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Temperature and salinity effects on ^{18}O fractionation for rapidly precipitated carbonates: Laboratory experiments with alkaline lake water

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The precipitation of lacustrine carbonates can occur relatively rapidly over large ranges of salinity, alkalinity and temperature. Few studies have directly addressed oxygen fractionation of stable isotopes during the formation of these carbonates. We present results from experiments that elucidate the factors which regulate the isotopic composition of carbonates precipitated from lake water. Water from Mono Lake was diluted by different amounts with Creek water from the Mono Basin. Carbonates were precipitated in these solutions by adding CaCl_2 solution or powder.

The experimental results show that rapidly precipitated inorganic calcite, typical of some lacustrine environments, may record equilibrium ^{18}O fractionation as has been demonstrated previously for slowly inorganically growing, or biologically precipitated carbonates. However, apparent disequilibrium fractionation is observed in carbonates precipitated rapidly from waters of extremely high salinities and low temperatures. This appears to result from the formation of carbonate polymorphs, such as gaylussite. Rapidly precipitated pure calcite exhibits ^{18}O enrichments with respect to predicted equilibrium values. The temperature correlation of ^{18}O fractionation appears to hold at relatively high temperatures ($>10^\circ\text{C}$) but the slope of the temperature/fractionation equation is salinity dependent, although the cause is presently unclear.

Introduction

Isotopic geothermometry has been widely used for studying paleoclimate and paleoceanography because there is a systematic temperature dependence of oxygen isotopic fractionation during carbonate precipitation. Since 1950, a number of empirical paleotemperature equations have been established for the marine carbonate system (Epstein et al., 1953; Craig, 1965; O'Neil et al., 1969; Horibe and Oba, 1972; Erez and Luz, 1983; Grossman and Ku, 1986). However, closed-basin lakes exhibit a large range of salinities, alkalinities and temperatures. Carbonates formed in such lakes may be inorganically precipitated (such as marl, seedreite, micrite, tufa and oolite) or biogenically precipitated (such as stromatolite- and oncolite-forming algae, molluscs, gastropod and ostracode shells). Although empirical evidence has confirmed a correlation between oxygen isotope frac-

tionations and temperature for lacustrine carbonates (Lister et al., 1991; Gasse et al., 1987; Fritz et al., 1987; Turner et al., 1983; Johnson et al., 1991; Schelske and Hodell, 1991; Li, 1995), the effects of salinity, alkalinity, temperature and precipitation rate on the fractionation are not completely defined.

During the last decade, stable isotopic records for carbonate sediments from closed-basin lakes have been used as a paleoclimatic proxy. The $\delta^{18}\text{O}$ records have been interpreted in terms of changes in hydrologic balance and temperature (Li, 1995; Phillips et al., 1992; Lister et al., 1991; Johnson et al., 1991; Gonfiantini, 1986). Fresh water carries calcium ions into lake water enriched in bicarbonate and carbonate ions (Kelts and Hsü, 1978). During warm seasons, dissolved calcium carbonate can reach supersaturation. At this point a fine-grained calcite precipitate often forms. This carbonate settles to the bottom as either rhythmically laminated or massive, white to yellowish gray marls (Kelts and Hsü, 1978; Brunskill and Hariss, 1969; Anderson and Dean, 1985; Pilskaln and Johnson, 1991). This precipitation process may be rapid. Summer "whittings" (seasonal clouding of the epilimnion by CaCO_3) have been observed in many closed-basin lakes (Brunskill, 1969; Strong and Eadie, 1978). Yet, few experimental data exist to directly address whether this carbonate forms in stable isotopic equilibrium with lake water. Our study was designed to test whether isotopic equilibrium is recorded by inorganically, rapidly precipitated lacustrine carbonates.

Previous work

McCrea (1950) first studied the oxygen isotopic fractionation of inorganically precipitated carbonate by measurements of CaCO_3 slowly precipitated from sea water over the temperature range 0 – 80°C . His work established the temperature coefficient of the $\text{CaC}^{18}\text{O}_3$ - H_2^{18}O fractionation. Epstein and others (1953) observed that the temperature coefficient of the $\text{CaC}^{18}\text{O}_3$ - H_2^{18}O fractionation determined from biologically precipitated calcite was essentially in agreement with McCrea's work for inorganically precipitated carbonate. Based on the measurements of the $\delta^{18}\text{O}$ of marine mollusc shells and the sea water temperature where the shells were formed, Epstein et al. (1951 and 1953) established a paleotemperature equation that relates the $\delta^{18}\text{O}$ of CO_2 released from carbonates by H_3PO_4 and the $\delta^{18}\text{O}$ of water (CO_2 equilibrated with water). This paleotemperature equation had been confirmed and slightly modified by other workers (Clayton, 1961; Craig, 1965; Tarutani et al., 1969; O'Neil et al., 1969).

