



Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates

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Abstract—A suite of divalent metal (Ca, Cd, Ba) carbonates was synthesized over the temperature range 10–40°C by the classical method of slowly bubbling N₂ through a bicarbonate solution. It was discovered that carbonates could be precipitated reproducibly in or out of isotopic equilibrium with the environmental solution by varying the concentrations of bicarbonate and cation. Precipitation rate had little or no influence on the isotopic composition of the product. Relatively high initial concentrations of up to 25 mM in both bicarbonate and cation were prepared by adding solid metal chlorides to solutions of NaHCO₃. On the basis of results of equilibrium experiments and a new determination of the acid fractionation factor, a new expression is proposed for the oxygen isotope fractionation between calcite and water at low temperatures:

$$1000\ln\alpha(\text{Calcite-H}_2\text{O}) = 18.03(10^3T^{-1}) - 32.42$$

where α is the fractionation factor, and T is in kelvins. Combining new data for low-temperature precipitations and the high-temperature equilibrium fractionations published by O'Neil et al. (1969) results in a revised expression for the oxygen isotope fractionation between octavite (CdCO₃) and water from 0° to 500°C:

$$1000\ln\alpha(\text{CdCO}_3\text{-H}_2\text{O}) = 2.76(10^6T^{-2}) - 3.96$$

The ability to produce nonequilibrium carbonates allowed assessment to be made, for the first time, of the temperature dependence of nonequilibrium stable isotope fractionations in mineral systems. The temperature coefficients of $\alpha(\text{carbonate-water})$ for nonequilibrium divalent metal carbonates are greater than those for equilibrium carbonates, a finding that may bear on the interpretation of analyses of biogenic carbonates forming out of isotopic equilibrium in nature.

New determinations of acid fractionation factors ($1000\ln\alpha$) at 25°C for calcite (10.44 ± 0.10), aragonite (11.01 ± 0.01), and witherite (10.57 ± 0.16) are mildly to strongly different from those published by Sharma and Clayton (1965) and point to a control on this fractionation by some physical property of the mineral. Reproducible values for octavite (CdCO₃) varied from 11.18 to 13.60 depending on the conditions of preparation of the carbonate. These new values need to be considered in determinations of absolute ¹⁸O/¹⁶O ratios of international reference standards and in relating analyses of carbonates to those of waters, silicates, and oxides. Copyright © 1997 Elsevier Science Ltd

1. INTRODUCTION

In his pioneering study of theoretical and experimental aspects of the oxygen isotope geochemistry of calcium carbonate, McCrea (1950) used two different batches of seawater for his experiments and obtained two different equations for the fractionation of ¹⁸O/¹⁶O between inorganically precipitated CaCO₃ and H₂O as a function of temperature. No explanation was provided for why the two equations were so different. Epstein et al. (1951, 1953), working in the same laboratory, developed an analogous carbonate-water oxygen isotope temperature scale by analyzing biogenic carbonates precipitated by marine organisms living either in thermostated tanks in the laboratory or under natural conditions in localities where the seasonal surface temperatures were known. The oxygen isotope temperature scale obtained from the biogenic carbonates was in good agreement with one of the McCrea (1950) equations.

For over 40 years major advances in paleoceanography and paleoclimatology have been made using the oxygen isotope paleotemperature scale of Epstein et al. (1953) or a slight modification of it. Throughout the intervening years a

number of complications of the method have been recognized and addressed. Among the most important of these are (1) validity of the original calibrations, (2) influence of polymorphic form and chemical composition of the CaCO₃ shell or cement on equilibrium fractionation factors, (3) kinetic effects of both biological (vital) and physical origin, (4) reliability of acid fractionation factors, (5) temperature dependence of nonequilibrium fractionations, and (6) recognition of diagenetic processes that alter the original isotopic compositions.

In an attempt to address some of the above concerns through laboratory experimentation, O'Neil et al. (1969) measured oxygen isotope fractionations between alkaline-earth carbonates and water over the temperature range 0–500°C. They concluded that (1) the temperature coefficient for the CaCO₃-H₂O fractionation published by Epstein et al. (1953) was almost the same as that determined from their inorganic precipitation experiments and one of the equations of McCrea (1950), (2) there are significant oxygen isotope fractionations of up to a few permil between the various alkaline earth carbonates at low temperatures, and (3) both cationic size and mass are important in controlling isotopic

fractionation in carbonate-water systems. Tarutani et al. (1969) made further studies of synthetic carbonates by slowly precipitating calcite, aragonite, and magnesian calcite from various bicarbonate solutions. Their results suggested that, relative to calcite at 25°C, aragonite was enriched in ^{18}O by 0.6‰ and magnesian carbonates were enriched by 0.06‰/mol% Mg. Their data for inorganically precipitated carbonate were in accord with the $\text{CaCO}_3\text{-H}_2\text{O}$ calibrations of Epstein et al. (1953) and O'Neil et al. (1969).

Tarutani et al. (1969) also reported that precipitations from solutions with higher initial calcium concentrations tended to yield larger fractionations and explained this observation as a disequilibrium phenomenon rather than one arising from variations in the equilibrium constant in response to changes in some other parameter like ionic strength or pH. They measured low isotopic ratios from the outer parts of single precipitations of the carbonates by sequential isotopic analysis and did not observe any change in the fractionation factor determined using solutions containing 36 g NaCl/L. If this anomalous phenomenon were caused by rapid precipitation in the first stage of precipitation, the early calcium carbonate should have had nearly the same (or lighter) isotopic composition as the HCO_3^- ion in solution according to McCrea (1950). That is, the isotopic ratio should have increased from the inner parts of the crystals to the outer parts, because ^{16}O species would tend to precipitate faster than ^{18}O species as a result of the more rapid diffusion of the isotopically lighter species to the crystal surface (Turner, 1982). The higher fractionation factor observed at higher concentrations implies that there is some other factor which influences the attainment of isotopic equilibrium for carbonates precipitated from aqueous solutions. In a similar vein, O'Neil et al. (1969) also reported that the $^{18}\text{O}/^{16}\text{O}$ fractionation between carbonates and water decreased with time during a single precipitation experiment but offered no explanation for this phenomenon.

Golyshv et al. (1981) concluded from theoretical considerations that the isotopic properties of carbonates are determined primarily by the cationic radius and that, in contrast to the findings of O'Neil et al. (1969), the mass effect becomes substantial only for ions with large masses like those of Ba^{2+} and Pb^{2+} . The Cd^{2+} cation takes on special significance in this respect as it has almost the same ionic radius as Ca^{2+} in carbonate crystals but has a much larger mass. The influence of these parameters on the equilibrium isotopic properties of carbonates and other minerals needs further testing by laboratory experiment.

Horibe and Oba (1972) reported that aragonite was depleted in ^{18}O relative to calcite in mollusks grown at various temperatures and Zheng (unpubl. data), using the increment method of semi-empirical calculations (Schütze, 1980), suggested that aragonite should be significantly depleted in ^{18}O relative to calcite at low temperatures. Sommer and Rye (1978) and Grossman and Ku (1986), however, showed that the aragonitic foraminifer *Hogelundia* was enriched in ^{18}O relative to the calcitic foraminifer *Uvigerina*. The aragonite-calcite fractionation is now generally accepted to be positive at low temperatures. From their analyses of natural samples, Sommer and Rye (1978) proposed an aragonite-

calcite paleotemperature scale, but Grossman and Ku (1986) found no temperature dependence of this fractionation in their oxygen isotope measurements of aragonitic and calcitic foraminifera. Furthermore, they argued that the high temperature data of *Hogelundia* reported by Sommer and Rye (1978) were 2–3‰ higher than expected on the basis of experimental results, because the foraminifera grew during a glacial period when the isotopic composition of seawater was heavier.

The power and potential of oxygen isotope analysis of biogenic carbonates remains secure, but uncertainties still remain in the minds of most active workers in the field about the reliability of proposed isotopic temperature scales and the factors that influence them. The most commonly accepted oxygen isotope paleotemperature scale in use today for biogenic carbonates is that proposed by Grossman and Ku (1986) and will be discussed in more detail below. Clearly there are important unresolved conflicts among the results of published calculations, measurements of natural carbonates, and measurements of laboratory synthesized carbonates. In the present study we report results of laboratory experiments designed to make further tests of the importance of some chemical and physical conditions of precipitation to equilibrium and kinetic isotope effects in carbonate-water systems. Carbonates were precipitated in and out of isotopic equilibrium at three different low temperatures. The importance of rate of precipitation and initial concentrations of bicarbonate and cation was reinvestigated. In addition, the temperature dependence of nonequilibrium fractionations were determined for the first time for mineral-water systems. Barium and cadmium carbonates, while relatively rare in nature, were investigated because of their importance to the overall understanding of the oxygen isotope chemistry of carbonates. The CaCO_3 polymorph vaterite was also synthesized and its isotopic properties determined.

