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An experimental study of oxygen isotope fractionation between inorganically precipitated aragonite and water at low temperatures

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Abstract—To determine oxygen isotope fractionation between aragonite and water, aragonite was slowly precipitated from $Ca(HCO_3)_2$ solution at 0 to 50°C in the presence of Mg^{2+} or $SO_4^{\ 2-}$. The phase compositions and morphologies of synthetic minerals were detected by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The effects of aragonite precipitation rate and excess dissolved CO_2 gas in the initial $Ca(HCO_3)_2$ solution on oxygen isotope fractionation between aragonite and water were investigated. For the $CaCO_3$ minerals slowly precipitated by the $CaCO_3$ or $NaHCO_3$ dissolution method at 0 to 50°C, the XRD and SEM analyses show that the rate of aragonite precipitation increased with temperature. Correspondingly, oxygen isotope fractionations between aragonite and water deviated progressively farther from equilibrium. Additionally, an excess of dissolved CO_2 gas in the initial $Ca(HCO_3)_2$ solution results in an increase in apparent oxygen isotope fractionations. As a consequence, the experimentally determined oxygen isotope fractionations at 50°C indicate disequilibrium, whereas the relatively lower fractionation values obtained at 0 and 25°C from the solution with less dissolved CO_2 gas and low precipitation rates indicate a closer approach to equilibrium. Combining the lower values at 0 and 25°C with previous data derived from a two-step overgrowth technique at 50 and 70°C, a fractionation equation for the aragonite-water system at 0 to 70°C is obtained as follows:

$$10^3\ln\alpha = 20.44 \times 10^3/T - 41.48.$$

This equation represents the first experimental calibration of oxygen isotope fractionation between inorganically precipitated aragonite and water at low temperatures. By considering the kinetic mechanism of oxygen isotope disequilibrium, we argue that this equation is a close proxy for thermodynamic equilibrium fractionation in the low-temperature mineral. Therefore, the discrepancies in $CaCO_3$-H_2O fractionation factors between different synthesis experiments may imply that some of the studies reflect steady-state fractionations during aragonite precipitation and subsequent polymorphic transition to calcite at different run conditions. *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

Calcium carbonate is one of the most important minerals in reconstructing paleoclimate and paleoenvironment by means of oxygen isotope analysis. A large amount of data have been accumulated for oxygen isotope fractionation in $CaCO_3$-H_2O systems since the classic work of Urey (1947) that laid out the theoretical basis of isotopic fractionation in the carbonate. However, there are still discrepancies among theoretical calculations, experimental measurements, and natural observations of oxygen isotope fractionation factors between two $CaCO_3$ polymorphs, calcite and aragonite. Whereas Epstein et al. (1953) noted no significant difference in $\delta^{18}O$ values between aragonitic and calcitic layers in an abalone shell, Tarutani et al. (1969) observed from a reexamination that the aragonitic layers were actually depleted in ^{18}O relative to the calcitic layers. Similarly, Horibe and Oba (1972) reported an ^{18}O enrichment in calcite relative to aragonite for mollusks grown at temperatures of ~5, 15, and 23°C. Behrens and Land (1972) also showed that calcite is enriched in ^{18}O relative to coexisting aragonite. In contrast, a number of authors reported that aragonite in some biogenic carbonates is enriched in ^{18}O relative to calcite (e.g., Sommer and Rye, 1978; Grossman and Ku, 1981, 1986; Grossman, 1982; Jones et al., 1983; Aharon, 1991; Barrera et al., 1994; Rahimpour-Bonab et al., 1997; Thorrold et al., 1997; Boehm et al., 2000).

Statistical-mechanical calculations predict that carbon and oxygen isotope fractionations should occur between calcite and aragonite because of differences in the internal vibrational frequencies of the carbonate ions in the two polymorphs (Huang and Kerr, 1960; Schroeder et al., 1962). The theoretical calculation of Tarutani et al. (1969) suggested that aragonite should be enriched in ^{18}O relative to calcite by 0.8‰ at 25°C. However, the authors illustrated that the results of such calculations depend on the choice of one of the several published sets of vibrational frequencies. Hulston (1978) and O'Neil (1986) further pointed out that the statistical-mechanical methods are valid only for ideal gases, and additional approximations and assumptions are required for calculations involving solids and liquids. Zheng (1999) systematically calculated oxygen isotope fractionation factors between carbonates by means of the modified increment method and noted that calcite is enriched in ^{18}O by 4.5‰ relative to aragonite at 25°C.

Experimental calibrations of the $CaCO_3$-H_2O fractionation factors have commonly been conducted at low temperatures via the decomposition of $Ca(HCO_3)_2$ in aqueous solutions. The available results show good agreement among those deter-

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mined by McCrea (1950) for aragonite and a mixture of aragonite and calcite, by Tarutani et al. (1969) for a mixture of vaterite and calcite, and by O'Neil et al. (1969) and Kim and O'Neil (1997) for calcite. These fractionation factors are also close to the calculations of Zheng (1999) and the observations on natural samples by Patterson et al. (1993) for the aragonite-water system, but smaller than those calculated by the statistical-mechanical methods for the calcite-water system (Bottinga, 1968; Kieffer, 1982; Chacko et al., 1991). The experimental calibrations of McCrea (1950), Tarutani et al. (1969), O'Neil et al. (1969), and Kim and O'Neil (1997) showed that there are negligible fractionations between $CaCO_3$ polymorphs at low temperatures, whereas the inorganic precipitation experiment of Tarutani et al. (1969) from $Ca(HCO_3)_2$ solution in the presence of Mg^{2+} yielded an ^{18}O enrichment of 0.6‰ in aragonite relative to calcite at 25°C.

Because aragonite is a metastable polymorph of $CaCO_3$, it is easily susceptible to polymorphic transition to stable calcite. The rate of such a transition is much faster in the aqueous solution than in the dry state (Wary and Daniels, 1957; Fyfe and Bischoff, 1965; Deleuze and Brantley, 1997; Zhou and Zheng, 2001). This has complicated the calibrations of oxygen isotope fractionation factors between calcite and water by means of either precipitation experiments or natural observations. Because of the widespread applications of the $CaCO_3$-H_2O thermometer to the reconstruction of paleoclimate, resolution of the controversy concerning the aragonite-water oxygen isotope fractionation is needed. A companion study of Zhou and Zheng (2002) has experimentally clarified the kinetic mechanism of oxygen isotope disequilibrium in precipitated aragonite and witherite. Their results show that the duration of CO_3^{2-}-H_2O isotope exchange in the precipitation experiments is critical in achieving isotopic equilibration between precipitated carbonate and water.

The purposes of this work are to study the influence of carbonate precipitation rate on oxygen isotope fractionation by chemical synthesis methods and to determine the equilibrium fractionation factors between aragonite and water during inorganic precipitation of $CaCO_3$. We use scanning electron microscopy (SEM) micromorphologic analysis of synthesized minerals to evaluate whether thermodynamic equilibrium is attained. We then report the first experimentally determined thermodynamic equilibrium fractionation relationship for the aragonite-water system.

2. EXPERIMENTAL METHODS

2.1. Aragonite Synthesis

In principle, aragonite can be synthesized by either the overgrowth technique (Zhou and Zheng, 1998) or slow precipitation from a $Ca(HCO_3)_2$ solution in the presence of Mg^{2+} or SO_4^{2-} (Bischoff and Fyfe, 1968; Zhou and Zheng, 2001). The present study has employed the slow precipitation method, in which $Ca(HCO_3)_2$ solutions were prepared by dissolving solid $CaCO_3$ in water with CO_2 bubbling for a long time (3 d) to obtain sufficient amounts of $Ca(HCO_3)_2$, by dissolving solid $Ca(HCO_3)_2$ in water, or by dissolving $NaHCO_3$ in water with CO_2 bubbling for a short time (10 to 20 min) to prevent the immediate precipitation of $CaCO_3$ when $CaCl_2$ was added to the solutions. The detailed experimental conditions and the phase compositions of the synthesized minerals are listed in Tables 1 to 4. According to the difference in the procedures of preparing the $Ca(HCO_3)_2$ solutions, synthesis methods are grouped into three types as summarized below.

