

# CARBONATE PRECIPITATION IN PYRAMID LAKE, NEVADA

## Probable Control by Magnesium Ion

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### ABSTRACT

Magnesium ion inhibition of calcium carbonate (calcite) formation explains present day controls on carbonate formation in Pyramid Lake. Concentrations of magnesium ion are sufficient to reduce calcium carbonate nucleation rates and calcite formation rates in present-day supersaturated lake water. Calcium carbonate nucleation and crystal growth measurements in the presence of magnesium ion are consistent with whole-lake whiting and carbonate mound formation in and around Pyramid Lake.

### INTRODUCTION

Calcium carbonate mineralization occurs in hardwater lakes of the United States and elsewhere.<sup>1-4</sup> Pyramid Lake, Nevada, a present-day lake remnant of paleolake Lahontan, in contrast to other hardwater lakes, has unique physical and chemical characteristics which modify in-lake calcium carbonate mineralization (Figures 1 and 2).<sup>5-8</sup> Other high-salinity and high-alkalinity lakes in this region of the Great Basin are remnants of paleolakes Lahontan (Walker Lake) or Russell (Mono Lake) (Figure 1). Like Pyramid Lake, Walker Lake and Mono Lake exhibit unusual carbonate mineralization.

An ongoing research question involving carbonate mineralization reactions in surface waters, with significance in the areas of global carbon budgets and global warming, concerns the appearance of massive amounts of suspended calcium carbonate in surface waters (whittings).<sup>9-13</sup> Much concerning the nature of whittings remains uncertain. Pyramid Lake appears to be an appropriate location to investigate the mechanism of whiting formation and the water conditions that cause whittings to happen. Carbonate mineralization processes in specific lakes and lake basins depend strongly on a number of geochemical and biological factors. To investigate specific processes, such as calcium carbonate precipitation within a water column, it is useful to study lakes where these processes are well developed.

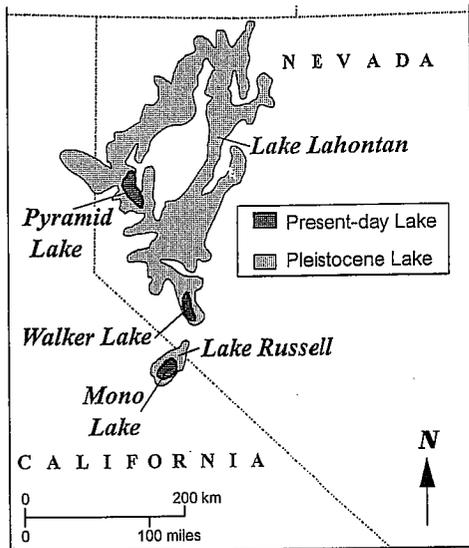


Figure 1. Remnant highly-saline, highly-lakes, Pyramid Lake, Walker Lake, and Mo and the paleolakes Lake Lahontan and Lake (Redrawn from Bishoff et al., 1993).

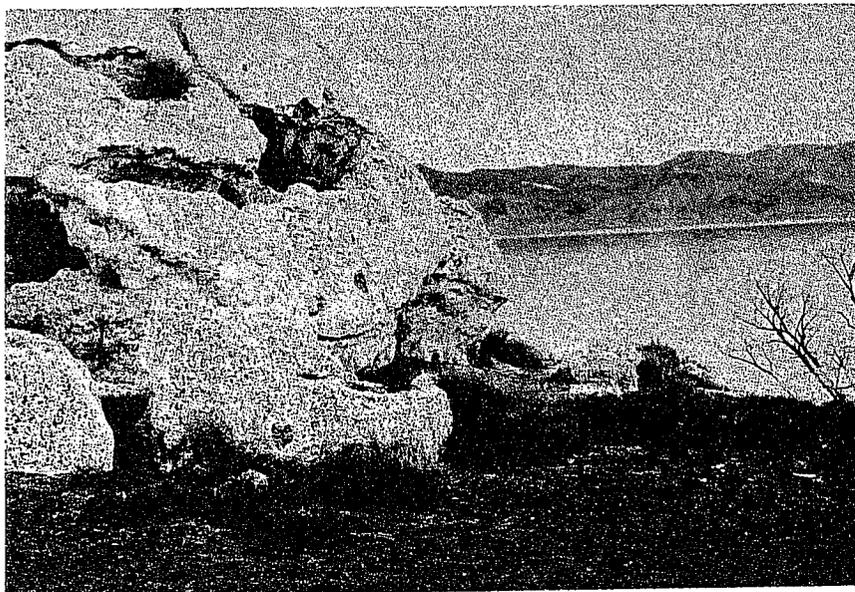


Figure 2. View of Pyramid Lake from the shore (Photograph by author, 1992). Characteristic large mounds are on the left and are well above the present lake level. A tree close to the present lake scale.