2. EXPERIMENTAL METHODS

2.1. Preparation of Solutions

A series of Na-X-Cl-HCO_3 solutions was made in deionized water at equimolar concentrations of XCl_2 ($\text{X} = \text{Ca}^{2+}$, Cd^{2+} , or Ba^{2+}) and NaHCO_3 ranging from 5 to 25 mM depending on the solubility product of the carbonate. Purified CO_2 gas ($P = 1\text{ bar}$) was normally bubbled through stirred deionized water at room temperature for 10 min in order to adjust the pH down to a value of about 6.0 and enhance solubility. The NaHCO_3 was then added and, after 10 min, the chloride was added. Stirring was continued for an additional 10 min to insure that all salts were completely dissolved. The specific chlorides were used to make the various carbonates; for example, barium chloride for witherite and cadmium chloride for octavite. An alternate method of preparation, used by O'Neil et al. (1969) and Tarutani et al. (1969), was also employed. Solid carbonate was added to 400 mL of stirred deionized water, and CO_2 gas was bubbled through the water to dissolve the carbonate to saturation. After a minimum of 2 h of bubbling with CO_2 gas, undissolved carbonates were removed by vacuum filtration, and the saturated divalent metal bicarbonate solution stored in a bottle. For CaCO_3 , however, solutions prepared this way always produced a mixture of calcite and vaterite, and in small amounts. This method of preparation of bicarbonate solutions was, therefore, not used in preparing the majority of carbonates examined in this study.

2.2. Synthesis of Carbonates

After the bicarbonate solutions were prepared, one aliquot of solution was taken for $\delta^{18}\text{O}$ analysis, and 100 or 200 mL of the solution

was placed in a specially designed vessel that was thermostated for at least 1 h in a constant temperature bath ($\pm 0.1^\circ\text{C}$) to ensure that the specified temperature was established before precipitation started. Pre-purified nitrogen gas was then bubbled slowly through the solutions to remove CO_2 thus promoting supersaturation and slow precipitation of the carbonates. The N_2 was saturated with water vapor of the same oxygen isotope composition as the water vapor leaving the precipitating solution in order to maintain constant isotopic composition of the solution. The bubbling rate of N_2 was controlled by a regulator attached to the tank and was monitored by counting the bubbles for periods of 30 s. Precipitations were performed at 10, 25, and 40°C .

The time required for the first appearance of precipitate depended on the composition of the solution, temperature, and bubbling rate, but it took at least one day and a maximum of five days to generate sufficient material ($\sim 10 \text{ mg } \text{XCO}_3$) for both X-ray diffraction and isotopic analysis. Upon completion of the experiment, a 2 mL aliquot of the final solution was taken for $\delta^{18}\text{O}$ analysis. The solid carbonate, precipitated on the walls and at the bottom of the vessel, was removed using a rubber policeman, filtered, rinsed several times with deionized water, ethyl alcohol, and then dried on filter paper for at least $\sim 2 \text{ h}$ at 80°C prior to storage for isotopic analysis. The mineralogy of every precipitate was identified by X-ray diffraction analysis, and some of the precipitates were examined by scanning electron microscopy.

2.3. Release of Total Oxygen in Carbonates

To obtain $^{18}\text{O}/^{16}\text{O}$ ratios of total oxygen of the carbonates, the carbonates were decomposed thermally on a conventional silicate extraction line, and the oxide residue was fluorinated to release its oxygen. Carbonate samples were placed in Ni tubes and degassed at 100°C for at least 3 h. After complete degassing, the valves on the tubes were closed and the samples were heated at 600°C over-

night. The thermally liberated CO_2 gas was collected, and its volume and isotopic composition were measured. The metal oxide remaining in the Ni tube was then reacted with ClF_3 at 600°C for 12 h. Oxygen obtained from the reaction with ClF_3 was converted to CO_2 , and its volume and isotopic composition were measured. Generally, the yield obtained from the sum of oxygen released on thermal decomposition and fluorination of the remaining oxide was 97–100%. Combined with the data from the phosphoric acid reaction, acid fractionation factors were obtained.

2.4. Oxygen Isotope Measurements

All isotopic measurements were made on CO_2 gas using a Finnigan Delta S isotope ratio mass spectrometer. $\delta^{18}\text{O}$ values were normalized to the recommended values for the international reference standards NBS-19, SMOW, and SLAP. Carbonates were analyzed at 25°C using the classical procedure of McCrea (1950). Acid fractionation factors used in this paper are 1.01050 for calcite, 1.01063 for witherite, and 1.01146 for octavite, modified from the values reported by Sharma and Clayton (1965). The previously accepted value of 1.01025 for calcite was used only once in this paper when making comparisons between results obtained in this study and those published earlier (Fig. 1).

Solutions were analyzed by the CO_2 - H_2O equilibration method (Cohn and Urey, 1938) using a modification of the vacutainer method of Socki et al. (1992). The equilibrated CO_2 gas was extracted and analyzed on the mass spectrometer, and a CO_2 - H_2O fractionation factor (α) of 1.0412 (O'Neil et al., 1975) was applied to obtain the isotopic composition of the water itself. The oxygen isotope fractionation factor α between two substances A and B is defined as

$$\alpha = (^{18}\text{O}/^{16}\text{O})_{\text{A}} / (^{18}\text{O}/^{16}\text{O})_{\text{B}}$$

For theoretical and practical reasons the function $1000 \ln \alpha$ is nor-

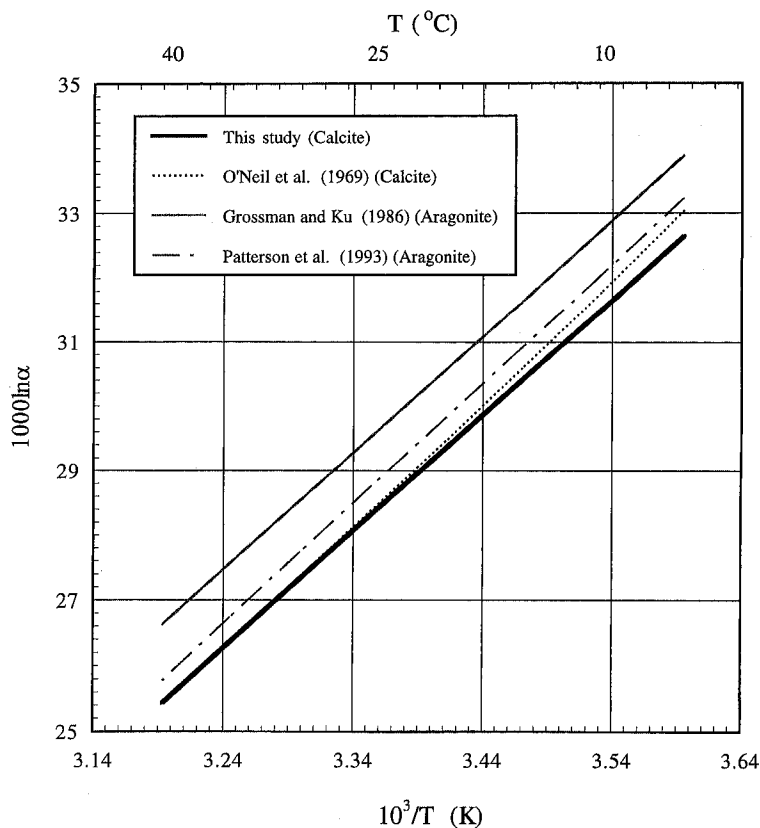


Fig. 1. Comparison of fractionation curves for CaCO_3 - H_2O at low temperatures.

mally employed in this paper. Oxygen isotope compositions of both carbonates and waters are reported in the familiar $\delta^{18}\text{O}$ notation relative to the SMOW standard.