In a detailed study of slowly precipitated inorganic carbonates, Tarutani et al. (1969) investigated the effects of calcite-aragonite polymorphism, salinity of the aqueous phase, magnesium solid solution in calcite and other factors on stable isotopic fractionation. The precipitation method they used was to slowly remove CO_2 from saturated calcium bicarbonate solutions by a finely dispersed stream of nitrogen through the solution. The results of their experiments showed: (1) an ^{18}O enrichment of about 0.6‰ in aragonite compared

to calcite at 25°C; (2) no significant difference in the $\delta^{18}\text{O}$ of carbonates precipitated at different NaCl concentrations (0–36 g/l) solutions; (3) magnesian calcites exhibit a larger ^{18}O fractionation relative to pure calcite; and (4) the differences in isotopic fractionation between inorganic and biogenic carbonates are very small. O'Neil et al. (1969) used the same method developed by Clayton for determining the oxygen isotopic fractionation between carbonate and water at high temperature. Inorganic carbonates were precipitated slowly at 0, 25, 60 and 100 to 700°C. Based on their work, O'Neil et al. (1969) developed a paleotemperature equation that described ^{18}O fractionations between calcite and water between 0–500°C.

In nature, the salinities of closed-basin lakes often exceed that of normal sea water. Alkalinities of these brines may also be higher than in sea water. Since there is no experimental data, we wanted to test whether isotopic fractionations of carbonate precipitated from such waters is linearly related to temperature, as observed for normal marine carbonates. We also wish to investigate whether the temperature dependence of isotopic fractionation is influenced by alkalinity and salinity.

Experimental method

Two sets of calcite precipitation experiments were carried out in the laboratory. In all the experiments, we used Mono Lake water and Rush Creek water. Mono Lake is a hypersaline and alkaline closed-basin lake in the Great Basin, California; Rush Creek is a major tributary in the Mono Basin. The salinity of Mono Lake is about 84‰ (90 g/l TDS), alkalinity is about 600 meq/l, pH is about 9.7, and $\delta^{18}\text{O}$ is -4.5‰. The snow melt stream water of Rush Creek used for the experiments had a salinity of 0.02‰, alkalinity of 0.4 meq/l, pH of 7.67, and $\delta^{18}\text{O}$ of -15‰ (Li, 1995). In each experiment, we mixed different portions of the lake water and the creek water to form solutions of specific salinities and alkalinities. The $\delta^{18}\text{O}$ value of each mixture was calculated by:

$$\delta_m = \delta_L f_L + \delta_R f_R \quad (1)$$

where δ_L , δ_R and δ_m are the $\delta^{18}\text{O}$ values of the lake water, the Rush Creek water and the mixture, respectively. f_L and f_R represent the fractions of the lake water and the creek water, respectively. The salinity and alkalinity of each mixture were calculated in a similar manner.

Mixtures of lake and creek water were prepared in large (0.6–4 liter) glass beakers and maintained in thermostated environments regulated to $\pm 1^\circ\text{C}$. These were covered to minimize exchange with atmospheric gases. Although the lake water is about 9-fold supersaturated for calcite, no detectable precipitate was obtained from this water, even when maintained at 37°C for two weeks. In order to initiate carbonate precipitation we increased the very low (Ca^{2+}) by adding either reagent grade CaCl_2 powder or CaCl_2 solution into each mixture. The CaCl_2 solution was made by dissolving CaCl_2 in the creek water.

