Aquat Geochem (2012) 18:95–113
DOI 10.1007/s10498-011-9150-3

ORIGINAL PAPER

Calcium Carbonate Nucleation in an Alkaline Lake Surface Water, Pyramid Lake, Nevada, USA

Michael M. Reddy · Anthony Hoch

Received: 30 March 2011 / Accepted: 15 November 2011 / Published online: 7 December 2011
© U.S. Government 2011

Abstract Calcium concentration and calcite supersaturation (Ω) needed for calcium carbonate nucleation and crystal growth in Pyramid Lake (PL) surface water were determined during August of 1997, 2000, and 2001. PL surface water has Ω values of 10–16. Notwithstanding high Ω, calcium carbonate growth did not occur on aragonite single crystals suspended PL surface water for several months. However, calcium solution addition to PL surface-water samples caused reproducible calcium carbonate mineral nucleation and crystal growth. Mean PL surface-water calcium concentration at nucleation was 2.33 mM ($n = 10$), a value about nine times higher than the ambient PL surface-water calcium concentration (0.26 mM); mean Ω at nucleation (109 with a standard deviation of 8) is about eight times the PL surface-water Ω. Calcium concentration and Ω regulated the calcium carbonate formation in PL nucleation experiments and surface water. Unfiltered samples nucleated at lower Ω than filtered samples. Calcium concentration and Ω at nucleation for experiments in the presence of added particles were within one standard deviation of the mean for all samples. Calcium carbonate formation rates followed a simple rate expression of the form, rate (mM/min) $= A\ (\Omega) + B$. The best fit rate equation "Rate (Δ mM/Δ min) $= -0.0026\ \Omega + 0.0175$ ($r = 0.904$, $n = 10$)" was statistically significant at greater than the 0.01 confidence level and gives, after rearrangement, Ω at zero rate of 6.7. Nucleation in PL surface water and morphology of calcium carbonate particles formed in PL nucleation experiments and in PL surface-water samples suggest crystal growth inhibition by multiple substances present in PL surface water mediates PL calcium carbonate formation, but there is insufficient information to determine the chemical nature of all inhibitors.

M. M. Reddy (✉) · A. Hoch
US Geological Survey (USGS), National Research Program (NRP), Central Branch (CB),
Denver Federal Center, P.O. Box 25046, MS 403, Lakewood, CO 80225, USA
e-mail: mmreddy@usgs.gov

A. Hoch
e-mail: tony.hoch@wy.nacdnet.net

Present Address:
A. Hoch
Laramie Rivers Conservation District, 1050 North Third Street, Laramie, WY, USA

Keywords Pyramid Lake, Nevada, USA · Calcium carbonate · Nucleation · Calcium carbonate nucleation · Supersaturation · Mineral formation inhibition

1 Introduction

Calcium carbonate mineral formation is a significant component of the global carbon cycling system, mediating carbonate sediment formation and carbon sequestration in oceans, lakes, surface water, and groundwater (Dittrich and Obst 2004; Sarmiento and Gruber 2006; Higgins et al. 2009). Carbonate mineral formation in lakes is influenced by calcium carbonate precipitation, crystal growth, and dissolution (Dean and Fouch 1983; Galat and Jacobsen 1985; Reddy 1986, 1995; Hodell et al. 1998). However, little information exists concerning critical elements of mineral formation, calcium ion concentration, and calcite supersaturation (Ω) levels at the onset of carbonate mineral nucleation in lakes, surface water, and groundwater.

The calcium carbonate polymorphs calcite and aragonite occur widely in natural systems; other polymorphs such as vaterite, monohydrocalcite (Rosen et al. 2004), hexahydrocalcite (Bischoff et al. 1993), and amorphous calcium carbonate (Addadi et al. 2003) occur much less frequently. Understanding, characterizing, and predicting calcium carbonate mineral formation in alkaline lakes and other locations such as the deep sea sediment–water interface (Higgins et al. 2009) requires understanding of mineral formation factors (Reddy 1986): mineral solution Ω; mineral nucleation; crystal growth; mineral aggregation and transformation; and inhibition of mineral nucleation and growth by specific chemical substances. Field studies and laboratory investigations suggest that calcite growth-rate inhibitors facilitate unstable calcium carbonate polymorph formation (Bischoff et al. 1993; Rosen et al. 2004) by reducing calcite growth rates via absorption at growth sites on the calcite surface (Nancollas and Reddy 1971; Nancollas and Reddy 1974; He et al. 1999; Reddy and Hoch 2000, 2001).

Carbonate mineral formation in natural waters has been studied extensively (Weyl 1961; Reynolds 1978; Wetzel and White 1985; Herman and Lorah 1988; Herman 1989; McConnaughey et al. 1994; Reddy 1995; Plummer et al. 2000; Schuster et al. 2003). Cloud (1962) summarized early experiments dealing with calcium carbonate precipitation from seawater and concluded that precipitation is a function of parent solution Ω. Chave and Seuss (1970) proposed that magnesium ion and dissolved organic matter in solution inhibit calcium carbonate precipitation from seawater. Otsuki and Wetzel (1974) concluded that pH (in natural microenvironments) may exceed nine due to photosynthetic activity, facilitating calcium carbonate formation. McConnaughey et al. (1994), Arp et al. (1999), and Dittrich and Obst (2004) studied calcium carbonate formation in lacustrine environments. McConnaughey et al. (1994) examined the importance of biological processes in lake-water calcium carbonate formation process and hypothesized that algae alter water pH adjacent to algal cells, which shifts Ω during photosynthesis leading to calcium carbonate formation in a hard-water lake.

Organic and inorganic particles (termed "heteronuclei") facilitate calcium carbonate nucleation in supersaturated lake water. Arp et al. (1999) suggested that biofilm exopolymers enhance carbonate mineral formation at Pyramid Lake (PL) in highly supersaturated mixing zones of thermal spring water. Whole lake whitings (massive calcium carbonate precipitation causing lake water turbidity), such as those occurring in PL, are well documented, but poorly explained (Hodell et al. 1998).

The >150 m deep PL exhibits occasional surface-water whiting events during late summer (August) when lake waters are warmest. Hypotheses for whiting events include calcium carbonate nucleation triggered by nanoplankton (Galat and Jacobsen 1985; Lebo et al. 1993); carbonate nucleation caused by increased pH and concomitant elevated Ω associated with biological productivity (Kelts and Hsü 1978; McKenzie 1982; Dean and Fouch 1983); or calcium carbonate nucleation due to mixing of cool spring waters with warm epilimnion waters (Runnells 1969; Kelts and Hsü 1978; Galat and Jacobsen 1985; Lebo et al. 1993). Information is sparse concerning PL calcium concentrations or calcium carbonate mineral Ω levels at the time and location of "whole lake whitings" or during calcium carbonate formation at near-shore locations.

The purpose of this report is to extend previous work on calcium carbonate formation in surface waters (McConnaughey et al. 1994), and modeling and laboratory investigations of PL surface water (summarized in Reddy 1995). Onsite and laboratory nucleation and crystal growth procedures (described in Reddy 1986; Kile et al. 2000) were used to quantify PL surface-water calcium concentration and Ω initiating calcium carbonate nucleation. Preliminary single crystal growth experiments in 1992 and 1993 examined aragonite formation in ambient PL surface water. The geochemical conditions necessary for calcium carbonate nucleation and crystal growth in PL surface water were determined for samples collected during August of 1997, 2000, and 2001. Calcium carbonate particle mineralogy and morphology, important indicators of PL carbonate formation processes, were determined from filtered PL surface water samples obtained in August 1992 and 2000, and for calcium carbonate formed during nucleation experiments in 1997, 2000, and 2001.