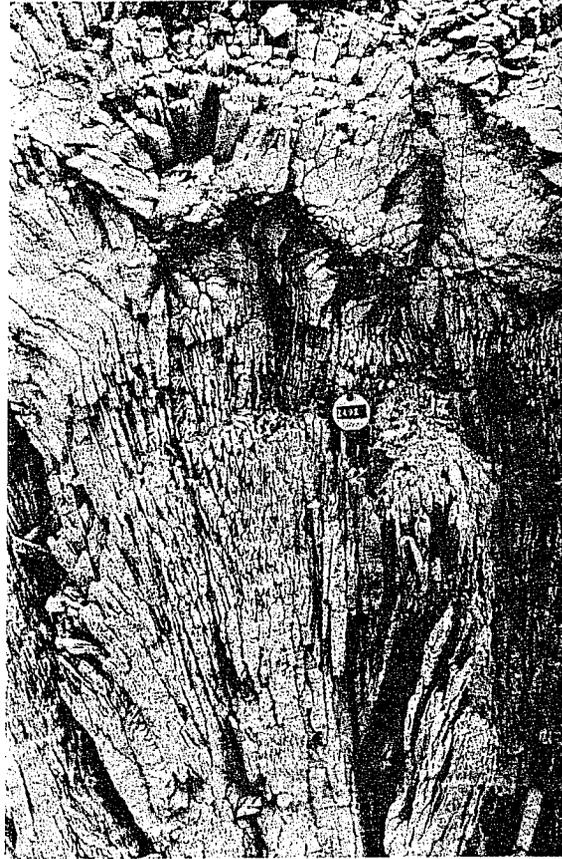


Figure 3. A cross-section of a carbonate mound along the shore of Pyramid Lake exhibiting the characteristic radial distribution of crystals found near the mound center. The key at the center of the photo is about one inch in diameter (photograph by author, 1992).

Calcium carbonate mineralization in Pyramid Lake differs from carbonate formation in less-saline, less-alkaline lakes in several respects, including:

- The occurrence of large carbonate mounds in the near-shore region (Figures 2 and 3)
- The formation of a less stable form of calcium carbonate (aragonite) rather than the thermodynamically stable polymorph calcite.<sup>14</sup>
- The occurrence of massive calcium carbonate precipitation episodes, whittings, throughout the Pyramid Lake water column.<sup>14</sup>

Carbonate mineralization at Pyramid Lake, from analogy to laboratory studies of calcium carbonate formation, is regulated by specific chemical factors:

- Water column supersaturation,
- Carbonate mineral nucleation and crystal growth rates, and
- The presence of inhibitors such as magnesium and phosphate ions.<sup>1,15,16,17,18,19,20</sup>

The working hypothesis of this paper is that Pyramid Lake magnesium ion concentrations control calcium carbonate formation rates. Laboratory and in-lake calcium carbonate formation studies at Pyramid Lake are in progress to test this hypothesis. Field studies were

## PURPOSE

This report outlines calcium carbonate nucleation and crystal growth kinetics in the presence and absence of magnesium ion. From analogy with these laboratory measurements it is reasonable to consider that carbonate nucleation (homogeneous nucleation from supersaturated lake water) and crystallization (crystal growth at a mineral surface from a metastable supersaturated solution)<sup>22</sup> are the basis for carbonate formation in the Pyramid Lake Basin. Nucleation leads to whittings; crystallization leads to carbonate mound formation.