3. RESULTS AND DISCUSSION

3.1. Temperature Dependence of Equilibrium Fractionations

3.1.1. Calcium carbonates

The various fractionation curves proposed for the $\text{CaCO}_3\text{-H}_2\text{O}$ system (both calcite and aragonite) are shown in Fig. 1. A recent determination was made by Patterson et al. (1993) who measured the oxygen isotope composition of aragonitic otoliths from freshwater fish that lived in waters of known temperature and isotopic composition. They obtained the following relation for the temperature dependence of the fractionation factor $\alpha(\text{CaCO}_3\text{-H}_2\text{O})$:

$$1000\ln\alpha = 18.56(10^3T^{-1}) - 33.49$$

where T is in kelvins. They also recalculated the paleotemperature equation of Grossman and Ku (1986) to fit a T^{-1} relation and obtained the following:

$$1000\ln\alpha = 18.07(10^3T^{-1}) - 31.08$$

Patterson et al. (1993) state that the slopes of these equations are indistinguishable, but that the intercept differs by approximately +2.5 because of seasonal changes in bottom water temperature, the isotopic composition of water, analytical errors, and unexplained metabolic effects. In Fig. 1 we compare the curve determined in the present study for calcite (using an acid fractionation factor of 1.01025) with the previously published curve for this system determined by O'Neil et al. (1969) and the two curves determined for biogenic aragonite. The temperature coefficient (slope) for our data on this plot is indeed very close to that of Grossman and Ku (1986) even though one is for calcite, and the other is for aragonite. The implication of this observation is that $\alpha(\text{aragonite-calcite})$ does not change with temperature over the low temperature range investigated, a conclusion that has some basis in theory. If aragonite is indeed enriched by 0.6‰ relative to calcite at 25°C as observed in the laboratory experiments of Tarutani et al. (1969), however, the data of Patterson et al. (1993) are much more in accord with our experimental data for calcite than those of Grossman and Ku (1986) whose implied difference between aragonite and calcite would be much too high at approximately 1.2‰. Because of the importance of oxygen isotope analyses of natural carbonates in several aspects of earth science, further experimental work on these systems is warranted.

Our new data for inorganically precipitated calcite at low initial concentrations of 5 mM are in good accord with those of O'Neil et al. (1969) above 25°C, but there is a relatively large difference in the datasets around 10°C (Fig. 1). We propose that the fractionation curve for calcite-water determined in the present study is the most reliable curve for this system on the basis of several considerations including (1) the similarity of the slope of our new curve to those determined for biogenic carbonates, (2) the large number of experiments performed provided improved statistics, (3) the

fractionations were determined over a large temperature range and are internally consistent, and (4) the conditions of the present experiments were tightly constrained to produce only calcite, the stable polymorph of CaCO_3 . These are only plausibility arguments as attainment of isotopic equilibrium can not be proved.

It should be noted that an acid fractionation factor of 1.01050 (see Table 5) was used in the new determination of the calcite-water calibration that is shown in Fig. 2 and represented by the following expression:

$$1000\ln\alpha(\text{Calcite-H}_2\text{O}) = 18.03(10^3T^{-1}) - 32.42$$

3.1.2. Barium carbonate

A few checks were made of the reliability of equilibrium oxygen isotope fractionations between carbonates and water determined by the synthesis approach (Table 2). Results of our new determinations were compared to those made many years ago in a different laboratory. O'Neil et al. (1969) argued that the data they obtained by slow precipitations of carbonates at low temperatures were equilibrium data because they were in good accord with data for high-temperature recrystallization experiments for which equilibrium could be proved by reversing the curves. Our new low-temperature data for $\text{BaCO}_3\text{-H}_2\text{O}$ agree remarkably well with those published by O'Neil et al. (1969) almost 30 years ago. The (corrected) high-temperature data of O'Neil et al. (1969) for BaCO_3 (witherite) are combined with our low temperature data in Fig. 3 using the new determination of the acid fractionation factor for witherite (see Table 5). The relation obtained:

$$1000\ln\alpha(\text{BaCO}_3\text{-H}_2\text{O}) = 2.63(10^6T^{-2}) - 4.04$$

is the same as that of O'Neil et al. (1969) within experimental error. T^{-2} is normally used to relate fractionation factors over very large temperature ranges that include high temperatures (e.g., O'Neil, 1986). This confirmation provides needed credence to the approach as results of very few experiments of this type have been reported.

3.1.3. Cadmium carbonate

One of the most important carbonate systems to examine is $\text{CdCO}_3\text{-H}_2\text{O}$ as the radius of the Cd^{2+} ion is almost identical to that of Ca^{2+} in carbonates. With our present techniques, the importance of cationic radius to the isotopic properties of divalent metal carbonates can be assessed at low temperatures where fractionation factors are larger and more sensitive to changes in temperature and other parameters. O'Neil et al. (1969) were unable to synthesize CdCO_3 at low temperatures by the method they used because of the low solubility of octavite. In this study, low-temperature oxygen isotope fractionation factors for the $\text{CdCO}_3\text{-H}_2\text{O}$ system were obtained for the first time by slow synthesis from Na-Cd-Cl-HCO_3 solutions (Table 3). Because of the large range of values obtained in the present study (see Table 5), the one value of the acid fractionation factor ($\alpha = 1.01146$) that agreed with the value published by Sharma and Clayton (1965) was used in calculating the $\delta^{18}\text{O}$ values of CdCO_3 . Again the (corrected) high temperature equilibrium oxygen

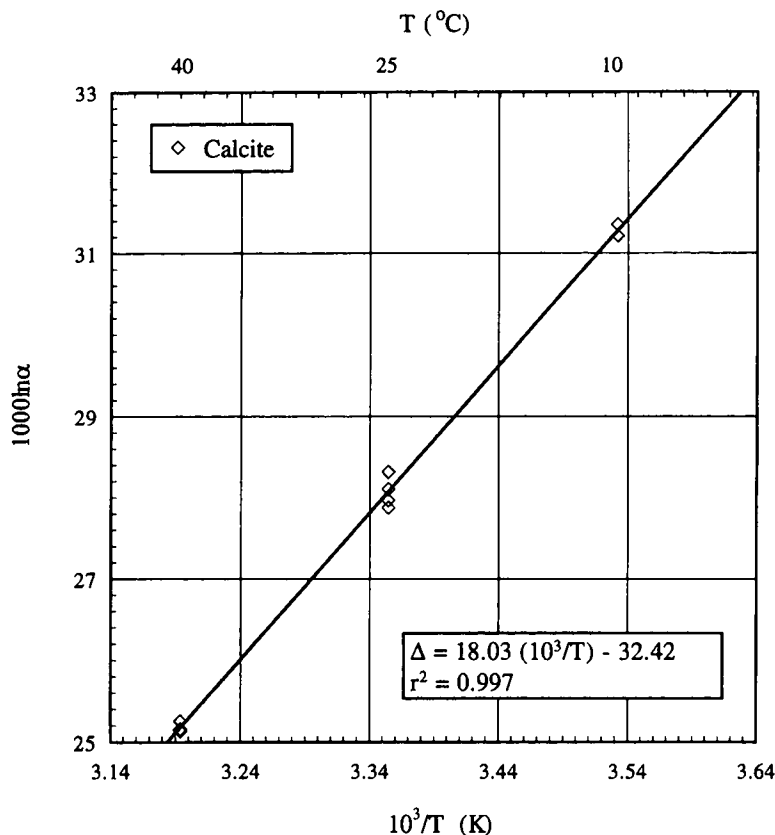


Fig. 2. Relation between $\Delta = 10^3 \ln \alpha(\text{calcite-water})$ and temperature at the lowest initial concentrations of Ca^{2+} and HCO_3^- (5 mM).

isotope fractionations obtained by O'Neil et al. (1969) were in excellent accord with the low temperature fractionations we obtained by our methods and combined to produce the following relation shown in Fig. 4:

$$1000 \ln \alpha(\text{CdCO}_3\text{-H}_2\text{O}) = 2.76(10^6 T^{-2}) - 3.96$$

In this case, however, the above relation is significantly different from the extrapolated high-temperature data published earlier, once again emphasizing the danger of extrapolating any type of chemical data obtained at high temperatures to low temperatures as was performed by O'Neil et al. (1969) in the absence of low-temperature data for this system. Despite the important change in the fractionation curve for $\text{CdCO}_3\text{-H}_2\text{O}$, the point made in the earlier study was confirmed: relative to cationic mass, the cationic radius plays a minor role in determining the oxygen isotope properties of carbonates.

3.2. Nonequilibrium Carbonates

3.2.1. Synthesis of nonequilibrium carbonates

It was noticed early on that the oxygen isotope fractionation factors between synthetic carbonates and water varied significantly with initial concentrations of the bicarbonate solutions. The higher the initial concentrations of metal ion

and bicarbonate, the larger were the fractionation factors, and reproducibly so. Solutions prepared with divalent metal chlorides and NaHCO_3 have much higher ionic strengths than those prepared by dissolving solid carbonates in water, and thus we were able to prepare relatively concentrated bicarbonate solutions of up to 25 mM for the more soluble carbonates like calcite and witherite. At these concentrations the solutes would have a negligible effect on the oxygen isotope activity of the water (e.g., O'Neil and Truesdell, 1991). The low solubility of octavite precluded preparation of such concentrated solutions.