2 Study Area

The study location, PL, a large, closed-basin lake at the terminus of the Truckee River within Piaute Tribal lands, north of Reno, Nevada, is a remnant of Pleistocene Lake Lahontan (Fig. 1) (Hamilton-Galat and Galat 1983; Lebo et al. 1993; Reddy 1995; Tenzer et al. 1997). Near-shore sampling sites were at the PL Natural Resource Building, Sutcliffe, Nevada (August, 1997, and August, 2000), at Wizard Cove at the north end of PL (August, 1997), and at a mid-lake location in the North Basin of PL (August, 2001) (Fig. 1) (Table 1). PL surface water is alkaline (a sodium-chloride-bicarbonate type water) with a pH of nine or greater.

3 Methods

Water analyses and calcium carbonate nucleation measurements use grab samples from the upper 1 m of PL. Surface water samples are supersaturated with respect to calcium carbonate minerals and atmospheric carbon dioxide and may be unstable because of calcium carbonate formation; therefore, calcium carbonate nucleation measurements are completed as soon as possible after sample collection.

3.1 Aragonite Single Crystal Growth Measurements

Calcification in PL was estimated by periodically weighing aragonite single crystals suspended inside dialysis bags located within the PL epilimion near the Natural Resource

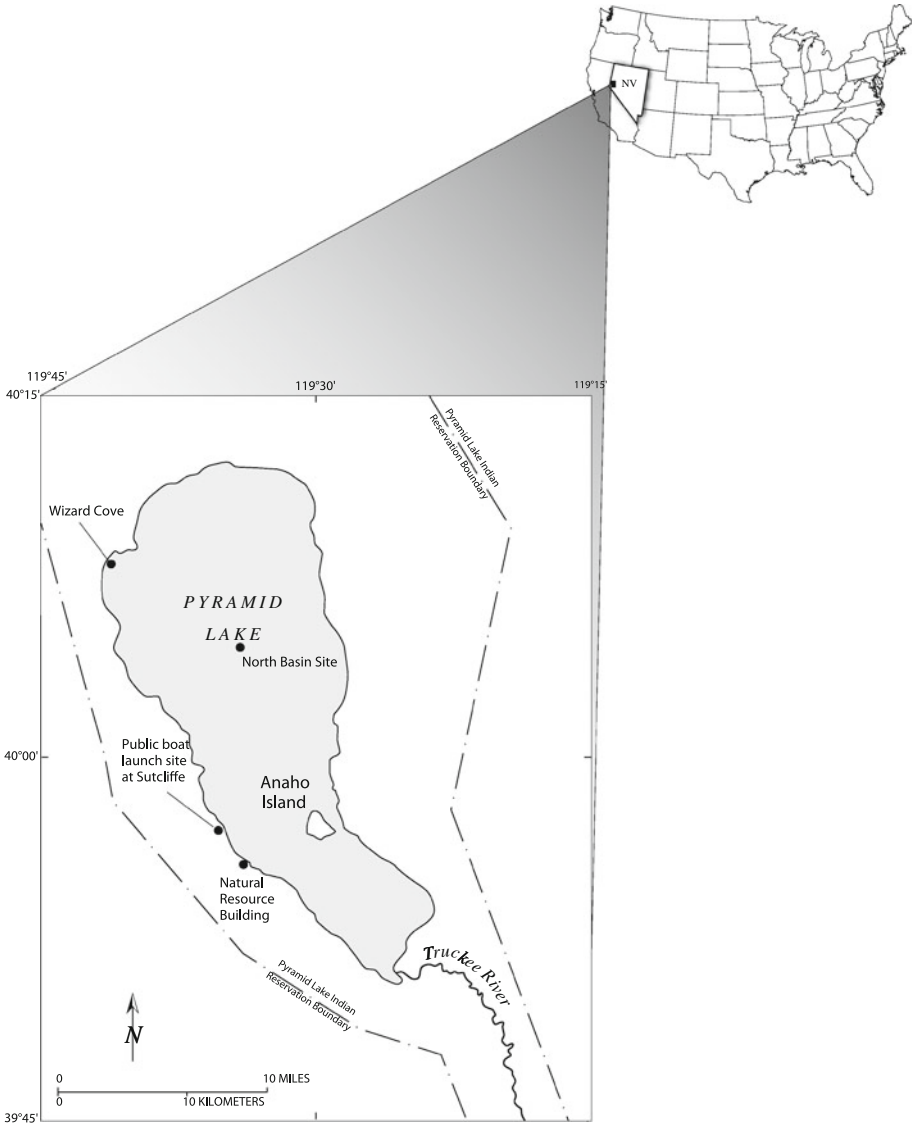

Fig. 1 Map of Pyramid Lake and vicinity showing sample collection sites

Building (McConnaughey et al. 1994). These qualitative experiments used large aragonite single crystals (Ward Scientific Company, Rochester, New York).

3.2 Precipitation Experiment

Experimental details and solution preparation information are similar to laboratory calcium carbonate nucleation experiments done previously (Reddy 1986; Kile et al. 2000). Stock 0.1 M calcium chloride solution was added from a Grade A burette to a 100-mL lake water

Table 1 Pyramid Lake nucleation sample collection information for samples from Wizard Cove (WC), near the Natural resource Building (NRB), and the North Basin (NB)

Sample number	Collection—measurement date	Sample location	Sample treatment	Sample amendment
PL-1	8/15/1997	WC	Filtered 0.1 μm pore size	
PL-2	8/15/1997	WC	Unfiltered	
PL-3	8/18/1997	WC	Filtered 0.1 μm pore size	Single addition of 2 mL calcium solution
PL-4	8/19/1997	NRB	Filtered 0.1 μm pore size	
PL-5	8/19/1997	NRB	Filtered 0.1 μm pore size	w/algal particles added
PL-6	8/19/1997	NRB	Filtered 0.1 μm pore size	
PL-7	8/19/1997	NRB	Filtered 0.1 μm pore size	w/algal particles added
NCL00 1	8/25/2000	NRB	Filtered 0.45 μm pore size	
NCL00 2	8/25/2000	NRB	Unfiltered	
NCL00 3	8/25/2000	NRB	Unfiltered	Sample warmed
NCL01 1	8/22/2001	NB	Unfiltered	
NCL01 2	8/22/2001	NB	Filtered 0.45-um pore size	

Sample number, collection date, measurement date, location, treatment, and amendment

sample in a magnetically stirred 250-mL Erlenmeyer flask on site or in the project laboratory within a few days of sample collection.

Water used for reagent preparation, obtained by mixed-bed ion exchange and carbon adsorption purification prior to use, had very low conductance (greater than 15 mega ohm resistance) and was free of trace ionic impurities. Reagents were American Chemical Society Reagent Grade or equivalent. Glassware was grade A. Filtered and unfiltered PL water samples were used in the titration experiments. Some experiments were amended with particulates obtained from a fish-holding pond adjacent to the Natural Resource Building (Fig. 1).

During each PL surface water titration, calcium chloride addition (one drop per 15 s) increased calcium concentration slowly, avoiding high-localized Ω. Some nucleation experiments used twice this addition rate. At nucleation, sample turbidity dramatically increased within a one-drop addition of the stock calcium chloride solution to the sample. Temperature and pH were measured during the titration with a Fisher Scientific Accumet 1002 pH meter and an Orion gel pH electrode with automated temperature compensation calibrated with standard buffers prior to use.

3.3 Isolation of Particles Used to Amend Nucleation Experiments

During August 1997, 3 L of a PL fish-holding pond water (experiencing an algal bloom) were filtered (0.45-μm pore-size filter). Particles retained by the filter were washed with pond water into 250 mL of pond water (about a tenfold increase in the PL pond water

particulate concentration). Nucleation measurements in the presence of particles were done by using material from a 50-mL portion of this pond water concentrate collected on a 0.45-μm-pore-size filter. Filtered particles were scraped into a 100-mL sample of filtered PL water sample used for the titration. Particulate material in PL during late summer consists of small organic-rich particles and bacteria-detritus aggregates that form from in-lake sources (Hamilton-Galat and Galat 1983; Tenzer et al. 1997). Particle concentration was not directly measured on the sample used for this qualitative (enhanced algal particle concentration) nucleation experiment. Solution amended by particles isolated from the pond were used to test the hypothesis that algal particulate material (including biofilm exopolymers) produced during an algal bloom would enhance calcium carbonate nucleation and crystal growth in PL surface water.