## SCOPE

Discussion in this report will be limited to laboratory studies dealing with nucleation and crystal growth of calcium carbonate in the presence and absence of magnesium ion at 25°C. Summaries of Pyramid Lake water chemical analyses used here are published data.<sup>23,24</sup> The average Pyramid Lake alkalinity calculated using the published data of Benson agrees well with the recently measured lake alkalinity.<sup>25</sup> A survey of carbonate deposits in the Pyramid Lake Basin is available.<sup>25</sup>

## BACKGROUND

Calcium carbonate formation in a test tube or in a lake is initiated by nucleation, involving formation of unstable polymorphs and hydrates.<sup>22</sup> Unstable calcium carbonate polymorphs will ultimately transform to calcite, the thermodynamically stable form of calcium carbonate at standard temperature and pressure. Unstable polymorphs may persist in solution for extended intervals in the presence of substances (termed "inhibitors") which inhibit the formation of a thermodynamically more-stable phase. Typical inhibitors include magnesium and phosphate ions, both of which reduce calcite formation rates.<sup>22</sup> Solution temperature influences formation of unstable calcium carbonate polymorphs and subsequent transformation. Calcite forms at 25 °C in inhibitor-free solutions with moderate supersaturations (supersaturation values of 10 to 20). Calcite formation in the presence of magnesium ion enhances the formation of unstable calcium carbonate polymorphs. Natural waters which have unusual solution compositions (i.e., high concentrations of magnesium or phosphate ions) often form unstable calcium carbonate polymorphs. Calcium carbonate nucleation rates differ among polymorphs and hydrates; nucleation rates increase dramatically with increasing calcium carbonate solution supersaturation (Figure 4.).

## CALCIUM CARBONATE NUCLEATION

A convenient measure of calcium carbonate nucleation is the time necessary to form a solid carbonate from a supersaturated solution. This time, referred to as "induction time," is measured by changes in solution light scattering and composition. Nucleation is difficult to characterize because of the presence of heterogeneous nucleation sites<sup>22</sup> because growth often accompanies nucleation.

Magnesium ion controls, in part, calcium carbonate induction times and nucleation. Induction times increase as the solution magnesium ion concentration and magnesium to calcium ion ratio increase (Figure 4). Average Pyramid Lake magnesium ion concentration (about  $4 \times 10^{-3}$  moles per liter, and magnesium-to-calcium ion ratio about 20) is sufficient to increase the calcium carbonate induction time and to reduce calcium carbonate nucleation (Figure 4). For supersaturation of 25, changing solution magnesium to calcium ratios 0-1 roughly doubles the induction time. At lower supersaturations (i.e., about 20) or at high magnesium-to-calcium ion ratios, induction times were about three times that of the magnesium free solution. Elevated lakewater magnesium concentration increases calcium carbonate induction times, reducing nucleation rates. Removal of the magnesium ion from lake water due to calcium carbonate nucleation (as a mixed calcium-magnesium carbonate) increases the nucleation rates.

Magnesium ion content and polymorphic composition of nucleated calcium carbonate has been reported elsewhere.<sup>16</sup> Briefly, the predominate crystalline components of precipitate, over a range of magnesium ion concentrations and supersaturations, were vaterite and aragonite. Formation of calcite from the metastable solutions was retarded by magnesium ion. Some aged solutions containing low concentrations of magnesium ion developed calcite as a final precipitate. In these experiments, vaterite (which was initially formed) was transformed to calcite during the course of the experiment. Magnesium content of the nucleated carbonate phase was a function of nucleation and ripening conditions.<sup>16</sup> Magnesium ion content was greatest for the initial precipitate. As the precipitate aged, its magnesium ion content decreased.<sup>16</sup> Nucleation sensitivity to a solution calcium carbonate supersaturation has confounded past attempts to predict the onset and duration of whittings in Pyramid Lake.<sup>14</sup> Supersaturation is currently (1994) below the critical value for nucleation (10) except during summer (Figure 5). Supersaturations were calculated over a range of temperatures and calcium ion concentrations with WATEQ4F.<sup>26</sup> Temperatures varied from 0 to 25°C for both calcite and aragonite supersaturation (Figure 5). Maximum supersaturation for calcite (at 25°C) is above 10 while that for aragonite is less than 1. In the absence of magnesium ion, calcite would nucleate and grow in present-day Pyramid Lake water. However, since calcite formation is inhibited, lake supersaturations can increase to about 10. Lake whittings would be expected to occur only when the supersaturation with respect to aragonite is above 10.