After adding additional Ca^{2+} , the precipitation process took place very rapidly (CaCO_3 precipitate was visible immediately). The carbonate precipitates were allowed to settle for three hours, and the supernatant liquids were decanted. The glass beakers were placed in an oven and dried at 60°C. At this temperature, there should not be an inversion from aragonite to calcite, because XRD analyses showed that aragonite deposited in lake sediments remained unchanged even when dried at 75°C. The dried carbonates were analyzed isotopically in an automated carbonate preparation device attached to a VG Prism M.S. In this device, carbonate reactions were conducted sequentially in a common acid bath maintained at 90°C. Reactions were carried out for 10 minutes. The CO_2 gas was purified and allowed to enter the M.S. where it was compared to a standard working gas. Standards were run in conjunction with each of the automated runs. The precision ($\pm 1\sigma$) of 23 replicate standards was 0.10‰ for $\delta^{18}\text{O}$ and 0.09‰ for $\delta^{13}\text{C}$. However, the $\delta^{13}\text{C}$ data does not provide pertinent information and is not presented.

Results and discussion

Experiment-I

This experiment explored the correlation between oxygen isotopic fractionation in carbonates and temperature. Samples ME-6 and -7 were made from 1 liter of the lake water and 3.67 liters of the creek water whereas samples ME-8, -9 and -10 were made from 1 liter of the lake water and 2 liters of the creek water. No precipitate was obtained from the mixtures after one week. Then, we added 2 ml of Ca^{2+} solution with a concentration of 0.272 M each mixture. Precipitation took place immediately. Table 1 lists the experimental conditions and the results. Duplicate analyses of ME-6B indicate that the error of stable isotope measurements is very small. A linear correlation of the $\delta^{18}\text{O}$ difference between carbonate and water with temperature is shown in Figure 1 (excluding sample ME-6B). The resulting regression equation has a slope similar to the paleotemperature equations obtained in previous studies (Table 2). This intriguing

Table 1 Temperature and salinity effects on the isotopic fractionation between rapidly precipitated carbonate and water. The carbonate precipitate was made by adding 2 ml of CaCl_2 solution (0.27M) into each mixture.

Sample	Temperature (°C)	Salinity (‰)	$\delta^{18}\text{O}$ (‰ PDB)	δ_w (‰)	$\delta_c - \delta_w$ for $\delta^{18}\text{O}$
ME-6B	0 $\pm$ 1	84	-3.16	-0.5	-2.7
	0 $\pm$ 1	84	-3.06	-0.5	-2.6
a ME-6	0 $\pm$ 1	18	-6.52	-11.2	4.7
a ME-7	10 $\pm$ 0.5	18	-8.68	-11.2	2.5
b ME-8	18 $\pm$ 0.4	26	-10.03	-9.9	-0.1
b ME-9	25 $\pm$ 0.2	26	-11.80	-9.9	-1.9
b ME-10	35 $\pm$ 0.2	26	-12.87	-9.9	-3.0

- a. Prepared with 1 liter lake water and 3.67 liter creek water
b. Prepared with 1 liter lake water and 2 liter creek water

Table 2 Comparison of temperature correlation obtained from this study with the previous studies.

Regressions: $\delta_c - \delta_w = A - BT$				
Salinity	Carbonate	A	B	Data source
Sea water	Calcite	3.95	0.232	Epstein et al.; O'Neil et al.
Sea water	Aragonite	4.68	0.221	Grossman and Ku
18–28‰	Calcite	4.50	0.231	Fig. 1 in this work

ing result suggests that the temperature dependence of ^{18}O fractionation appears to hold even at a rapid precipitation rate.

Sample ME-6B exhibits values that fall off from the straight line. We analyzed the X-ray diffraction pattern (XRD) for these carbonates in order to assess whether these disequilibrium values were influenced by the presence of a non calcite phase. The carbonate phase of ME-6B is very complicated while the other samples have very pure calcite (Figure 2). ME-6B sample contains mainly gaylussite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$), minor calcite, and perhaps a small amount of aragonite. The solution used to precipitate this sample was pure lake water. Note that the solutions used for other samples have much lower salinity values (18–28‰), closer to that of sea water.