3.4 Solution Chemical Analysis

Analysis of PL surface water was performed following standard analytical procedures of the US Geological Survey (USGS) at the USGS National Research Program (NRP) Laboratory in Boulder, CO. Details of onsite and laboratory procedures and quality assurance techniques, detection limits for laboratory and onsite analyses, and summary statistics for reference samples, distilled water field blanks, and laboratory blanks analyses are given in Reddy et al. (1989). For example, alkalinity determinations in this laboratory for the USGS standard reference sample M-4 gave a mean of 0.535 meq/L with a standard deviation of 0.014 meq/L (a relative standard deviation of 2.6% for $n = 63$). This value compares with the reference mean value of 0.540 meq/L with a standard deviation of 0.022 (a relative standard deviation of 4.1% for $n = 48$). A chemical analysis of filtered PL surface water for a sample collected at Wizard Cove on August 26, 2000 is given in Table 2.

Calcium concentration, pH, specific conductance, and alkalinity were determined onsite and in the USGS NRP Boulder Laboratory before, and occasionally following, calcium carbonate nucleation in surface-water samples. Onsite PL surface-water calcium concentrations are determined by ethylenediaminetetraacetic acid (EDTA)/calcein titration (Diehl 1964). Alkalinity measurements were done by using a Hach titrator to a fixed end point of 4.5. Sample pH and temperature were determined at intervals during calcium addition.

Table 2 Chemical analysis for a Pyramid Lake surface water sample collected at Wizard Cove on August 26, 2000

Parameter	Units	Value
Temperature	°C	21.1
Conductance	mS/cm	8.0
pH		8.99
Ionic strength	equ/L	0.0826
Calcium	mg/L	11.4
Magnesium	mg/L	104
Sodium	mg/L	1,421
Potassium	mg/L	126
Sulfate	mg/L	285
Chloride	mg/L	2,108
Alkalinity	meq/L	21.6
Alkalinity	mg HCO_3/L	1,320
SiO_2	mg/L	0.75

Prior to calcium carbonate nucleation, calcium and carbonate concentrations at each time are calculated from the initial PL concentrations and volume of added 0.1 M calcium chloride solution assuming mass balance in solution. Sample pH and alkalinity decreased slightly following each calcium addition to the PL surface-water sample. Calcium carbonate growth in PL surface water is estimated by changes in solution pH following nucleation.

3.5 Solution Supersaturation

Calcium carbonate formation is followed in terms of Ω, a parameter that describes calcium carbonate mineral formation tendency and equilibrium in a solution, and is defined as:

$$\Omega = \left[\mathrm{Ca}^{+2}\right]\left[\mathrm{CO}_3^{-2}\right]/K_{\mathrm{sp}}$$

where brackets refer to ion activities in solution, and K_{sp} is the calcite thermodynamic solubility product at the sample temperature. Chemical speciation of PL surface water is done using PHREEQC to determine concentrations, activities, Ω values, and carbon dioxide partial pressures. Ion activity products (IAP) (i.e., $[\mathrm{Ca}^{+2}][\mathrm{CO}_3^{-2}]$) and Ωs are calculated with PHREEQC (Version 2) and the Phreeqc.dat database (Parkhurst and Appelo 1999) using measured lake water chemical parameters (i.e., sample temperature, pH, total calcium concentration, and alkalinity) and a PL surface-water composition (i.e., major, minor, and trace ions) for the remaining chemical constituents, assuming a closed system. Input conditions and PL water concentrations are used in the PHREEQC input file to calculate the solution species distribution. During each titration, calcium concentration and Ω increased with calcium chloride stock solution addition until nucleation occurred. At the onset of calcium carbonate nucleation sample pH, calcium concentration, alkalinity, and Ω decreased without additional calcium titrant because of calcium carbonate mineral formation. Solution pH following nucleation is used to estimate calcium carbonate formation in solution, the calcium concentration in solution, and the Ω value at each pH measurement using the geochemical modeling features of PHREEQC.

3.6 Calcium Carbonate Formation Rate

Calcium carbonate formation rates are calculated as the ratio of the difference in solution calcium concentration (mM), divided by the difference in time (min), for two measured solution pH values. Ω values are calculated at each measured pH.

3.7 Calcium Carbonate Examination by Scanning Electron Microscopy (SEM), Environmental Scanning Electron Microscopy (ESEM), and Optical Microscopy (OM)

SEM, ESEM, or OM was used to characterize particles isolated on filters from nucleation experiments and from filtered PL surface-water samples. Particles formed in nucleation experiments were examined using a SEM at the Denver Federal Center, Lakewood, Colorado, under a 20-kV, 64-μA beam over a range of magnifications up to about 20,000 times magnification. Electron micrographs of PL surface-water particles and PL sediments were obtained using an Electroscan model E2 ESEM at the University of Southern Mississippi, Hattiesberg, Mississippi, and a SEM at Lawrence University. Particle composition was

determined by energy dispersive X-ray (EDAX) analysis. Optical microscopy identified selected particle morphology and mineralogy for measurements in 2000 and 2001.

4 Results and Discussion

4.1 Pyramid Lake Supersaturation

Pyramid Lake surface water chemical composition (Table 2) has high Ω (i.e., 10–16). These Ω values are near the calcium carbonate spontaneous precipitation metastability limit (Reddy 1986, 1995). Qualitative experiments verified the absence of calcium carbonate growth in PL surface water by using aragonite single crystals (Ward Scientific Company, Rochester, New York). Seven aragonite crystals were suspended in PL (adjacent to the Natural Resource Building, Fig. 1) from August 21, 1992 to October 2, 1992 and two crystals were deployed from February 13, 1993 to May 16, 1993. These single crystals did not increase in weight (average weight loss was −0.22725 g in 1992 and −0.0092 g in 1993 for crystal weighing between 50 and 100 g), demonstrating the absence of calcium carbonate formation in calcium carbonate supersaturated PL surface water.

4.2 Nucleation Measurements

Nucleation measurements were conducted with PL surface-water samples from two locations (Fig. 1) during August 1997 and 2000, and from a mid-lake location (the North Basin of PL) in August 2001 (12 samples in total over 3 years (Table 3)). During each titration, calcium concentration and Ω increased and pH and alkalinity decreased until nucleation. Two nucleation experiments had different conditions and were not used in statistical comparisons of the data set. Experiment PL-3 was not a titration experiment, 2 mL of 0.1 M calcium chloride solution was added at one time, and precipitation occurred overnight. Experiment NCL00 3 was warmed by sunlight during the titration procedure.

Pyramid Lake surface-water calcium and alkalinity concentration changes following nucleation in the presence and absence of added particles are consistent with the formation of calcium carbonate in the supersaturated lake water. Energy dispersive x-ray analysis and

Table 3 Initial PL surface-water sample total calcium concentration, alkalinity, pH, and initial/nucleation temperature (±0.2°C)

Sample number	pH	Ca (mM)	Alkalinity, mg $CaCO_3$/L	Temp (°C)
PL-1	9.08	0.271	1,087	26.1/26.3
PL-2	9.09	0.271	1,087	25.5/25.7
PL-3	8.98	0.271	1,087	25/28.5
PL-4	9.20	0.293	1,067	22/22
PL-5	9.21	0.293	1,067	22/23.3
PL-6	9.17	0.252	1,067	23.3/23.3
PL-7	9.18	0.253	1,067	23.3/23.3
NCL00 1	9.11	0.271	1,020	24.7
NCL00 2	9.12	0.271	1,020	24.6/25.2
NCL00 3	9.11	0.271	1,020	26.7/31.4
NCL01 1	9.09	0.242	1,010	27/27
NCL01 2	9.12	0.242	1,010	26.5/26.5