The fractionation factors measured for solutions with different initial concentrations differed by as much as 2–3 permil at a given temperature. Clearly there is only one equilibrium fractionation at any temperature, so most of the carbonates precipitated from these solutions of varying concentration were forming out of oxygen isotope equilibrium with the water. Only limited criteria were available to use in selecting which direction of change (i.e., larger or smaller fractionations), if any, was in the direction toward equilibrium. The bicarbonate solutions used in previous work, for which equilibrium was assumed, were relatively dilute because they were made by dissolving the solid carbonate in CO_2 -charged water. In addition, as the concentrations of our Na-X-Cl-HCO_3 solutions were lowered, the fractionation factors rapidly decreased to what appeared to be a limiting value. (Experiments will be made with extremely dilute solu-

Table 1. Data for calcite experiments.

Sample	Temp. (°C)	$\delta^{18}\text{O}$ (Water)	$\delta^{18}\text{O}$ (CaCO_3)	$\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$	$10^3 \ln \alpha$	Init. conc. (mM)
ST-18	10	-7.74	25.56	1.03356	33.01	15
ST-20	10	-7.74	25.69	1.03369	33.14	25
ST-24	10	-7.74	26.50	1.03451	33.93	25
ST-25	10	-7.74	26.64	1.03465	34.06	25
ST-36	10	-7.74	25.32	1.03332	32.77	25
ST-37	10	-7.74	25.46	1.03346	32.91	25
ST-38-S	10	-8.30	25.86	1.03445	33.87	25
ST-38-N	10	-8.30	25.12	1.03370	33.14	25
ST-39	10	-8.30	25.72	1.03430	33.73	25
ST-52-10	10	-8.12	23.47	1.03185	31.35	5
ST-54-10	10	-8.23	23.21	1.03170	31.21	5
ST-18	25	-7.74	21.52	1.02949	29.06	15
ST-19	25	-7.74	21.19	1.02916	28.74	15
ST-20	25	-7.74	22.06	1.03003	29.59	25
ST-22	25	-7.74	21.45	1.02942	28.99	15
ST-24	25	-7.74	21.58	1.02955	29.12	25
ST-25	25	-7.74	21.97	1.02994	29.50	25
ST-36	25	-7.74	21.51	1.02948	29.05	25
ST-37	25	-7.74	21.65	1.02962	29.19	25
ST-38-S	25	-8.30	21.46	1.03001	29.57	25
ST-38-N	25	-8.30	21.15	1.02970	29.26	25
ST-39	25	-8.30	21.32	1.02987	29.43	25
ST-45-25-N	25	-8.30	19.73	1.02826	27.87	5
ST-50-25	25	-8.25	20.23	1.02872	28.31	5
ST-52-25	25	-8.12	20.00	1.02835	27.96	5
ST-54-25	25	-8.23	20.03	1.02849	28.10	5
ST-18	40	-7.74	18.06	1.02600	25.67	15
ST-20	40	-7.74	18.40	1.02634	26.00	25
ST-22	40	-7.74	17.94	1.02588	25.55	15
ST-24	40	-7.74	18.41	1.02635	26.01	25
ST-25	40	-7.74	18.42	1.02636	26.02	25
ST-36	40	-7.74	18.82	1.02677	26.42	25
ST-37	40	-7.74	18.60	1.02655	26.20	25
ST-38-S	40	-8.30	18.11	1.02663	26.28	25
ST-38-N	40	-8.30	17.98	1.02650	26.15	25
ST-39	40	-8.30	18.01	1.02653	26.18	25
ST-50-40	40	-8.20	17.06	1.02547	25.15	5
ST-52-40	40	-8.12	17.24	1.02557	25.25	5
ST-54-40	40	-8.23	17.01	1.02545	25.13	5

Temp. = Temperature.

Init. conc. = Initial concentration (Ca^{2+}) = (HCO_3).

Table 2. Data for witherite experiments.

Sample	Temp. (°C)	$\delta^{18}\text{O}$ (Water)	$\delta^{18}\text{O}$ (BaCO_3)	$\alpha_{\text{BaCO}_3\text{-H}_2\text{O}}$	$10^3 \ln \alpha$	Init. conc. (mM)
C30-10	10	-7.80	23.12	1.03116	30.69	25
C32-10	10	-7.80	22.61	1.03065	30.19	15
C33-10	10	-7.80	22.68	1.03072	30.26	15
C34-10	10	-7.80	22.51	1.03055	30.09	15
C48-10-N	10	-8.30	20.58	1.02912	28.71	5
C49-10-N	10	-8.30	20.80	1.02934	28.92	5
C30-25	25	-7.80	19.19	1.02720	26.84	25
C32-25	25	-7.80	18.83	1.02684	26.49	15
C33-25	25	-7.80	19.05	1.02706	26.70	15
C34-25	25	-7.80	18.84	1.02685	26.50	15
C48-25-N	25	-8.30	17.52	1.02604	25.70	5
C49-25-N	25	-8.30	17.36	1.02587	25.55	5
C32-40	40	-7.80	15.76	1.02375	23.47	15
C33-40	40	-7.80	15.82	1.02381	23.53	15
C34-40	40	-7.80	15.75	1.02374	23.46	15
C49-40-N	40	-8.30	14.43	1.02292	22.66	5

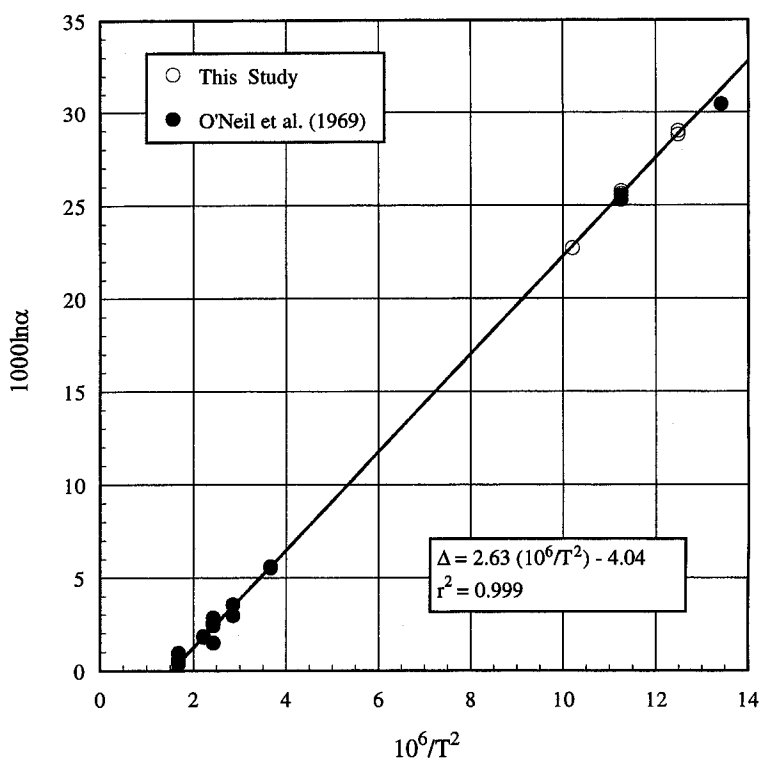


Fig. 3. Oxygen isotope fractionation between barium carbonate and water. The initial concentrations of Ba^{2+} and HCO_3^- were 5 mM. High temperature data from O'Neil et al. (1969).

tions in the future to test that we have indeed reached a limiting value.) On the basis of analyses of natural materials, the larger fractionation factors measured were greater than deemed possible. Finally we place emphasis on those conditions of precipitation that produce only calcite, the stable phase. Taking all these points into consideration, we judge the smallest fractionation factors obtained to be the best representations of equilibrium fractionation factors. This

judgment may seem counterintuitive to those who would expect kinetically-controlled, nonequilibrium fractionations to be too small (i.e., the carbonate would be isotopically too light) as is seen in some biogenic carbonates like coralline carbonate. It is well to point out that the good reproducibility obtained for the fractionation factors of what we interpret to be nonequilibrium carbonates may indeed be reflecting some equilibrium system we have not yet identified.

Table 3. Data for octavite experiments.

Sample	Temp. (°C)	$\delta^{18}\text{O}$ (Water)	$\delta^{18}\text{O}$ (CdCO_3)	$\alpha_{\text{CdCO}_3\text{-H}_2\text{O}}$	$10^3 \ln \alpha$	Init. conc. (mM)
40-10	10	-8.30	22.43	1.03099	30.52	5
42-10	10	-8.30	22.45	1.03101	30.54	10
44-10	10	-8.30	22.35	1.03091	30.44	5
46-10	10	-8.30	22.51	1.03107	30.60	5/10
51-10	10	-8.30	22.53	1.03109	30.61	5
40-25	25	-8.30	18.73	1.02726	26.89	5
42-25	25	-8.30	19.39	1.02792	27.54	10
44-25	25	-8.30	18.89	1.02742	27.05	5
46-25	25	-8.17	19.18	1.02758	27.20	5/10
51-25	25	-8.30	19.08	1.02761	27.23	5
53-25	25	-8.30	19.15	1.02768	27.30	5
40-40	40	-8.30	15.85	1.02435	24.06	5
42-40	40	-8.30	16.49	1.02500	24.69	10
44-40	40	-8.13	15.90	1.02423	23.94	5
46-40	40	-8.30	16.13	1.02463	24.34	5/10
51-40	40	-8.30	16.13	1.02463	24.34	5
53-40	40	-8.30	16.32	1.02483	24.52	5

Temp. = Temperature.