## CALCIUM CARBONATE (CALCITE) CRYSTAL GROWTH

A seeded growth method has been used to characterize the rate of calcite formation from metastable supersaturated solutions. Crystal growth data has been interpreted using a parabolic rate equation which relates the crystal growth to the product of three terms: 1) the growth surface available for reaction; 2) the crystal growth rate constant; and 3) the square of the reaction driving force.<sup>16,22</sup> This rate law, which has a parabolic reaction driving force term indicating that the rate determining step is a surface reaction, allows a convenient representation of inhibitor ions influence on calcite formation rates.<sup>16,22</sup> During carbonate mound formation, the initial calcium carbonate polymorphs and their subsequent transformation are uncertain. Also, lake water and inflow spring water chemical compositions at the time of mound formation are not known. In this report, only the growth of calcite is considered. Additional studies of other polymorphs and hydrates are important for application of lake deposits in paleoclimate reconstruction partly because isotope fractionation factors may be regulated by the polymorphic composition of the carbonate deposits.

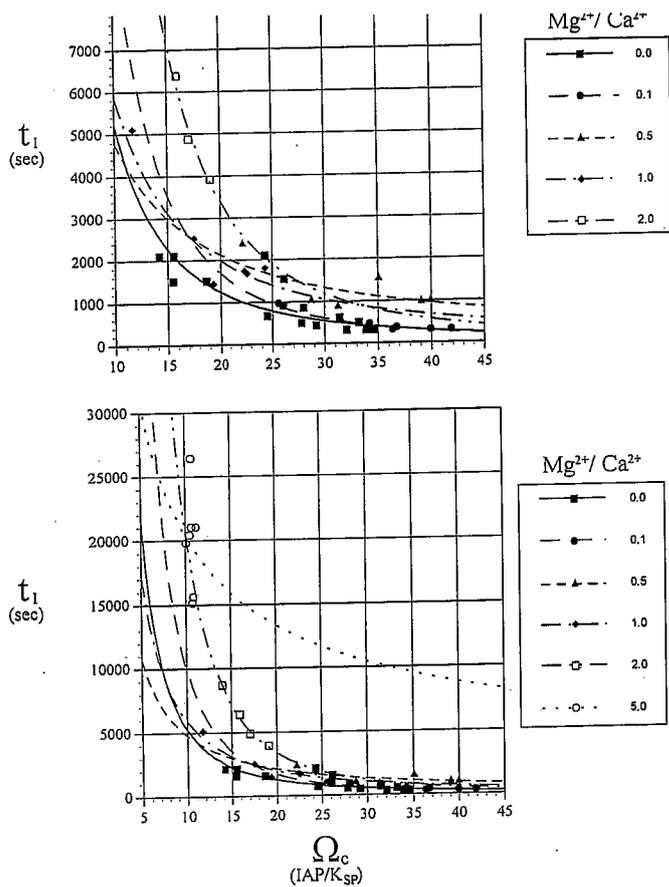


Figure 4. Calcium carbonate induction time, in seconds, plotted as a function of supersaturation for a solution containing 4 millimolar total carbonate ion concentration and a range of solution magnesium ion to calcium ion concentration ratios.<sup>16</sup> A. Induction times for solutions containing magnesium ion to calcium ion concentration ratios from 0 to 2. B. Induction times for solutions containing magnesium ion to calcium ion concentration ratios from 0 to 5.

Solution supersaturation, the solution variable directly controlling nucleation, defined as the ratio of the calcium carbonate ion activity product to the calcium carbonate (calcite) solubility product (details of the calculation are discussed in reference 16). Nucleation rate is inversely proportional to the induction time; as induction time increases, nucleation rate decreases.

As supersaturation values decrease to about 10, the time for calcium carbonate nucleation becomes large, and the nucleation rates become very small (Figure 4). Solutions with supersaturations less than 10 are termed "metastable". This designation implies that carbonate minerals will not form in such solutions without the presence of a suitable growth surface or substrate. In the presence of a carbonate surface, calcium carbonate may precipitate from a metastable solution. Carbonate mineral formation will continue until the solution reaches equilibrium (i.e., calcite saturation). In Pyramid Lake, carbonate mineral growth from metastable supersaturated solution formed large carbonate mounds (Figures 2 and :

