of free and complexed Mg<sup>2+</sup> ions, over the range of concentrations investigated in this set of experiments, does not significantly influence the oxygen isotope fractionation between synthetic aragonite and water. It should be noted, however, that experimental data presented in Fig. 2 for the forced CO<sub>2</sub> degassing method were taken from the *Experiment 2* group dataset only (Table 1) as data from the *Experiment 1* group were excluded for reasons detailed in Section 3.1 (i.e., systematic discrepancy with the latter group of results).

### 3.2.2. Passive CO<sub>2</sub> degassing method

Even though the presence of Mg<sup>2+</sup> (up to 100 mmolal) did not affect the oxygen isotope fractionation between aragonite and water in the forced degassing experiment (Section 3.2.1), a further investigation was carried out in which aragonite was precipitated by the passive CO<sub>2</sub> degassing method in the presence of up to 902.5 mmolal (or ~0.9 molal) Mg<sup>2+</sup> at 25 °C. Data compiled in Table 2 show that the  $\delta^{18}\text{O}_{\text{water}}$  values of the Na–Ca–Mg–Cl–HCO<sub>3</sub> solutions (i.e.,  $\delta^{18}\text{O}_{\text{water}}$ ) with 902.5 mmolal Mg<sup>2+</sup> are about 1‰ lower than those ( $\delta^{18}\text{O}_{\text{preparation water}}$ ) of the water in which the salts are dissolved whereas those of the 20–60 mmolal Mg<sup>2+</sup> solutions are statistically indistinguishable from their parental or preparation water. The discrepancy between the isotopic ratios of the water in the dilute and concentrated Mg<sup>2+</sup> solutions is due to an “isotope salt effect” on the aqueous salt solutions. It should be noted that the Na–Ca–Mg–Cl–HCO<sub>3</sub> solutions described in Table 2 were prepared by dissolving a magnesium chloride hexahydrate (MgCl<sub>2</sub>·6H<sub>2</sub>O) salt. The number of water molecules contributed to the solutions by the hydrated salt was negligible for the solutions containing 20–60 mmolal Mg<sup>2+</sup> but comprised a significant fraction (9.7%) of the total water in the case of the 902.5 mmolal Mg<sup>2+</sup> solutions. Oxygen isotope salt effects determined experimentally by the CO<sub>2</sub>–H<sub>2</sub>O equilibration technique in this study from a 500 mmolal and a 1000 mmolal MgCl<sub>2</sub> solution were –0.53‰ and –1.10‰, respectively at 25 °C. Consequently, the oxygen isotope ratios of the preparation water (Nanopure water plus hydration waters from the salt) reported as  $\delta^{18}\text{O}_{\text{preparation water}}$  in Table 2 for the Na–Ca–Mg–Cl–HCO<sub>3</sub> solutions with 902.5 mmolal Mg<sup>2+</sup> were estimated on the basis of the –1.0‰ oxygen isotope salt effect.

The 1000ln  $\alpha_{\text{aragonite-water}}$  values, calculated from the  $\delta^{18}\text{O}_{\text{preparation water}}$  values (isotope composition ratios) for the Na–Ca–Mg–Cl–HCO<sub>3</sub> solutions with 902.5 mmolal Mg<sup>2+</sup> at 25 °C, are almost 0.6‰ smaller than those obtained from the solutions with 20 mmolal Mg<sup>2+</sup> (Table 3 and Fig. 2). The oxygen isotope salt effect in aqueous saline solutions was thoroughly investigated by O’Neil and Truesdell (1991) and Horita et al. (1993a,b). O’Neil and Truesdell (1991) proposed two mechanisms to explain this phenomenon when the isotopic composition of water is determined by the CO<sub>2</sub>–H<sub>2</sub>O equilibration technique: fractionation among the three oxygen-bearing species (bound or solvation water, free water, and CO<sub>2</sub>) in the system, and modification of the structure of water in the presence of ions. It can be inferred from the first mechanism that Mg<sup>2+</sup> ions,

being structure-makers, will preferentially attract  $^{18}\text{O}$ -rich water molecules to their hydration spheres, leaving the free water, and aragonite that will precipitate from this system, isotopically light. Consequently, smaller aragonite–water oxygen isotope fractionations, or negative isotope salt effects, are expected from solutions with high  $\text{Mg}^{2+}$  concentrations relative to those obtained from pure water or dilute solutions.