Table 4 Summary of Pyramid Lake water calcium carbonate nucleation results

Sample number	mLs added causing nucleation in 100 mL PL water	Calcium concentration (mM) at Nucleation	Estimated supersaturation at nucleation
PL-1	2.1	2.32	106
PL-2	2	2.23	103
PL-3*	(2)	(2.23)	
PL-4	2.2	2.40	119
PL-5	2	2.25	113
PL-6	2.35	2.58	123
PL-7	2.2	2.40	117
NCL00 1	2.2	2.37	105
NCL00 2	2	2.18	99
NCL00 3**	(1.6)	(1.80)	
NCL01 1	2	2.18	101
NCL01 2	2.2	2.37	105
Mean	2.125	2.33	109
SD	0.123	0.123	8

Sample number, mLs of 0.1 M calcium chloride solution added to 100 mL of lake water sample to cause nucleation, calcium concentration (mM) in PL surface-water sample at nucleation, and estimated lake water Ω at nucleation

* Not included in statistical average. Two mL of 0.1 M calcium solution added rapidly at the start of the experiment

** Not included in statistical average. Sample warmed by direct sunlight during titration. Starting temperature 26.7°C; temperature at nucleation 31.4°C. Sample temperature increased about 0.5°C per minute during the 9.75-min titration

optical microscopy of particles formed during the nucleation experiments also confirmed formation of calcium carbonate.

Mean calcium solution volume causing turbidity in a 100-mL aliquot of PL surface-water samples was 2.13 mL with a standard deviation of 0.12 mL. One standard deviation confidence levels for the volume needed to cause nucleation are 2.01–2.25 mL (Table 4). At nucleation, the PL surface water sample became turbid, titrant addition stopped, and sample pH, calcium concentration, alkalinity, and Ω decreased (Fig. 2).

Time to nucleation is determined by titrant addition rate and by induction time after each addition (see Reddy 1986 for induction time measurements on metastable calcium carbonate supersaturated solutions). Mean time to nucleation was 10 min (range from 9 to 11.6 min) for 10 samples with a standard deviation of 0.9 min. The difference between time to nucleation for filtered and unfiltered samples was not statistically significant at the 95% confidence level. More rapid titrant addition gave shorter nucleation times (7–10 min, mean 8.3 min, standard deviation 1.5 min, $n = 3$) and caused nucleation with a smaller calcium addition and a smaller Ω at nucleation (70–80).

Carbon dioxide partial pressure of PL surface water varies during the calcium titration. For example, the sample PL-1 had a carbon dioxide partial pressure of 645 mbar at the start of the titration. This value is greater than the atmospheric value and suggests that PL surface water will outgas carbon dioxide. At the point of nucleation, solution pH decreased from 9.08 to 9.0 and solution carbon dioxide partial pressure increased to 741 mbar. At the

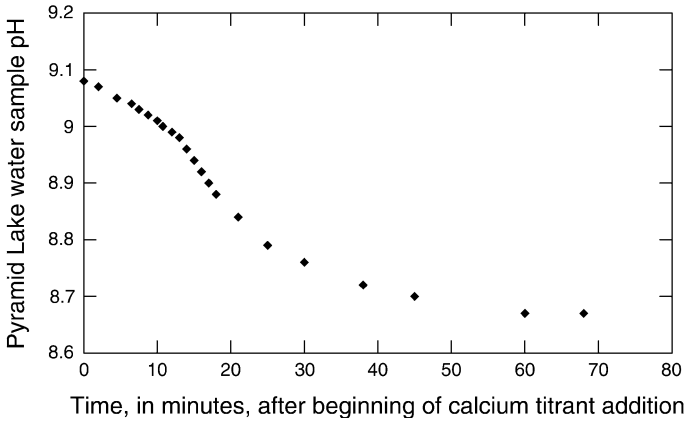

Fig. 2 Pyramid Lake surface-water pH during a titration of a 100 mL PL surface-water sample (PL-1) with 0.1 M calcium chloride solution plotted versus time. Nucleation occurred and calcium addition stopped 9 min after the start of calcium addition

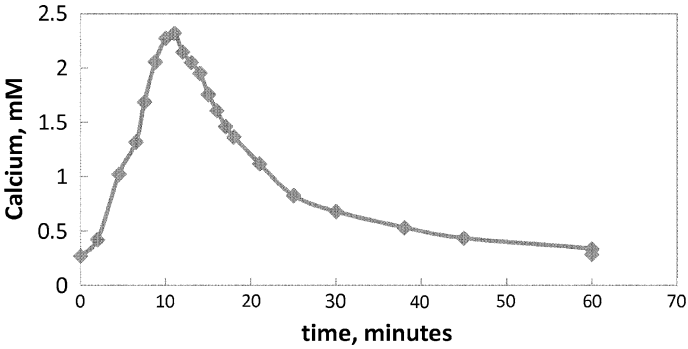

Fig. 3 Calcium concentration (in mM) during a titration of a 100 mL PL surface-water sample (PL-1) with 0.1 M calcium chloride solution plotted versus time in minutes. Calcium concentration increases until carbonate nucleation occurs and then decreases

termination of the experiment, solution pH is 8.66 and solution carbon dioxide partial pressure is 1,700 mbar. This value is well above the atmospheric value. Calculated carbon dioxide partial pressure (using PHREEQC) of the PL surface water used in the nucleation experiment solution at the start of the titration is about twice the atmospheric value and increases to about five times the atmospheric value at the end of the nucleation experiment.

4.3 Calcium Concentration in PL Surface Water at Nucleation

Calcium addition to PL surface water increases calcium concentration to the point of calcium carbonate nucleation (Fig. 3) and then calcium concentration decreases. In one experiment, calcium concentration decreased from 2.32 mM (Experiment PL1, Table 4) at nucleation to 0.45 mM 49 min after nucleation, and to 0.30 mM 67 min after nucleation. In a second experiment, calcium concentration decreased from 2.23 mM (Experiment PL2, Table 4) at nucleation to 0.32 mM 70 min after nucleation. Mean PL surface-water calcium concentration at nucleation was 2.33 mM for ten samples (standard deviation of

0.12 mM). This value is nine times the initial calcium concentration in the PL surface-water sample (0.271 mM).

Calcium concentration initiating calcium carbonate nucleation in PL surface water during August in each of the 3 years was reliable and reproducible. Mean calcium concentration causing calcium carbonate nucleation in filtered PL surface-water sample is 2.41 mM (standard deviation of 0.10 mM, $n = 5$), whereas the mean of 5 unfiltered PL surface-water samples (including the particle amended experiments) is 2.25 mM (standard deviation 0.09 mM). The results of an unpaired t test comparing the filtered and unfiltered sample calcium concentration at nucleation gave $t = 2.65$ (standard deviation of 0.1 mM, $n = 10$). The P value of this result is 0.029 (significant at the 95% confidence level), suggesting that unfiltered samples required a lower calcium concentration to cause nucleation—particles larger than the filter pore size facilitate calcium carbonate nucleation in PL surface water.

4.4 Nucleation Ω

In titration experiments, the starting mean Ω was 14 ± 2 for 10 samples. Added titrant increased Ω from the initial value to the Ω at carbonate nucleation (Fig. 4). Following nucleation, alkalinity, calcium, pH, and Ω decrease. For example, 1 h after nucleation experiment PL-1 has a Ω value of less than 10 (Fig. 4). Mean Ω at nucleation is 109 (range = 99–123, $n = 10$, with a standard deviation of 8). The range of Ω values one standard deviation above and below the mean Ω value is 101–115. High Ω values required for calcium carbonate nucleation in PL surface water implies nucleation and crystal growth rate inhibition by dissolved substances present in PL surface water (in addition to magnesium ion, Reddy 1995). Variation in Ω at nucleation may reflect variability in calcium carbonate crystal-growth inhibitor concentrations in PL surface water. Reddy and Leenheer (2011) demonstrate that fulvic acid isolated from Big Soda Lake, an alkaline, high-pH lake near Fallon, Nevada, is an effective calcite growth-rate inhibitor at low milligram per liter concentrations.

