

## The effect of polymorphism and magnesium substitution on oxygen isotope fractionation between calcium carbonate and water

TOSHIKAZU TARUTANI\*

Enrico Fermi Institute, University of Chicago, Chicago 60637

ROBERT N. CLAYTON

Enrico Fermi Institute, and Departments of Chemistry and Geophysical Sciences  
University of Chicago, Chicago 60637

and

TOSHIKO K. MAYEDA

Enrico Fermi Institute, University of Chicago, Chicago 60637

(Received 30 August 1968; accepted in revised form 15 April 1969)

**Abstract**—Calcite, aragonite and magnesian calcite were slowly precipitated from aqueous bicarbonate solutions, and oxygen isotope fractionation factors between the precipitate and water were measured. For calcite–water at 25°C and 0°C,  $1000 \ln \alpha = 28.1$  and  $33.7$ , respectively, both values in excellent agreement with the Urey–Epstein paleotemperature scale. Aragonite–water at 25°C gave  $28.7$ , implying a small but significant fractionation between aragonite and calcite.  $O^{18}$  also concentrates in magnesian calcite, relative to pure calcite precipitated under the same conditions, by  $0.06\%$  for each mole-percent  $MgCO_3$  in calcite.

### INTRODUCTION

FROM theoretical calculations, UREY (1947) predicted that the temperature coefficient of the equilibrium constant for oxygen isotope exchange between calcium carbonate and water would be large enough to permit establishment of a geological thermometer based on that exchange reaction. The first experimental measurements of this temperature coefficient (MCCREA, 1950) were based on inorganic precipitation of aragonite or an aragonite–calcite mixture from sea water over the temperature range 0–80°C.

The currently accepted calibration of the calcium carbonate–water paleothermometer was provided by EPSTEIN *et al.* (1953) on the basis of calcium carbonate (calcite and aragonite) deposited by marine invertebrates, in some cases grown in thermostatted tanks, in other cases taken from natural environments of known temperatures. The remarkable accuracy, sensitivity and usefulness of the carbonate–water paleotemperature scale have been demonstrated by a large number of significant papers published over the last fifteen years.

The purpose of the present study is to investigate some of the possible second-order effects which may influence the oxygen isotope distribution in calcium carbonate–water systems in nature. An attempt is made to answer several

---

\* Present address: Department of Chemistry, Kyushu University, Fukuoka, Japan.

questions:

- (1) What is the effect of calcite–aragonite polymorphism?
- (2) What is the effect of magnesium solid solution in calcite?
- (3) What is the effect of salinity of the aqueous phase?
- (4) Are there significant isotopic differences between biologically and inorganically precipitated carbonates?
- (5) What can be said with regard to the attainment of isotopic equilibrium in the precipitation of calcium carbonate from aqueous solutions?

There is no *a priori* reason why calcite and aragonite should behave identically in isotope exchange reactions. In a calculation of isotopic partition function ratios, following the theoretical treatments of UREY (1947), BIGELEISEN and MAYER (1947), and MCCREA (1950), one would use, in part, the internal vibration frequencies of the carbonate ions, which are significantly different for the two polymorphs (HUANG and KERR, 1960; ADLER and KERR, 1963; SCHROEDER *et al.*, 1962). A calculation based on the observed vibrational frequencies predicts an enrichment of both  $O^{18}$  and  $C^{13}$  in aragonite relative to calcite by a few tenths permil (O'NEIL *et al.*, 1969). Separate analyses of the pearly layer (aragonite) and the prismatic layer (calcite) from the shell of an abalone, *Haliotis Rufescens*, grown at constant temperature suggest that the aragonite–calcite fractionations are not this large (EPSTEIN *et al.*, 1953; EPSTEIN, 1959).

MCCREA's (1950) statement that no relationship was observed between isotopic composition and crystal structure must be evaluated in light of the range of as much as one permil which he observed for carbonates precipitated at the same temperature.

