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Kinetic mechanism of oxygen isotope disequilibrium in precipitated witherite and aragonite at low temperatures: An experimental study

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Abstract—To study what dictates oxygen isotope equilibrium fractionation between inorganic carbonate and water during carbonate precipitation from aqueous solutions, a direct precipitation approach was used to synthesize witherite, and an overgrowth technique was used to synthesize aragonite. The experiments were conducted at 50 and 70°C by one- and two-step approaches, respectively, with a difference in the time of oxygen isotope exchange between dissolved carbonate and water before carbonate precipitation. The two-step approach involved sufficient time to achieve oxygen isotope equilibrium between dissolved carbonate and water, whereas the one-step approach did not. The measured witherite-water fractionations are systematically lower than the aragonite-water fractionations regardless of exchange time between dissolved carbonate and water, pointing to cation effect on oxygen isotope partitioning between the barium and calcium carbonates when precipitating them from the solutions. The two-step approach experiments provide the equilibrium fractionations between the precipitated carbonates and water, whereas the one-step experiments do not. The present experiments show that approaching equilibrium oxygen isotope fractionation between precipitated carbonate and water proceeds via the following two processes:

1. Oxygen isotope exchange between $[CO_3]^{2-}$ and H_2O:

$$[C^{16}O_3]^{2-} + 2H_2^{18}O = [C^{18}O_2^{16}O]^{2-} + 2H_2^{16}O \qquad (1)$$
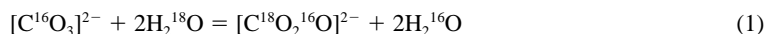
2. A combination of divalent metal cation M^{2+} with the $[CO_3]^{2-}$ to form carbonate:

$$M^{2+} + [C^{18}O_2^{16}O]^{2-} + H_2^{18}O = MC^{18}O_3 + H_2^{16}O \qquad (2)$$
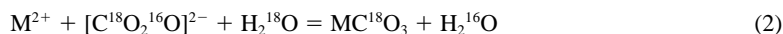
Reaction 1 is the rate-limiting step for equilibrium oxygen isotope fractionation between carbonate and water, and reaction 2 bears the structural effect of carbonate crystallization on oxygen isotope fractionation during carbonate precipitation. The present results show that the time of $[CO_3]^{2-}$-H_2O isotope exchange in the precipitation experiments is of critical importance in dictating the extent of isotopic equilibration between precipitated carbonate and water. If the time of oxygen isotope exchange between $[CO_3]^{2-}$ and H_2O is long enough to attain equilibrium before carbonate precipitation, the precipitated carbonate is able to achieve isotopic equilibration with water. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

Carbonate is one of the most common minerals in shallow marine sediments. Oxygen isotope data for carbonate assemblages have been used extensively to understand their origin and precipitation temperature from seawater. Since the pioneering study of McCrea (1950) to calibrate the oxygen isotope geothermometer involving calcium carbonates, a great number of laboratory experiments, empirical estimates, and theoretical calculations have been performed in the last five decades. It has been the general consensus that carbonate is enriched in ^{18}O relative to H_2O but depleted in ^{18}O relative to the dissolved CO_2 at thermodynamic equilibrium; oxygen isotope fractionation among crystalline carbonates is principally determined by structural and cationic effects (O'Neil et al., 1969; Tarutani et al., 1969; Zheng, 1999).

Precipitation experiments have been applied widely to calibration of oxygen isotope fractionation factors between calcium carbonate and water at low temperatures. Principal ap-

proaches are to synthesize calcium carbonate via slow decomposition of $Ca(HCO_3)_2$ or rapid precipitation of $CaCO_3$ by adding $CaCl_2$ to $NaHCO_3$-Na_2CO_3 solutions (e.g., McCrea, 1950; O'Neil et al., 1969; Tarutani et al., 1969; Kim and O' Neil, 1997). All of the experiments involve hydrolysis of carbonate to bicarbonate, carbonic acid, and dissolved CO_2. The steps of oxygen isotope exchange take place among carbonic acid, H_2O and CO_2, and among CO_2, bicarbonate, and hydroxide. Equilibrium isotope partitioning is obtained when $CaCO_3$ precipitates slowly from solution; rapid precipitation fosters disequilibrium (McCrea, 1950; O'Neil et al., 1969; Romanek et al., 1992). As outlined by Usdowski et al. (1991), the strongest fractionation is caused by the isotope exchange between CO_2 and H_2O, and the smallest fractionation occurs between dissolved and gaseous CO_2; the fractionation between the dissolved carbonate species and H_2O is intermediate and decreases in magnitude in the order of H_2CO_3, $[HCO_3]^-$, and $[CO_3]^{2-}$. Zeebe (1999) has observed recently that oxygen isotope fractionation between $CaCO_3$ and H_2O depends not only on the temperature but also on the pH of the solution from which it is formed.

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However, there is still great controversy with respect to the direction and magnitude of oxygen isotope fractionations between calcium carbonates (the polymorphs of $CaCO_3$, calcite, and aragonite). The precipitation experiments of Tarutani et al. (1969) and Kim and O'Neil (1997) as well as the natural observation of Sommer and Rye (1978), Grossman and Ku (1986), Aharon (1991), Barrera et al. (1994), Rahimpour-Bonab et al. (1997), Thorrold et al. (1997), and Boehm et al. (2000) suggest that calcite is depleted in ^{18}O relative to aragonite. In contrast, the natural observations of Epstein et al. (1953), Behrens and Land (1972), Horibe and Oba (1972) as well as the theoretical calculations of Zheng (1999) show that calcite is enriched in ^{18}O relative to aragonite. Furthermore, the empirical estimates of Patterson et al. (1993) for the aragonite-water system at 3.2 to 30.3°C are very close to the experimental calibrations of O'Neil et al. (1969) as well as Kim and O'Neil (1997) for the calcite-water system at the low temperature. A potential drawback of these comparisons is that a different genesis of carbonates was involved: Precipitation experiments were responsible for inorganic carbonates, whereas the natural observations were based on biogenic carbonates. Therefore, it has often been questioned whether the oxygen isotope partitioning in biogenic carbonate is exactly the same as for inorganic carbonate, whether there is oxygen isotope inheritance during polymorphic transition from aragonite to calcite, and whether oxygen isotope equilibrium fractionations have been attained between $CaCO_3$ and H_2O in laboratory experiments and natural observations of interest.