Nucleation Ω was reliable and reproducible. Mean PL surface-water nucleation Ω for five filtered samples is 112 (standard deviation of 9). Two of five filtered samples have nucleation Ω above the mean value of all samples. Mean Ω for five unfiltered samples (including two particle-amended experiments) is 107 (standard deviation of 8). A t test comparing the Ω nucleation for filtered and unfiltered samples gave $t = 2.66$ ($n = 10$). The difference between the filtered and unfiltered samples is

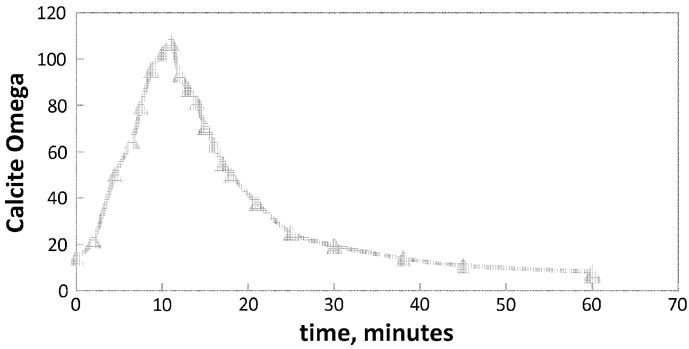

Fig. 4 Plot of estimated Ω for a titration of a 100 mL PL surface-water sample (PL-1) with 0.1 M calcium chloride solution versus time in minutes. Ω increases to calcium carbonate nucleation and then decreases

significant at the 0.05 probability level. As PL surface water Ω approaches values near 110, nucleation occurs with a concomitant increase in sample turbidity. Nucleation caused by increased Ω indicates that calcium carbonate formation will also occur by increasing terms in the IAP (i.e., carbonate and/or increasing both calcium and carbonate concentrations).

PL calcium carbonate nucleation requires Ω greater than Ω in laboratory nucleation experiments with well-controlled conditions and metastable supersaturated solutions. For example, metastable supersaturated solutions with Ω values in the range of 10–20 typically have induction times of 10 min (Reddy 1986). Persistent high Ω values in PL surface water suggest that nucleation and growth rate inhibitors, in addition to magnesium ion (Reddy 1995), are present in PL surface water.

4.5 Calcium Carbonate Formation Rates

Calcite crystallization-growth rates follow an empirical rate law of the form

$$\text{Rate} = k(\Omega - 1)^n \tag{1}$$

where "k" and "n" are constants (Nancollas and Reddy 1971; Reddy 1986).

Calcium carbonate formation rates measured in PL nucleation experiments follows a similar equation.

$$\text{Rate}(\text{in}\,\Delta\,\text{mM}/\Delta\,\text{min}) = A\,\Omega + B \tag{2}$$

where A and B are constants and $n = 1$.

A least squares best fit of the data from $\Omega = 75$ to $\Omega = 8$ (ten measurements) for the nucleation experiment PL-1 gives

$$\text{Rate}\,(\Delta\,\text{mM}/\Delta\,\text{min}) = -0.0026\,\Omega + 0.0175\,(r = 0.904) \tag{3}$$

The rate equation relation is significant at greater than the 0.01 confidence level, and the statistical significance is evidence for the applicability of this equation for description of calcium carbonate nucleation and growth in PL surface water. During the PL nucleation experiments, crystal mass increases and precipitate specific surface area changes. The constant A, which is proportional to the reaction rate constant (k) and the surface area available for growth (s, in m^2/gm), suggests that complimentary changes in k and s occur during calcium carbonate formation. Constants A and B in Eq. 2, after rearrangement, give Ω at zero calcium carbonate formation rate. At zero rate

$$\text{Rate} = 0 = -0.0026\,\Omega + 0.0175 \tag{4}$$

$$\Omega = 0.0175/0.0026 = 6.73 \tag{5}$$

This Ω value at zero growth rate is 6.73 times greater than the calcite equilibrium value and corresponds to the IAP of the final crystalline phase in the experiment.

At the onset of nucleation (Ω values from 100 to 84), calcium carbonate formation rates follow a similar expression (for three measurements)

$$\text{Rate} = -0.018\,\Omega + 0.0564\,(r = 0.928) \tag{6}$$

This relationship, not significant at the 0.1 significance level, suggests that initially a more soluble precursor carbonate forms in PL surface water at high Ω. The Ω at zero growth rate (31.3) is greater than the final value observed at lower Ω (i.e., 6.73), suggesting that the

initial phase formed at high Ω is unstable and transforms to the more stable final phase as the reaction proceeds.

4.6 Influence of Particles on Calcium Carbonate Nucleation

Particle influence on carbonate mineral nucleation in PL surface water (Arp et al. 1999) was examined using particle-amended filtered PL surface water (Experiments PL-5 and PL-7, Table 4). These experiments contrast with control nucleation experiments using filtered PL water (PL-4 and PL-6, Table 4). Mean calcium concentration at nucleation for two experiments done with added particles (Experiments PL-5 and PL-7, Table 4) was 2.33 ± 0.07 mM, while the mean for filtered control experiments (PL-4 and PL-6, Table 4) was 2.49 ± 0.09 mM. Mean Ω at nucleation for the two experiments done with added particles was 115 ± 2. In comparison, mean Ω for filtered control experiments was 121 ± 2. Both calcium concentration and Ω at nucleation are less than the values for filtered control experiments, supporting the hypothesis that particulate material present in PL surface water facilitates calcium carbonate nucleation. Nucleation experiments with added particles (PL-5 Ω at nucleation = 113; PL-7 Ω at nucleation = 117), were within one standard deviation of the mean value for all samples (mean, standard deviation, 109 ± 8).

Calcium carbonate formed in supersaturated PL surface water, in the presence and absence of particle amendments, had similar calcium carbonate crystal morphology—predominantly stubby orthorhombic prisms with oval, spherical, and twinned aragonite plates with aggregates of sub micrometer material (Fig. 5). Particle edge lengths were

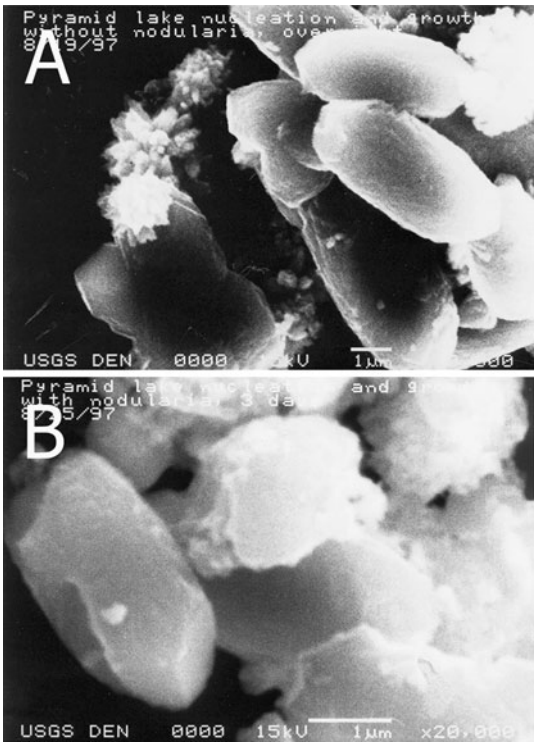

Fig. 5 Scanning electron microscopy images of calcium carbonate particles formed in a PL surface-water sample during nucleation experiments (Magnification bar shown on each figure). **a** Control experiment—nucleation in a filtered (0.1-um-pore-size filter) sample (Experiment PL-3, particles sampled after standing overnight) in the absence of algae; **b** Calcium carbonate nucleation in a filtered (0.1-um-pore-size filter) sample (Experiment PL-5, particles sampled 3 days after nucleation) with particle amended PL surface water

3–8 μm and sub micrometer particles aggregates are 1–3 μm in diameter. Optical microscopy of particles from nucleation experiments in 2000 and 2001 indicated particles found in all experiments were aragonite averaging about 3 μm in length with a few up to 5 μm. Similarity of carbonate particles formed in the presence (Fig. 5b) and absence of particles (Fig. 5a) demonstrates that particles present in PL surface water have little influence on nucleated calcium carbonate morphology and mineralogy.