Magnesium in metastable solid solution in calcite is common in marine organisms. Typical high-magnesian calcite may contain ~15 mole per cent  $MgCO_3$ . Oxygen isotope fractionations among alkaline earth carbonates precipitated at 25°C have been measured, and are found to be on the order of a few permil:  $CaCO_3$ – $SrCO_3$  1.2‰,  $CaCO_3$ – $BaCO_3$  3.6‰ (O'NEIL *et al.*, 1969). Dolomite–calcite fractionations of 4–7‰ at 25°C have been estimated by extrapolation of high-temperature experiments (NORTHROP and CLAYTON, 1966; O'NEIL and EPSTEIN, 1966a). From these results it is expected that magnesian calcites should show a larger isotope fractionation relative to water than pure calcite.

The paleothermometer calibrations of EPSTEIN *et al.* (1953) were carried out in sea water. It has generally been assumed that the same fractionations would be observed in fresh or hypersaline waters. Because of the possibility of significant alteration of the structure of water by complex formation (TAUBE, 1954), it is desirable to test this assumption.

It was noted by EPSTEIN *et al.* (1953) that the temperature coefficient of the calcium carbonate–water isotopic thermometer determined from biologically precipitated carbonate was “essentially in agreement” with the temperature coefficient measured by MCCREA (1950) for inorganically precipitated calcium carbonate. We have attempted to verify this observation, and to detect any small differences which might exist, either in the temperature coefficient, or in the absolute magnitude of the fractionation factor.

UREY *et al.* (1951) discussed the possibility that organisms might deposit

calcium carbonate out of isotopic equilibrium with sea-water. It is now known that some organisms do indeed exert a "vital effect" (LOWENSTAM and EPSTEIN, 1954; WEBER and RAUP, 1966). The close correspondence between fractionations observed for a number of different invertebrates and for inorganically precipitated carbonate (EPSTEIN *et al.*, 1953) argues for a close approach to equilibrium between the carbonate and water in these instances. A stronger case is provided by the fact that a simple two-parameter equation was an excellent fit to the high-temperature exchange equilibrium data of CLAYTON (1961) as well as to the low-temperature data of EPSTEIN *et al.* (1953).

## EXPERIMENTAL PROCEDURES

### *Materials*

Calcium bicarbonate solutions were prepared by passing carbon dioxide at one atmosphere pressure through a suspension of reagent grade calcium carbonate in distilled water. After standing at room temperature for one hour or longer, the solution was filtered to remove excess calcium carbonate. Magnesium bicarbonate solutions were prepared by the same procedure, using reagent grade basic magnesium carbonate. Concentrations of the calcium and magnesium bicarbonate solutions were determined by EDTA titration.

Solutions of malate and pyruvate were prepared by addition of sodium hydroxide to solutions of malic acid and pyruvic acid to bring the pH to 7, following the procedure of KITANO and HOOD (1965).

### *Slow precipitation of carbonates*

Five hundred milliliters of calcium bicarbonate solution (with or without added magnesium salts or organic acid solutions) was placed in a gas washing bottle with a fritted disc, and was maintained at 25°C in a constant temperature water bath or at 0°C in an ice-water bath. Carbon dioxide was slowly removed from the solution by a finely dispersed stream of nitrogen which had been passed through water of the same isotopic composition as the solution so as to avoid changing the isotopic composition of the solution by evaporation. After a period of several hours or days the precipitated carbonate was removed from the vessel, washed with water and acetone and dried for one hour at 100°C.

The polymorphic form of the precipitated calcium carbonate is sensitive to conditions of precipitation, such as rate and temperature (WRAY and DANIELS, 1957) and presence of other substances in solution (KITANO and HOOD, 1965). Under the conditions employed here, pure calcium bicarbonate solutions gave calcite, or calcite-vaterite mixtures. It is not clear what determines their proportions. In one precipitation where both were formed, successive sampling at various times showed that both phases continued to form throughout the experiment.