The mechanism of oxygen isotope exchange between carbonate, dissolved carbonates, CO_2, and H_2O was studied by precipitation experiments (e.g., McCrea, 1950; McConnaughey, 1989; Usdowski et al., 1991). McConnaughey (1989) developed a mechanistic model of kinetic isotope disequilibrium in biogenic carbonates and concluded that disequilibrium fractionation occurs when $CaCO_3$ precipitation is fast enough that $[CO_3]^{2-}$ units in the crystal are buried before they isotopically equilibrate with H_2O. Equilibration can be divided into two phases: $[CO_3]^{2-}$ exchange between crystal and solution, and oxygen isotope exchange between dissolved $[CO_3]^{2-}$ and H_2O. Furthermore, McConnaughey (1989) predicted that the slow exchange of oxygen isotopes between dissolved $[CO_3]^{2-}$ and H_2O is the most likely step to prevent oxygen equilibrium during $CaCO_3$ precipitation. His experiments showed that isotopic equilibration during biologic calcification occurs through CO_2 exchange across the calcifying membrane and by the admixture of ambient waters containing $[HCO_3]^-$ into the calcifying fluids.

Although the prediction of McConnaughey (1989) was confined to biologic carbonates, it is possible that his model is also applicable to inorganically precipitated carbonate. Because the behavior of oxygen isotope partitioning in $CaCO_3$ is considerably different from that in the dissolved carbonates ($[HCO_3]^-$ and $[CO_3]^{2-}$) at equilibrium (McCrea, 1950; Usdowski and Hoefs, 1993), it can be tested whether oxygen isotope equilibrium between dissolved carbonates and H_2O have predominated in the achievement of equilibrium fractionation between carbonate and water. This paper reports the results of synthesis experiments in which witherite and aragonite were precipitated from aqueous solutions at low temperatures. The results provide the first experimental evidence for the kinetic mechanism

of oxygen isotope disequilibrium fractionation between inorganic carbonate and water.

2. EXPERIMENTAL METHODS

The alkaline earth metal carbonates in the aragonite group include aragonite, strontianite, and witherite. The experimental determinations of O'Neil et al. (1969) and the theoretical calculations of Zheng (1999) showed the following sequence of ^{18}O enrichment in the aragonite-group carbonate at isotopic equilibrium: aragonite > strontianite > witherite. In the present experiments, witherite was synthesized by the direct precipitation method, and aragonite was synthesized using the overgrowth technique (Zhou and Zheng, 1998). Witherite and aragonite were chosen because they have larger oxygen isotope fractionations relative to strontianite, thereby reducing experimental errors.

2.1. Synthesis of Witherite

One- and two-step approaches were respectively established to precipitate witherite directly with a difference in the time of oxygen isotope exchange between dissolved carbonate and water before witherite precipitation. The two-step approach requires relatively long durations to achieve oxygen isotope equilibrium between dissolved carbonate and water, whereas the one-step approach does not.

2.1.1. One-step approach

A 0.1 mol/L 200 mL of Na_2CO_3 (2.12 g, analytical reagent grade) solution was thermostated in a given temperature (50 or 70°C) water bath under constant magnetic stirring. After thermal equilibration (thermostated ~15–20 min), 0.5M 50 mL of $BaCl_2$ solution prepared with analytical reagent-grade $BaCl_2 \cdot 2H_2O$ (slight excess relative to the Na_2CO_3 solution), and having the same temperature as the Na_2CO_3 solution, was dropped into the Na_2CO_3 solution under constant magnetic stirring. After a reaction period (aged for 5 min), the precipitate was filtered using a Buchner filter, rinsed three times with deionized water and once with acetone, then dried in a 110°C oven for 12 h. The synthesized witherite and the filtrates were stored in capped glass bottles for isotopic analysis.

2.1.2. Two-step approach

An aliquot of 2.12-g Na_2CO_3 (analytical reagent grade) was dissolved in 200 mL deionized water. This Na_2CO_3 solution was sealed in a glass bottle and maintained in a water bath at a given temperature (50 or 70°C) for oxygen isotope exchange for given durations (at least 20 d). Then, 0.5 mol/L 50 mL of $BaCl_2$ solution, having the same temperature as the exchanged Na_2CO_3 solution, was dropped into the exchanged Na_2CO_3 solution with constant magnetic stirring to form a witherite precipitate. The remaining procedures are the same as those in the one-step approach above.

2.2. Synthesis of Aragonite

Thermodynamically, aragonite is a metastable variety of $CaCO_3$. Solid-state transformation of aragonite to calcite is slow even by geologic standards (Kunzler and Goodell, 1970). But in aqueous solution, it can spontaneously and rapidly convert to calcite, except when affected by specific chemical inhibitors (Berner, 1971). The present experiments follow the overgrowth technique by Zhou and Zheng (1998) for aragonite synthesis, but have been slightly modified for the purpose of calibrating isotope fractionation factors.