Although previous studies have demonstrated that in many lakes the majority of primary carbonate forms in the epilimnion during warm seasons (Li, 1995; Newton and Grossman, 1988; Schelske and Hodell, 1991; Kelts and Hsü, 1978), Bischoff et al. (1991) reported that gaylussite is currently precipitating in Mono Lake dur-

Figure 1 Temperature correlation of ^{18}O fractionation between the rapidly precipitated carbonate and its equilibrated solution. The linear relationship has a slope similar to those obtained by Epstein et al. (1953) for marine biogenic carbonates, and by O'Neil et al. (1969) for slowly inorganically precipitated carbonates. Sample ME-6B (Open circle) contains mainly gaylussite and was eliminated from the regression.

ing the winter and suggest this is due to high salinities of the lake. Our experimental results confirm Bischoff et al.'s suggestion that gaylussite may form if salinity is high ($>55\%$) and temperature is low ($<5^\circ\text{C}$) (ME-6B). There is no previous study to address the isotopic fractionation between gaylussite and water. With this single experiment it is impossible to conclude what the real ^{18}O fractionation is, but it does suggest that the $\delta^{18}\text{O}$ of gaylussite is much lighter than that of calcite. This result indicates that this apparent disequilibrium is mainly due to impure carbonate multi-phases caused by high salinity ($>55\%$) and extremely low temperatures ($\sim 0^\circ\text{C}$). Fortunately, these extremely high salinities are not common in the nature and most carbonates in the lake sediments precipitate in the warm seasons, so that the formation of gaylussite should be minor in lacustrine sediments. Our future work will attempt to constrain the isotopic fractionations between gaylussite and water.

Experiment-II

In Experiment-I, Ca^{2+} solution was added to 0.5 liter of the creek-lake water mixture in order to make CaCO_3 precipitate. Because the Ca^{2+} solution was made with creek water which has a lower salinity and lighter $\delta^{18}\text{O}$ value than these of the mixture, it is possible that the salinity and isotopic composition may have been altered at the

Figure 2 a. XRD analysis of Sample ME-6B, showing the carbonate phase contains mainly gaylussite, minor calcite and little aragonite. b. XRD analyses of Samples ME-6A to ME-10, showing these samples consist of pure calcite. G = Gaylussite, C = Calcite, A = Aragonite, and H = Halite.

locus of precipitation. Although our results did not show evidence for such an effect, Experiment-II was carried out to avoid this possibility by adding ~ 0.5 g of CaCl_2 powder to each mixture while stirring the solution vigorously, maintaining isotopic homogeneity and uniform salinity in the solution. This experiment was designed to investigate the effects of temperature and salinity on oxygen isotopic fractionation and was conducted at eight different salinities and eight different temperatures (Table 3). Note that we cannot distinguish the effects of salinity and alkalinity separately because these variables are correlated. We discuss the effect of salinity but recognize it may also reflect an alkalinity effect.

Table 3 lists all experimental results and the comparison of these results with the predicted equilibrium $\delta^{18}\text{O}$ values calculated from the equation of Epstein et al. (1953). Three observations can be drawn from the comparison: (1) the ^{18}O fractionations for samples precipitated at salinities less than 50% are much larger than predicted for equilibrium fractionations; (2) at extremely high salinity ($>70\%$) and low temperature ($<10^\circ\text{C}$), the measured $\delta^{18}\text{O}$ values are lighter than the predicted equilibrium value, but are much closer to predicted equilibrium values than those at lower salinities; (3) as salinity decreases, the degree of disequilibrium fractionation increases. The largest disequilibrium occurs at the lowest salinity.

Figure 3 shows the effect of salinity on ^{18}O fractionation for these experiments. In all cases except at 0°C temperature, the ^{18}O fractionations are linearly correlated with salinity of the aqueous phase. The average salinity effect on the ^{18}O fractionation between

Table 4 Temperature correlations of ^{18}O fractionation under different salinities. The temperature equations are fitted from Figure 4. Sample numbers in *italic* represent that the results of these samples are not included for fitting.

Salinity (‰)	Temperature (°C)								Temperature correlation
	0±1	5±0.5	10±0.5	15±0.5	20±0.2	25±0.2	30±0.2	37±0.2	
84.1	ME-19	ME-27	ME-35	ME-43	ME-51	ME-59	ME-67	ME-75	$\delta_c - \delta_w = 14.6 - 0.22T$, R2 = 0.99
75.7	ME-20	ME-28	ME-36	ME-44	ME-52	ME-60	ME-68	ME-76	$\delta_c - \delta_w = 12.8 - 0.19T$, R2 = 0.99
67.3	ME-21	ME-29	ME-37	ME-45	ME-53	ME-61	ME-69	ME-77	$\delta_c - \delta_w = 10.9 - 0.18T$, R2 = 0.97
57.2	ME-22	ME-30	ME-38	ME-46	ME-54	ME-62	ME-70	ME-78	$\delta_c - \delta_w = 7.4 - 0.12T$, R2 = 0.97
42.1	ME-23	ME-31	ME-39	ME-47	ME-55	ME-63	ME-71	ME-79	$\delta_c - \delta_w = 5.4 - 0.12T$, R2 = 0.95
26.9	ME-24	ME-32	ME-40	ME-48	ME-56	ME-64	ME-72	ME-80	$\delta_c - \delta_w = 4.1 - 0.13T$, R2 = 0.98
16.8	ME-25	ME-33	ME-41	ME-49	ME-57	ME-65	ME-73	ME-81	$\delta_c - \delta_w = 2.7 - 0.12T$, R2 = 0.99
8.4	ME-26	ME-34	ME-42	ME-50	ME-58	ME-66	ME-74	ME-82	$\delta_c - \delta_w = 1.5 - 0.12T$, R2 = 0.99