Solutions of calcium bicarbonate containing magnesium ion (added as magnesium chloride solution) gave aragonite (occasionally containing a minor amount of calcite), as was shown by KITANO and HOOD (1965).

Products were identified by microscopic examination, and by X-ray diffraction. Magnesium content of magnesian calcites was determined from the *d*-spacing of the 112 diffraction line, using a Norelco diffractometer with silicon as an internal standard.

Isotopic analysis of carbonates was done by the phosphoric acid procedure of MCCREA (1950). Water samples were analyzed by equilibration of the final solution with carbon dioxide (COHN and UREY, 1938). Mass spectrometer results were corrected for value mixing, background, and mass-44 tail, and corrections for C<sup>13</sup> variations were made according to the formulas of CRAIG (1957). Analyses of carbon dioxide from carbonates were corrected by a factor of 1.01025 (modified after SHARMA and CLAYTON, 1965) to take account of the isotopic fractionation in the phosphoric acid reaction. This factor is not significantly different for calcite and aragonite, as was verified in the present work by analysis of a sample before and after conversion from aragonite to calcite by heating in vacuum for one hour at 410°C. The same value was used for

magnesian calcites. Analyses of water were calculated using the factor 1.04073 for equilibrium between carbon dioxide gas and liquid water at 25°C (O'NEIL and EPSTEIN, 1966b).

## RESULTS AND DISCUSSION

### Calcite, 25°C

Results of isotopic analyses of precipitates from pure calcium bicarbonate solutions are given in Table 1. The range of observed values of the calcium carbonate-water fractionation at 25°C is from 27.90 to 28.75 (expressed as  $1000 \ln \alpha$ , where  $\alpha = \frac{(O^{18}/O^{16}) \text{ calcium carbonate}}{(O^{18}/O^{16}) \text{ water}}$ ). It was observed from microscopic and X-ray examination that several of the samples contained vaterite as well as

Table 1. Calcite precipitation at 25°C

Expt. No.	Init. Ca <sup>2+</sup> conc. (mg/l)	N <sub>2</sub> flow rate (ml/min)	Time (hr)	CaCO <sub>3</sub> wt. (mg)	1000 ln $\alpha$	Vaterite*	Remarks
C1	220	10	18	45	28.33	2	
C2	250	10	18	115	28.59	2	
C3	280	10	18	120	28.50	2	
C4	300	10	22	115	28.22	1	
C5	315	10	24	152	28.37	1	NaCl 36 g/l
C6	390	10	18	295	27.97	1	
C7	290	1	42	70	28.56	2	
C8	310	1	43	78	28.43	1	
C9	182	1	68	142	28.40	1	
C10	320	1	65	130	28.29	1	
C11	220	1	90	60	28.10	0	
C12	241	1	90	142	27.90	0	
C13	262	1	90	126	28.16	0	
C14	290	1	90	205	28.47	2	
C15	310	1	90	135	28.38	0	
C16	320	1	92	115	28.75	0	NaCl 36 g/l
C17	340	1	90	125	28.74	0	
C18	390	1	90	357	28.73	0	
C19	218	10†	137	22.5	28.49	1	
C20	310	10†	138	165	28.43	1	
C21	420	10†	137	292	28.75	0	
C22	218	10†	232	22.5	28.17	0	
C23	310	10†	208	80	28.46	0	
C24	420	10†	209	345	28.65	0	

\* Visual estimate of vaterite fraction: 0 < 5%; 1 5-30%; 2 30-50%.

† N<sub>2</sub> flow at this rate 10 min per day, then shut off.

calcite, as indicated in column 7 of Table 1. In two cases, samples C2 and C7, the two polymorphs were separated by heavy liquids and analyzed. In each case the vaterite phase was found to be enriched in O<sup>18</sup> by 0.5‰ and in C<sup>13</sup> by 0.6‰ relative to the associated calcite. Since it was not practicable to carry out this separation on all vaterite-containing samples, results from such samples were not further considered.