The  $1000\ln\alpha_{\text{aragonite-water}}$  values calculated from the  $\delta^{18}\text{O}_{\text{water}}$  values (isotope activity ratios) of the Na–Ca–Mg–Cl– $\text{HCO}_3$  solutions in the presence of 902.5 mmolal  $\text{Mg}^{2+}$  are approximately 0.4‰ larger than those from the solutions containing 20 mmolal  $\text{Mg}^{2+}$  (Table 3 and Fig. 2). This small, but unexpected, discrepancy is beyond the analytical error of  $\pm 0.13\text{‰}$  and, thus, is interpreted as an *apparent activity*-based oxygen isotope salt effect resulting from the presence of  $\text{Mg}^{2+}$  ions or its ion-pairs on the aragonite–water fractionation factor. In general, isotope salt effects on the fractionation factor are not anticipated when isotope activity ratios of the solution are used for the calculations of the fractionation factor. In view of these observations and despite a lack of evidence, we propose that our anomalous *apparent activity*-based oxygen isotope salt effect of  $\sim 0.4\text{‰}$  implies that (1) the isotope activity ratios ( $\delta^{18}\text{O}_{\text{water}}$  values in Table 3) of concentrated solutions determined by the  $\text{CO}_2$ – $\text{H}_2\text{O}$  equilibration technique do not reflect the true isotope activity ratios of concentrated solutions when other phases, such as aragonite, are present in the system or (2) the presence of high concentrations of  $\text{Mg}^{2+}$  ions modifies the mechanism(s) of aragonite precipitation and results in its relative enrichment in  $^{18}\text{O}$ .

The influence of NaCl,  $\text{CaCl}_2$ , and dissolved minerals on the oxygen isotope fractionation in mineral–water systems at high pressure and temperatures were recently investigated by Hu and Clayton (2003). At 15 kbar, they observed that the oxygen isotope salt effect of a 5 molal  $\text{CaCl}_2$  solution is  $-0.68\text{‰}$  at 600 °C and  $-0.61\text{‰}$  at 750 °C, compared to  $-0.15\text{‰}$  and  $-0.22\text{‰}$  for a 6.2 molal NaCl solution at the same temperatures in the quartz–water system. Conversely, they reported a negligible influence of NaCl concentrations (up to 37 molal) on the calcite–water oxygen isotope fractionation at 15 kbar between 300 and 750 °C. Kim and O’Neil (1997) also reported salt effects (non-equilibrium isotope effects of up to  $+1.6\text{‰}$  on the calcite–water fractionation at 25 °C) on the oxygen isotope fractionation between abiogenic divalent metal carbonates and aqueous bicarbonate and metal chloride solutions at low temperatures (10, 25, and 40 °C). The mechanism(s) of oxygen isotope salt effects in mineral–water systems remains unclear in spite of the mounting evidence and database.

### 3.3. Influence of precipitation rate on aragonite–water fractionation

Precise determinations of the aragonite precipitation rates from the three different homogeneous nucleation methods employed in this study (see descriptions in Section 2.1.) is not practical because (1) the number and size of the nuclei on which aragonite-growth proceeds is unpredictable and (2) the surface area of the growing aragonite varies

during the course of the precipitation. Alternative synthesis methods, involving heterogeneous nucleation (e.g., seeded precipitation), from which the precipitation rate can be quantitatively characterized, have been reported in the literature and successfully applied to kinetic studies of carbonate minerals (Zhong and Mucci, 1993, 1994). These heterogeneous nucleation methods could not be employed in this study because the contribution of the seed material to the isotopic composition of the bulk precipitate (seed + overgrowth) would inevitably interfere with the accurate determination of the  $\delta^{18}\text{O}$  signature of aragonite overgrowths.