Init. conc. = Initial concentration (X^{2+}) = (HCO_3).

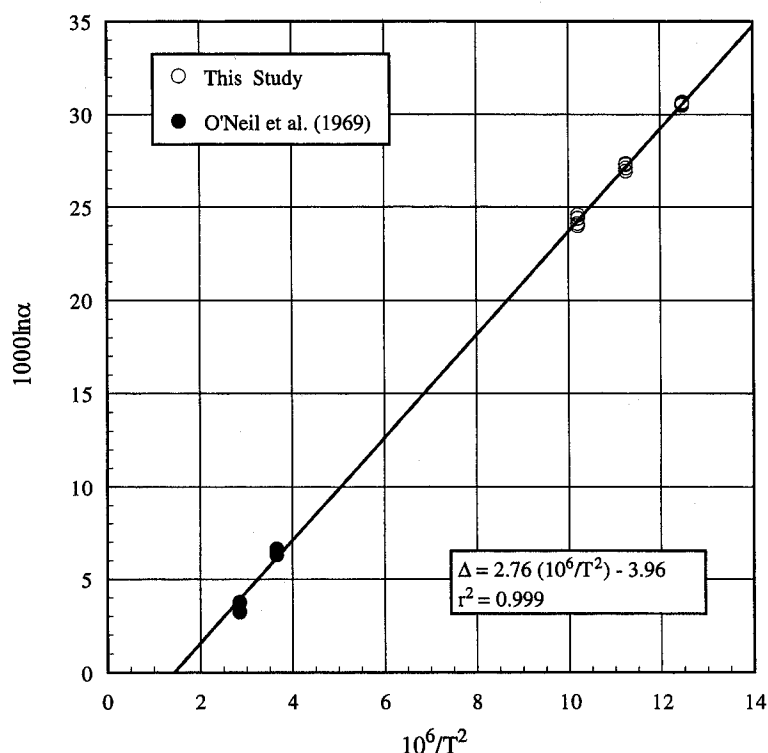


Fig. 4. Oxygen isotope fractionation between cadmium carbonate and water. The initial concentrations of Cd^{2+} and HCO_3^- were 5 mM. High temperature data from O'Neil et al. (1969).

3.2.2. Physical properties of nonequilibrium carbonates

In an attempt to understand the nature of the carbonates precipitated out of isotopic equilibrium with water, the products were examined under the petrographic microscope, with the scanning electron microscope (SEM) and by X-ray diffraction (XRD) analysis. The crystallinities of the synthetic carbonates, determined from ratios of specific peak heights on the diffractograms, were identical to those of natural minerals so that any difference in fractionation factors (between carbonates and water or between acid-liberated CO_2 and carbonate) could not be explained by poor crystallinity of synthetic materials. The expected external forms of the minerals (e.g., well-formed rhombs of calcite) were always observed under the scanning electron microscope.

The only identifiable change in physical property of the products obtained was a variation in crystal size. For calcite and witherite, the lower the initial concentration and the higher the temperature of precipitation, the larger the crystal size. For octavite, there was a slight increase in crystal size with increasing temperature but, in contrast to the other minerals examined, there was a marked increase in crystal size with increasing initial concentration. In addition, the size of the octavite crystals was markedly smaller than those of the other minerals regardless of the conditions of precipitation. The length of time required for the first appearance of precipitate was shorter (minimum 5 h; maximum 2 days) for octavite than for calcite and witherite (minimum 10 h; maximum 5 days). The precipitation rates were always slow and the precipitations were allowed to proceed for several days, de-

pending on the mineral, in order to obtain enough material for analysis.

3.2.3. Temperature dependence of α

The ability to prepare carbonates out of isotopic equilibrium in a reproducible fashion provided us with the opportunity to test the assumption often made that the temperature coefficient of the $\text{CaCO}_3\text{-H}_2\text{O}$ fractionation is the same whether the carbonate is precipitated in or out of equilibrium. Using this assumption, some workers have used changes in the oxygen isotope compositions of coralline carbonate, for example, to reflect changes in temperature of the environmental waters (e.g., Druffel, 1985; Shen et al., 1992; Dunbar et al., 1994). In fact, on theoretical grounds, it is even possible that the fractionation factors of materials precipitated out of equilibrium would be temperature independent or only weakly so. The fractionation curves we determined for these carbonates are the first ever reported for nonequilibrium mineral systems.

The oxygen isotope fractionations measured between nonequilibrium calcite and water from 10° to 40°C are given in Table 1 and shown in Figs. 5 and 6. The most striking features of the data are the unusually large fractionations that increase with increasing initial concentrations and their regular decrease with increasing temperature. The slopes of the nonequilibrium fractionation curves are much steeper than those of the assumed equilibrium curve (Fig. 6). In addition, the slopes of the two nonequilibrium curves are almost identical and readily distinguishable from the equilib-

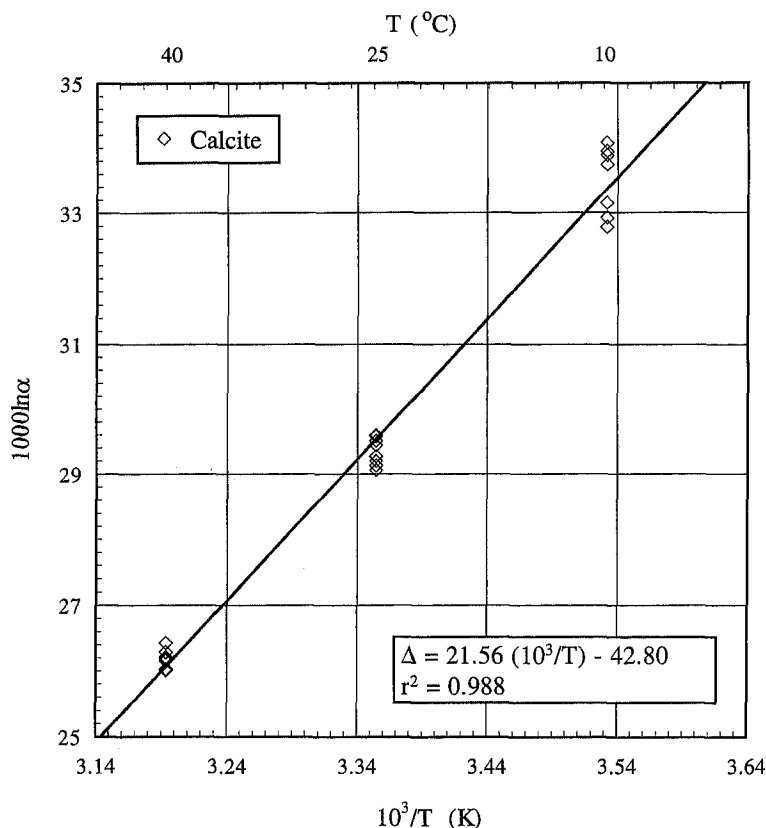


Fig. 5. Relation between $\Delta = 10^3 \ln \alpha$ (calcite-water) and temperature at the highest initial concentrations of Ca^{2+} and HCO_3^- (25 mM).

rium slope. If the results of these experiments can be applied to natural biogenic carbonate systems, and that application is questionable, the practical effect would be that a given change in $\delta^{18}\text{O}$ of nonequilibrium carbonate like coralline carbonate would correspond to a smaller change in temperature than indicated from the conventional oxygen isotope paleotemperature curves in use. All else being equal, a change of 1 permil in $\delta^{18}\text{O}$ of nonequilibrium carbonate would correspond to a change of about 3°C whereas the same change in $\delta^{18}\text{O}$ for an equilibrium carbonate would correspond to a change of about 4°C .

Attempts were also made to synthesize nonequilibrium witherite and octavite. The data are given in Tables 2 and 3 and the fractionation curves are shown in Figs. 7 and 8. Witherite is soluble enough that the relatively highly concentrated solutions necessary for nonequilibrium precipitation could be prepared. Again the fractionation factors for the nonequilibrium cases were higher, but the difference between the data for initial concentrations of 15 and 25 mM were not as pronounced as they were for calcite and significant only at the lowest temperature where fractionations are highest in general. Octavite is the least soluble carbonate examined in this study, and only relatively dilute solutions could be prepared. In this case, the difference between probable nonequilibrium and equilibrium precipitations could be seen only at the highest temperatures, a phenomenon completely unexpected and difficult to understand. In any event,

the observation that equilibrium precipitation is favored from solutions that are relatively dilute, or initially undersaturated with respect to the solid carbonate, was confirmed as a general phenomenon for all carbonates and perhaps for other minerals as well.