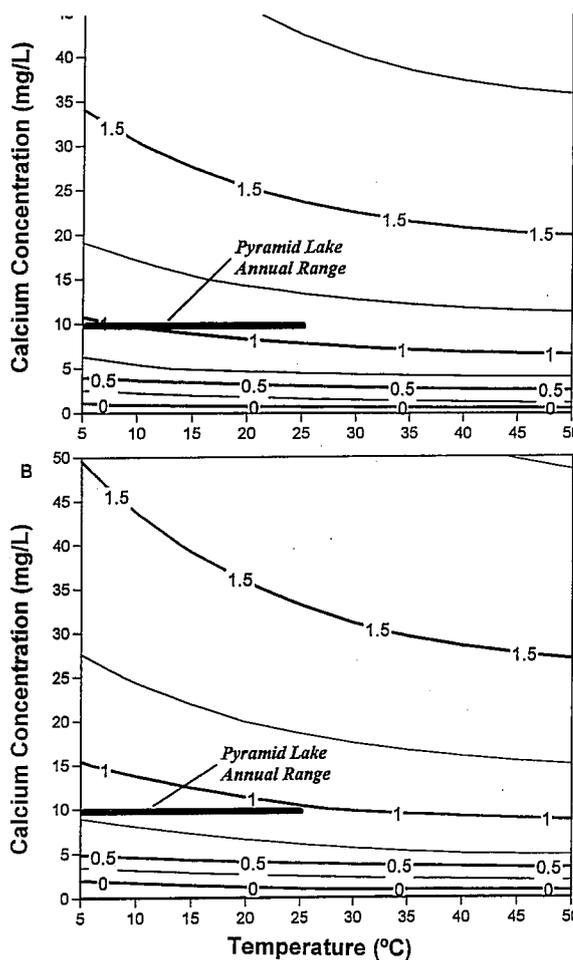


Figure 5. Saturation indices for Pyramid Lake, Log (Ion Activity Product/Solubility Product) calculated with WATEQ4F.<sup>26</sup> Supersaturation isopleths (in log units) are plotted as a function of lake water calcium concentration and temperature. The Pyramid Lake temperature range was 0 to 25°C. A) Saturation indices calculated with respect to calcite as the mineral phase. B) Saturation indices calculated with respect to aragonite as the mineral phase.

## CALCIUM CARBONATE FORMATION INHIBITORS

At a fixed calcium carbonate supersaturation level and temperature, inhibitor concentration levels regulate carbonate mineral polymorphic compositions and formation rates (Figure 6).<sup>15,27</sup>

Following nucleation, or in the presence of a suitable growth surface, calcium carbonate minerals form in supersaturated solution. Unlike calcite crystal growth on pure calcite seed crystals in magnesium-free solutions, calcite growth in solutions containing 10 moles per liter magnesium is dramatically reduced (Figure 6). As shown in Figure 6, for the solution containing 1 millimolar magnesium ion, neither solution pH nor calcium ion concentration decrease during the experiment. In the absence of magnesium ion, the solution rapidly approaches calcite equilibrium. Crystal growth is inhibited more than crystal nucleation by millimolar magnesium ion concentrations (compare Figure 6 with Figure 4 presumably because nucleation involves several polymorphs, only some of which are sensitive to magnesium ion growth inhibition).

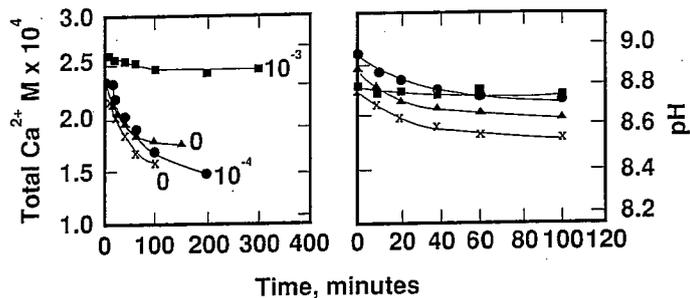
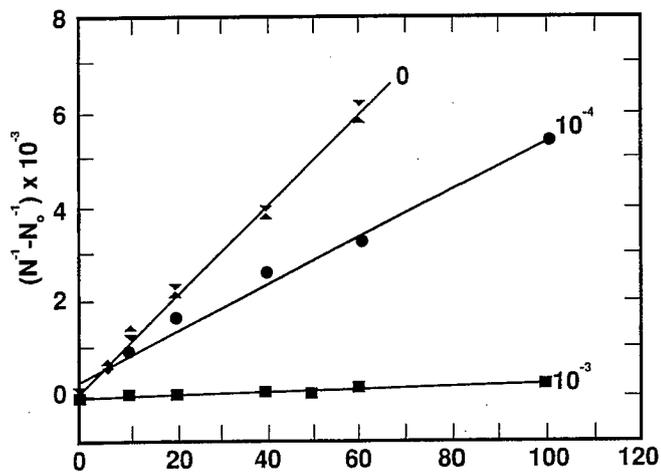