2.1.1. *$CaCO_3$ dissolution*

To 500 mL deionized water,1.25 g of analytical-grade reagent or synthesized $CaCO_3$ solid were added. The suspension of $CaCO_3$ was placed in either a constant temperature water bath or a 0°C ice-water bath and stirred by magnetic stirrer to ensure a constant temperature. Then CO_2 gas was bubbled through the suspension for 3 d to dissolve $CaCO_3$, forming a $Ca(HCO_3)_2$ solution. To minimize the loss of water as vapor because of the bubbling, the CO_2 gas was first passed through water of the same isotopic composition as that of the solution used. The $Ca(HCO_3)_2$ solution was then vacuum filtered to remove undissolved $CaCO_3$ solid. A given amount of analytical regent-grade $MgCl_2 \cdot 2H_2O$ was added to the $Ca(HCO_3)_2$ solution prepared above. After the dissolution of $MgCl_2 \cdot 2H_2O$ without formation of any precipitate, the flasks containing the $Ca(HCO_3)_2$ and $MgCl_2$ solution were placed in the constant temperature water bath or the 0°C ice-water bath to slowly precipitate $CaCO_3$ minerals. The phase compositions of the synthesized minerals are listed in Table 1.

To test the effect of Mg^{2+} concentration on oxygen isotope fractionation at 25°C, a $Ca(HCO_3)_2$ solution containing 2.5 g of analytical-grade reagent $CaCO_3$ per 1050 mL of deionized water was used, and the following procedures were adopted in the synthesis experiments. The 1050-mL $Ca(HCO_3)_2$ solution was divided into volumes of 500 mL, 250 mL, and 250 mL to which different amounts of $MgCl_2 \cdot 6H_2O$ were added. The remaining steps were similar to those described above. The same runs were also carried out at 50°C. The phase compositions of the synthesized minerals are listed in Table 2.

To investigate the dependence of oxygen isotope fractionation on $Ca(HCO_3)_2$ concentration, a 1050-mL $Ca(HCO_3)_2$ solution was prepared at 25°C using the same procedures as described above. In this case, solutions with different concentrations of $Ca(HCO_3)_2$ were prepared by diluting the $Ca(HCO_3)_2$ solution with deionized water. An appropriate amount of $MgCl_2 \cdot 6H_2O$ was added to the specifically diluted $Ca(HCO_3)_2$ solution to ensure that the final Mg^{2+} concentration in the diluted $Ca(HCO_3)_2$ solution was 0.032 mol/L. The phase compositions of the synthesized minerals are listed in Table 3. Samples 97CB42 (0.8*n* mol/L), 97CB43 (0.6*n* mol/L), 97CB44 (0.2*n* mol/L), 97CB45 (0.2*n* mol/L), and 97CB46 (1.0*n* mol/L), where the suffix *n* denotes the initial concentration of $Ca(HCO_3)_2$ in the starting solution, were slowly precipitated at 25°C for 90 d. Among them, samples 97CB44 (0.2*n* mol/L) and 97CB45 (0.2*n* mol/L) yielded insufficient $CaCO_3$ precipitate for X-ray diffraction (XRD) and isotopic analyses and were not considered further.

2.1.2. *$NaHCO_3$ dissolution*

A given amount of analytical-grade reagent $NaHCO_3$ was dissolved in 200 mL deionized water. Then, CO_2 was bubbled through the $NaHCO_3$ solution for 10 to 20 min. A given amount of analytical-grade reagent $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 2H_2O$ was dissolved in 250 mL deionized water. The two solutions were transferred into a 500-mL volumetric flask and diluted to 500 mL with the deionized water to obtain the desired $Ca(HCO_3)_2$ solution containing Mg^{2+} ions. This solution was placed in a 25°C water bath to slowly precipitate $CaCO_3$. The phase compositions of the synthesized minerals are listed in Table 4.

To investigate the effect of dissolved amounts of CO_2 gas in aqueous solution on oxygen isotope fractionation between aragonite and water, an apparatus was designed to control the amount of CO_2 flow through the $NaHCO_3$ solution (Fig. 1), and thus, a series of special experiments were carried out. To 200 mL deionized water, 2.1 g of analytical regent-grade $NaHCO_3$ were added. Then, CO_2 was bubbled through this solution for 60 min. As schematically shown in Fig. 1, the amount of dissolved CO_2 gas in container 1 is more than that in container 2. The remaining synthesis steps are similar to the above-described procedures. The detailed run conditions are listed in Table 4. Samples 97CB17 and 97CB18 were precipitated from the $Ca(HCO_3)_2$ solutions in containers 1 and 2, respectively. The XRD analyses show that sample 97CB17 is an approximately equal mixture of aragonite and calcite, whereas sample 97CB18 is pure aragonite. These observations suggest that low concentrations of dissolved CO_2 favor aragonite formation, consistent with previous conclusions by Berner et al. (1983) and Lasaga et al. (1985).

Table 1. Mineralogy and experimental conditions of calcium carbonate synthesized by the $CaCO_3$ dissolution method.

Sample	T (°C)	Precipitation time (d)	Mg^{2+} concentration (mol/L)	Mineralogy[†]	Remarks[‡]
97CB23	0	80	0.016	Cc	a
97CB23.2	0	115	0.016	Arg + Cc	a
97CB26	0	70	0.128	Arg + Cc	b
97CB33	0	45	0.192	Arg + Cc + Vt (T)	b
97CB33.2	0	60	0.192	Arg + Cc (M)	b
97CB34	0	65	0.224	Arg + Cc (M) + Vt (T)	b
98CB01	0	90	0.192	Arg + Cc + Vt (T)	b
98CB02	0	90	0.224	Arg + Cc + Vt (T)	b
97CB19	25	30	0.016	Arg + Cc	b
97CB20	25	30	0.016	Arg + Cc (M)	b
97CB20.2	25	80	0.016	Arg + Cc (T)	b
97CB22	25	30	0.016	Arg + Cc (M)	a
97CB22.2	25	80	0.016	Arg + Cc (T)	a
97CB24	25	68	0.064	Arg	b
97CB25	25	68	0.064	Arg	a
97CB28	25	68	0.032	Arg	b
98CB06	25	60	0.064	Arg	c
98CB07	25	60	0	Cc	c
97CB29	50	68	0.032	Arg	c
97CB30	50	68	0.032	Arg	c

[†] Abbreviations Arg, Cc, and Vt denote aragonite, calcite and vaterite, respectively; M and T denote the micro amount and trace amount in the $CaCO_3$ mixture, respectively; and Arg + Cc denotes the approximately equal amounts of aragonite and calcite;

[‡] Symbols a, b, and c denote the carbon and oxygen isotope compositions of three different initial $CaCO_3$ solids, respectively.

2.1.3. *$Ca(HCO_3)_2$ dissolution in the presence of dissolved sulfate*

A sample was slowly precipitated from $Ca(HCO_3)_2$ solution in the presence of dissolved SO_4^{2-}. To 400 mL of deionized water, 5.88 g of $CaCl_2 \cdot 2H_2O$ were added. The solution was then placed in a 50°C water bath. A stoichiometric amount of Na_2SO_4 was dissolved in 400 mL deionized water, and then the solution of Na_2SO_4 was thermostatically kept in the 50°C water bath. The solution of $CaCl_2$ was added drop by drop to the solution of Na_2SO_4 that was stirred vigorously to form $CaSO_4$ precipitate. Then 3.36 g of $NaHCO_3$ were added to the suspension of $CaSO_4$ and stirred for 5 h. The solution of Ca^{2+}-Na^{+}-HCO_3^{-}-SO_4^{2-} was then obtained by filtration. This solution was maintained in the 50°C water bath again for 80 d to form $CaCO_3$ precipitate. Sample 97CB09W was derived from the mineral precipitating on the wall of the reaction vessel, and XRD analysis shows that it is pure aragonite.

In all synthesis runs at 25 and 50°C, water-flowing condensers were used to minimize the loss of water vapor during the thermostatic precipitation. We observed that in general, mineral precipitation started to take place after 4 weeks at 0°C and after 1 week at 25°C, but overnight at 50°C. In all cases, final mineral precipitates were obtained by vacuum filtration and rinsed three times with deionized water and once with acetone. The precipitate slurry was dried under an infrared lamp for 5 h, followed by 12 h in a 110°C vacuum oven. Carbonate yields estimated by weighing after filtration were $> 80\%$ and proportional to $Ca(HCO_3)_2$ concentration.

2.2. Mineral Detection and Characterization

The phase composition and structure of $CaCO_3$ precipitates were characterized by XRD using a Rigaku Dmax X-ray diffractometer with graphite monochromatized Cu K_α radiation ($\lambda = 0.154178$ nm). The morphology of synthesized $CaCO_3$ was investigated using a Hitachi S-650 scanning electron microscope. When crystals of calcite (or vaterite) are too small to be observable within aragonite matrix by SEM, XRD detection still shows the presence of calcite (or vaterite). In this case, “micro amount” is used to denote that the mineral is detectable by XRD with strong peaks, whereas “trace amount” denotes that the mineral is detectable by XRD with weak peaks.