3.3. Effect of Precipitation Rate on $\text{CaCO}_3\text{-H}_2\text{O}$ Fractionation

3.3.1. Biogenic carbonate

The effect of the rate of precipitation on carbon isotope fractionation has been studied many times and, for most geologic processes, carbon isotope fractionation is believed to be independent of rate (Romanek et al., 1992), except for a few unusual cases (e.g., O'Neil and Barnes, 1971). On the other hand, only a few studies have been made of the effect of precipitation rate on oxygen isotope fractionation between carbonates and water. Most of these investigations dealt with natural biogenic samples such as corals, and only one experimental study, using inorganically synthesized material, was made by Tarutani et al. (1969). The importance of precipitation rate to the fractionation of both stable isotope and elemental ratios between natural carbonates, and their environmental solutions remains controversial.

McConnaughey (1989a) sampled skeletal materials from corals that grew at two different sites and reported a correla-

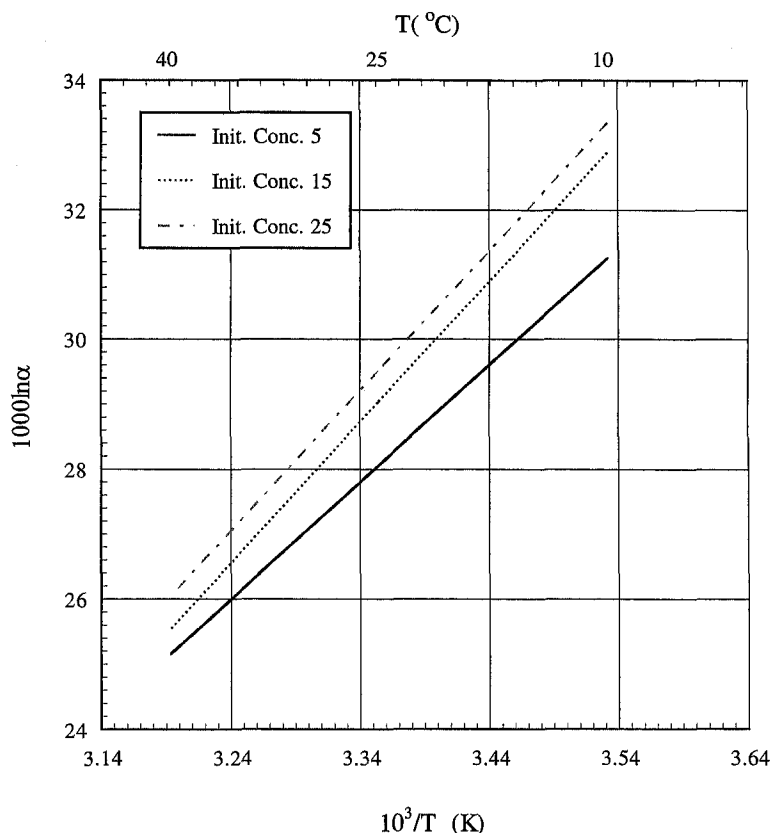


Fig. 6. Relation between $\Delta = 10^3 \ln \alpha (\text{calcite-water})$ and temperature at different initial concentrations of Ca^{2+} and HCO_3^- .

tion between the $\delta^{18}\text{O}$ value of skeletal carbonate and growth rate of the coral. The $\delta^{18}\text{O}$ values are lower than equilibrium values and remain constant between 15 mm/yr and 5 mm/yr and then increase dramatically as the growth rate decreases. The $\delta^{18}\text{O}$ values approach equilibrium values at growth rates below 2 mm/yr. In contrast, De Villers et al. (1995) found a notable effect of growth rate on $\delta^{18}\text{O}$ values and Sr/Ca ratios in corals that grew at 6 mm/yr and 12 mm/yr and argued against the McConnaughey (1989a) suggestion that the $\delta^{18}\text{O}$ value is independent of growth rate over the range of 5 mm/yr to 15 mm/yr. From the trace element literature, the consensus view at the present time is that the slower the precipitation rate, the closer is the approach to chemical equilibrium (e.g., Dromgoole and Walter, 1990).

3.3.2. Inorganic carbonate

Tarutani et al. (1969) synthesized inorganic carbonates at two different growth rates by changing the N_2 flow rate. In contrast to the results obtained for biogenic carbonates, these authors did not detect any influence of precipitation rate on the oxygen isotope fractionation factor between CaCO_3 and H_2O . In our experiments, we reinvestigated a possible relation between oxygen isotope fractionation and growth rate at 25°C using an apparatus specially configured to test two different types of bubbling (Fig. 9). In Type I bubbling, relatively large bubbles are generated, one at a time, by

passing the N_2 through a tube with no constriction. Type II bubbling is characterized by the production of many smaller bubbles when the N_2 passes through a fine frit located at the bottom of the vessel. Because the apparatus is connected up in series, the same amount of nitrogen gas flows through both sections of the apparatus, but vastly different sizes and numbers of bubbles are generated in the two sections. The final pH of the solutions where Type II bubbles were generated was about 0.5 units higher than that of the other solution, which means that Type II bubbles remove CO_2 more efficiently than Type I bubbles as anticipated. We used two different N_2 flow rates to precipitate pure calcite from the bicarbonate solution. Slow is defined as approximately 10 bubbles per 30 s, and fast as 24 bubbles/30 s. The flow rate was held constant throughout the duration of the experiment. After several tests, we chose between 9 and 24 bubbles per 30 s flow rates to obtain calcite-only precipitation. Precipitations, made with higher than 24 or lower than 10 bubbles/30 s flow rates, produced mixtures of calcite and vaterite. Our bubbling rates are only qualitatively related to actual rates of precipitation.

The relation between precipitation (bubbling) rate and oxygen isotope fractionation is shown in Fig. 10. The pH values of the final solutions are plotted as well. The pH of the starting solution was 5.6, and the final pH values were between 7.5 and 8.5, depending on the flow rate. As CO_2 is carried away in the stream of nitrogen, the pH of the solution

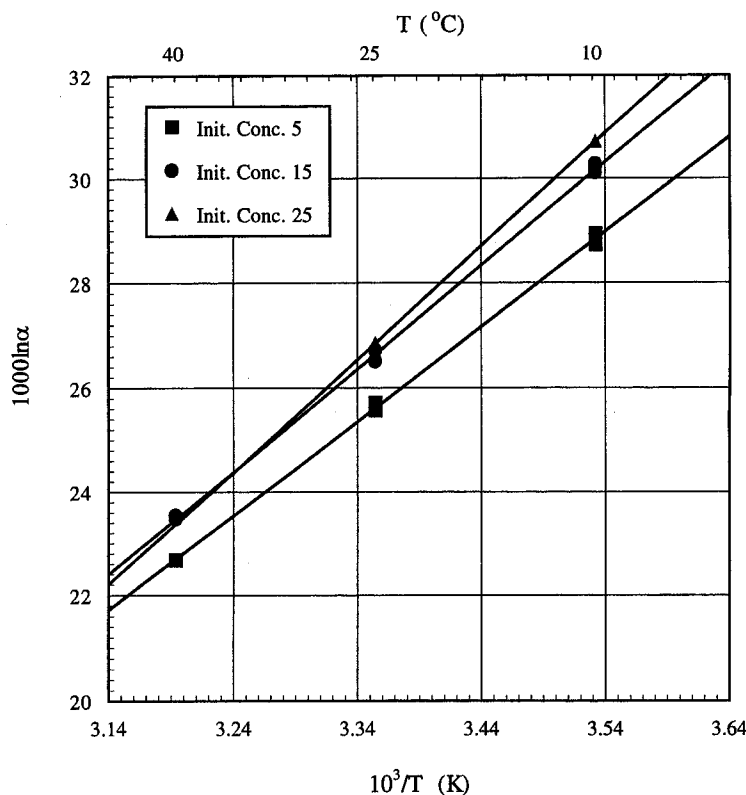


Fig. 7. Relation between $\Delta = 10^3 \ln \alpha$ (witherite-water) and temperature at different initial concentrations of Ba^{2+} and HCO_3^- .

gradually increases until the requisite supersaturation occurs, and the CaCO_3 precipitates. As can be seen in Fig. 10, the rate of precipitation has little bearing on the oxygen isotope fractionation within the flow rate range of calcite-only precipitation. It is noteworthy that inorganic calcite was not isotopically light compared to the calcite precipitated by McConnaughey (1989a,b). According to McConnaughey (1989b), isotopic disequilibrium between synthetic carbonates and water occurs when CO_2 undergoes reactions to form HCO_3^- . It seems clear from the results of the present experiments and those performed earlier by Tarutani et al. (1969) that precipitation rate has little or no bearing on the oxygen isotope fractionation between calcite and water. Caution should be exercised, as always, comparing the results of laboratory systems to those of natural systems, particularly when biological reactions are involved. Also of importance is the fact that our experiments were specifically controlled to produce the thermodynamically stable polymorph of CaCO_3 whereas the coralline data are for aragonite. It is also possible that the rate of precipitation was not changed enough in the experiments to produce a measurable effect, but as described below, when the rate of precipitation is very rapid, vaterite-calcite mixtures were produced.