Figure 6. Total calcium concentration and pH of the supersaturated solution plotted as a function of time for seeded crystal growth in the presence and absence of added magnesium ion. Molar concentrations of added magnesium ions are indicated at the end of the curves.<sup>18</sup>

Inhibition of calcite growth by magnesium ion would be expected to occur in Pyramid Lake. The parabolic growth rate expression<sup>16</sup> describes the effect of magnesium ion concentration levels on calcite formation rates. Rate data for calcium carbonate seeded growth in the presence and absence of magnesium ion plotted as the integrated rate function versus time illustrates calcite growth rate reduction (Figure 7) by magnesium ion. Line slopes in Figure 7 are proportional to the calcite growth rate constant; the decrease in slope with increasing magnesium concentration demonstrates calcite growth rate reduction in solutions containing 10<sup>-3</sup> moles per liter magnesium ion. The Pyramid Lake average magnesium ion concentration is four times the highest magnesium ion concentration shown in Figure 7, and would thus be expected to strongly inhibit calcite growth. The carbonate polymorphs found in Pyramid Lake surface sediments and water is aragonite, not calcite.<sup>28</sup>

Calcite crystal growth reduction caused by magnesium ion is shown for a range of magnesium concentrations by plotting the reduced rate constant ( $k/k_0$ ) versus magnesium



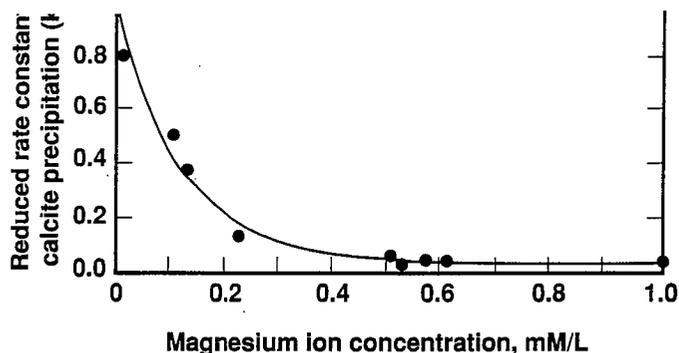


Figure 8. Calcite crystallization reduced-rate constant ( $k/k_0$ ) as a function of the concentration of magnesium ions in solution.<sup>16</sup>

ion concentration (Figure 8). The calcite reduced growth rate constant (the ratio of the rate constant in the presence and absence of magnesium ion) decreases with increasing magnesium concentration to very low values at magnesium concentrations greater than one millimolar.

It is not clear from laboratory studies how locally elevated supersaturation, developed by high calcium concentration spring water inputs and their subsequent modification by mixing with lake water, modifies carbonate growth inhibition. At present (1994), the location at the north shore of Pyramid Lake exhibits carbonate formation.<sup>29</sup> Lake water magnesium ion concentrations stabilize elevated calcium concentrations and supersaturations allowing mineralization where spring inputs cause locally elevated supersaturation.

Most springs along the shore of Pyramid Lake are not at present associated with carbonate precipitation. Hot springs at the north end of Pyramid Lake have high calcium and low magnesium and alkalinity concentrations.<sup>25</sup> Calculations suggest that mixing of low-alkalinity, calcium rich spring water with Pyramid Lake water leads to non-linear variation in supersaturation as a function of the mixing ratios. Supersaturation of some mixtures is above that of lake water, suggesting that maximum supersaturation and mineralization occurs in the lake water / spring water mixing zone. Mixing zone precipitation may lead to detailed crystal morphology present in Pyramid Lake carbonate mounds (Figure 2).