2.3. Isotope Analysis

Oxygen and carbon isotope analyses of carbonates were conducted by the conventional phosphoric acid method (McCrea, 1950). The oxygen isotope analyses of water were performed by the classical CO_2-H_2O equilibration method (Cohn and Urey, 1938). Isotope ratio measurements were made on CO_2 gas in a Delta+ mass spectrometer at the University of Science and Technology of China. The acid

Table 2. Dependence of oxygen isotope fractionations on Mg^{2+} concentration in the aragonite-water system.

Sample	T (°C)	Precipitation time (d)	Mineralogy	Mg^{2+} (mol/L)	$10^3\ln\alpha$	Remarks
98CB04	25	60	Cc	0	28.31	c[†]
98CB05	25	60	Arg + Cc (M)	0.016	28.64	c
98CB03	25	60	Arg + Cc (T)	0.032	28.50	c
97CB49	50	60	Arg	0.032	24.38	c
97CB50a	50	60	Arg	0.064	24.23	c
97CB50b	50	60	Arg	0.064	24.26	c

[†] Symbol c is the same as that in the column of remarks in Table 1.

Table 3. Dependence of oxygen isotope fractionations on $Ca(HCO_3)_2$ concentrations in the aragonite-water system.

Sample	T (°C)	Precipitation time (d)	Mineralogy	$Ca(HCO_3)_2$ (mol/L)	$10^3\ln\alpha$	Remarks
97CB43	25	90	Arg	$0.6n$[†]	27.99	b[‡]
97CB43W	25	90	Arg	$0.6n$	27.75	b
97CB42W	25	90	Arg	$0.8n$	28.20	b
97CB46	25	90	Arg	$1.0n$	28.03	b
97CB46W	25	90	Arg	$1.0n$	28.18	b

[†] Suffix n after number denotes the $Ca(HCO_3)_2$ concentration in the starting solution.

[‡] Symbol b is the same as that in the column of remarks in Table 1.

fractionation factor of 25°C used in this study is 1.01034 for aragonite and the mixture of aragonite and calcite and 1.01025 for calcite (Sharma and Clayton, 1965). The equilibrium fractionation factor of oxygen isotopes for the CO_2-H_2O system at 25°C is 1.0412 (O'Neil et al., 1975; Friedman and O'Neil, 1977). The oxygen and carbon isotope ratios of both carbonates and water are reported in the $\delta^{18}O$ and $\delta^{13}C$ notations relative to Vienna standard mean ocean water (VSMOW) and Vienna Peedee belemnite (VPDB) standards, respectively. The $\delta^{18}O$ analytical uncertainties for both carbonate and water are $< \pm 0.2‰$ (2σ). The oxygen isotope fractionation factor α between carbonate and water is defined as

$$\alpha = (\delta^{18}O_{CaCO_3} + 1000)/(\delta^{18}O_{H_2O} + 1000),$$

where $\delta^{18}O_{CaCO3}$ and $\delta^{18}O_{H2}O$ denote the oxygen isotope compositions of calcium carbonate and water, respectively. For theoretical and practical reasons, the function $10_3\ln\alpha$ vs. $10_3/T$ is employed in this paper.

Three different $CaCO_3$ solids were used as starting materials, and their carbon and oxygen isotope compositions are as follows: (1) synthesized $CaCO_3$, $\delta^{13}C = -13.57‰$ and $\delta^{18}O = 17.99‰$; (2) analytical-grade reagent, $\delta^{13}C = -6.03‰$ and $\delta^{18}O = 25.60‰$; and (3) analytical-grade reagent, $\delta^{13}C = -15.82‰$ and $\delta^{18}O = 23.67‰$. Starting waters of different $\delta^{18}O$ values were used in the synthesis experiments, and the $\delta^{18}O$ values of final waters are essentially the same (i.e., within $\pm 0.2‰$) as the starting waters, except for the case when a large amount of CO_2 was dissolved in water by means of the $CaCO_3$ dissolution method. The $\delta^{18}O$ values of the final waters and final $CaCO_3$ precipitates were used in the calculation of fractionations. Consequently, uncertainties in $\delta^{18}O$ measurements of the starting materials do not affect the errors of fractionation factors.

3. RESULTS

3.1. Synthesis of $CaCO_3$ Minerals

As shown in Tables 1 to 4, the phase compositions of synthesized $CaCO_3$ minerals by the different methods vary generally from pure calcite through a mixture of calcite and aragonite to pure aragonite with increasing Mg^{2+} concentrations in the solutions. This suggests that the presence of Mg^{2+} ions in the $Ca(HCO_3)_2$ solutions favors the formation of metastable aragonite (Tables 1 and 4). Similarly, the formation of aragonite is also favored by increasing experimental temperature (Table 1). At similar Mg^{2+} concentrations, aragonite formed at both 25 and 50°C, but the coexisting phases of calcite and aragonite occurred with minor vaterite at 0°C (Table 1). The formation of aragonite also depends on $Ca(HCO_3)_2$ concentration and the amount of dissolved CO_2 gas in the initial $Ca(HCO_3)_2$ solutions. Samples 97CB23.2 and 97CB33.2 at 0°C and samples 97CB20.2 and 97CB22.2 at 25°C in Table 1 were precipitated from the filtrates of corresponding samples 97CB23, 97CB33, 97CB20, and 97CB22, respectively. The $Ca(HCO_3)_2$ concentrations and the amounts of dissolved CO_2 gas in the former solutions are significantly lower than those in the latter ones because of $CaCO_3$ precipitation and slow escape of CO_2. The XRD analysis shows that the contents of aragonite in the former are higher than those in the latter, indicating that the aragonite content in $CaCO_3$ minerals increases with decreasing $Ca(HCO_3)_2$ concentration and decreasing amount of dissolved CO_2 gas.

The morphology of $CaCO_3$ crystals synthesized by the slow precipitation method was investigated by SEM in detail, and typical examples are shown in Fig. 2. The minerals synthesized at 0 and 25°C occur in the form of aggregate of a single phase. For pure calcite or aragonite, the single crystals are rhombohedral or rodlike. The mixture of calcite and aragonite is composed of crystalline rhombs and rods. The morphologies of both aragonite and calcite are similar to those formed in nature. Compared with aragonite synthesized at 0 and 25°C, aragonite synthesized at 50°C consists of dispersed rod-like single crystals almost without aggregation. The single crystals of aragonite synthesized at 50°C are larger than those synthesized at 0 and 25°C under the same experimental conditions. Because aragonite precipitation took place after 4 weeks at 0°C, after 1 week at 25°C, and overnight at 50°C, it appears that with increasing experimental temperature, the decomposition rate of $Ca(HCO_3)_2$ is enhanced, and single crystals of aragonite grow much faster.

The SEM observations help identify whether equilibrium oxygen isotope fractionation is likely to have achieved between aragonite and water. In general, the slower the rate of the mineral formation, the closer the mineral is to isotope equilibrium (e.g., McCrea, 1950; Kim and O'Neil, 1997). Furthermore, the yields of minerals formed at 0 and 25°C are lower than those at 50°C. This also indicates that the rate of $Ca(HCO_3)_2$ decomposition increases with temperature.

3.2. Effects of Mg^{2+} and $Ca(HCO_3)_2$ Concentrations on Oxygen Isotope Fractionation Between Aragonite and Water

3.2.1. *Mg^{2+} concentration*

Bischoff and Fyfe (1968) investigated the influence of Mg^{2+} in solution on polymorphic transition process from aragonite to calcite in detail. Their experiments showed that the presence of Mg^{2+} in the solution could inhibit the transition process from aragonite to calcite. They also pointed out that the Mg^{2+}, which can stabilize aragonite, also favors the formation of aragonite. On the other hand, other experiments showed that Mg^{2+} is readily incorporated into the structure of $CaCO_3$ to form mag-

Table 4. Mineralogy and experimental conditions of calcium carbonate synthesized by the $NaHCO_3$ dissolution method.

Sample	T (°C)	Bubbling CO_2 time (min)	$CaCl_2$ (mol/L)	$NaHCO_3$ (mol/L)	Mg^{2+} (mol/L)	Precipitation time (d)	Mineralogy
97CB01	25	10	0.025	0.015	0.375	60	Arg
97CB02	25	10	0.050	0.030	1.000	60	Arg
97CB03	25	20	0.025	0.060	1.000	60	Arg
97CB04	25	20	0.050	0.015	1.000	60	Arg
97CB05	25	15	0.050	0.030	1.000	60	Arg
97CB17	25	60	0.025	0.050	0.016	33	Arg + Cc
97CB18	25	60	0.025	0.050	0.032	33	Arg

nesian calcite (Tarutani et al., 1969; Chen et al., 1979). Furthermore, ions having larger radii than Ca^{2+} prefer to be incorporated into the structure of aragonite, whereas those having smaller radii are repelled by aragonite and thus not incorporated into its lattice (Deleuze and Brantley, 1997). However, the effect of Mg^{2+} on oxygen isotope fractionation between aragonite and water is unclear.