Carbonate nucleation was measured in warmed PL surface water (NCL00 3, Table 4) (26.7–31.4°C at nucleation, about 0.5°C per minute over the 10-min titration). The volume of titrant needed for nucleation (1.6 mL), the calcium concentration at nucleation (1.8 mM), and the Ω value at nucleation (75) for this experiment are below the average for these parameters measured using the standard procedure where temperature was constant during the titration. Calcium concentration and Ω at nucleation for the warmed experiment are below the three standard deviation values for the mean values of these parameters for the unheated experiments. Sample warming reduces the required calcium concentration and Ω needed for carbonate nucleation. Pyramid Lake surface water Ω increases slightly with temperature over the range of 25–30°C (Fig. 5 in Reddy 1995) and this increase in Ω is insufficient to explain the markedly enhanced nucleation in this warmed experiment.

4.7 Morphology of Calcium Carbonate Particles from Filtered PL Surface Water

Morphology and mineralogy of calcium carbonate formed during PL calcium addition experiments, and formed in PL surface water, are characteristic of mineral formation process in PL. Calcium carbonate particle morphology in a PL surface-water sample collected in the North Basin in August 2000 following a multi-year increase in PL-surface elevation (Fig. 6a) is similar to the carbonate particle morphology observed in the nucleation experiments (Fig. 5). The particle shown in Fig. 6a has similar morphology and major and minor diameters (4 and 2 μm) as the carbonate particles from the nucleation experiments (particle size range from 3 to 8 μm in diameter, Fig. 5), suggesting that it was formed in PL surface-water conditions similar to the nucleation experiment (i.e., high Ω). In contrast to the particle morphology shown in Fig. 6a, other particles collected in the same way, at the same location and on the same date (Fig. 6b–d) display morphology characteristics similar to calcite precipitated in laboratory experiments at low Ω. Calcite rhombohedral particles shown in Fig. 6b (14–20 μm edge length) have jagged edges suggesting erosion of the particles. Particles in Fig. 6c, d are smaller calcite rhombs with regular sharp edges (length of 4–6 μm). Particles shown in Fig. 6b, c, d may form in locations where PL lake water is mixing with lower magnesium-containing spring water leading to the formation of calcite at intermediate Ω. Carbonate particle morphology variations shown in Fig. 6 may be due to different mineral formation processes occurring at different times or in different areas of PL surface water. Aragonite precipitation occurs in most parts of the lake, whereas calcite precipitates near underwater springs; algal organic matter and inorganic carbonate precipitation from lake water are the dominant sediment components in PL. Different combinations of source and distribution processes (Tenzer et al. 1997) affect sediments and their formation in surface waters in different parts of PL.

Carbonate particles from PL surface water exhibit varied morphology over time and location. For example, in contrast to particles collected on filters in August of 2000 (Fig. 6), large aragonite crystals (Fig. 7a) were present in near-shore surface-water sample collected during August of 1992 (following a multi-year decrease in PL surface elevation)

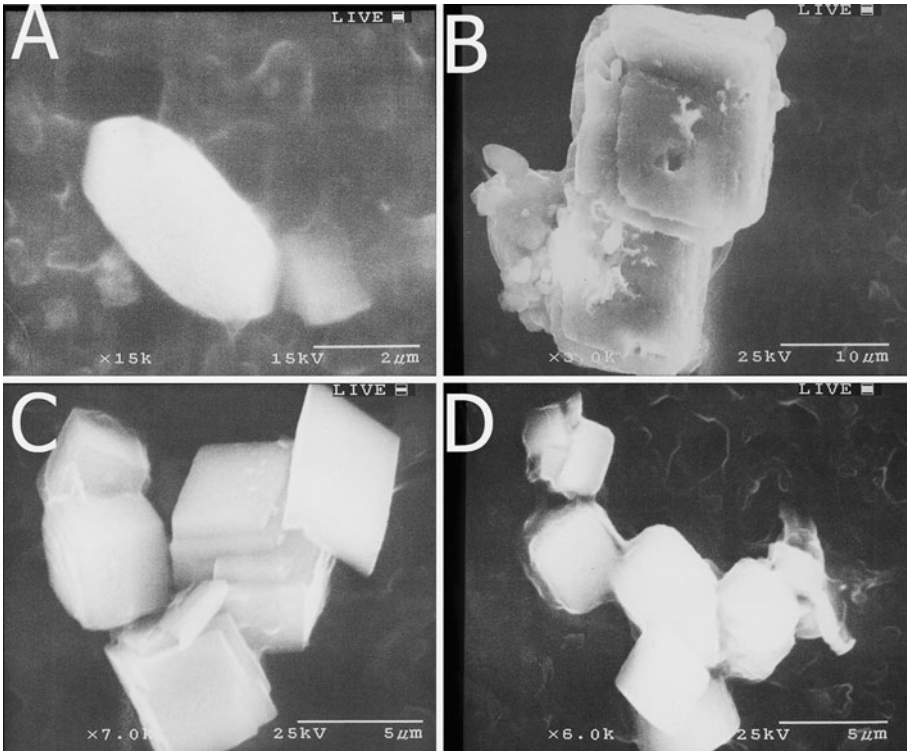

Fig. 6 SEM images of calcium carbonate particles in a (North Basin) PL surface-water sample collected during August 2000. **a** Aragonite particle, **b** calcite particle, **c** calcite particle, and **d** calcite particle

adjacent to the Natural Resources Building. Year-to-year changes in PL elevation and Ω may influence calcium carbonate mineral growth rates and crystal size. The 25-μm width and 75-μm length of one aragonite particle in Fig. 7a suggests that this particle formed by aragonite nucleation and growth at low Ω in the presence of calcite crystal-growth inhibitors because aragonite crystal size is related to the Ω value in the growth solution. In solutions containing sufficient magnesium concentration to inhibit calcite growth, high Ω favors formation of small aragonite crystals, while at lower Ω larger aragonite crystals form. Aragonite crystals of the size exhibited in Fig. 7a form in low Ω solutions (Reddy and Nancollas 1976). Additional calcium carbonate particles collected in August 1992 (Fig. 7b, c) have smaller size than the aragonite crystals shown in Fig. 7a. Near-shore particles (Fig. 7b, c) have edge lengths of 20–25 μm and the mid-lake particle has edge length of 6–8 μm. Aragonite occurrence and persistence in PL surface water is due to the high concentrations of magnesium ion present in PL surface water (Table 2) (Reddy 1986, 1995). All PL surface water carbonate particles exhibit EDAX spectra characteristic of calcium carbonate. Particle morphology from SEM micrographs indicates that PL surface-water carbonate particles are calcite and aragonite.