2.2.1. Preparation of seed crystal $SrCO_3$

A given amount of analytical reagent-grade Na_2CO_3 was weighed and prepared as a given concentration of Na_2CO_3 solution. Similarly, a given amount of analytical reagent-grade $SrCl_2 \cdot 6H_2O$ was weighed and prepared as a given concentration of $SrCl_2$ solution. The solution of $SrCl_2$ was added dropwise to the Na_2CO_3 solution to precipitate $SrCO_3$. The precipitate was filtered and washed three times with deionized water and once with acetone. After being dried in a 110°C
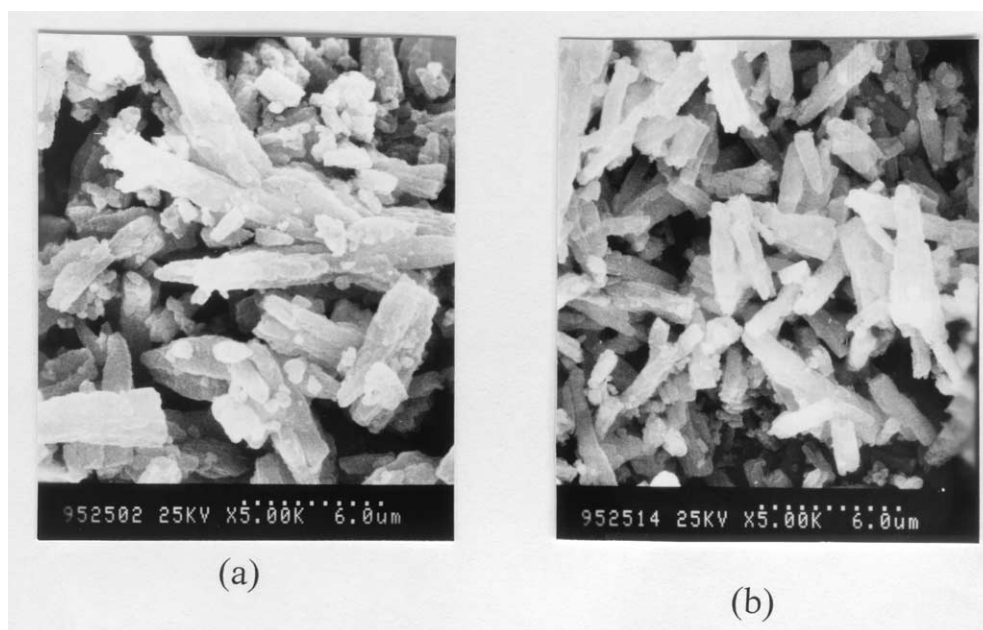
Fig. 1. Typical SEM photographs of aragonite synthesized at (a) 50°C and (b) 70°C, respectively.

oven for 24 h, the $SrCO_3$ precipitate was stored in a small capped glass bottle for later use. The isotopic compositions of the $SrCO_3$ crystal seeds are $\delta^{13}C = -8.92‰$ (relative to PDB) and $\delta^{18}O = 20.08‰$ (relative to SMOW).

2.2.2. One-step approach

Crystal seeds of $SrCO_3$ weighing 15 to 20 mg, which account for < 1 wt.% of the theoretical amount of the precipitated aragonite, were added to 0.1 mol/L 200 mL of Na_2CO_3 (2.12 g, analytical reagent grade) solution. The suspension of $SrCO_3$ and Na_2CO_3 was dispersed ultrasonically for 20 to 30 min to improve the efficiency of the seeds and then placed in a constant temperature (50 or 70°C) water bath. After being thermostated ~15 to 20 min, 0.5M 50 mL of $CaCl_2$ solution (slight excess relative to the Na_2CO_3 solution), having the same temperature as the solution of $SrCO_3$ and Na_2CO_3, was dropped into the Na_2CO_3 solution and continuously stirred magnetically. After ageing for 5 min, the precipitate was filtered using a Buchner filter, rinsed three times with deionized water and once with acetone, and then dried in a 110°C oven for 12 h. The synthesized aragonite and the filtrates were stored in capped glass bottles for later isotopic analysis.

2.2.3. Two-step approach

An aliquot of 2.12-g Na_2CO_3 (analytical reagent grade) was dissolved in 150 mL of deionized water. This Na_2CO_3 solution was sealed in a glass bottle and was maintained in a given temperature (50 or 70°C) water bath to exchange for a given time (at least 10 d). Then, an aliquot of 15 to 20 mg of $SrCO_3$ crystal seeds was added to 50 mL of deionized water. This $SrCO_3$ solution was dispersed ultrasonically for 20 to 30 min and then thermostated at the same temperatures as the Na_2CO_3 solution. After being thermostated, the $SrCO_3$ suspension was added to the Na_2CO_3 solution to make the final concentration of Na_2CO_3 the same as that in the one-step approach. The remaining procedures are the same as those in the one-step experiments; however, two kinds of Na_2CO_3 with different isotope ratios were used: (1) $\delta^{13}C = -9.48‰$ (relative to PDB) and $\delta^{18}O = 20.20‰$ (relative to SMOW), and (2) $\delta^{13}C = -14.39‰$ (relative to PDB) and $\delta^{18}O = 15.83‰$ (relative to SMOW). The carbon and oxygen isotope ratios of Na_2CO_3 were analyzed according to the conventional phosphoric acid method (McCrea, 1950) by using the acid fractionation factor of

1.01025 at 25°C for calcite (Sharma and Clayton, 1965), because the acid fractionation factor for Na_2CO_3 is not available at the present time.

2.3. Mineral Identification

The phase composition and structure of the precipitates were characterized by a Rigaku Dmax X-ray diffractometer with graphite monochromatized CuK_α radiation ($\lambda = 0.154178$ nm). The morphology of the synthesized calcium carbonate was observed by a Hitachi S-650 scanning electron microscope (SEM).