Samples 98CB03, 98CB04, and 98CB05 in our experiments were obtained at 25°C, in which sample 98CB04 is pure calcite because of the absence of Mg^{2+}. Similarly, samples 97CB49, 97CB50a, and 97CB50b were obtained at 50°C. The experimental conditions, mineralogy, and oxygen isotope fractionations between aragonite and water at the different Mg^{2+} concentrations are listed in Table 2. It appears that the variation in the $10^3\ln\alpha$ value is insignificant with increasing Mg^{2+} concentration within the experimental errors at either 25 or 50°C. In addition, the data for samples 97CB02, 97CB03, 97CB04, and 97CB05 in Table 5 also show no significant change in the $10^3\ln\alpha$ value even if the Mg^{2+} concentrations in the $Ca(HCO_3)_2$ solution are as high as 1.000 mol/L (Table 4). These results indicate that the Mg^{2+} concentration does not significantly affect oxygen isotope fractionation for the aragonite-water system.

Sample 97CB09W is a pure aragonite that was slowly precipitated at 50°C from $Ca(HCO_3)_2$ solution in the presence of dissolved sulfate. The measured fractionation value of 23.59‰ between this aragonite and water is slightly lower than but close to the fractionation values of 23.75 to 23.82‰ from the $CaCO_3$ dissolution method in the presence of Mg^{2+} (Table 5).

3.2.2. $Ca(HCO_3)_2$ concentration

Kim and O'Neil (1997) experimentally investigated the effect of Ca^{2+} and HCO_3^- concentrations on oxygen isotope fractionation between calcite and water. Their results showed that the fractionation between calcite and water decreases with decreasing concentrations of Ca^{2+} and HCO_3^-, and the effect depends on temperature. With respect to the formation rate of $CaCO_3$ minerals, the lower the concentrations of Ca^{2+} and/or HCO_3^-, the slower the precipitation rate of $CaCO_3$ minerals and the closer to equilibrium for the oxygen isotope fractionations between mineral and water.

To study the influence of $Ca(HCO_3)_2$ concentration on oxygen isotope fractionation between aragonite and water, our experiments were carried out at different $Ca(HCO_3)_2$ concentrations at 25°C. As listed in Table 3, $10^3\ln\alpha$ values vary from

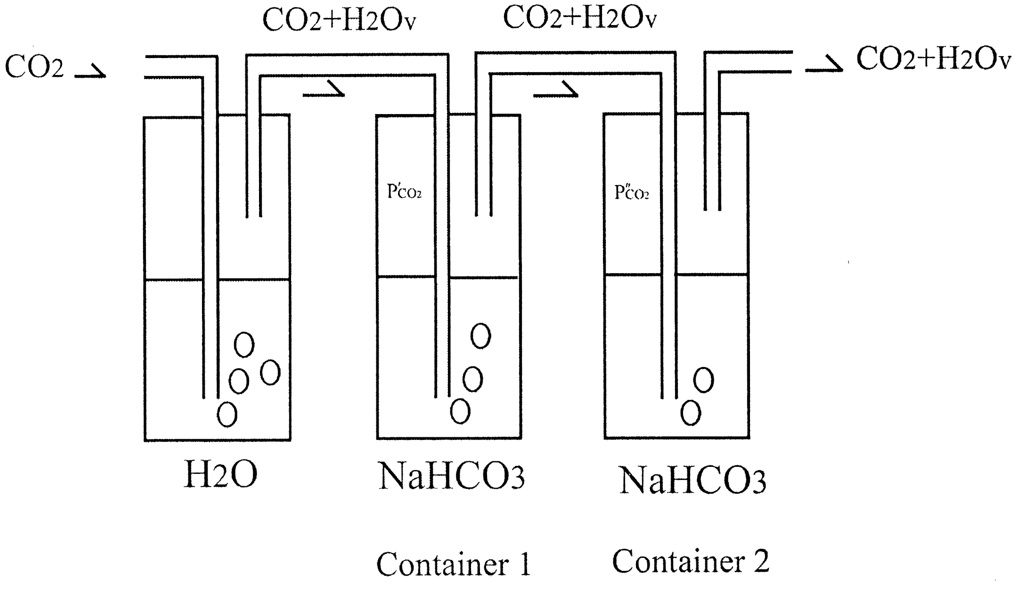

Fig. 1. Schematic diagram of the experimental apparatus used in the preparation of $Ca(HCO_3)_2$ solution at different pCO_2. The solution in container 1 contains a larger amount of dissolved CO_2 gas than that in container 2.

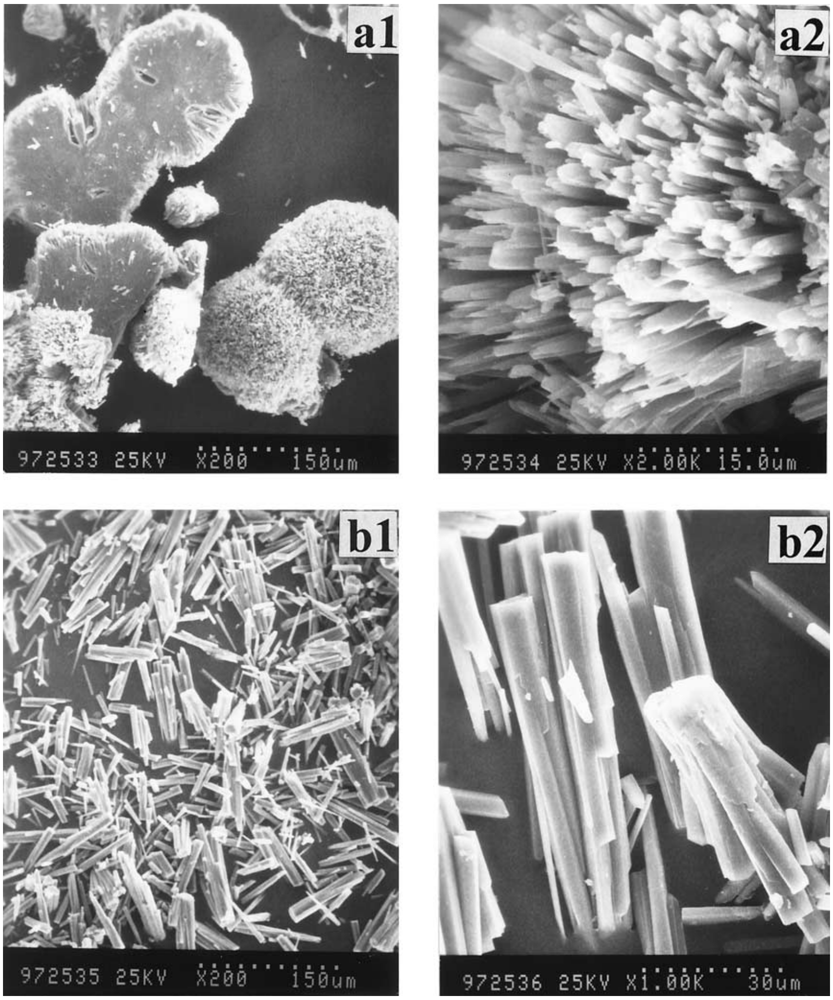

Fig. 2. Typical scanning electron microscopy photographs of aragonite minerals synthesized by the slow precipitation method at (a) 25°C and (b) 50°C. Photos a2 and b2 are enlargements of photos of a1 and b1, respectively.

28.20 to 27.75‰ with a change in $Ca(HCO_3)_2$ concentration from 0.6 to 1.0 times than the starting solution. It appears that within the experimental errors, the change in the oxygen isotope fractionation is almost unmeasurable with the change in $Ca(HCO_3)_2$ concentration. This indicates that the fractionation due to the change in the Ca^{2+} and HCO_3^- concentrations is negligible under the present experimental conditions.

3.3. Oxygen Isotope Fractionation in the $CaCO_3$-H_2O System

Because of the potential polymorphic transition of aragonite to calcite during $CaCO_3$ precipitation in the laboratory and nature, a series of synthesis experiments were carried out by the slow precipitation method to control their formation (Tables 1 to 4). Principally depending on Mg^{2+} concentration in the solutions and precipitation temperature, the synthesized products include pure aragonite, an aragonite-dominant phase with only very small amounts of calcite and/or vaterite, approximately equal mixtures of aragonite and calcite, and pure calcite. The phase compositions of $CaCO_3$ minerals were identified by the XRD analysis and SEM observation. For instance, the XRD pattern of sample 97CB22 shows the presence of the micro-amount of calcite within the aragonite matrix, but no rhombohedral crystal of calcite was observed by SEM. For sample 97CB19, on the other hand, the XRD pattern shows the coexistence of calcite and aragonite, and the SEM observation indicates the occurrence of both rhombohedral calcite and rodlike aragonite. Apparently, there are fewer SEM-observable calcite crystals in sample 97CB22 than in sample 97CB19.