Despite its limitations, a bulk precipitation rate (mg of  $\text{CaCO}_3$ /kg of solution/day) was calculated from most of the forced  $\text{CO}_2$  degassing experiments performed at 10, 25 and 40 °C as well as for the constant addition precipitations carried out at 25 °C (Tables 1 and 3). Results are presented in Fig. 3. Given an analytical error of  $\pm 0.13\text{‰}$ , Fig. 3 shows that the bulk precipitation rate does not affect the oxygen isotope fractionation between aragonite and water over the range ( $\sim 1$  up to  $\sim 15.5$  mg/kg/day) investigated. In other words, no apparent kinetic isotope effects are involved during the precipitations of inorganic aragonite under the experimental conditions of this study.

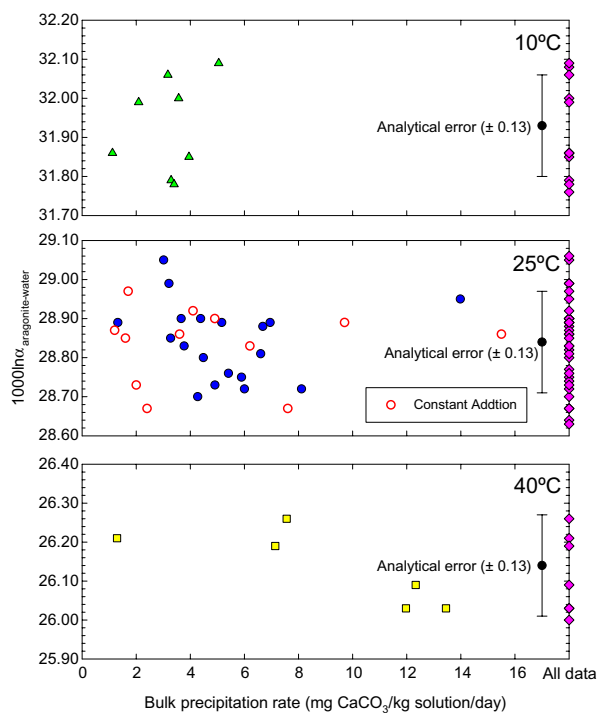


Fig. 3. Relation between  $1000\ln\alpha_{\text{aragonite-water}}$  and estimated bulk aragonite precipitation rate. Given an analytical error of  $\pm 0.13\text{‰}$ , no effect of the bulk precipitation rate was observed for aragonite precipitated from Na–Ca–Mg–Cl– $\text{HCO}_3$  solutions at 10, 25 and 40 °C by the forced  $\text{CO}_2$  degassing method as well as at 25 °C by the constant addition method. Diamond symbols shown on the right side of the graph represent all equilibrium aragonite–water oxygen isotope fractionations determined in this study, regardless of the aragonite synthesis protocol.



### 3.4. Influence of temperature on aragonite–water fractionation

#### 3.4.1. Inorganic aragonite

Aragonite was precipitated at five different temperatures (0, 5, 10, 25, and 40 °C) by at least one of the three methods described in Section 2.1 and the oxygen isotope fractionation factors between aragonite and water were experimentally determined (see Tables 1–3). An acid fractionation factor of 1.01063 (Kim et al., in press) was applied to calculate the oxygen isotope composition of the aragonite precipitates. Oxygen isotope fractionation factors obtained from experimental solutions containing <100 mmolal  $Mg^{2+}$  were included in the new determination of the aragonite–water calibration. The new calibration is shown in Fig. 4 and is represented by the following expression:

$$1000\ln\alpha_{\text{aragonite-water}} = 17.88 \pm 0.13(10^3/T) - 31.14 \pm 0.46 \quad (1)$$