2.4. Isotopic Analyses

Oxygen and carbon isotope analyses of carbonates were conducted according to the conventional phosphoric acid method (McCrea, 1950). The oxygen isotope analysis of water was performed by the classic CO_2-H_2O equilibration method (Cohn and Urey, 1938). Isotope ratio measurements were made on CO_2 gas using a Delta+ mass spectrometer. Acid fractionation factors used in this study are 1.01034 for aragonite and 1.01097 for witherite at 25°C (Sharma and Clayton, 1965). The equilibrium fractionation factor 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 compositions of both carbonates and water are reported in the familiar $\delta^{18}O$ and $\delta^{13}C$ notations relative to the SMOW and PDB standards, respectively. $\delta^{18}O$ analytical errors for both carbonates and water are better than $\pm$ 0.2‰. The 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 as same as the starting waters. The oxygen isotope fractionation factor is expressed in the conventional α notation: $\alpha = (\delta^{18}O_{carbonate} + 1000/(\delta^{18}O_{water} + 1000)$.

3. RESULTS

All of the synthesized carbonates were analyzed by X-ray diffraction (XRD) to ensure that the all samples used were pure witherite, strontianite, or aragonite. SEM photographs show that the synthesized aragonite is rod-like and ~2 to 6 μm in length (Fig. 1).

The oxygen isotope compositions of synthetic witherite and corresponding solution by the one- and two-step approaches are

Table 1. Oxygen isotope data of witherite synthesized by one-step approach and corresponding water.

Sample No.	Temp. (°C)	$\delta^{18}O$ (‰) H$_2$O	$\delta^{18}O$ (‰) BaCO$_3$	α	$10^3\ln\alpha$
98CB37	50	−5.13	17.71	1.02296	22.70
98CB38	50	−5.41	16.94	1.02247	22.22
98CB37B	50	−5.14	17.86	1.02312	22.86
98CB38B	50	−5.30	17.32	1.02274	22.49
98CB35	70	−5.30	13.28	1.01857	18.51
98CB35B	70	−5.42	13.24	1.01864	18.59
98CB36B	70	−5.43	13.30	1.01883	18.66

listed in Tables 1 and 2, respectively. Oxygen isotope fractionations ($10^3\ln\alpha$) between witherite and water derived from the one-step approach are 22.22 to 22.86‰ at 50°C and 18.51 to 18.66‰ at 70°. The $10^3\ln\alpha$ values from the two-step approach are 19.22 to 19.71‰ at 50°C and 16.40 to 17.31‰ at 70°C. As shown in Figure 2, the oxygen isotope fractionations between witherite and water, derived from the two-step approach experiments, are systematically ~1 to 2‰ lower than those from the one-step runs. The only difference between the one- and two-step approaches is the time of the isotopic exchange of $[CO_3]^{2-}$ with H$_2$O.

The oxygen isotope compositions of the synthetic aragonite and water obtained by the one- and two-step approaches are listed in Tables 3 and 4, respectively. Oxygen isotope fractionations ($10^3\ln\alpha$) between aragonite and water derived from the one-step approach are 23.53 to 24.33‰ at 50°C and 19.92 to 20.46‰ at 70°C. The $10^3\ln\alpha$ values from the two-step approach are 21.14 to 21.81‰ at 50°C and 18.36 to 18.95‰ at 70°C. Although the Na$_2$CO$_3$ or the water of the different isotope ratios were used as starting materials in the synthesis experiments, there is no measurable difference in the resultant $10^3\ln\alpha$ values between aragonite and water at the same temperatures. This suggests that the $\delta^{18}O$ values of the initial Na$_2$CO$_3$ or water have no effect on the oxygen isotope fractionation between carbonate and water in the two-step approach experiments. As depicted in Figure 2, the fractionation values obtained by the two-step approach are also systematically ~1 to 2‰ lower than those under the one-step approach at 50 to 70°C.

From Figure 2 it can be seen that the measured witherite-water fractionations are systematically lower than the arago-

nite-water fractionations, regardless of exchange time between dissolved carbonate and water. In other words, BaCO$_3$ has the same systematics of oxygen isotope partitioning as aragonitic CaCO$_3$, regardless of whether the oxygen isotope equilibration between $[CO_3]^{2-}$ and H$_2$O was attained or not. This points to the cationic effect on oxygen isotope partitioning between the Ba and Ca carbonates when precipitating them from aqueous solutions. This is also consistent with the previous experiments by O'Neil et al. (1969) as well as by Kim and O'Neil (1997).

4. DISCUSSION

The oxygen isotope fractionations between witherite and water were determined by O'Neil et al. (1969) via slow precipitation experiments at 0 and 25°C, respectively. A number of precipitation experiments were made by Kim and O'Neil (1997) at 10, 25, and 40°C to check the reliability of the equilibrium witherite-water fractionations. The calibration experiments in the different laboratories at the different times yield concordant results within the experimental errors. Zheng (1999) calculated oxygen isotope fractionation between witherite and water using the increment method. As shown in Figure 3, the present experimental results for the witherite-water system by the two-step approach are consistent not only with the previous experiments by O'Neil et al. (1969) and Kim and O'Neil (1997), but also with the theoretical calculations of Zheng (1999). This suggests that the two-step experiments have provided the equilibrium fractionations between witherite and water, whereas the one-step experiments have not. Taking the present two-step approach data together with the previous results of O'Neil et al. (1969) as well as Kim and O'Neil

Table 2. Oxygen isotope data of witherite synthesized by two-step approach and corresponding water.