For the pure aragonite and aragonite-dominant phases, the measured oxygen isotope fractionations between $CaCO_3$ and H_2O are 33.52 to 33.79‰ at 0°C, 26.92 to 28.64‰ at 25°C, and 23.59 to 24.38‰ at 50°C (Table 5). The fractionations derived from the different runs at 0 and 50°C are in agreement with each other within the analytical uncertainties (±0.2‰) at the same temperatures, but there is large scatter in the fractionations from the different runs at 25°C. Figure 3 illustrates the relationship of $10^3 \ln\alpha$ to $10_3/T$ for these data by a comparison with known data for the aragonite-water system.

As shown in Fig. 4, the data of Table 6 for oxygen isotope fractionations involving the calcite-aragonite mixtures and pure calcite are relatively scattered, from 32.66 to 33.79‰ at 0°C,

Table 5. Oxygen isotope compositions of water and coexisting aragonite and aragonite-calcite mixtures synthesized using the slow precipitation method.

			$CaCO_3$		H_2O		
Sample	T (°C)	Mineralogy	δ^{18}O (‰)	δ^{13}C (‰)	δ^{18}O (‰)	α	$10^3\ln\alpha$
97CB33W[†]	0	Arg + Cc (M)	20.04	−7.10	−13.59	1.03409	33.52
97CB33.2	0	Arg + Cc (M)	20.25	−1.57	−13.46	1.03417	33.60[‡]
97CB34W	0	Arg + Cc (M)	22.79	−8.15	−11.09	1.03426	33.69
97CB01	25	Arg	21.79	2.89	−5.64	1.02758	27.21[‡]
97CB02	25	Arg	22.97	3.57	−4.66	1.02776	27.38[‡]
97CB03	25	Arg	22.86	3.91	−5.07	1.02807	27.68[‡]
97CB04	25	Arg	22.63	4.04	−5.10	1.02787	27.49[‡]
97CB05	25	Arg	22.62	2.96	−5.09	1.02785	27.47[‡]
97CB18	25	Arg	20.94	−7.87	−6.60	1.02772	27.35[‡]
97CB20	25	Arg + Cc (M)	17.89	−14.04	−10.22	1.02840	28.00
97CB20.2	25	Arg + Cc (T)	17.75	−9.54	−9.28	1.02728	26.92[‡]
97CB22	25	Arg + Cc (M)	16.69	−8.72	−12.24	1.02868	28.27
97CB22.2	25	Arg + Cc (T)	15.50	−9.80	−12.16	1.02800	27.62[‡]
97CB24	25	Arg	17.22	−11.09	−10.56	1.02808	27.69
97CB25	25	Arg	18.70	−10.56	−9.76	1.02874	28.33
97CB28W	25	Arg	18.29	−11.65	−9.76	1.02833	27.93
97CB42W	25	Arg	20.91	−12.62	−7.48	1.02860	28.20
97CB43	25	Arg	22.75	−11.82	−5.48	1.02839	27.99
97CB43W	25	Arg	20.50	−11.92	−5.48	1.02813	27.75
97CB46	25	Arg	20.12	−9.20	−8.08	1.02843	28.03
97CB46W	25	Arg	20.27	−9.77	−8.08	1.02858	28.18
98CB03	25	Arg + Cc (T)	22.28	−14.43	−6.44	1.02891	28.50
98CB05	25	Arg + Cc (M)	22.40	−10.36	−6.47	1.02905	28.64
98CB06	25	Arg	20.96	−12.97	−7.74	1.02892	28.51
97CB09W	50	Arg	17.07	3.80	−6.65	1.02388	23.59
97CB29	50	Arg	15.02	−11.98	−8.87	1.02410	23.82
97CB30	50	Arg	14.78	−12.71	−9.04	1.02404	23.75
97CB49	50	Arg	17.66	−16.99	−6.85	1.02468	24.38
97CB50a	50	Arg	17.67	−16.93	−6.69	1.02452	24.23
97CB50b	50	Arg	17.81	−16.86	−6.58	1.02455	24.26

[†] Suffix W in the sample no. denotes the sample that was scraped from the wall of the reaction vessel.

[‡] The value was used in fitting Eqn. (1).

but fall within the narrow range of 28.07 to 28.23‰ at 25°C. The data at 25°C are not only in close agreement with the curve of Kim and O'Neil (1997) for calcite at 25°C (Fig. 4) but also indistinguishable from the higher fractionation values from our experiments for the pure aragonite and aragonite-dominant phases at 25°C (Table 5).

4. DISCUSSION

4.1. Oxygen Isotope Fractionation in the Aragonite-Water System

Tarutani et al. (1969) employed a similar precipitation method to synthesize aragonite and obtained an average $10^3\ln\alpha$ value of 29.19‰ at 25°C (recalculated using $\alpha CO_2\text{-}H_2O = 1.0412$ at 25°C). This fractionation value is slightly larger than the highest one of our data at 25°C in Table 5 (28.64‰ for sample 98CB05). The significant scatter in our data derived from the $CaCO_3$ dissolution method (Tables 5 and 6) may reflect disequilibrium fractionations between $CaCO_3$ and H_2O due to dissolution of excess CO_2 in the process of preparing of $Ca(HCO_3)_2$ solution (refer to Fig. 1 for the experimental procedures). Similar scatters were also observed by McCrea (1950, Table X) and by Kim and O'Neil (1997, Fig. 5).

The excess dissolved CO_2 gas may be largely present in the form of dissolved carbonate species of H_2CO_3, HCO_3^-, and CO_2 in $Ca(HCO_3)_2$ solutions. It would either slowly escape from the $Ca(HCO_3)_2$ solution during $CaCO_3$ precipitation or remain in the final solutions. It is expected that there are oxygen isotope equilibria among dissolved CO_2, $Ca(HCO_3)_2$, and $CaCO_3$ during $CaCO_3$ precipitation. CO_2 is enriched in ^{18}O relative to H_2O at thermodynamic equilibrium, and the escape of gaseous CO_2 could result in a residual solution that is depleted in ^{18}O. However, only a small amount of $CaCO_3$ precipitated from the relatively large $Ca(HCO_3)_2$ solution reservoirs, and therefore, the amount of CO_2 lost from the $Ca(HCO_3)_2$ solutions during $CaCO_3$ precipitation would be too small to affect the δ^{18}O values of the solution. CO_2 remaining in the final solution, nevertheless, will escape during pumping under vacuum as required for the measurement of the δ^{18}O value of H_2O. As a result, the measured δ^{18}O value of H_2O in the final solution is expected to be lower than the bulk δ^{18}O value of the final solution, leading to apparently higher fractionation values for the aragonite-water system. This is confirmed by the semiquantitative experiments that employed the $NaHCO_3$ dissolution method and the special apparatus in Fig. 1 for samples 97CB17 and 97CB18 in Table 4.

Samples 97CB17 and 97CB18 were synthesized at 25°C in containers 1 and 2, respectively. A $CaCO_3\text{-}H_2O$ fractionation of 28.23‰ is obtained for sample 97CB17 (Table 6), which is larger than a fractionation of 27.35‰ for sample 97CB18

(Table 5). This difference indicates that oxygen isotope fractionation between $CaCO_3$ and H_2O increases with increasing amount of gaseous CO_2 dissolved in the $Ca(HCO_3)_2$ solution because the solution in container 1 contains a larger amount of dissolved CO_2 gas than in container 2. In this context, the higher fractionation values reflect the effect of excess dissolved CO_2, whereas the lower fractionation values tend to approach thermodynamic equilibrium.

During the synthesis procedures, much longer time (3 d) was taken to bubble CO_2 in the $CaCO_3$ dissolution method than in the $NaHCO_3$ dissolution method (10 to 20 min). As a result, a much greater amount of gaseous CO_2 was dissolved into the $Ca(HCO_3)_2$ solutions in the $CaCO_3$ dissolution method than in the $NaHCO_3$ dissolution method. The oxygen isotope fractionation values derived from the $NaHCO_3$ dissolution method indeed show only a small scatter (27.21 to 27.68‰ at 25°C in Table 5). Because higher fractionation values are readily produced by the effect of excess dissolved CO_2, the relatively lower fractionation values derived from the $CaCO_3$ dissolution method for samples 97CB20.2 and 97CB22.2 at 25°C (26.92 and 27.62‰ in Table 5) and for sample 97CB33.2 at 0°C (33.60‰ in Table 5) are interpreted to be closer to thermodynamic equilibrium.