The slope of the new aragonite–water fractionation relation, shown in Fig. 4, is similar to that of the calcite–water calibration of Kim and O’Neil (1997), but aragonite is enriched in  $^{18}O$  relative to calcite over the temperature range investigated (0–40 °C). On the basis of this new aragonite–water fractionation relation and the calcite–water relation of Kim and O’Neil (1997), the aragonite–calcite fractionation at 25 °C is 0.78‰, a value slightly larger than the fractionation of 0.6‰ determined by Tarutani et al. (1969) but almost identical to the value of 0.79‰ calculated by the same authors from partition function ratios of the two polymorphs. It should be noted, however, that the experimental value of Tarutani et al. (1969) was derived using the same acid fractionation factor (1.01025) for both aragonite and calcite and, thus,

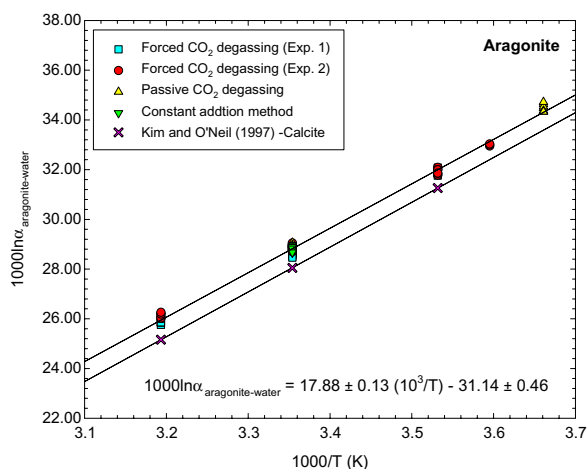


Fig. 4. Relation between  $1000\ln\alpha_{\text{aragonite-water}}$  and temperature. At least one of the three precipitation methods described in Section 2.1 was used to synthesize aragonite at any given temperature. The least squares fit to these data (Eq. (1)) is proposed for the temperature dependence of the equilibrium oxygen isotope fractionation between aragonite and water. A positive aragonite–calcite fractionation is also obtained over the temperature ranges investigated on the basis of Kim and O’Neil (1997)’s experimental determination of the calcite–water temperature calibration.

their aragonite–calcite fractionation is not 0.6‰ but a little smaller than the reported value. In contrast to these results, Zhou and Zheng (2003), who experimentally determined the inorganic aragonite–water oxygen isotope fractionation between 0 and 70 °C, reported a negative aragonite–calcite fractionation of  $-4.47\text{‰}$ . Kim and O’Neil (2005) have since proposed that several kinetic isotope fractionation mechanisms may explain the results of the aragonite precipitation experiments of Zhou and Zheng (2003).

#### 3.4.2. Comparison with biogenic aragonite

To facilitate a comparison of the results of this study with fractionation factors derived from analyses of biogenic carbonates, the aragonite–water fractionation factor determined in this study was recalculated using an acid fractionation factor of 1.01025 (Sharma and Clayton, 1965), a value in common use for calcite of any origin or physical state. This recalculation was required because most of the biogenic carbonate oxygen isotope analyses reported in previous studies were obtained following a high-temperature (>50 °C) reaction between the solid carbonate and  $H_3PO_4$  and normalized to accepted values for (calcite) international reference standards. The fractionation curves for the aragonite–water systems are shown in Fig. 5. In addition, published temperature dependencies for the oxygen isotope fractionation between aragonite and water are provided in Table 4. The biogenic aragonite–water curves of Grossman and Ku (1986), Thorrold et al. (1997), Radtke et al. (1996, 1998), White et al. (1999) and Böhm et al. (2000) are slightly different from each other but uniformly higher than the one generated in this study. In contrast, our temperature calibration lies higher than the curve constructed by Patterson et al. (1993) from analyses of freshwater otoliths.