The variation in observed fractionation factor, considerably outside experimental error, was uncorrelated with nitrogen flow rate, and thus was not considered to be related to rate of precipitation. There was, however a correlation with initial calcium concentration, with higher concentrations giving rise to larger fractionations. Attempts were made to determine whether the fractionation remained

constant throughout a precipitation experiment by interrupting the experiment several times to remove the precipitate for analysis. Unfortunately, these happened to be cases in which large amounts of vaterite and some aragonite were formed so that the results did not provide the required test. In two experiments, numbers C18 and C24, the total calcite product was reacted with phosphoric acid in the usual procedure for extraction of carbon dioxide for isotopic analysis, except that successively evolved fractions of carbon dioxide were removed at intervals of 15 or 30 min. The results are presented in Table 2. It can be seen from the large

Table 2. Sequential isotopic analysis of precipitated carbonates

Expt. No.	H <sub>3</sub> PO <sub>4</sub> react. time	CO <sub>2</sub> yield ( $\mu$ mole)	$\delta$ C <sup>13</sup> rel. PDB*	$\delta$ O <sup>18</sup> rel. SMOW	1000 ln $\alpha$ CaCO <sub>3</sub> -H <sub>2</sub> O
C18	5 min	26	-26.37	22.17	28.45
	15 min	80	-26.69	22.26	28.54
	30 min	120	-27.18	22.45	28.72
	60 min	180	-27.69	22.56	28.83
	24 hr	136	-28.37	22.49	28.76
C24	15 min	60	-26.87	22.00	28.28
	30 min	70	-27.20	22.25	28.53
	45 min	67	-27.52	22.34	28.62
	60 min	60	-27.68	22.44	28.71
	75 min	52	-27.86	22.46	28.73
	105 min	79	-27.95	22.65	28.92
	24 hr	72	-28.25	22.65	28.92
A5	5 min	249	-26.80	22.91	28.72
	10 min	128	-27.26	23.01	28.82
	60 min	59	-27.46	22.94	28.75

\* Isotopic compositions given in  $\delta$ -terminology, as deviations of isotopic ratio from standards in parts per thousand (permil, ‰). Carbon standard is the Chicago carbonate PDB; oxygen standard is Standard Mean Ocean Water (SMOW).

systematic trend in  $\delta$ C<sup>13</sup> values that the acid reaction proceeds in large part by stripping of grains from the outside in. The variation in C<sup>13</sup> content reflects the increase of  $\delta$ C<sup>13</sup> in the bicarbonate solution as isotopically lighter carbon dioxide is swept from it during precipitation. Hence the smaller trend visible in the O<sup>18</sup> data also reflects a lower  $\delta$ O<sup>18</sup> in the outer parts of the crystals than in the interiors. Since the oxygen reservoir in the solution is large, this effect can only be attributed to a small change in fractionation factor.

It is not clear whether the observed differences in fractionation factor represent departures from equilibrium or variations in the equilibrium constant in response to small changes in ionic concentration or pH. (Note that the pH of a saturated solution increases as the calcium concentration decreases.) If departures from equilibrium are significant, then they might be expected to be greatest at the beginning of precipitation when supersaturation and crystal imperfection might be important. The possibility of an effect of ionic concentration was investigated by means of a precipitation from a solution containing 36 g/l of sodium chloride (experiments C5 and C15). The resulting fractionations were not significantly different from results from other experiments of comparable calcium concentration.