Table 3 Results of experiment for salinity and temperature effects on stable isotopic equilibrium of rapid carbonate precipitation

Sample	L _w : C _w (ml)	Temp. (°C)	Salinity (‰)	δ ¹⁸ O _w (‰ SMOW)	δ ¹⁸ O _c (‰ PDB)	δ _c - δ _w for δ ¹⁸ O	δ _c - δ _{eq} * (‰ PDB)
ME-19	250 : 0	0±1	84.1	-0.5	3.16	3.66	-0.3
ME-20	225 : 25	0±1	75.7	-1.95	-1.63	0.32	-3.6
ME-21	200 : 50	0±1	67.3	-3.40	0.83	4.23	0.3
ME-22	170 : 80	0±1	57.2	-5.14	3.08	8.22	4.3
ME-23	125 : 125	0±1	42.1	-7.75	-0.16	7.59	3.6
ME-24	80 : 170	0±1	26.9	-10.36	-1.71	8.65	4.7
ME-25	50 : 200	0±1	16.8	-12.10	-1.28	10.82	6.9
ME-26	25 : 225	0±1	8.4	-13.55	-1.45	12.10	8.2
ME-27	250 : 0	5±0.5	84.1	-0.5	-1.43	-0.93	-3.7
ME-28	225 : 25	5±0.5	75.7	-1.95	-1.80	0.15	-2.6
ME-29	200 : 50	5±0.5	67.3	-3.40	-0.25	3.15	0.4
ME-30	170 : 80	5±0.5	57.2	-5.14	-2.26	2.88	0.1
ME-31	125 : 125	5±0.5	42.1	-7.75	-1.28	6.47	3.7
ME-32	80 : 170	5±0.5	26.9	-10.36	-1.29	9.07	6.3
ME-33	50 : 200	5±0.5	16.8	-12.10	-1.28	10.82	8.0
ME-34	25 : 225	5±0.5	8.4	-13.55	-1.21	12.34	9.6
ME-35	250 : 0	10±0.5	84.1	-0.5	-1.31	-0.81	-2.4
ME-36	225 : 25	10±0.5	75.7	-1.95	-2.08	-0.13	-1.8
ME-37	200 : 50	10±0.5	67.3	-3.40	-1.90	1.50	-0.1
ME-38	170 : 80	10±0.5	57.2	-5.14	-1.23	3.91	2.3
ME-39	125 : 125	10±0.5	42.1	-7.75	-1.80	5.95	4.3
ME-40	80 : 170	10±0.5	26.9	-10.36	-1.32	9.04	7.4
ME-41	50 : 200	10±0.5	16.8	-12.10	-1.23	10.87	9.2
ME-42	25 : 225	10±0.5	8.4	-13.55	-0.83	12.72	11.1
ME-43	250 : 0	15±0.5	84.1	-0.5	-0.69	-0.19	-0.7
ME-44	225 : 25	15±0.5	75.7	-1.95	-1.05	0.90	0.4
ME-45	200 : 50	15±0.5	67.3	-3.40	-1.07	2.33	1.9
ME-46	170 : 80	15±0.5	57.2	-5.14	-1.42	3.72	3.3