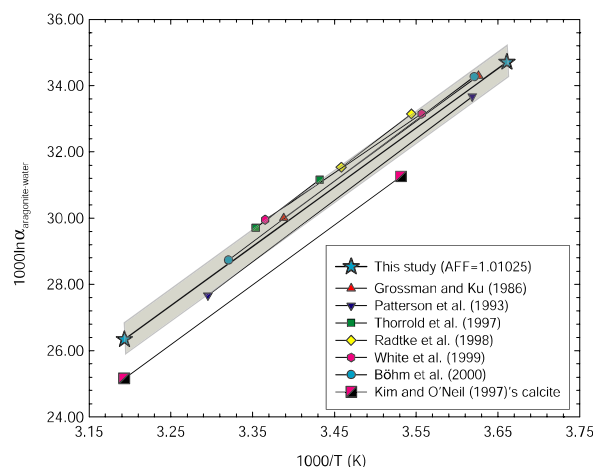


Fig. 5. Comparison of the new experimental aragonite–water calibration with previously reported fractionation relationships for biogenic aragonite–water at low temperatures. The shaded area around the new calibration curve represents the standard error ( $\pm 0.46\text{‰}$ ) of the regression analysis. The calcite–water isotope fractionation curve of Kim and O’Neil (1997) is added for comparison.

Table 4  
Comparison of published determinations of the aragonite–water fractionation

Authors	Temp. range (°C)	Equations
This study	0–40	$1000\ln\alpha = 17.88 (10^3/T) - 31.14$
Grossman and Ku (1986)	2.6–22	$1000\ln\alpha = 18.04 (10^3/T) - 31.12$
Patterson et al. (1993)	3.2–30.3	$1000\ln\alpha = 18.56 (10^3/T) - 33.49$
Thorrold et al. (1997)	18.2–25	$1000\ln\alpha = 18.56 (10^3/T) - 32.54$
Radtke et al. (1998)	9–16	$1000\ln\alpha = 18.70 (10^3/T) - 33.13$
White et al. (1999)	8–24	$1000\ln\alpha = 16.74 (10^3/T) - 26.39$
Böhm et al. (2000)	3–28	$1000\ln\alpha = 18.45 (10^3/T) - 32.54$

Temp., temperature.

Considering that the standard error of the least squares analysis (or curve fitting) for the intercept of our new calibration (Eq. (1)) is  $\pm 0.46$ , all the biogenic aragonite–water fractionation curves shown in Table 4 are statistically indistinguishable from our new abiogenic aragonite–water fractionation curve (see Fig. 5). The implications of these observations are threefold: (1) many modern biogenic aragonites are precipitated *at or very near* oxygen isotope equilibrium with ambient water, (2) where deviations from the oxygen isotope equilibrium are observed, the discrepancy can be accounted for by species specific vital (physiological and/or kinetic) effects operating during the precipitation of the biogenic aragonite, and (3) regardless of vital effects, the temperature coefficients of all the aragonite–water curves are, to all intents and purposes, the same. These conclusions are drawn on the assumption that abiogenic aragonite can be precipitated in oxygen isotope equilibrium with water using the methods applied in this study. Given the nature of the precipitation process, it is impossible to demonstrate that isotopic equilibrium was attained during this study. Nevertheless, the aragonite was precipitated relatively slowly, under well-constrained environmental conditions, from relatively dilute solutions and in the absence of vital or metabolic effects. In addition, the forced CO<sub>2</sub> degassing method employed in this study is almost identical to the one used by Kim and O’Neil (1997) to precipitate calcite in apparent isotopic equilibrium with its parent solution. Thus it is reasonable to assume that the aragonite synthesized in this study yields a reliable equilibrium aragonite–water fractionation that can be used as a reference point to elucidate the metabolic processes (vital effects) responsible for the isotopic disequilibrium of biogenic aragonite relative to their ambient fluids.