Sample No.	Temp. (°C)	Time* (d)	$\delta^{18}O$ (‰) H$_2$O	$\delta^{18}O$ (‰) BaCO$_3$	$\alpha_{BaCO3-Water}$	$10^3\ln\alpha$
97CB41	50	20	−7.83	11.72	1.01970	19.51
98CB08	50	60	−4.60	14.99	1.01968	19.49
98CB10	50	60	−4.59	15.22	1.01990	19.71
00CB08	50	20	1.98	21.42	1.01940	19.22
00CB09	50	20	−10.45	8.88	1.01953	19.35
97CB16	70	20	−6.98	9.44	1.01654	16.40
97CB38	70	20	−6.66	10.03	1.01680	16.66
98CB12	70	60	−2.32	14.67	1.01703	16.89
98CB13	70	60	−3.31	14.09	1.01746	17.31
00CB10	70	20	1.89	19.26	1.01734	17.19
00CB11	70	20	−10.54	6.66	1.01738	17.23

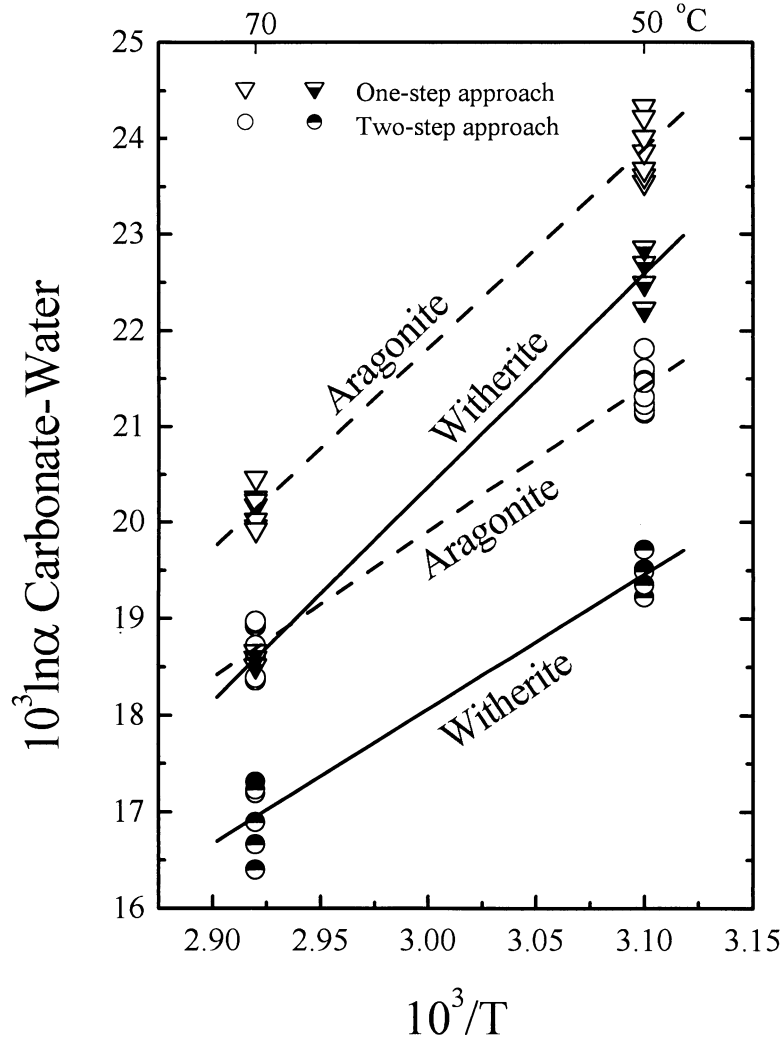* The time of exchange between $[CO_3]^{2-}$ and H$_2$O

Fig. 2. Oxygen isotope fractionations between witherite, aragonite, and water synthesized by one- and two-step experiments.

Table 3. Oxygen isotope data of aragonite synthesized by one-step approach and corresponding water.

Sample No.	Temp. (°C)	$\delta^{18}O$ (‰) H_2O	$\delta^{18}O$ (‰) $CaCO_3$	α	$10^3 ln\alpha$
95CB47	50	−3.17	20.56	1.02381	23.53
95CB49	50	−3.28	20.53	1.02389	23.61
95CB51	50	−3.08	20.81	1.02396	23.68
95CB109	50	−4.65	19.39	1.02415	23.86
95CB111	50	−3.95	20.58	1.02463	24.33
98CB39B	50	−5.38	18.79	1.02430	24.01
98CB41B	50	−5.23	19.16	1.02452	24.22
95CB54	70	−3.07	17.29	1.02042	20.22
95CB56	70	−2.93	17.43	1.02022	20.02
95CB57	70	−2.98	17.42	1.02046	20.25
95CB84	70	−3.04	17.57	1.02067	20.46
95CB104	70	−4.67	15.61	1.02038	20.17
98CB40B	70	−5.43	14.61	1.02015	19.95
98CB42B	70	−5.41	14.60	1.02012	19.92

(1997), a combined fractionation relation is obtained for the witherite-water system in the temperature range of 0 to 70°C: $10^3 ln\alpha = 18.81 \times 10^3/T - 38.22$, where the data of Kim and O'Neil (1997) have been recalculated by using the acid fractionation factor of 1.01097 (Sharma and Clayton, 1965) instead of 1.01063 (Kim and O'Neil, 1997). Errors in slope and intercept are 0.50 and 1.58, respectively.

As shown in Figure 3, the combined experimental curve for the witherite-water system is in excellent agreement with the calculated fractionations by Zheng (1999). Likewise, not only the oxygen isotope fractionations between aragonite and water derived from the two-step experiments are consistent with the theoretical calculations of Zheng (1999), but also the sequence and magnitude of ^{18}O enrichment in aragonite and witherite are concordant with the theoretical predictions. In addition, the aragonite-water fractionations were also measured by using Na_2CO_3 and waters of different isotope compositions as the starting materials. As listed in Table 4, the results agree with each other within the experimental errors. Therefore, the mea-

Table 4. Oxygen isotope data of aragonite synthesized by two-step approach corresponding water.