Kinetics and mechanism of $CaCO_3$-H_2O oxygen isotope fractionations must be taken into account in evaluating the aragonite-water fractionation data listed in Table 5. Although the data of Table 3 show that the change in concentrations of $Ca(HCO_3)_2$ solution under the present experimental conditions does not result in a measurable effect on oxygen isotope fractionation between aragonite and water, our experiments indicate that the higher the synthesis temperature, the faster the formation of $CaCO_3$ minerals. As previously described, equilibrium fractionation is favored in the lower temperature syntheses because of slower precipitation, whereas the disequilibrium prevailed at the higher temperature because of rapid precipitation.

Oxygen isotope fractionations between aragonite and water at 50 and 70°C have been determined by Zhou and Zheng (2002) using the one- and two-step approaches of the overgrowth technique. The measured $10^3\ln\alpha$ values by the one-step approach are 23.53 to 24.33‰ at 50°C and 19.92 to 20.46‰ at 70°C; those by the two-step approach are 21.14 to 21.81‰ at 50°C and 18.36 to 18.95‰ at 70°C. On the basis of these experimental results and carbonate solution chemistry, Zhou and Zheng (2002) deduced that two processes control oxygen isotope equilibrium: (1) oxygen isotope exchange between dissolved CO_3^{2-} and H_2O; and (2) structural effect of carbonate crystallization by combining divalent metal cation with CO_3^{2-}. The authors concluded that the two-step approach provided sufficient time to achieve oxygen isotope equilibrium between dissolved carbonate and water, whereas the one-step approach did not. As a result, the two-step approach experiments are capable of providing thermodynamic equilibrium fractionation data between the precipitated carbonates and water, whereas the one-step experiments are not. Consequently, the fractionation values of 21.14 to 21.81‰ from the two-step approach at 50°C were accepted as the equilibrium ones, whereas the values of 23.53 to 24.33‰ from the one-step approach were not. As shown in Fig. 3, the fractionation values of 23.59 to 24.38‰ derived from the slow precipitation experiments at 50°C in this study are in agreement with the fractionation values of 23.53 to 24.33‰ from the one-step overgrowth experiments at 50°C. Accordingly, we infer that the fractionations obtained from the present study at 50°C represent isotopic disequilibrium.

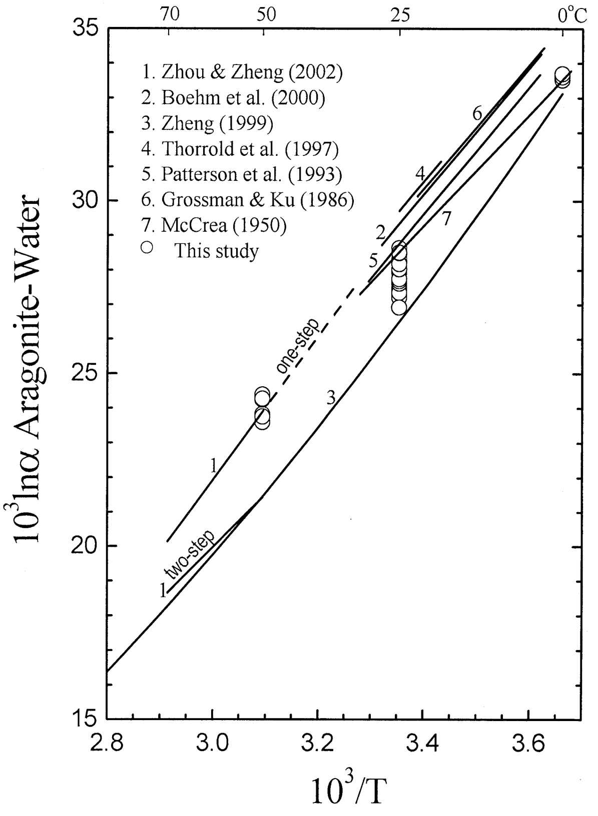

Fig. 3. Comparison of oxygen isotope fractionation factors between aragonite and water derived from the slow precipitation method in this study with those obtained by other methods. “One-step” and “two-step” denote the data from the one-step and two-step overgrowth experiments, respectively, of Zhou and Zheng (2002).

In both Tarutani et al.’s (1969) and the present experiments, the formation of aragonite involves the following chemical reactions:

$$2[HCO_3]^- \rightarrow [CO_3]^{2-} + CO_2\uparrow + H_2O, \qquad (I)$$

$$[CO_3]^{2-} + Ca^{2+} \rightarrow CaCO_3(s)\downarrow. \qquad (II)$$

Accompanied by the crystallization of the $CaCO_3$ minerals, processes of oxygen isotope exchange may proceed in the following reactions:

$$[HC^{18}O^{16}O_2]^- + [HC^{18}O_2{}^{16}O]^- \leftrightarrows [C^{18}O_2{}^{16}O]^{2-} + H_2{}^{16}O + C^{18}O^{16}O\uparrow, \qquad (III)$$

$$[C^{18}O_2{}^{16}O]^{2-} + H_2{}^{16}O \leftrightarrows [C^{18}O^{16}O_2]^{2-} + H_2{}^{18}O, \qquad (IV)$$

$$H_2{}^{18}O + [C^{18}O^{16}O_2]^{2-} + Ca^{2+} \leftrightarrows CaC^{18}O_2{}^{16}O(s)\downarrow + H_2{}^{16}O, \qquad (V)$$

where reaction III denotes the oxygen isotope exchange during HCO_3^- decomposition to CO_3^{2-} and H_2O, reaction IV means the isotope exchange and equilibration between CO_3^{2-} and

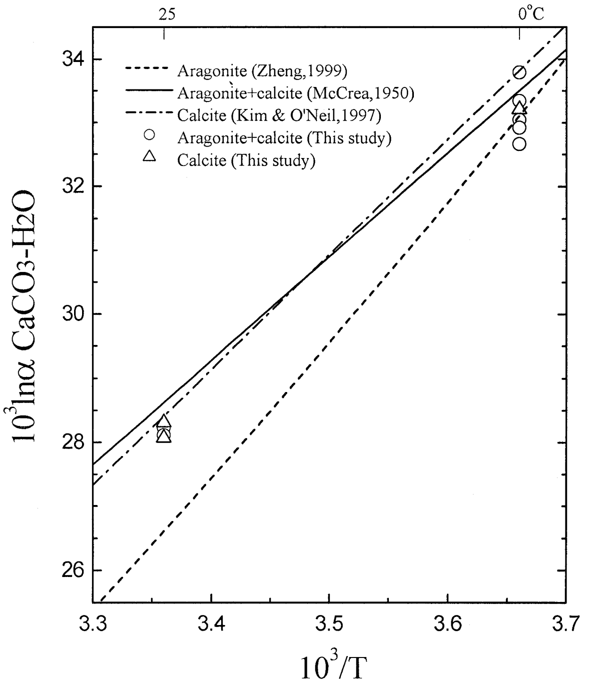

Fig. 4. Comparison of oxygen isotope fractionation factors between calcium carbonate and water derived from this study with those obtained by theoretical calculations (Zheng, 1999) and synthesis experiments (McCrea, 1950; Kim and O'Neil, 1997).

H_2O, and reaction V reflects the isotope exchange when the CO_3^{2-} equilibrating with H_2O is combined with Ca^{2+} to form aragonite crystals, i.e., structural effect on isotope fractionation during mineral crystallization.

McConnaughey (1989) argued that the slow rate of oxygen isotope exchange between CO_3^{2-} and H_2O is most likely to prevent oxygen isotope equilibrium during $CaCO_3$ precipitation. The two-step approach experiments of Zhou and Zheng (2002) at 50 and 70°C confirm McConnaughey's (1989) hypothesis: the achievement of equilibrium oxygen isotope fractionation between carbonates and water depends on the exchange and equilibration of CO_3^{2-} in solution with H_2O. This means that exchange reaction IV is the rate-limiting step of oxygen isotope equilibrium in the aragonite-water system. If reaction III proceeds rapidly, CO_3^{2-} derived from HCO_3^- decomposition in the solution cannot achieve isotopic equilibration with H_2O. The aragonite formed in this way is thus enriched in ^{18}O relative to that formed at isotope equilibrium between CO_3^{2-} and H_2O, because HCO_3^- is enriched in ^{18}O relative to CO_3^{2-} at the same temperature (McCrea, 1950; Usdowski and Hoefs, 1993, Zeebe, 1999). In this context, the lower fractionation values of 33.60‰ at 0°C and 26.92 to 27.68‰ at 25°C in Table 5 derived from the samples with less dissolved CO_2 gas in the initial $Ca(HCO_3)_2$ solution are interpreted to approach equilibrium values.