#### 4. CONCLUSIONS

On the basis of principles established for the determination of the temperature dependence of the equilibrium calcite–water fractionation (Kim and O’Neil, 1997) as well as a study of the influence of the pH on the aragonite–water fractionation (Kim et al., 2006), the equilibrium oxygen isotope aragonite–water fractionations were determined as a function of temperature between 0 and 40 °C. The least squares fit to these measurements yields the following equation:

$$1000\ln\alpha_{\text{aragonite–water}} = 17.88 \pm 0.13(10^3/T) - 31.14 \pm 0.46$$

This new temperature coefficient for the aragonite–water oxygen isotope fractionation will allow a more reliable reconstruction of past climate variations and provide a baseline for calibration of species-specific paleothermometers. In addition, by combining our new experimental data (equilibrium aragonite–water fractionation factors) and the calcite–water fractionation relationship established in previous studies, a positive aragonite–calcite fractionation ( $\sim 0.8\text{‰}$  at 25 °C) was obtained between 0 and 40 °C. The sign and magnitude of the aragonite–calcite oxygen isotope fractionation factors are consistent with the experimental results (0.6‰) and theoretical calculations (0.79‰) of Tarutani et al. (1969). Because the slopes of the aragonite–water and calcite–water expressions are very similar, the aragonite–calcite fractionation can not be used to determine temperatures of formation.

Finally, the influence of Mg<sup>2+</sup> ions and its ion-pairs on the oxygen isotope fractionation in the aragonite–water system at 25 °C was experimentally studied. On the basis of aragonite precipitation experiments conducted in the presence of 20 and 100 mmolal Mg<sup>2+</sup>, no oxygen isotope salt effect on the equilibrium aragonite–water oxygen isotope fractionation was observed. However, significant isotope salt effects were detected from aragonite precipitates synthesized from solutions containing 902.5 mmolal Mg<sup>2+</sup>. Potential mechanisms for the *composition*-based as well as the *activity*-based oxygen isotope salt effects observed in this study were discussed.

#### ACKNOWLEDGMENTS

This research was funded in part by a GSA Graduate Student Research Grant (No. 7714-04) to S.-T. Kim and NSERC Discovery grants to A.M. and C.H.-M. as well as NSF 9406067 to J.R. O’Neil. S.-T. Kim also acknowledges financial support from the Carl Reinhardt McGill Major Fellowship program as well as GEOTOP-UQAM-McGill fellowships during his residency at McGill University. The authors would like to thank Lora Wingate, Julie Leduc, and Constance Guignard for their assistance in the laboratory. Finally, this manuscript was greatly improved by constructive comments from Juske Horita, Ethan Grossman, and two anonymous reviewers. GEOTOP-UQAM-McGill publication No. 2007-0027.

#### REFERENCES

Beck W. C., Grossman E. L. and Morse J. W. (2005) Experimental studies of oxygen isotope fractionation in the carbonic acid