It is clearly improper simply to average the data when apparently real systematic trends exist. For the reasons given above, we tentatively conclude that the smaller fractionations, obtained in more dilute solutions and under more favorable

Table 3. Calcite precipitation at 0°C

Expt. No.	Init. Ca <sup>2+</sup> conc. (mg/l)	Time (hr)	CaCO <sub>3</sub> wt. (mg)	1000 ln $\alpha$	Remarks
C25	360	96	95	33.66	NaCl 23.5 g/l; Na <sub>2</sub> SO <sub>4</sub> 3.92 g/l
C26	340	96	95	33.75	

crystal growth conditions, more closely approach the equilibrium value. A value of  $1000 \ln \alpha = 28.1$  has been selected as the mean of the lowest four experimental values (C11, C12, C13, C22).

### Calcite, 0°C

Results of three precipitations of calcite from calcium bicarbonate solutions carried out in an ice bath at 0°C are given in Table 3. The solution in experiment No. C25 also contained 23.5 g/l NaCl and 3.92 g/l Na<sub>2</sub>SO<sub>4</sub>. With these limited data no significant differences were observed, so the mean value of  $1000 \ln \alpha = 33.7$  was taken.

### Aragonite, 25°C

The isotopic fractionations measured between aragonite and water are given in Table 4. They are identical, within experimental error, for all values of the calcium, magnesium and sodium concentrations studied and for a range of a factor of ten in precipitation rate. The stripping experiment for run A5 in Table 2 shows no change of O<sup>18</sup> content as the crystals grew. The mean value of  $1000 \ln \alpha$  is 28.71, implying a fractionation between aragonite and calcite of 0.6 at 25°C.

### Magnesian calcite, 25°C

Table 5 shows results of magnesian calcite precipitations.

Calcite precipitated in the presence of malate and pyruvate salts, gave a mean fractionation value of 27.8, i.e. 0.3 lower than the value from pure calcium bicarbonate experiments. The origin of this effect is unknown, and we have assumed it to be constant for all precipitations from malate or pyruvate solutions. The trend of isotopic fractionation with increasing magnesium in solid solution in calcite is shown in Fig. 1. The effect amounts to an increase of  $1000 \ln \alpha$  by 0.06 for each mole per cent MgCO<sub>3</sub> in calcite.

Table 4. Aragonite precipitation at 25°C

Expt. No.	Init. Ca <sup>2+</sup> conc. (mg/l)	Mg <sup>2+</sup> conc. (mg/l)	N <sub>2</sub> flow rate (ml/min)	Time (hr)	CaCO <sub>3</sub> wt. (mg)	1000 ln $\alpha$	Remarks
A1	270	480		91	110	28.68	NaCl 23.5 g/l; Na <sub>2</sub> SO <sub>4</sub> 3.92 g/l
A2	270	364		90	150	28.68	
A3	330	1535		72	120	28.71	
A4	300	480	10	19	124	28.78	
A5	310	480	10	19	145	28.68	
A6	260	480	1	89	82	28.59	N <sub>2</sub> flow 1 hr/day
A7	310	480	1	118	175	28.85	
A8	260	960	10	164	90	28.70	

Table 5. Magnesian calcite precipitation at 25°C

Expt. No.	Init. Ca <sup>++</sup> conc. (mg/l)	Mg <sup>++</sup> conc. (mg/l)*	Organic acid (g/l)†	Time (hr)	Mole % Mg in calcite	1000 ln $\alpha$	Remarks
MC-1	310	0	M 5	65		27.85	
MC-2	320	0	M 5	258		27.66	
MC-3	350	0	M 5	63		27.91	
MC-4	270	0	P 5	70		27.79	
MC-5	200	Cl 195	M 5	144	5.7	27.97	
MC-6	240	H 290	M 5	66	9.0	28.38	
MC-7	270	H 500	M 5	72	12.8	28.80	NaCl 36 g/l
MC-8	260	H 420	M 10	96	11.8	28.39	
MC-9	280	H 365	M 10	71	10.7	28.41	
MC-10	290	H 290	M 10	72	5.7	27.81	
MC-11	320	H 182	P 5	19	3.7	28.16	
MC-12	270	H 132	P 8	45	5.3	27.91	
MC-13	300	H 138	P 8	138	4.7	28.08	

\* Cl = magnesium chloride; H = magnesium bicarbonate.