3.4. Precipitation of Vaterite

Vaterite, one of the three polymorphs of calcium carbonate, was first identified in the repair tissue of young gastropods by Mayer and Weineck (1932). Regardless of its rarity

in nature, it is important to our understanding of the theory of isotopic fractionation to determine, if possible, the equilibrium isotopic properties of this mineral, if indeed equilibrium properties of an unstable mineral can be determined. We first synthesized vaterite using the method of Easton and Claugh (1986) because relatively large, well-formed crystals are produced very slowly (several days to a week). The beautiful crystals of vaterite produced, however, were isotopically very light and far removed from isotopic equilibrium with the water. The isotopic composition of such vaterite is clearly controlled by the differing rates of diffusion of the different isotopic species of CO_2 and useless for our purposes. This behavior is reported here only as an interesting curiosity.

Vaterite was always produced with calcite when a saturated calcium bicarbonate solution was prepared by dissolving CaCO_3 . In contrast, only calcite was precipitated from solutions containing relatively high concentrations of CaCl_2 and NaHCO_3 . For solutions less concentrated in chloride, either mixtures of calcite and vaterite, or pure calcite was synthesized. While it is not clear which factors control the proportion of the two polymorphic forms of CaCO_3 , it was a general observation that the proportion of vaterite, precipitated from dilute Na-Ca-Cl- HCO_3 solutions, increased when the precipitation rate was very slow. Rather special physical and chemical conditions seem to be necessary for the vaterite polymorph to precipitate, presumably due to its high instability in aqueous solutions.

Tarutani et al. (1969) reported that aragonite was enriched

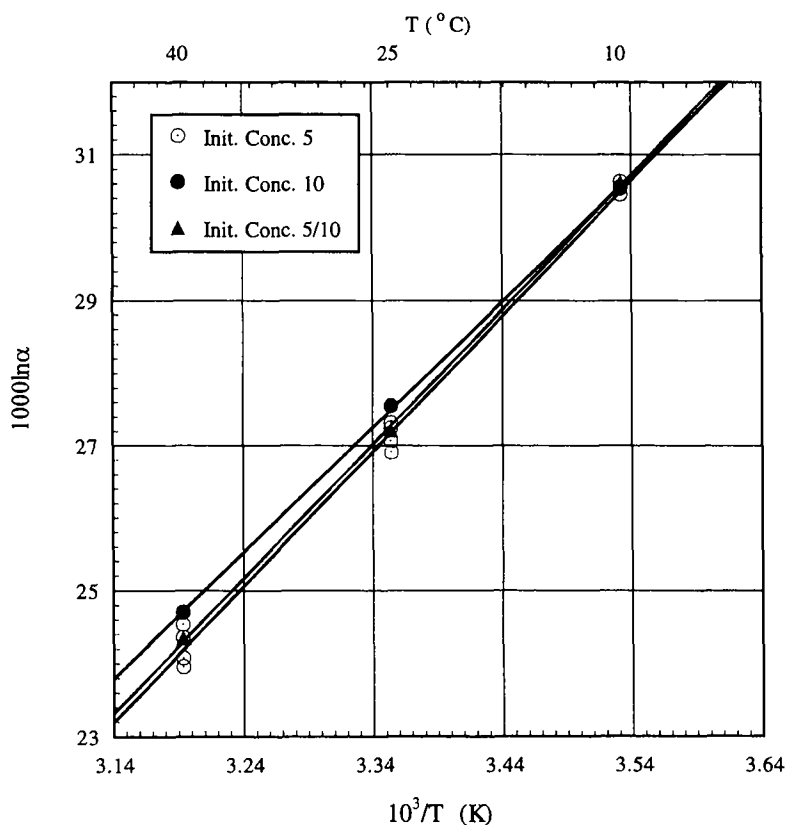


Fig. 8. Relation between $\Delta = 10^3 \ln \alpha(\text{octavite-water})$ and temperature at different initial concentrations of Cd^{2+} and HCO_3^- .

by 0.6‰ relative to calcite at 25°C; furthermore, they mentioned that vaterite was enriched in ^{18}O by 0.5‰ relative to the associated calcite that was separated from mixtures of the two polymorphs produced in two separate experiments at 25°C. In the present study, oxygen isotope compositions were measured of preparations of pure vaterite and of vaterite-calcite mixtures of different proportions at 25 and 40°C (Table 4). At both temperatures, vaterite was found to be 0.6‰ enriched relative to calcite, confirming the earlier results of Tarutani et al. (1969), but with the additional intriguing suggestion that the vaterite-calcite fractionation is temperature independent, at least over this range of 15°. Because of the theoretical significance of these preliminary data, additional experiments on this question are warranted and will

be conducted over a larger range of temperatures at a later date. It is well to keep in mind at this juncture that vaterite is a thermodynamically unstable mineral under the conditions of the experiment and that it is not possible to prove that isotopic equilibrium was attained between vaterite and water in these experiments.

3.5. Acid Fractionation Factors

The oxygen isotope composition of carbonates can be analyzed in a variety of ways, but some modification of the original phosphoric acid reaction developed by McCrea (1950) is used in almost every stable isotope laboratory in the world. CO_2 liberated by the reaction of the acid with the carbonate constitutes only two-thirds of the oxygen in the carbonate so an acid fractionation factor must be applied to the analysis of the CO_2 to obtain the isotopic composition of the carbonate. At 25°C the liberated CO_2 is around 10‰ heavier than the carbonate, and this number will vary by a couple of permil depending on the carbonate and the temperature of the reaction. Accurate knowledge of the acid fractionation factors is essential to interpreting natural data not only for the CaCO_3 polymorphs but for other common carbonates like dolomite, rhodochrosite, ankerite, and siderite.

Sharma and Clayton (1965) measured the $^{18}\text{O}/^{16}\text{O}$ ratios of total oxygen of alkaline earth and transition metal carbonates and concluded that acid fractionation factors depend on the chemical composition of the carbonates. O'Neil (1986)

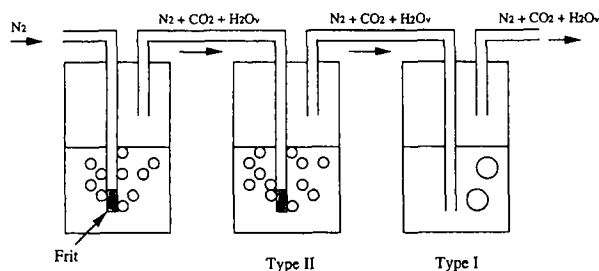


Fig. 9. Apparatus used in the synthesis of divalent carbonates illustrating two different types of bubbling employed. See text.

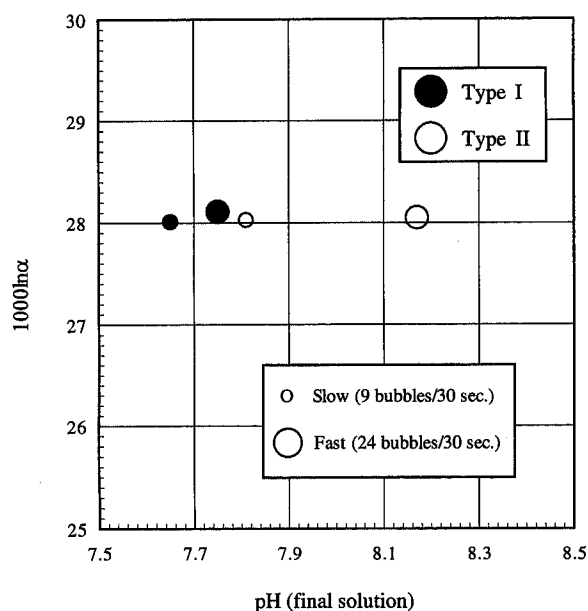


Fig. 10. Effect of bubbling rate and type on $10^3 \ln \alpha$ (calcite-water) at 25°C.

argued from some unpublished data that poorly crystallized naturally-occurring materials like certain protodolomites and some laboratory synthesized carbonates seemed to have acid fractionation factors that were similar to that of calcite as if the rate of reaction was as important or more important than the chemical composition of the carbonate. O'Neil (1986) suggested, furthermore, that if the same acid fractionation factor were applied to all synthetic carbonates, there would be no significant oxygen isotope fractionation between CaCO_3 and CdCO_3 , and thus the cationic radius would be the controlling factor in determining the magnitude of the

fractionation factor between divalent metal carbonates and water.