- system at 15°, 25°, and 40 °C. *Geochim. Cosmochim. Acta* **69**, 3493–3503.
- Böhm F., Joachimski M. M., Dullo W. C., Eisenhauer A., Lehnert H., Reitner J. and Worheide G. (2000) Oxygen isotope fractionation in marine aragonite of coralline sponges. *Geochim. Cosmochim. Acta* **64**, 1695–1703.
- Cohn M. and Urey H. C. (1938) Oxygen exchange reactions of organic compounds and water. *J. Am. Chem. Soc.* **60**, 679–687.
- Davis K. J., Dove P. M. and De Yoreo J. J. (2000) The role of  $Mg^{2+}$  as an impurity in calcite growth. *Science* **290**, 1134–1137.
- Golyshev S. I., Padalko N. L. and Pechenkin S. A. (1981) Fractionation of stable isotopes of carbon and oxygen in carbonate systems. *Geochem. Intl.* **18**, 85–99.
- González L. A. and Lohmann K. C. (1985) Carbon and oxygen isotopic composition of Holocene reefal carbonates. *Geology* **13**, 811–814.
- Grossman E. L. and Ku T. L. (1986) Oxygen and carbon isotope fractionation in biogenic aragonite—temperature effects. *Chem. Geol.* **59**, 59–74.
- Hartley G. and Mucci A. (1996) The influence of  $P_{CO_2}$  on the partitioning of magnesium in calcite overgrowths precipitated from artificial seawater at 25°C and 1 atm total pressure. *Geochim. Cosmochim. Acta* **60**, 315–324.
- Helgeson H. C. (1969) Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Am. J. Sci.* **267**, 729–804.
- Horibe Y. and Oba T. (1972) Temperature scales of aragonite–water and calcite–water systems. *Fossils*(23/24), 69–79.
- Horita J., Cole D. R. and Wesolowski D. J. (1993a) The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: II. Vapor–liquid water equilibration of mixed salt solutions from 50 to 100 °C and geochemical implications. *Geochim. Cosmochim. Acta* **57**, 4703–4711.
- Horita J., Wesolowski D. J. and Cole D. R. (1993b) The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: I. Vapor–liquid water equilibration of single salt solutions from 50 to 100 °C. *Geochim. Cosmochim. Acta* **57**, 2797–2817.
- Hu G. and Clayton R. N. (2003) Oxygen isotope salt effects at high pressure and high temperature and the calibration of oxygen isotope geothermometers. *Geochim. Cosmochim. Acta* **67**, 3227–3246.
- Kim S.-T., Hillaire-Marcel C. and Mucci A. (2006) Mechanisms of equilibrium and kinetic oxygen isotope effects in synthetic aragonite at 25 °C. *Geochim. Cosmochim. Acta* **70**, 5790–5801.
- Kim, S.-T., Mucci, A. and Taylor, B. E. (in press) Phosphoric acid fractionation factors for calcite and aragonite between 25 and 75 °C: Revisited. *Chem. Geol.*
- Kim S.-T. and O’Neil J. R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta* **61**, 3461–3475.
- Kim S.-T. and O’Neil J. R. (2005) Comment on “An experimental study of oxygen isotope fractionation between inorganically precipitated aragonite and water at low temperatures” by G.-T. Zhou and Y.-F. Zheng. *Geochim. Cosmochim. Acta* **69**, 3195–3197.
- Lécuyer C., Reynard B. and Martineau F. (2004) Stable isotope fractionation between mollusc shells and marine waters from Martinique Island. *Chem. Geol.* **213**, 293–305.
- Lippmann F. (1973) *Sedimentary Carbonate Minerals*. Springer-Verlag, Berlin, New York.
- McConnaughey T. (1989a)  $^{13}C$  and  $^{18}O$  isotopic disequilibrium in biological carbonates: I. Patterns. *Geochim. Cosmochim. Acta* **53**, 151–162.
- McConnaughey T. (1989b)  $^{13}C$  and  $^{18}O$  isotopic disequilibrium in biological carbonates: II. In vitro simulation of kinetic isotope effects. *Geochim. Cosmochim. Acta* **53**, 163–171.
- McConnaughey T. A. (2003) Sub-equilibrium oxygen-18 and carbon-13 levels in biological carbonates: carbonate and kinetic models. *Coral Reefs* **22**, 316–327.
- McCrea J. M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* **18**, 849–853.
- Morse J. W., Wang Q. W. and Tsio M. Y. (1997) Influences of temperature and Mg:Ca ratio on  $CaCO_3$  precipitates from seawater. *Geology* **25**, 85–87.