Carbonate particle morphology observed in the calcium-addition experiments (Fig. 5) differed from particle morphologies associated with calcium carbonate formed in pure solutions (Reddy 1986; Kile et al. 2000). Morphological differences between calcium carbonate nucleation in pure solutions and nucleation in PL surface water suggests the

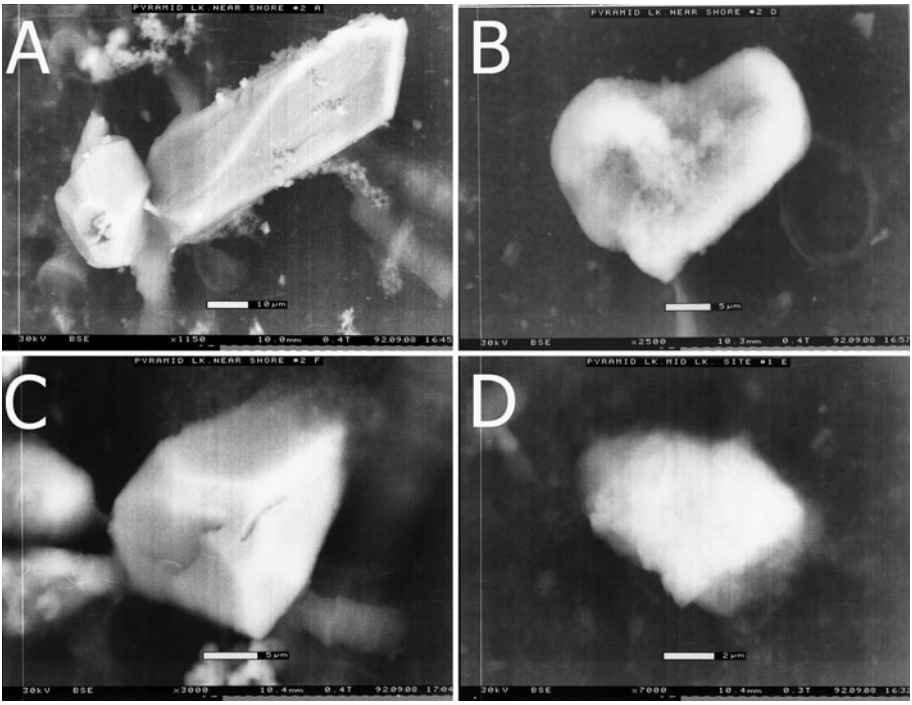

Fig. 7 Calcium carbonate particles from PL surface-water samples collected near shore at the Natural Resource Building (August 1992) (**a**, **b**, and **c**) and from a mid-lake location (**d**)

presence of multiple crystal-growth rate–inhibiting substances, in addition to magnesium ion, in PL surface water. Calcite growth morphology in the presence of a single growth rate–inhibiting substance, such as a polycarboxylic acid, exhibits discontinuous growth layers on the mineral surface (Reddy and Hoch 2001). In contrast, precipitates formed in highly supersaturated PL surface water with or without added algae do not exhibit discontinuous growth layers.

Calcite rhombs, with a 5-μm edge length and a narrow size distribution and/or vaterite are formed in low Ω, magnesium-free solutions (Kile et al. 2000). Calcium carbonate particle morphology differences observed for particles formed during PL nucleation experiments (Fig. 5) and in PL surface water in comparison (Figs. 6, 7) with calcite rhombs produced in laboratory experiments suggests the presence of multiple crystal nucleation and growth inhibiting substances in PL. In support of this hypothesis, Didymus et al. (1993) report that low molecular weight and macromolecular organic additives influence the morphology of calcium carbonate formed from supersaturated solutions. Moreover, elevated dissolved organic carbon (DOC) concentrations in PL surface water (e.g., 10 mg/L DOC, Hamilton-Galat and Galat 1983) are consistent with DOC in PL surface water reducing calcium carbonate nucleation and crystal growth rates and influencing calcium carbonate particle morphology in PL surface water (Reddy and Hoch 2000).

Other investigators suggest dissolved organic substances mediate and/or modify calcium carbonate reaction rates in surface water and groundwater. Plummer et al. (2000) report calcite growth inhibition by DOC in a natural system near calcite equilibrium.

Numerous dissolved organic and inorganic substances reduce calcite growth rates at low concentrations (microgram to milligram per liter concentrations) in the supersaturated solution (Reddy and Nancollas 1973; Reddy 1975, 1977, 1978, 1986, 1995; Reddy and Nancollas 1976; Reddy and Wang 1980; Reddy and Hoch 2000, 2001; Reddy and Leenheer 2011). Growth rate inhibition depends on chemical functionality and structure. Interaction of growing calcium carbonate minerals with crystal growth-rate inhibiting substances influences crystal size, crystal morphology, and mineral polymorphic composition (Reddy and Hoch 2000, 2001; Leenheer and Reddy 2008). Recently, De Yoreo and Dove (2004) proposed that interactions between organic growth rate modifiers and edges of individual steps on existing crystal faces modify crystal growth morphology.

5 Conclusions

Pyramid Lake surface water has consistently high Ω values (i.e., 10–16). Aragonite single crystals, suspended in PL surface water for varying lengths of time, verified the absence of calcium carbonate growth in supersaturated PL surface water. However, increasing PL calcium concentration and Ω allowed reproducible determination of calcium concentration and Ω needed for calcium carbonate nucleation and crystal growth. Mean PL surface-water calcium concentration at nucleation (2.33 mM ($n = 10$) with a standard deviation of 0.12 mM) is about nine times the ambient PL surface-water calcium concentration (0.26 mM); mean Ω (109 with a standard deviation of 8) is about eight times the PL surface-water Ω at the start of the titration experiment.

Calcium concentration and Ω at nucleation differed between filtered and unfiltered PL water at two sites over 3 years—unfiltered samples nucleated at lower calcium concentration and lower Ω than filtered samples. At nucleation, in the presence of added particles, calcium concentration and Ω were less than the values for the filtered control experiment, but the difference was within one standard deviation of the mean values for all samples. Calcium carbonate particles formed in the presence and absence of PL surface water particles had similar morphology. Calcium carbonate formation rates follow a simple rate expression. The best-fit rate equation is statistically significant at greater than the 0.01 confidence level and gives after rearrangement $\Omega = 6.7$ at zero rate. Differences in calcium carbonate particle morphology between nucleation and crystal growth in pure solutions suggest that multiple dissolved inhibiting substances mediate calcium carbonate formation in PL. However, there is insufficient information to determine the chemical nature of all calcium carbonate nucleation and crystal growth inhibitors present in PL surface water.

Acknowledgments The authors acknowledge help and encouragement of the PL Paiute Tribal Council and the PL Natural Resource Building staff during this work. Fieldwork was done with the assistance of David Fellenz (a USGS Volunteer, Lawrence University, Appleton, WI), Micaela Reddy (USGS Volunteer, Denver, CO), Julie Reddy (USGS Volunteer, Denver, CO), and Paul Schuster (USGS, NRP, CB, Boulder, CO). George Molino of Cutthroat Charters, Reno, NV, and Dan Mosley of the Pyramid Lake Piaute Tribe Environmental Department, Nixon, NV facilitated lake-water sampling logistics. Scott Charlton (USGS, NRP, BRR, CB, Denver, CO) assisted in data analysis and chemical speciation calculation. Charmaine Gunther (USGS, NRP, CB, Denver, CO) assisted in the preparation of the report. Review comments by David Parkhurst (USGS, NRP, CB, Denver, CO) and David Naftz (USGS, WRD, Salt Lake City, UT) and an anonymous reviewer significantly improved the manuscript. Anthony Hoch held a National Research Council-USGS Research Fellowship during this research. Funding for the work is by the USGS, NRP. The use of trade names and product names in this paper is for identification purposes only, and does not constitute endorsement by the USGS.

References

Addadi L, Raz S, Weiner S (2003) Taking advantage of disorder: amorphous calcium carbonate and its roles in biomineralization. Adv Mater 15:959–970

Arp G, Thiel V, Reimer A, Michaelis W, Reitner J (1999) Biofilm exopolymers control microbialite formation at thermal springs discharging into the alkaline Pyramid Lake, Nevada, USA. Sediment Geol 126:159–176

Bischoff JL, Stine S, Rosenbauer RJ, Fitzpatrick JA, Stafford TW Jr (1993) Ikaite precipitation by mixing of shoreline springs and lake water, Mono Lake, California, USA. Geochim Cosmochim Acta 57:3855–3865

Chave K, Seuss E (1970) Calcium carbonate supersaturation in seawater: effects of dissolved organic matter. Limnol Oceanogr 15:633–637

Cloud PE Jr (1962) Environment of calcium carbonate deposition west of Andros Island, Bahamas. U.S. Geol. Surv Professional Paper 350, p 138

De Yoreo JJ, Dove PM (2004) Shaping crystals with biomolecules. Science 306:1301–1302

Dean WE, Fouch TD (1983) Lacustrine environment. In: Scholle PA, Bebout DG, Moore CH (eds) Carbonate depositional environments, AAPG Memoir 33. The American Association of Petroleum Geologists, Tulsa, pp 98–130