ME-47	125 : 125	15±0.5	42.1	-7.75	-1.96	5.79	5.3
ME-48	80 : 170	15±0.5	26.9	-10.36	-1.83	8.53	8.1
ME-49	50 : 200	15±0.5	16.8	-12.10	-2.13	9.97	9.5
ME-50	25 : 225	15±0.5	8.4	-13.55	-2.61	10.94	10.5
ME-51	250 : 0	20±0.2	84.1	-0.5	-1.44	-0.94	-0.3
ME-52	225 : 25	20±0.2	75.7	-1.95	-1.61	0.34	1.0
ME-53	200 : 50	20±0.2	67.3	-3.40	-1.88	1.52	2.2
ME-54	170 : 80	20±0.2	57.2	-5.14	-2.12	3.02	3.7
ME-55	125 : 125	20±0.2	42.1	-7.75	-2.33	5.42	6.1
ME-56	80 : 170	20±0.2	26.9	-10.36	-2.65	7.71	8.4
ME-57	50 : 200	20±0.2	16.8	-12.10	-2.89	9.21	9.9
ME-58	25 : 225	20±0.2	8.4	-13.55	-3.58	9.97	10.7
ME-59	250 : 0	25±0.2	84.1	-0.5	-1.78	-1.28	0.6
ME-60	225 : 25	25±0.2	75.7	-1.95	-2.22	-0.27	1.6
ME-61	200 : 50	25±0.2	67.3	-3.40	-2.52	0.88	2.7
ME-62	170 : 80	25±0.2	57.2	-5.14	-3.11	2.03	3.9
ME-63	125 : 125	25±0.2	42.1	-7.75	-3.66	4.09	5.9
ME-64	80 : 170	25±0.2	26.9	-10.36	-4.28	6.08	7.9
ME-65	50 : 200	25±0.2	16.8	-12.10	-4.99	7.11	9.0
ME-66	25 : 225	25±0.2	8.4	-13.55	-6.19	7.36	9.2
ME-67	250 : 0	30±0.2	84.1	-0.5	-2.36	-1.86	1.2
ME-68	225 : 25	30±0.2	75.7	-1.95	-2.65	-0.70	2.3
ME-69	200 : 50	30±0.2	67.3	-3.40	-2.78	0.62	3.6
ME-70	170 : 80	30±0.2	57.2	-5.14	-3.07	2.07	5.1
ME-71	125 : 125	30±0.2	42.1	-7.75	-4.11	3.64	6.7
ME-72	80 : 170	30±0.2	26.9	-10.36	-4.66	5.70	8.7
ME-73	50 : 200	30±0.2	16.8	-12.10	-4.87	7.23	10.2
ME-74	25 : 225	30±0.2	8.4	-13.55	-5.60	7.95	11.0
ME-75	250 : 0	37±0.2	84.1	-0.5	-3.30	-2.80	1.8
ME-76	225 : 25	37±0.2	75.7	-1.95	-3.67	-1.72	2.9
ME-77	200 : 50	37±0.2	67.3	-3.40	-4.19	-0.79	3.8
ME-78	170 : 80	37±0.2	57.2	-5.14	-4.56	0.58	5.2
ME-79	125 : 125	37±0.2	42.1	-7.75	-4.79	2.96	7.6