Sample No.	Temp. (°C)	Time* (d)	$\delta^{18}O$ (‰) H_2O	$\delta^{13}C$ (‰) $CaCO_3$	$\delta^{18}O$ (‰) $CaCO_3$	α	$10^3 \ln\alpha$	Remarks[#]
95CB117	50	10	−6.25	−9.30	15.33	1.02172	21.48	(1)
97CB39	50	20	−7.79	−9.43	13.80	1.02176	21.53	(1)
97CB40	50	20	−7.82	−9.16	13.84	1.02183	21.60	(1)
98CB09	50	60	−4.51	−9.02	17.44	1.02205	21.81	(1)
98CB19	50	10	−4.01	−9.26	17.61	1.02171	21.47	(1)
98CB22	50	10	−3.92	−14.10	17.36	1.02136	21.14	(2)
98CB23	50	10	−4.12	−14.12	17.18	1.02139	21.16	(2)
98CB24	50	10	−4.09	−14.16	17.28	1.02146	21.23	(2)
95CB116	70	10	−6.25	−9.25	12.73	1.01910	18.92	(1)
97CB11	70	20	−5.74	−9.22	12.68	1.01853	18.36	(1)
97CB36	70	20	−7.37	−9.51	11.26	1.01877	18.59	(1)
97CB37	70	20	−6.82	−9.48	11.61	1.01856	18.39	(1)
98CB28	70	10	−3.85	−14.30	14.94	1.01890	18.72	(2)
98CB29	70	10	−3.67	−14.31	15.39	1.01913	18.95	(2)

* The time of exchange between $[CO_3]^{2-}$ and H_2O.
[#] The carbon and oxygen isotope ratios of starting Na_2CO_3: (1) $\delta^{13}C = -9.48$‰ and $\delta^{18}O = 20.20$‰; (2) $\delta^{13}C = -14.39$‰ and $\delta^{18}O = 15.83$‰.

sured $10^3\ln\alpha$ values for the aragonite-water system derived from the two-step experiments can be interpreted to represent equilibrium fractionations, corresponding to the following fractionation equation at 50 to 70°C: $10^3\ln\alpha = 15.37 \times 10^3/T - 26.14$. Errors in slope and intercept are 0.73 and 2.19, respectively. An extrapolation of the present calibration to 25°C gives a fractionation of 25.41‰ between aragonite and water, which is significantly lower than the previously experimental determination of 29.19‰ by Tarutani et al. (1969) after recalculation by using $\alpha_{CO2-H2O} = 1.01042$. It is unclear why there is such a discrepancy between the two experimental calibrations. Kim and O'Neil (1997) observed that the temperature coefficients of α(carbonate-water) for disequilibrium divalent metal carbonates are greater than those for equilibrium carbonates. Our experiments in the one- and two-step approaches appear to have confirmed their results. Similar results were also obtained by Melchiorre and Criss (1999) who determined oxygen isotope fractionations between malachite and water via synthesis experiments by means of rapid and slow precipitation approaches, respectively.

According to the experimental study of Mills and Urey (1940), the half time of the isotopic exchange toward equilibrium between $[CO_3]^{2-}$ and H_2O is 28 h at 25°C and pH 11 and decreases with decreasing pH. Therefore, the $[CO_3]^{2-}$-H_2O isotope exchange in our two-step approach experiments was fast because of the higher run temperatures (at 50 and 70°C) and has thus achieved isotopic equilibrium because of the much longer run time (> 10 d), whereas the $[CO_3]^{2-}$-H_2O exchange in the one-step approach experiments was not as significant because of the very short exchange time (< 20 min) and, thus, was not able to attain isotopic equilibrium. In this regard, if the equilibration of oxygen isotope exchange between $[CO_3]^{2-}$ and H_2O has occurred before carbonate precipitation, the carbonate precipitated is able to achieve oxygen isotope equilibrium with water.

McCrea (1950) pointed out that the oxygen isotope compositions of carbonate from rapid precipitation depend on those of the solution and dissolved $[CO_3]^{2-}$. In other words, the carbonate formed by rapid precipitation inherits the oxygen isotope compositions of $[CO_3]^{2-}$ in the solution, being indepen-

dent of the varieties of crystalline carbonate. It appears that our results conflict with McCrea (1950). Although he did not describe his experimental conditions in detail, he discussed the time dependence of oxygen isotope exchange and equilibration between Na_2CO_3 and H_2O, and stated that the half-time of reaction between $NaCO_3$ and H_2O is 28 h as given by Mills and Urey (1940). In his other experiments of rapid precipitation, the mixed solution of Na_2CO_3 and $NaHCO_3$ had exchanged oxygen isotopes with H_2O at constant temperature for at least 5 d before precipitation. Thus, it is inferred that oxygen isotope exchange between Na_2CO_3-$NaHCO_3$ and H_2O in the McCrea (1950) experiments has taken place sufficiently to approach equilibrium, similar to our two-step approach runs. To resolve the apparent disagreement, the experimental procedures adopted by McCrea (1950) are outlined briefly as follows.

The two kinds of mixed solutions of 0.049M Na_2CO_3 and 0.00034M $NaHCO_3$ were prepared by McCrea (1950) using waters of different isotope compositions. $CaCO_3$, $SrCO_3$, and $BaCO_3$ were precipitated rapidly. The phosphoric acid method was used to extract CO_2 from the samples for oxygen isotope analysis. The results were presented relative to PDB in his Table VI as listed in our Table 5 and recalculated relative to SMOW. It appears from the data of McCrea (1950) that the $\delta^{18}O$ values for the three different varieties of carbonate are indistinguishable within experimental errors.