Didymus JM, Oliver P, Mann S, DeVries AL, Hauschka PV, Westbroek P (1993) Influence of low-molecular-weight and macromolecular organic additives on the morphology of calcium carbonate. J Chem Soc Faraday Trans 89:2891–2900

Diehl H (1964) Calcein, calmagite, and *o, o′*-dihydroxyazobenzene. Titrimetric, colorimetric, and fluorometric reagents for calcium and magnesium. The G. Frederick Smith Chemical Company, Columbus

Dittrich M, Obst M (2004) Are picoplankton responsible for calcite precipitation in lakes? Ambio 33:553–558

Galat DL, Jacobsen RL (1985) Recurrent aragonite precipitation in saline-alkaline Pyramid Lake, Nevada. Arch Hydrobiol 105:137–159

Hamilton-Galat K, Galat DL (1983) Seasonal variation of nutrients, organic carbon, ATP, and microbial standing crops in a vertical profile of Pyramid Lake, Nevada. Hydrobiologia 105:27–43

He S, Kan AT, Tomson MB (1999) Inhibition of calcium carbonate precipitation in NaCl brines from 25 to 90°C. Appl Geochem 14:17–25

Herman JS (1989) A geochemical model of calcite precipitation and CO_2 outgassing in karst streams. In: Miles DL (ed) Water-Rock Interaction, WRI-6. Balkema, Rotterdam, pp 301–304

Herman JS, Lorah MM (1988) Calcite precipitation rates in the field: measurement and prediction for a travertine-depositing stream. Geochim Cosmochim Acta 52:2347–2355

Higgins JA, Fischer WW, Schrag DP (2009) Oxygenation of the ocean and sediments: consequences for the seafloor carbonate factory. Earth Planet Sci Lett 284:25–33

Hodell DA, Schelske CL, Fahnenstiel GL, Robbins LL (1998) Biological induced calcite and its isotopic composition in Lake Ontario. Limnol Oceanogr 43:187–199

Kelts K, Hsü KJ (1978) Freshwater carbonate sedimentation. In: Lerman A (ed) Lakes: chemistry, geology, physics, chapter 9. Springer, New York, pp 294–323

Kile DE, Eberl DD, Hoch AR, Reddy MM (2000) An assessment of calcite crystal growth mechanisms based on crystal size distributions. Geochem Cosmochim Acta 64:2937–2950

Lebo ME, Reuter JE, Rhodes CL, Goldman CR (1993) Pyramid Lake, Nevada water quality study 1989-1993. Volume II. Limnological Description. University of California, Davis

Leenheer JA, Reddy MM (2008) Co-precipitation of dissolved organic matter by calcium carbonate in Pyramid Lake, Nevada. Ann Environ Sci 2:11–25

McConnaughey TA, LaBaugh JW, Rosenberry DO, Striegl RG, Reddy MM, Schuster PF, Carter V (1994) Carbon budget for a groundwater-fed lake: calcification supports summer photosynthesis. Limnol Oceanogr 39:1319–1332

McKenzie JA (1982) Carbon-13 cycle in Lake Greifen: a model for restricted ocean basins. In: Schlanger SO, Cita MB (eds) Nature and origin of cretaceous carbon-rich facies. Academic Press, Harcourt Brace Jovanovich, London, pp 197–207

Nancollas GH, Reddy MM (1971) The crystallization of calcium carbonate II. Calcite growth mechanism. J Colloid Interf Sci 37:824–830

Nancollas GH, Reddy MM (1974) The kinetics of crystallization of scale-forming minerals. Soc Petrol Eng J 14:117–126

Otsuki A, Wetzel RG (1974) Calcium and total alkalinity budgets and calcium carbonate precipitation of a small hard-water lake. Arch Hydrobiol (74):14–30

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey, Water-Resources Investigations Report 99-4259, 312 p

Plummer LN, Busenberg E, Riggs AC (2000) In situ growth of calcite at Devils Hole, Nevada: comparison of field and laboratory rates to a 500,000 year record of near-equilibrium calcite growth. Aquat Geochem 6:257–274

Reddy MM (1975) Kinetics of calcium carbonate formation. Proc Int Assoc Theor Appl Limnol 19:429–438

Reddy MM (1977) Crystallization of calcium carbonate in the presence of trace concentrations of phosphorus-containing anions I. Inhibition by phosphate and glycerophosphate ions at pH 8.8 and 25°C. J Cryst Growth 41:287–295

Reddy MM (1978) Kinetic inhibition of calcium carbonate formation by wastewater constituents. In: Rubin AJ (ed) The chemistry of waste-water technology (Chapter 3). Ann Arbor Science Publishers, Inc., Ann Arbor, pp 31–58

Reddy MM (1986) Effect of magnesium ion on calcium carbonate nucleation and crystal growth in dilute aqueous solutions at 25°C. In: Mumpton FA (ed) Studies in digenesis. U.S. Geological Survey Bulletin 1578, Denver, pp 169–182

Reddy MM (1995) Carbonate precipitation in Pyramid Lake, Nevada. In: Amjad Z (ed) Mineral scale formation and inhibition. Plenum Press, New York, pp 21–32

Reddy MM, Hoch AR (2000) Calcite crystal growth rate inhibition by aquatic humic substances. In: Amjad Z (ed) Advances in crystal growth inhibition technologies. Kluwer, New York, pp 107–121

Reddy MM, Hoch AR (2001) Calcite crystal growth rate inhibition by polycarboxylic acids. J Colloid Interf Sci 235:365–370

Reddy MM, Leenheer J (2011) Calcite growth rate inhibition by fulvic acids isolated from Big Soda Lake, Nevada, USA, the Suwannee River, Georgia, USA, and by Polycarboxylic Acids. Ann Environ Sci 5:41–53

Reddy MM, Nancollas GH (1973) Calcite crystal growth inhibition by phosphonates. Desalination 12:61–73

Reddy MM, Nancollas GH (1976) The crystallization of calcium carbonate IV. The effect of magnesium, strontium, and sulfate ions. J Cryst Growth 35:33–38

Reddy MM, Wang KK (1980) Crystallization of calcium carbonate in the presence of metal ions. I. Inhibition by magnesium ion at pH 8.8 and 25°C. J Cryst Growth 50:470–480

Reddy MM, Schuster PF, Harte JJ (1989) Summary of data from onsite and laboratory analyses of precipitation runoff from carbonate-stone surfaces. National Acid Precipitation Assessment Program, June 1984 to November 1987, U.S. Geological Survey Open File Report, 89-246, 19 p

Reynolds RC Jr (1978) Polyphenol inhibition of calcite precipitation in Lake Powell. Limnol Oceanogr 23:585–597

Rosen MR, Arehart GB, Lico MS (2004) Exceptionally fast growth rate of <100-yr-old tufa, Big Soda Lake, Nevada: Implications for using tufa as a paleoclimate proxy. Geology 32:409–412

Runnells DD (1969) Diagenesis, chemical sediments, and the mixing of natural water. J Sediment Petrol 39:1188–1201

Sarmiento JL, Gruber N (2006) Ocean biogeochemical dynamics. Princeton University Press, Princeton, p 503

Schuster PF, Reddy MM, LaBaugh JW, Parkhurst RS, Rosenberry DO, Winter TC, Antweiler RC, Dean WE (2003) Characterization of lake water and ground water movement in the littoral zone of Williams Lake, a closed-basin lake in north-central Minnesota. Hydrol Process 17:823–838

Tenzer GE, Meyers PA, Knoop P (1997) Sources and distribution of organic and carbonate carbon in surface sediments of Pyramid Lake, Nevada. J Sediment Res 67:884–890

Wetzel RG, White WS (1985) Alteration of iron-$CaCO_3$ precipitation by yellow organic acids of aquatic angiosperm origin. Arch Hydrobiol 104:247–251

Weyl PK (1961) The carbonate saturometer. J Geol 69:32–44