† M = malic acid; P = pyruvic acid.

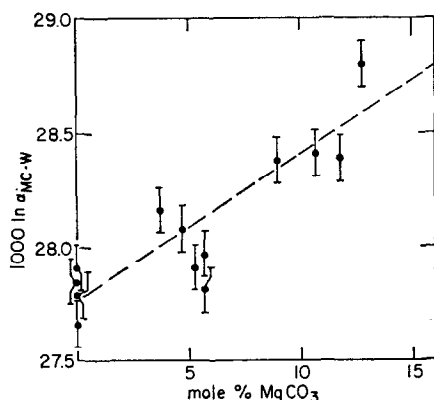


Fig. 1. Fractionation factors for magnesian calcite-water.

### Comparison with biogenic carbonates

The calibration of the paleotemperature scale of EPSTEIN *et al.* (1953) was given in terms of  $\delta$ -values of  $\text{CO}_2$  from carbonates and of  $\text{CO}_2$  equilibrated with water. Now that the fractionation factors associated with the two analytical procedures are known, their experimental values can be recalculated to give carbonate-water fractionation factors. In the work of EPSTEIN *et al.*, the  $\delta$ -values of both  $\text{CO}_2$  liberated from carbonates by  $\text{H}_3\text{PO}_4$  and water- $\text{CO}_2$  were very near that of the mass spectrometer working standard, so corrections proportional to  $\delta$  were insignificant. However, in the calculation of fractionation factors, corrections must be made for dilution of water oxygen by  $\text{CO}_2$  oxygen, and for the  $\delta\text{C}^{13}$  difference between the equilibration  $\text{CO}_2$  and the mass spectrometer standard (CRAIG, 1957). Taking  $\delta\text{C}^{13} = -29.2\text{‰}$  and  $\delta\text{O}^{18} = -14.9\text{‰}$ , both relative to PDB (CRAIG, 1957) the correction to the water analysis is  $-0.18\text{‰}$ . A sample

recalculation of the data of EPSTEIN *et al.* is as follows:

For sample 18(a), Table 7, page 1324, raw  $\delta(\text{carbonate}) - \text{raw } \delta(\text{water}) = 1.46\text{‰}$ .

Correcting for water analysis as above,  $\delta_c - \delta_w = 1.64$ .

Then

$$\alpha = \frac{(1.00164)(1.04070)}{1.01025} = 1.03183$$

where 1.04070 is the  $\text{CO}_{2(g)} - \text{H}_2\text{O}_{(l)}$  equilibrium fractionation factor (O'NEIL and EPSTEIN, 1966b), and 1.01025 is the  $\text{CO}_2 - \text{CaCO}_3$  kinetic fractionation factor (modified from SHARMA and CLAYTON, 1965).

The biogenic carbonate data are compared with the inorganic precipitation data in Fig. 2. The agreement with the calcite line is remarkably close. However, the

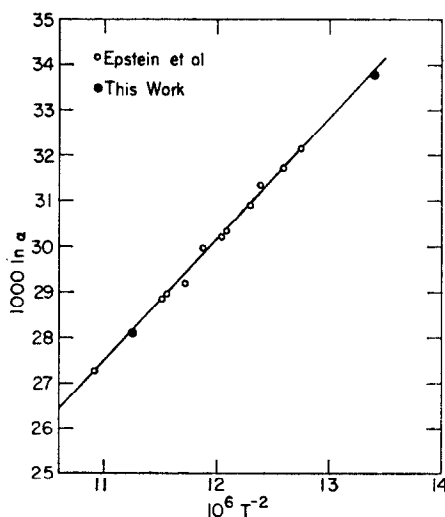


Fig. 2. Comparison of precipitation results with paleotemperature calibration of EPSTEIN *et al.* (1953).

data of EPSTEIN *et al.* were derived from analysis of both calcite and aragonite, taken in some cases from different parts of the same shell. Inspection of the analytical results in Table 7 of their paper leads to the conclusion that if any systematic difference exists between coexisting calcite and aragonite, it is small and in the opposite direction to that reported in the present study. If our conclusions about the magnitude and direction of the equilibrium calcite-aragonite fractionation are correct, then the implication is either that there is a vital effect on the isotopic fractionation in the biological precipitation of aragonite, or that there is a difference in behavior of calcite and aragonite in the analytical treatments, possibly in the helium roasting step.