In an attempt to resolve such apparent conflicts, we repeated the experiments of Sharma and Clayton (1965) for a few selected carbonates using the method described in section 2.3. For repeat determinations of the same preparation, reproducibility was generally excellent (e.g., 11.16, 11.23; 11.21, 11.15; 11.96, 11.82) so this method appears to be reliable. In agreement with the findings of Sharma and Clayton (1965), there are differences in acid fractionation factors (25°C) among the carbonates, but the values obtained in the present study are different from those obtained earlier, and sometimes they are significantly different (Table 5).

The most disturbing conclusion reached from the new determinations is that the fractionation factors obtained depended on the material used. Most of the materials examined were the carbonates synthesized in this study. Note that there is a tendency for $1000 \ln \alpha$ to increase with decreasing temperature of precipitation of the carbonate. A glaring example of this variation is provided by the determinations of $1000 \ln \alpha$ for octavite, a well-crystallized mineral that we concluded was precipitating in near equilibrium in all cases. The values range widely from an average value of 11.18 for two determinations using a commercial preparation (sample CdCO_3 of Table 5) to a single determination of 13.60 for sample 42-10. The (corrected) value reported by Sharma and Clayton (1965) for this mineral was 11.39, a value close to the value we obtained for the commercial preparation. Our average value for witherite is 10.57 ± 0.16 and is 0.34 per mil smaller than the value reported by Sharma and Clayton (1965). Variation of over 2 permil in the fractionation factor for a mineral like octavite means that such a variation could exist for other minerals as well, including the polymorphs of CaCO_3 .

The average of our eight determinations of the acid fractionation factor for calcite is 10.44 with an average deviation

Table 4. Data for other experiments.

Sample	Temp. (°C)	$\delta^{18}\text{O}$ (Water)	$\delta^{18}\text{O}$ (CaCO_3)	$\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$	$10^3 \ln \alpha$	Mineralogy
Calcite-Vaterite Mixtures						
60-R1-S	25	-8.30	20.15	1.02869	28.28	Mixture
60-R2-S	25	-8.30	20.59	1.02913	28.72	Mixture
60-R3-S	25	-8.30	20.66	1.02920	28.78	Mixture
60-R1-N	25	-8.30	20.44	1.02898	28.57	Mixture
60-R2-N	25	-8.30	20.78	1.02932	28.90	Vaterite
60-R3-N	25	-8.30	20.29	1.02883	28.42	Mixture
45-40-N	40	-8.30	17.85	1.02637	26.03	Vaterite
58-25-N	25	-8.30	20.76	1.02930	28.88	Mixture
58-40-N	40	-8.30	17.81	1.02633	25.99	Mixture
58-25-S	25	-8.30	20.92	1.02946	29.04	Mixture
58-40-S	40	-8.30	17.80	1.02632	25.98	Mixture
Rate Effect						
C61-R1-N	25	-8.30	19.97	1.02851	28.11	Calcite
C61-R2-N	25	-8.30	19.87	1.02841	28.01	Calcite
C61-R1-S	25	-8.30	19.91	1.02845	28.05	Calcite
C61-R2-S	25	-8.30	19.89	1.02843	28.03	Calcite

Temp. = Temperature.

Mixture = Calcite and Vaterite Mixture.

Table 5. Acid fractionation factors.

Sample	$\delta^{18}\text{O}$ (CO_2)	$\delta^{18}\text{O}$ (XCO_3)	$\alpha(\text{CO}_2\text{-XCO}_3)$	$10^3 \ln \alpha$	Mineralogy
LV3	36.40	25.57	1.01056	10.50	Calcite
24-10	37.28	26.48	1.01052	10.47	Calcite
24-10	37.28	26.50	1.01050	10.44	Calcite
47-10	36.42	25.36	1.01078	10.72	Calcite
38-25-N	31.87	21.22	1.01043	10.38	Calcite
47-25	31.82	21.07	1.01052	10.47	Calcite
38-40-N	28.67	18.24	1.01024	10.19	Calcite
38-40-N	28.67	18.05	1.01043	10.38	Calcite
syn-arag-1	21.77	10.60	1.01105	10.99	Aragonite
syn-arag-2	21.88	10.69	1.01108	11.02	Aragonite
CdCO_3	28.03	16.62	1.01122	11.16	Octavite
CdCO_3	28.03	16.54	1.01130	11.23	Octavite
44-10	33.97	20.35	1.01335	13.26	Octavite
42-10	34.08	20.12	1.01369	13.60	Octavite
46-10	34.23	21.02	1.01294	12.85	Octavite
44-25	30.47	17.59	1.01267	12.59	Octavite
42-25	30.98	18.00	1.01275	12.67	Octavite
46-25	30.86	18.61	1.01203	11.96	Octavite
46-25	30.86	18.75	1.01189	11.82	Octavite
44-40	27.45	15.68	1.01159	11.52	Octavite
42-40	28.05	15.71	1.01214	12.07	Octavite
46-40	27.77	16.31	1.01127	11.21	Octavite
46-40	27.77	16.37	1.01122	11.15	Octavite
32-10	33.48	22.52	1.01072	10.66	Witherite
32-10	33.48	22.40	1.01084	10.78	Witherite
32-25	29.66	18.67	1.01078	10.73	Witherite
32-25	29.66	18.95	1.01051	10.45	Witherite
49-25-N	28.18	17.33	1.01066	10.60	Witherite
32-40	26.56	16.12	1.01027	10.22	Witherite

X = cation (Ca^{2+} , Cd^{2+} , Ba^{2+}).

of ± 0.10 . This value is 0.24 permil larger than that reported by Sharma and Clayton (1965). Our value of 11.01 ± 0.01 for aragonite is significantly larger than the value of 10.29 reported by Sharma and Clayton (1965). Because the same fractionation factor, correct or not, is used in the analysis of all natural carbonates, the significant differences we are reporting for determinations of acid fractionation factors are usually of minor importance in the resolution of specific geochemical problems. Where these differences become important is in the matter of standards, absolute isotopic ratios, and relating oxygen isotope analyses of carbonates to those of water, silicates, and oxides.

4. CONCLUSIONS

Carbonates slowly precipitated at a given temperature from solutions of different initial concentrations of cation and bicarbonate have markedly different oxygen isotope compositions. Carbonates precipitated from the more concentrated solutions employed in this study are interpreted to have formed under nonequilibrium conditions. Previous workers using the N_2 bubbling technique of carbonate precipitation noted that vaterite-calcite mixtures of various uncontrollable proportions were the rule. By choosing appropriate conditions of precipitation, it is possible to produce pure calcite that is in apparent isotopic equilibrium with the water. A new expression is proposed for the calcite-water fractionation at low temperatures:

$$1000 \ln \alpha(\text{Calcite-H}_2\text{O}) = 18.03(10^3 T^{-1}) - 32.42$$

An expression that combines present low-temperature fractionations with the equilibrium high-temperature fractionations of O'Neil et al. (1969) is also proposed for the octavite-water fractionation over the temperature range of 0–500°C:

$$1000 \ln \alpha(\text{CdCO}_3\text{-H}_2\text{O}) = 2.76(10^6 T^{-2}) - 3.96$$

New determinations of acid fractionation factors ($1000 \ln \alpha$) at 25°C for calcite (10.44 ± 0.10), aragonite (11.01 ± 0.01), and witherite (10.57 ± 0.16) are mildly to strongly different from those published by Sharma and Clayton (1965) and point to a control on this fractionation by some physical property of the mineral. Reproducible values for octavite (CdCO_3) varied from 11.18 to 13.60 depending on the conditions of preparation of the carbonate. While these differences will not affect the interpretation of oxygen isotope variations among natural carbonates in any major way, these new values will need to be considered in establishing absolute $^{18}\text{O}/^{16}\text{O}$ ratios of international reference standards and in relating analyses of carbonates to those of waters, silicates, and oxides.

Stable isotope geochemists use a number of published fractionation factors that may be seriously in error, not only for carbonates as shown in the present study, but possibly for other systems as well. It is accepted that new determinations of thermodynamic or physical constants are often different from those published previously, but ideally these differences will be small. Some of the differences observed in the present study are important and concern the CaCO_3

polymorphs, arguably the most studied mineral in the field of stable isotope geochemistry. Further determinations of the type presented here are necessary to confirm or disprove frequently used fractionation factors.

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