By combining the lower fractionation values obtained using the smaller amounts of dissolved CO_2 gas at 0 and 25°C for the aragonite-dominant phase (Table 5) with those equilibrium values for pure aragonite derived from the two-step overgrowth method at 50 and 70°C (Zhou and Zheng, 2002), a new fractionation equation for the aragonite−water system is obtained by least squares fitting over a temperature range of 0 to 70°C, as shown in Fig. 5:

$$10^3 \ln\alpha = 20.44 \times 10^3/T - 41.48. \tag{1}$$

Eqn. 1 may be used as a close proxy for equilibrium fractionation between inorganically precipitated aragonite and water. This is because not only have a large number of the experiments provided the improved statistics, but also all the samples used in this regression are nearly pure aragonite.

4.2. Comparison With Previous Data for the Aragonite-Water System

McCrea (1950) synthesized nearly pure aragonite and an approximately equal mixture of aragonite and calcite in a seawater solution at −1.2 to 31.8°C by the slow decomposition of $Ca(HCO_3)_2$. Epstein et al. (1953) gave the $\delta^{18}O$ value of −9.6‰ for the Florida water used by McCrea (1950). We have thus recalculated the experimental results of McCrea (1950) using the acid fractionation factor of 1.01034 for the aragonite and $10^3\ln\alpha = 1.0412$ for the CO_2-H_2O system and obtained the following fractionation relation:

$$10^3 \ln\alpha = 16.26 \times 10^3/T - 26.01. \tag{2}$$

Patterson et al. (1993) determined the oxygen isotopic fractionations between aragonitic otoliths and water from which

Table 6. Oxygen isotope compositions of water and coexisting calcite and ~50:50 calcite-aragonite mixtures synthesized using the slow precipitation method.

Sample	T (°C)	Mineralogy	$CaCO_3$ $\delta^{18}O$ (‰)	$CaCO_3$ $\delta^{13}C$ (‰)	H_2O $\delta^{18}O$ (‰)	α	$10^3\ln\alpha$
97CB23	0	Cc	20.77	−8.90	−12.57	1.03376	33.21
97CB23.2	0	Arg + Cc	20.56	−4.49	−12.23	1.03319	32.66
97CB26	0	Arg + Cc	22.34	−4.17	−11.63	1.03436	33.79
97CB33	0	Arg + Cc	19.76	−7.84	−13.59	1.03380	33.24
98CB01	0	Arg + Cc	25.74	−8.44	−7.59	1.03358	33.04
98CB02	0	Arg + Cc	25.65	−9.13	−7.54	1.03344	32.92
97CB17	25	Arg + Cc	20.90	−6.82	−7.52	1.02864	28.23
97CB19	25	Arg + Cc	16.25	−13.28	−11.92	1.02851	28.11
98CB04	25	Cc	22.07	−14.33	−6.46	1.02872	28.31
98CB07	25	Cc	20.50	−14.32	−7.75	1.02847	28.07

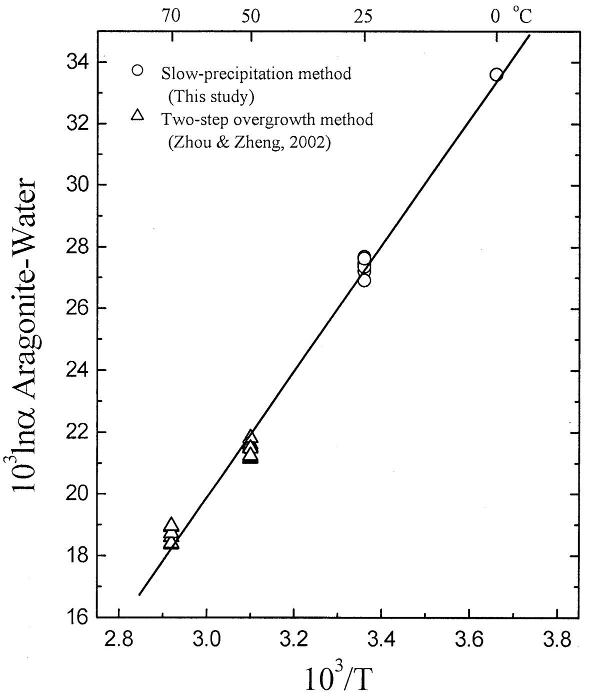

Fig. 5. Oxygen isotope fractionation factors between aragonite and water obtained by combining the results from the slow precipitation experiments at 0 and 25°C in this study with the two-step overgrowth experiments of Zhou and Zheng (2002) at 50 and 70°C.

they grew, yielding an empirical fractionation relationship over a temperature range of 3.2 to 30.3°C:

$$10^3\ln\alpha = 18.56 \times 10^3/T - 33.49. \quad (3)$$

Patterson et al. (1993) also recalculated the paleotemperature equation of Grossman and Ku (1986) to fit a $1/T$ relation and obtained the following equation in a temperature range of 2.6 to 22°C:

$$10^3\ln\alpha = 18.07 \times 10^3/T - 31.08. \quad (4)$$

As stated by Patterson et al. (1993), the slopes of Eqn. 3 and 4 are indistinguishable, but the intercepts differ by ~2.5‰ because of seasonal change in bottom water temperature, the isotopic composition of water, analytical errors, and unexplained metabolic effects. To test the validity of Eqn. 3, Patterson et al. (1993) used a modern shallow-water eurythermic species from Sandusky Bay in Lake Erie. The temperatures calculated from the carbonate $\delta^{18}O$ values agree with meteorological records from the Sandusky Bay Weather Station for the same time period.

Thorrold et al. (1997) also established an empirical relationship for oxygen isotope fractionation in the otolith aragonite reared in a temperature range of 18.2 to 25°C:

$$10^3\ln\alpha = 18.56 \times 10^3/T - 32.54. \quad (5)$$

This fractionation relationship is very close to that of Grossman and Ku (1986). The slopes between the equations of Thorrold et al. (1997) and Patterson et al. (1993) are indistinguishable, but Thorrold et al. (1997) also could not explain why there is the significant difference in the intercept.

Zheng (1999) applied the increment method to the systematic calculations of oxygen isotope fractionation factors between carbonates and water over a temperature range of 0 to 1200°C and obtained a theoretical relationship for the aragonite-water system:

$$10^3\ln\alpha = 3.91 \times 10^6/T^2 - 5.79 \times 10^3/T + 1.92. \quad (6)$$

The validity of the increment method for carbonates is proven not only by agreement with high-temperature exchange experiments but also by internal concordance within calcite and aragonite groups.

Boehm et al. (2000) combined their sponge data with the temperate and cold water equilibrium values from mollusks and foraminifera to obtain a fractionation relation for the aragonite-water system in a temperature range of 3 to 28°C:

$$10^3\ln\alpha = 18.45 \times 10^3/T - 32.54. \quad (7)$$

This equation is in agreement with both Eqn. 4 from Grossman and Ku (1986) and Eqn. 5 from Thorrold et al. (1997).

Zhou and Zheng (2002) have experimentally determined the aragonite-water fractionations by means of the overgrowth method at 50 and 70°C and obtained the following equations for the one-step and two-step approaches, respectively:

$$10^3\ln\alpha_{\text{one-step}} = 20.79 \times 10^3/T - 40.45, \quad (8a)$$

$$10^3\ln\alpha_{\text{two-step}} = 15.37 \times 10^3/T - 26.14, \quad (8b)$$

where Eqn. 8a for the one-step approach is obtained by fitting the experimental data of Zhou and Zheng (2002).

As shown in Fig. 3, there are significant differences among the above calibrations for the aragonite-water system. Nevertheless, both the curve derived from the two-step overgrowth experiments of Zhou and Zheng (2002) and that for Eqn. 1 in Fig. 6 are consistent with the theoretical calculations of Zheng (1999), whereas the data from the one-step overgrowth experiments of Zhou and Zheng (2002) are broadly comparable with the experimental and empirical results of Boehm et al. (2000), Thorrold et al. (1997), Patterson et al. (1993), Grossman and Ku (1986), and McCrea (1950). In other words, these experimental, empirical, and theoretical calibrations fall into the two groups. Because the fractionation factors from the two-step approach at 50 and 70°C have been demonstrated by Zhou and Zheng (2002) to represent equilibrium, it is reasonable to conclude that Eqn. 1 from this study provides a close proxy for the equilibrium fractionation between inorganically precipitated aragonite and water at 0 to 70°C.