However, it must be pointed out that McCrea (1950) did not take into account the difference in acid fractionation factors among the different varieties of carbonate. Using the acid fractionation factors of 1.01025 for $CaCO_3$, 1.01049 for $SrCO_3$, and 1.01097 for $BaCO_3$ at 25°C (Sharma and Clayton, 1965), we recalculated the data of McCrea (1950) as listed in the parentheses in Table 5. The recalculated results show that the oxygen isotope fractionations are not negligible between $CaCO_3$ and $BaCO_3$ and between $SrCO_3$ and $BaCO_3$. The fractionations between $CaCO_3$ and $BaCO_3$ are 0.97 to 0.82‰, which are close to the results from the present experiments and are in agreement with the theoretical calculations of Zheng (1999). We note that there is no significant fractionation between $CaCO_3$ and $SrCO_3$ in the recalculated data. This may be due to small equilibrium fractionations between aragonite and
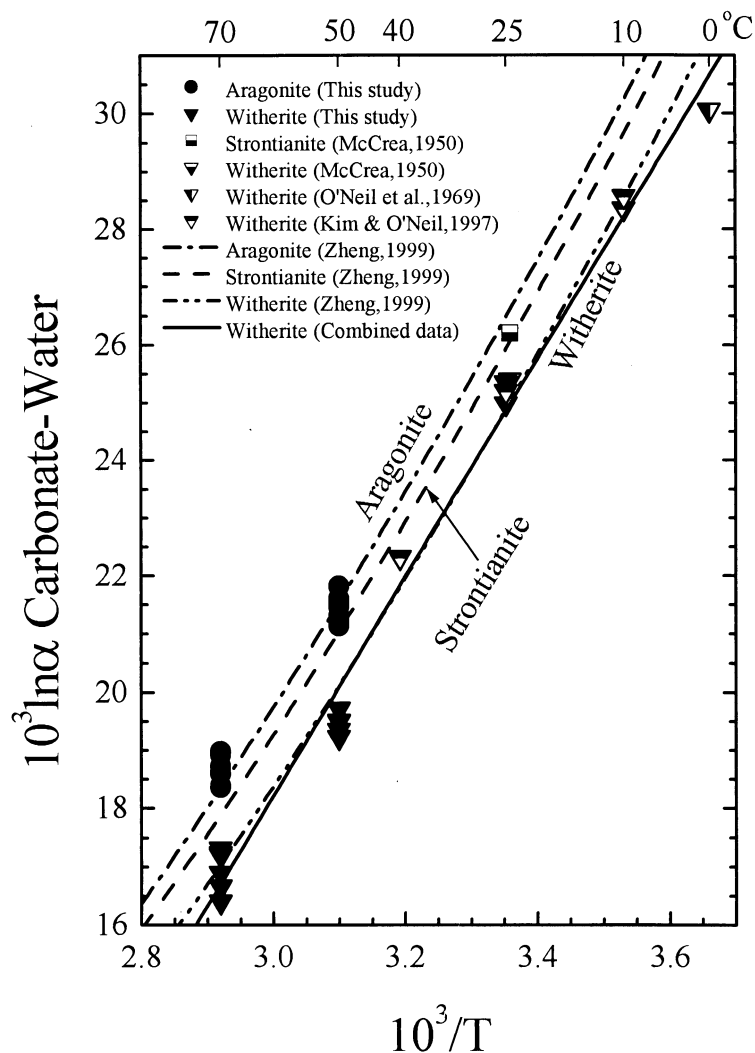
Fig. 3. Comparison of the experimental calibrations for oxygen isotope fractionation between aragonite, strontianite, witherite, and water with the theoretical calculations. The solid curve denotes the combined data from the present experiments with the previous precipitation experiments by O'Neil et al. (1969) as well as by Kim and O'Neil (1997) for the witherite-water system.

strontianite (Zheng, 1999) and possible experimental errors (± 0.2‰). Apparently, the carbonates precipitated rapidly by Mc-Crea (1950) did not inherit the oxygen isotope compositions of $[CO_3]^{2-}$ in the solutions. Instead, his results showed the structural effect on oxygen isotope partitioning between Ca, Sr, and

Table 5. Oxygen isotope data of rapidly precipitated carbonates (McCrea, 1950).

Sample	$\delta^{18}O$ (‰) (in Florida coastal water)	$\delta^{18}O$ (‰) (in Lake Michigan water)
$CaCO_3$	27.59	20.01
$SrCO_3$	27.72 (27.48)*	20.23 (19.99)*
$BaCO_3$	27.34 (26.62)*	19.91 (19.19)*

* The data in the parentheses represent modified values according to different acid fractionation factors.

Ba carbonates during their crystallization. This is also consistent with the experimental determinations of O'Neil et al. (1969) and the theoretical calculations of Zheng (1999).
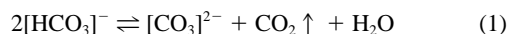
The water used in the experiments of McCrea (1950) was Lake Michigan water, for which the oxygen isotope composition was not given by the author. Nevertheless, Epstein et al. (1951) reported a $\delta^{18}O$ value of $-6.2‰$ for Lake Michigan water (relative to SMOW). We have thus recalculated the oxygen isotope fractionations between strontianite, witherite, and water from the data of McCrea (1950) at 25°C as shown in Figure 3. It appears that the experimental results from McCrea (1950) are not only in agreement with the experimental data of O'Neil et al. (1969), but also match the theoretical calculations by Zheng (1999) with reasonable internal agreement for oxygen isotope fractionations among the Ca, Sr, and Ba carbonates.

The present data in Figure 2 show clearly that there are the systematic differences in oxygen isotope fractionation between
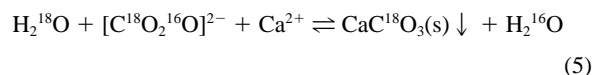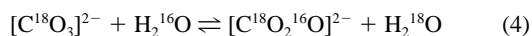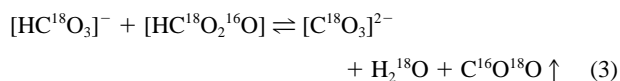
witherite, aragonite, and water acquired from the different experimental approaches. Furthermore, the results from the two-step approach represent the equilibrium fractionations between aragonite, witherite, and water, whereas those from the one-step approach do not. This provides tight constraints on the kinetic mechanism of oxygen isotope disequilibrium fractionation between carbonate and water.