The lake water (L_w) is from the surface of Mono Lake in 1993 with alkalinity of 600 meq/L, salinity of 84‰, and δ¹⁸O value of 0.5±0.3‰ (SMOW). The creek water (C_w) is taken from Rush Creek 3 km away from the lake shoreline in 1993, with alkalinity of 0.4 meq/L, salinity of 0.02‰, and δ¹⁸O of -15±1‰. The carbonate precipitation were made by adding ~0.5g CaCl₂ power into each mixture.

*: δ_{eq} is calculated from the average equation obtained by Epstein et al. (1953) and O'Neil et al. (1969).

δ_c - δ_w = 3.95 - 0.232T, where T is water temperature (°C), δ_w is δ¹⁸O_w (‰, PDB; by adding 0.22‰ on SMOW scale to obtain PDB scale), and δ_c is δ_c (‰, PDB).

Figure 3 Salinity effect on the ^{18}O fractionation between the rapidly precipitated carbonate and CO_2 equilibrated with the solution at different temperature. δ_w is the $\delta^{18}\text{O}$ of CO_2 extracted from the carbonate by acid reaction. δ_w is the $\delta^{18}\text{O}$ of CO_2 equilibrated with the water.

rapidly precipitated carbonate and its solution under different temperature ranges can be approximated as:

$$\delta_c - \delta_w = 13.96 - 0.179S; \text{ at } 5\text{--}10^\circ\text{C} \quad (2)$$

$$\delta_c - \delta_w = 11.94 - 0.149S; \text{ at } 15\text{--}20^\circ\text{C} \quad (3)$$

$$\delta_c - \delta_w = 8.67 - 0.125S; \text{ at } 20\text{--}37^\circ\text{C} \quad (4)$$

where S represents salinity of the aqueous phase (‰), δ_c is the $\delta^{18}\text{O}$ of CO_2 extracted from the carbonate precipitated from the aqueous phase (PDB), and δ_w is the $\delta^{18}\text{O}$ of CO_2 equilibrated with the aqueous phase (PDB). As salinity increases, the ^{18}O fractionation between carbonate and water decreases (Figure 3).

While the above observations illustrate the disequilibrium for rapid precipitation, we would like to know if the fractionation is still strongly temperature dependent. Figure 4 and Table 4 show that the fractionation is strongly correlated with temperature range 10–37°C. However, the temperature dependences are very different from the paleotemperature equations obtained from previous studies (Epstein et al., 1953; O'Neil et al., 1969; Grossman and Ku, 1986) and the result of Experiment-I. From Table 4, we can see that the intercept of the temperature correlations increases with salinity, but the slope increases only when the salinity is greater than 67.3‰.

Although our understanding of the mechanism of the salinity and temperature effects on the ^{18}O fractionation for the rapidly precipitated carbonate is not complete, the disequilibrium may be caused by two factors: impure carbonate multi-phases and/or the fast growth rate of carbonate crystals which perturbs the isotopic exchange at the site of precipitation. We conducted XRD and SEM analyses on several samples to investigate the presence of carbonate multi-phases. XRD analyses indicate that all of the samples from Experiment-II are pure calcite. The formation of carbonate polymorphs, such as gaylussite formation, is not the mechanism leading to disequilibrium. Hence, the disequilibrium is probably caused by

insufficient isotopic exchange between precipitation and solution due to fast growth rate of carbonate crystals. O'Neil et al. (1969) stated that carbonate precipitated extremely rapidly would be expected to have the same $^{18}\text{O}/^{16}\text{O}$ ratio as the bicarbonate ion in solution. For rapid precipitation, CaCO_3 precipitates so fast that the combined carbonate ions in the crystals do not have a chance to exchange isotopes with the water. Presently, we cannot answer the questions about why the rapidly precipitated carbonates do not exhibit isotope fractionations predicted from the equilibrium equation, and why this disequilibrium is a function of temperature and salinity. We were not able to measure possible differences in precipitation rates between the various salinity experiments. Therefore, we cannot say whether precipitation rate influences the degree of disequilibrium. To answer these questions, we need to know what are the ^{18}O fractionations among water, CO_2 , bicarbonate and carbonate ions, as well as the precipitated carbonate and measure precipitation rates.

Conclusions

The temperature dependence of ^{18}O fractionation may prevail in saline lake system because our results for rapid precipitation from Experiment-I agree with previous studies for slowly inorganically precipitated and biologically precipitated carbonates. In this experiment, a solution with high concentration of CaCl_2 was added to mixtures of Mono Lake and Rush Creek waters. However, in extremely saline (>70‰) and low temperatures (<10°C) solution, disequilibrium

Figure 4 Temperature correlation of the ^{18}O fractionation between the rapidly precipitated carbonate and CO_2 equilibrated with the solution at different salinities. Data points in the outlined squares were not used for the linear fits. The dashed line represents the temperature correlation obtained by Epstein et al. (1953) and O'Neil et al. (1969) for seawater (Salinity = 35‰).

rium fractionation may occur because of formation of carbonate polymorphs such as gaylussite. The first $\delta^{18}\text{O}$ measurement of gaylussite formed under hypersaline and alkaline water at low temperature is depleted in ^{18}O relative to calcite.

Experiments in which calcite was precipitated by addition of CaCl_2 powder to mixtures of lake and creek waters were often far from equilibrium. These experiments exhibited ^{18}O fractionation that was strongly dependent on both temperature and salinity. Presently, we cannot explain the mechanism causing the large disequilibrium ^{18}O fractionation in these experiments. It is necessary to investigate in-situ temperature correlations between carbonate and water for lake systems in order to accurately reconstruct paleo-climatic variability.

Acknowledgments

We appreciate Professor T.-L. Ku (USC) for his helpful discussion. This work was supported by NSF grants ATM-9303587 and OCE-9314192.

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