4.3. Oxygen Isotope Fractionation in $CaCO_3$-H_2O Systems

Calculations of reduced partition function ratios for oxygen isotopes in calcite were conducted by Bottinga (1968) (Eqn. 9), Shiro and Sakai (1972) (Eqn. 10), Kieffer (1982) (Eqn. 11), and Chacko et al. (1991) (Eqn. 12) by means of statistical-mechanical methods. By combination with reduced partition function ratios for oxygen isotopes in water (Hattori and Halas, 1982),

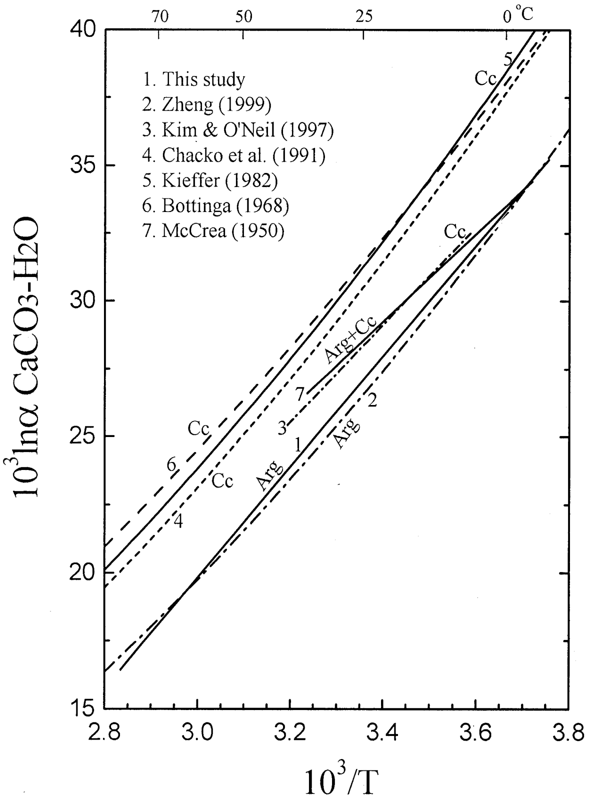

Fig. 6. Comparison of calculated oxygen isotope fractionations for the $CaCO_3$-H_2O systems by Bottinga (1968), Kieffer (1982), Chacko et al. (1991), and Zheng (1999) with the experimental data of McCrea (1950), Kim and O'Neil (1997), and this study.

theoretical fractionation equations for the calcite-water system are obtained as follows:

$$10^3 \ln\alpha = 3.16 \times 10^6/T^2 - 0.61 \times 10^3/T - 2.11, \quad (9)$$

$$10^3 \ln\alpha = 3.04 \times 10^6/T^2 - 1.10 \times 10^3/T - 1.65, \quad (10)$$

$$10^3 \ln\alpha = 4.01 \times 10^6/T^2 - 4.66 \times 10^3/T + 1.71, \quad (11)$$

$$10^3 \ln\alpha = 4.12 \times 10^6/T^2 - 5.51 \times 10^3/T + 2.57. \quad (12)$$

These equations have been recalculated by applying the assumption of Zheng (1993) that, when calculating mineral-water fractionation factors ($10^3\ln\alpha$) from the reduced partition function ratios ($10^3\ln\beta$) of the mineral and water, given mineral-water interaction factors must be introduced to cancel out the isotope effects of dissolved minerals in aqueous solutions. As shown by Zheng (1999), the revised curve of Kieffer (1982) is in agreement with the results obtained by the hydrothermal exchange experiments of O'Neil et al. (1969) at the high temperatures of 60 to 500°C. It is also close to the other theoretical curves of the statistical-mechanical calculations by Bottinga (1968) and Chacko et al. (1991), as depicted in Fig. 6.

Kim and O'Neil (1997) synthesized pure calcite in the system of Ca^{2+}-Na^+-Cl^--HCO_3^--H_2O with both Ca^{2+} and HCO_3^- concentrations of 0.0005 mol/L and obtained an oxygen isotope fractionation relation (recalculated using the acid fractionation factor of 1.01025) for the calcite-water system over a temperature range of 10 to 40°C:

$$10^3 \ln\alpha = 18.03 \times 10^3/T - 32.17. \quad (13)$$

As shown in Fig. 6, this fractionation relation significantly differs from the theoretical calculations for calcite, but it is close to the fractionations of McCrea (1950) for pure aragonite and aragonite-calcite mixtures. The fractionations from the present study at 0 and 25°C concerning the pure calcite and calcite-aragonite mixtures (Fig. 4 and Table 6) are also comparable with the higher fractionation values that were determined for the pure aragonite and aragonite-dominant phases (Fig. 3).

The synthesis method for calcite used by Kim and O'Neil (1997) is identical to that in the present study, all being via chemical reactions I and II. Although the authors emphasized that the synthesized mineral is pure calcite, it is well known that aragonite in aqueous solutions can very easily convert to stable calcite. In aqueous solutions, the infant aragonite precipitate spontaneously transforms into calcite after aging for only 24 h at 50 and 70°C (Zhou and Zheng, 2001). A preliminary experiment shows negligible oxygen isotope fractionation between the primary aragonite and its transformed, secondary calcite (Zhou, 1999). If the calcite of Kim and O'Neil (1997) would result from the polymorphic transition of aragonite during $CaCO_3$ precipitation, there could be the oxygen isotope inheritance in the transition process (Zheng, 1999). In this regard, the similarity in fractionation among the calcite of Kim and O'Neil (1997), the pure aragonite and aragonite-calcite mixtures of McCrea (1950); and the calcite, calcite-aragonite mixtures and aragonite from the present study is not accidental but inevitable. Therefore, the discrepancies in the $CaCO_3$-H_2O fractionation factors between the different synthesis experiments may reflect a metastable, steady-state "equilibrium" during aragonite precipitation under the each run conditions. The so-called steady-state equilibrium refers to a kinetically controlled transition state at nonequilibrium during the processes of isotope exchange reactions, whereas the thermodynamic equilibrium corresponds to the minimum free energy for isotope exchange reactions.

It appears that there is sufficient complexity in calibrating oxygen isotope fractionations for the calcite-aragonite-water systems by means of the inorganic chemical experiments. The complexity of biogenic carbonates thus remains to be resolved. Isotope disequilibrium is common in most biogenic carbonates (e.g., Swart, 1983) and is considered to be a result of either kinetic or metabolic effects. The kinetic effect may result from discrimination against heavier carbon and oxygen isotopes during the hydration and hydroxylation of CO_2 (McConnaughey, 1989). By reviewing a large number of studies on oxygen isotope fractionation between biogenic carbonates and water (Shackleton and Opdyke, 1973; Van Donk, 1977; Kahn, 1979; Fairbanks et al., 1980; Kahn and Williams, 1981; Erez and Honjo, 1981; Duplessy et al., 1981), Erez and Luz (1983) pointed out that the following factors may result in disequilibrium oxygen isotope fractionation between biogenic carbonate and water: (1) incorrect temperatures and/or oxygen isotope compositions of the water were estimated by the workers, (2) the analyses of planktonic samples were made on materials that contain large quantities of protoplasmic (organic) matter, or (3) disequilibrium fractionation values in plankton samples occurred in the earlier stages of the growth of planktonic foraminifera. Berger et al. (1978) suggested that when individuals are young, their metabolic activity is more intense, and the metabolic CO_2 portion of the skeleton is larger than that for old ones. Metabolic (growth) rates are known to be generally faster at higher temperatures within reasonable temperature limits (Moberly, 1968). This could also contribute to disequilibrium fractionations.

The effects of metabolic activity on oxygen isotope fractionation are unpredictable, and therefore, caution is advised in using oxygen isotope fractionations between biogenic $CaCO_3$ and H_2O for the purpose of calibrating thermodynamic equilibrium fractionation. In the case of biogenic carbonates, as long as the species-special offset from equilibrium is known and remains constant over the temperature range of interest, environmental information can still be accurately interpreted from skeletal records (e.g., Wellington and Durbar, 1995; Leder et al., 1996). For example, the empirical paleotemperature equation of the aragonitic otoliths–water system by Patterson et al. (1993) is evidently applicable to the estimation of seasonal temperature variations of seawater, even though the equation may not represent thermodynamic equilibrium. Nevertheless, the equation reflects the steady-state “equilibrium,” an objective phenomena in nature. On the other hand, the aragonite-water fractionation factors obtained from this study involve the inorganic precipitation of aragonite in an approximately ideal solution system. Therefore, they provide a close proxy for thermodynamic equilibrium.

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