5. IMPLICATIONS FOR KINETIC MECHANISM

In general, the chemical reactions involving $CaCO_3$ formation via the slow decomposition of $Ca(HCO_3)_2$ can be expressed as follows:

$$2[HCO_3]^- \rightleftharpoons [CO_3]^{2-} + CO_2 \uparrow + H_2O \qquad (1)$$

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

During the crystallization of $CaCO_3$ minerals, oxygen isotope exchange may proceed in the following ways:

$$[HC^{18}O_3]^- + [HC^{18}O_2{}^{16}O] \rightleftharpoons [C^{18}O_3]^{2-}$$
$$+ H_2{}^{18}O + C^{16}O^{18}O \uparrow \quad (3)$$

$$[C^{18}O_3]^{2-} + H_2{}^{16}O \rightleftharpoons [C^{18}O_2{}^{16}O]^{2-} + H_2{}^{18}O \qquad (4)$$

$$H_2{}^{18}O + [C^{18}O_2{}^{16}O]^{2-} + Ca^{2+} \rightleftharpoons CaC^{18}O_3(s) \downarrow + H_2{}^{16}O$$
$$(5)$$

where reaction 3 denotes the oxygen isotope exchange during $[HCO_3]^-$ decomposition to $[CO_3]^{2-}$ and H_2O. Reaction 4 means the isotopic exchange and equilibrium between $[CO_3]^{2-}$ and H_2O. Reaction 5 reflects the oxygen isotope exchange when $[CO_3]^{2-}$, equilibrating with H_2O, combines with Ca^{2+} to form $CaCO_3$ mineral. A critical question concerning the exchange reactions is: What dictates the isotopic equilibrium fractionation between carbonate and water during carbonate precipitation?
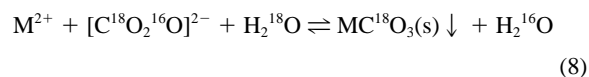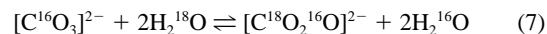
McCrea (1950) and O'Neil et al. (1969) observed that the rapidly precipitated $CaCO_3$ shows the same oxygen isotope composition as $[HCO_3]^-$ in solution. This implies that if the reaction of carbonate precipitation proceeds rapidly, the $[CO_3]^{2-}$ formed from $[HCO_3]^-$ decomposition would not have sufficient time to exchange oxygen isotopes with water to achieve equilibrium fractionation and would combine rapidly with Ca^{2+} in the solution to precipitate $CaCO_3$. As a consequence, the $CaCO_3$ precipitate can inherit the oxygen isotope composition of the dissolved carbonates in the solution, resulting in a significant deviation of the measured fractionations between $CaCO_3$ and H_2O from those equilibrium values. Therefore, the kinetic mechanism of oxygen isotope disequilibrium fractionation during these reactions is of critical importance in interpreting the experimental results, particularly in assessing whether isotope equilibrium has been achieved between carbonate and water.

It is known under the present experimental conditions that the precipitation of the Ca and Ba carbonates follows the reaction:

$$M^{2+} + [CO_3]^{2-} = MCO_3(s) \downarrow \qquad (6)$$

where M denotes a divalent metal cation like Ca or Ba. In the processes of carbonate formation, oxygen isotope fractionation involve the following isotope exchange reactions:

$$[C^{16}O_3]^{2-} + 2H_2{}^{18}O \rightleftharpoons [C^{18}O_2{}^{16}O]^{2-} + 2H_2{}^{16}O \qquad (7)$$

$$M^{2+} + [C^{18}O_2{}^{16}O]^{2-} + H_2{}^{18}O \rightleftharpoons MC^{18}O_3(s) \downarrow + H_2{}^{16}O$$
$$(8)$$

where reactions 7 and 8 have similar implications to reactions 4 and 5, i.e., reaction 7 represents the isotopic exchange and equilibrium between $[CO_3]^{2-}$ and H_2O. Reaction 8 reflects the structural effect on oxygen isotope partitioning during carbonate crystallization. Because the rate of isotope exchange between $[CO_3]^{2-}$ and H_2O is slower than that caused by the structural effect in the processes of mineral crystallization, reaction 7 will take a longer time to achieve isotope equilibration relative to reaction 8.

According to the kinetics of chemical reaction, the reaction rate of a complex chemical system is determined by the slowest step. Evidently, isotope exchange reaction 7 is the rate-limiting step in the synthesis experiments of interest and, thus, dictates the degree of isotope exchange toward equilibrium between carbonate and water. Nevertheless, the magnitude of final fractionation depends on exchange reactions 7 and 8. As shown in Figure 3, the experimental fractionations for the carbonate-water systems obtained by the two-step approach are equilibrium fractionations, because the isotope exchange between $[CO_3]^{2-}$ and H_2O proceeded over 10 d (Tables 2, 4).

In the one-step experiments, however, there was not enough time to achieve the oxygen isotope equilibration because the isotopic exchange between $[CO_3]^{2-}$ and H_2O was conducted for a rather short period (< 20 min). In this regard, the experimental results from the one-step approach represent disequilibrium fractionations. Although there is the structural effect on oxygen isotope partitioning between aragonite and witherite during rapid precipitation, the final fractionations for the carbonate-water systems are still in isotopic disequilibrium because the oxygen isotope exchange between $[CO_3]^{2-}$ and H_2O was significantly out of equilibrium.

The present experimental study shows that the previous prediction by McConnaughey (1989) for biologic carbonates is applicable to inorganically precipitated carbonates. In other words, the slow exchange of oxygen isotopes between dissolved carbonates and water can prevent oxygen isotope equilibrium during the timescales of biologic and inorganic $CaCO_3$ precipitation. It is evident that the rate-limiting step of achieving oxygen isotope equilibrium fractionation between carbonate and water is the attainment of the isotopic equilibrium between dissolved $[CO_3]^{2-}$ and H_2O before carbonate precipitation from aqueous solutions.

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