## MECHANISM OF MAGNESIUM ION INHIBITION OF CALCITE FORMATION

In studies of natural phenomena, such as calcium carbonate formation inhibition in lakes, it is useful to characterize the process mechanism. Magnesium ion inhibition of calcite crystal growth has been interpreted in terms of a Langmuir adsorption isotherm model (Figure 9). The Langmuir model assumes that inhibitor ions adsorb at crystal growth sites on the calcite surface.<sup>15,16,27</sup> This model may also apply to magnesium ion calcite crystal

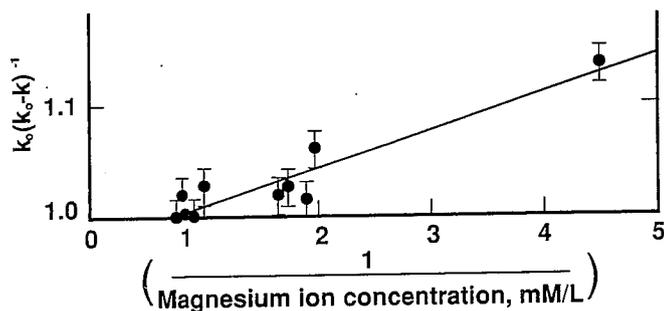


Figure 9. Langmuir isotherm plot of  $k_0/(k_0-k)$  as a function of the reciprocal of the added magnesium concentration in solution for calcite seeded crystallization.<sup>16</sup>

growth inhibition in present-day Pyramid Lake. The Langmuir model for phosphate glycerophosphate<sup>15</sup> indicated that the current Pyramid Lake phosphate concentration (one micromolar at the sediment-water interface<sup>25</sup>) will reduce the calcite crystal growth constant only slightly. Although phosphate is an effective calcite growth inhibitor, concentration in Pyramid Lake surface water is too low to impact calcite reaction. Pyramid Lake sediment phosphate concentrations are higher (up to 0.5 millimolar) and inhibit calcite crystal growth.<sup>25</sup> Mono Lake carbonate mineralization is regulated by the water column phosphate concentrations.<sup>24</sup>

## IN-LAKE CALCIUM CARBONATE CRYSTALLIZATION RATES

A test of calcium carbonate formation inhibition in Pyramid Lake, using an in situ crystal growth experiment, was begun in the summer of 1992. This procedure measured calcite and aragonite crystal growth rates for single crystals suspended in Pyramid Lake water. Initial results from August and September 1992 (no growth in the supersaturated lake water) suggests the importance of crystal growth inhibitors, such as magnesium ion, in reducing calcium carbonate formation from Pyramid Lake onto a carbonate surface. Field observations demonstrated carbonate deposition on an artificial substrate at a site of spring input (Micaela B. Reddy, personal communication, 1993). A can was observed to be encrusted with a mineral deposit. At this location carbonate mineralization occurred over the last few years. Additional laboratory and field experiments are in progress to evaluate the role of magnesium ion inhibition of carbonate formation in Pyramid Lake.

## CONCLUSIONS

Magnesium ion inhibits calcium carbonate nucleation and calcite crystal growth. Calcium carbonate formation inhibition by magnesium ion concentrations in Pyramid Lake water (about  $4 \times 10^{-3}$  moles per liter) at the maximum summer lake supersaturation (about supersaturations of 10) is consistent with laboratory data.

Calcium carbonate nucleation is reduced by millimolar magnesium ion concentrations. Induction times, compared to magnesium free solutions, increase in solutions containing millimolar magnesium ion. Whittings in Pyramid Lake result from calcium carbonate

that at that time supersaturations were well above 10. Elevated Pyramid Lake supersaturations may reflect high calcium ion loads transported to the lake during peak discharge. Carbonate nucleation studies of lake water may have application in characterizing and predicting Pyramid Lake whiting episodes. Continued research in this area is warranted.

Present-day Pyramid Lake maximum supersaturation occurs in late summer, corresponding to the maximum lake water temperature, and is below the value necessary for nucleation. An increase in maximum summer supersaturation appears to be necessary to cause whiting episodes now (1994). Whittings in other large lakes (i.e., the North American Great Lakes) occur at lower supersaturations, presumably because inhibitor concentrations in these lakes are lower than in Pyramid Lake.<sup>3</sup> Crystal growth kinetic characterization is the key to understanding carbonate formation in and about Pyramid Lake, and at other Great Basin Lakes. Continued research on the influence of inhibitors on carbonate mineralization reaction rates is needed.

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