- Mucci A. and Morse J. W. (1983) The incorporation of  $Mg^{2+}$  and  $Sr^{2+}$  into calcite overgrowths: influences of growth rate and solution composition. *Geochim. Cosmochim. Acta* **47**, 217–233.
- O’Neil J. R., Adami L. H. and Epstein S. (1975) Revised value for the  $O^{18}$  fractionation between  $CO_2$  and  $H_2O$  at 25°C. *J. Res. US Geol. Surv.* **3**, 623–624.
- O’Neil, J. R. and Truesdell, A. H. (1991) Oxygen isotope fractionation studies of solute-water interactions. In *Stable Isotope Geochemistry: A Tribute to Samuel Epstein* (eds. H. P. Taylor Jr., J. R. O’Neil and I. R. Kaplan). The Geochemical Society, San Antonio, pp. 17–25.
- Patterson W. P., Smith G. R. and Lohmann K. C. (1993) Continental paleothermometry and seasonality using the isotopic composition of aragonitic otoliths of freshwater fishes. In *Climate Change in Continental Isotopic Records*, vol. 78 (eds. P. K. Swart, K. C. Lohmann, J. McKenzie and S. Savin). *Geophys. Monogr. Ser.*, pp. 191–202.
- Pytkowicz R. M. (1973) Calcium-carbonate retention in supersaturated seawater. *Am. J. Sci.* **273**, 515–522.
- Radtke R. L., Showers W., Moksness E. and Lenz P. (1996) Environmental information stored in otoliths: insights from stable isotopes. *Mar. Biol.* **127**, 161–170.
- Radtke R. L., Showers W., Moksness E. and Lenz P. (1998) Corrigendum: environmental information stored in otoliths: insights from stable isotopes (Mar. Biol. 127:161–170, 1996). *Mar. Biol.* **132**, 347–348.
- Rahimpour-Bonab H., Bone Y. and Moussavi-Harami R. (1997) Stable isotope aspects of modern molluscs, brachiopods, and marine cements from cool-water carbonates, Lacepede Shelf, South Australia. *Geochim. Cosmochim. Acta* **61**, 207–218.
- Reddy M. M. and Wang K. K. (1980) Crystallization of calcium-carbonate in the presence of metal-ions. I. Inhibition by magnesium-ion at pH 8.8 and 25°C. *J. Cryst. Growth* **50**, 470–480.
- Sharma T. and Clayton R. N. (1965) Measurement of  $O^{18}/O^{16}$  ratios of total oxygen of carbonates. *Geochim. Cosmochim. Acta* **29**, 1347–1353.
- Socki R. A., Karlsson H. R. and Gibson E. K. (1992) Extraction technique for the determination of O-18 in water using preevacuated glass vials. *Anal. Chem.* **64**, 829–831.
- Tarutani T., Clayton R. N. and Mayeda T. K. (1969) Effect of polymorphism and magnesium substitution on oxygen isotope fractionation between calcium carbonate and water. *Geochim. Cosmochim. Acta* **33**, 987–996.
- Thorrold S. R., Campana S. E., Jones C. M. and Swart P. K. (1997) Factors determining  $\delta^{13}C$  and  $\delta^{18}O$  fractionation in aragonitic otoliths of marine fish. *Geochim. Cosmochim. Acta* **61**, 2909–2919.
- Weber J. N. and Woodhead P. M. (1970) Carbon and oxygen isotope fractionation in skeletal carbonate of reef-building corals. *Chem. Geol.* **6**, 93–117.
- Weber J. N. and Woodhead P. M. (1972) Temperature dependence of oxygen-18 concentration in reef coral carbonates. *J. Geophys. Res.* **77**, 463–473.
- White R. M. P., Dennis P. F. and Atkinson T. C. (1999) Experimental calibration and field investigation of the oxygen isotopic fractionation between biogenic aragonite and water. *Rapid Commun. Mass Spectrom.* **13**, 1242–1247.

- Zheng Y. F. (1999) Oxygen isotope fractionation in carbonate and sulfate minerals. *Geochem. J.* **33**, 109–126.
- Zhong S. J. and Mucci A. (1993) Calcite precipitation in seawater using a constant addition technique: A new overall reaction kinetic expression. *Geochim. Cosmochim. Acta* **57**, 1409–1417.
- Zhou G. T. and Zheng Y. F. (2003) An experimental study of oxygen isotope fractionation between inorganically precipitated aragonite and water at low temperatures. *Geochim. Cosmochim. Acta* **67**, 387–399.
- Zuddas P. and Mucci A. (1994) Kinetics of calcite precipitation from seawater: I. A classical chemical kinetics description for strong electrolyte solutions. *Geochim. Cosmochim. Acta* **58**, 4353–4362.

*Associate editor:* Juske Horita