In any case the differences in isotopic fractionation between inorganic and biogenic carbonates are very small, lending strong support to the interpretation that both sets of data represent a close approach to isotopic equilibrium between carbonate and water.



*Comparison with theory*

Calculations of oxygen isotope equilibrium fractionations among various divalent metal carbonates have been presented by O'NEIL *et al.* (1969). The results of such calculations depend rather strongly on which of the several published sets of vibrational frequencies are chosen. It was found by BOTTINGA (1968) and O'NEIL *et al.* (1969) that the frequencies given by SCHROEDER *et al.* (1962) give reasonable agreement with experiment for the calcite-water system. The same was found to be the case for carbon isotope fractionation (RUBINSON and CLAYTON, 1969). The calculated aragonite-calcite fractionation at 25°C is:  $1000 \ln \alpha_{A-C} = 0.79$ , in good agreement with the experimental value of 0.6. All of the difference between the two polymorphs arises from differences in the internal vibration frequencies of the carbonate ion, the lattice contributions to the heat capacity being the same for both forms within experimental error.

## CONCLUSIONS

Inorganic precipitation of calcite from water at 0° and 25°C gives excellent agreement in fractionation factor and in its temperature coefficient with the results of biogenic carbonate precipitation which determine the oxygen isotope paleotemperature scale of EPSTEIN *et al.* (1953). A significant aragonite-calcite fractionation was found in the laboratory experiments, but has not been observed in organically precipitated carbonates. The reason for this discrepancy is not known. The magnitude of the difference, 0.6‰, corresponds to an apparent temperature difference of 2.6° if the standard paleotemperature calibration is used.

Magnesian calcites are found to have significantly larger calcite-water fractionations than pure calcites. The effect on paleotemperatures is an error of 0.26° per mole-per cent  $MgCO_3$ , and so might give rise to errors of 3 or 4° in high-magnesian calcites.

The results presented here do not satisfy any rigorous conditions for proof of equilibrium. Our conclusion that isotopic equilibrium has been closely approached is based on several lines of evidence: insensitivity of the measured values to large changes in precipitation rate, insensitivity to changes in ionic strength, close coincidence between results from biogenic and inorganically precipitated carbonates, good fit with high-temperature data, and good agreement between experiment and theory. None of these alone is very convincing, but their total impact makes an equilibrium interpretation reasonable.

There may be some question as to the propriety of discussing isotopic equilibrium involving phases which are metastable, as in the case of aragonite at 25°C, and one atmosphere pressure. Nothing in the experimental results suggests that metastability with respect to phase transitions has any influence on the isotope exchange equilibrium. Neither of the metastable phases, aragonite or vaterite, underwent a solid-state transition to calcite under the conditions of the experiment, nor was there any evidence of dissolution of these phases to precipitate the stable calcite.

*Acknowledgments*—This research was supported in part by National Science Foundation grants GP 2019 and GA 514.

## REFERENCES

- ADLER H. H. and KERR P. F. (1963) Infrared absorption frequency trends for anhydrous normal carbonates. *Amer. Mineral.* **48**, 124-137.
- BIGEISEN J. and MAYER M. G. (1947) Calculation of equilibrium constants for isotopic exchange reactions. *J. Chem. Phys.* **15**, 261-267.
- BOTTINGA Y. (1968) Calculation of fractionation factors for carbon and oxygen isotopic exchange in the system calcite-carbon dioxide-water. *J. Phys. Chem.* **72**, 800-808.
- CLAYTON R. N. (1961) Oxygen isotope fractionation between calcium carbonate and water. *J. Chem. Phys.* **34**, 724-726.
- COHN M. and UREY H. C. (1938) Oxygen exchange reactions of organic compounds and water. *J. Amer. Chem. Soc.* **60**, 679-687.
- CRAIG H. (1957) Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochim. Cosmochim. Acta* **12**, 133-149.
- EPSTEIN S., BUCHSBAUM R., LOWENSTAM H. A. and UREY H. C. (1953) Revised carbonate-water isotopic temperature scale. *Geol. Soc. Amer. Bull.* **64**, 1315-1326.
- EPSTEIN S. (1959) In *Researches in Geochemistry* (editor P. H. Abelson), p. 221. John Wiley.
- HUANG C. K. and KERR P. F. (1960) Infrared study of carbonate minerals. *Amer. Mineral.* **45**, 311-324.
- KITANO Y. and HOOD D. W. (1965) The influence of organic material on the polymorphic crystallization of calcium carbonate. *Geochim. Cosmochim. Acta* **29**, 29-42.
- LOWENSTAM H. A. and EPSTEIN S. (1954) Paleotemperatures of the post-Aptian Cretaceous as determined by the oxygen isotope method. *J. Geol.* **62**, 207-248.
- MC CREA J. M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* **18**, 849-857.
- NORTHROP D. A. and CLAYTON R. N. (1966) Oxygen-isotope fractionations in systems containing dolomite. *J. Geol.* **74**, 174-196.
- O'NEIL J. R., CLAYTON R. N. and MAYEDA T. K. (1969) Oxygen isotope fractionation in divalent metal carbonates. In preparation.
- O'NEIL J. R. and EPSTEIN S. (1966a) Oxygen isotope fractionation in the system dolomite-calcite-carbon dioxide. *Science* **152**, 198-201.
- O'NEIL J. R. and EPSTEIN S. (1966b) A method for oxygen isotope analysis of milligram quantities of water and some of its applications. *J. Geophys. Res.* **71**, 4955-4961.
- RUBINSON M. and CLAYTON R. N. (1969) Carbon-13 fractionation between aragonite and calcite. *Geochim. Cosmochim. Acta* **33**, 997-1002.
- SCHROEDER R. A., WEIR C. E. and LIPPINCOTT E. R. (1962) Lattice frequencies and rotational barriers for inorganic carbonates and nitrates from low temperature infrared spectroscopy. *J. Res. U.S. Nat. Bur. Stand.* **66A**, 407-434.
- SHARMA T. and CLAYTON R. N. (1965) Measurement of  $O^{18}/O^{16}$  ratios of total oxygen of carbonates. *Geochim. Cosmochim. Acta* **29**, 1347-1353.
- TAUBE H. (1954) Use of oxygen isotope effects in the study of hydration of ions. *J. Phys. Chem.* **58**, 523-528.
- UREY H. C. (1947) The thermodynamic properties of isotopic substances. *J. Chem. Soc (London)* 562-581.
- UREY H. C., LOWENSTAM H. A., EPSTEIN S. and MCKINNEY C. R. (1951) Measurement of paleotemperatures and temperatures of the Upper Cretaceous of England, Denmark and the Southeastern United States. *Geol. Soc. Amer. Bull.* **62**, 399-416.
- WEBER J. N. and RAUP D. M. (1966) Fractionation of the stable isotopes of carbon and oxygen in marine calcareous organisms—the Echinoidea. Part I. Variation of  $C^{13}$  and  $O^{18}$  content within individuals. *Geochim. Cosmochim. Acta* **30**, 681-704.
- WRAY J. L. and DANIELS F. (1957) Precipitation of calcite and aragonite. *J. Amer. Chem. Soc.* **79**, 2031-2034.