Mineralogy and Morphology of Calcium Carbonate as a Function of Magnesium Concentration in Artificial Seawater

AHMED I. RUSHDI

Department of Oceanography, Faculty of Science,
Sana'a University, Sana'a, Republic of Yemen

ABSTRACT. Magnesium ions in solution affected the mineralogy and the morphology of calcium carbonate from which they precipitated. Low magnesium calcite was precipitated from a solution of low ionic products with respect to carbonate and Mg:Ca concentration ratio of less than 3:1. Aragonite was formed in a solution of Mg:Ca concentration ratio of more than 4:1. However, the increase of carbonate concentrations in the presence of magnesium ions enhanced the formation of magnesian calcite over aragonite. The co-existence of magnesian calcite, aragonite and vaterite indicated a kinetic control precipitation. This was also shown by the increased MgCO<sub>3</sub> content of magnesian calcite with the increase of carbonate concentrations in solution.

The presence of magnesium ions in artificial seawater produced acicular rather than the equant carbonate crystals, which produced in magnesium-free artificial seawater. Furthermore, the size of the crystals decreased with the increase of magnesium ions in the test solution.

Introduction

The mineralogy and morphology of the carbonate precipitate in solution are mainly influenced by the rates of dissolution and reprecipitation, which are controlled by the nucleation and the growth of the solid phases. It has been suggested that the presence of magnesium ions in solution inhibit the precipitation of calcium carbonate (Pytkowicz 1965 and 1973), retard the nucleation of calcite during the dissolution of aragonite (Bischoff 1968; Bischoff and Fyfe 1968), enhance the spontaneous precipitation of aragonite over calcite at high supersaturation (Taft and Harbaugh 1964;
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Analysis. XRD analysis were performed from 24° to 34° at 0.02°/sec using Cu α radiation. The mole percent MgCO₃ (mole % MgCO₃) in calcite was calculated from the empirical relationship obtained by Chave (1952).

Subsequently to the XRD analysis, each precipitate was dissolved in HCl (0.10n) and the concentration of Mg²⁺ was determined by atomic absorption spectroscopy (AAS). To estimate the residual Mg²⁺ in calcite, it was assumed that pure aragonite had a maximum 1.5 mole % MgCO₃. Pure aragonite that was precipitated from the test solution was then used as standard by dissolving a known amount in HCl and determining its mole % MgCO₃. The weight percent (wt%) of calcite in the mixture was calculated from each sample from the following equation:

\[
\text{wt% calcite} = \left[ \left( b \times \frac{84.321}{24.321} \right) + \left( b \times \frac{100.089}{24.321} \right) \right] \times \left[ \frac{(100 - a)}{a} \right]
\]

where \( a \) is the mole % MgCO₃ in calcite, calculated from XRD analysis and \( b \) is the wt% of Mg²⁺ in the total sample, determined by AAS. Therefore, the wt% of aragonite is 100 – wt% calcite.

Other precipitation runs were kept in a water bath for 35 days at a temperature of 25.0 ± 0.4°C. They were examined by XRD during the 35 days to test the transformation of their mineralogy. The XRD runs were made once each week up to about a month. In this case, the same method above was used to determine the mole % MgCO₃ and the wt% of calcite in each sample. Quantities of the transient vaterite and of aragonite were determined from the intensity ratio of aragonite to vaterite plus aragonite:

\[
\frac{(\text{arag.} \text{2θ})}{(\text{arag.} \text{2θ}) + (\text{vaterite} \text{2θ})} = \frac{I_{\text{arag.}}}{I_{\text{vaterite}} + I_{\text{arag.}}}
\]

\( I \) is the height at 2 theta for each mineral from XRD, assuming that the height is a function of the amount of the mineral in the mixture.

Twelve samples from these homogeneous precipitates were selected for the morphological and size examination. The samples were selected from low and high ionic products of carbonates and at Mg:Ca ratios in solution from 0 to 5, to test the effect of these parameters, that is, of the Mg:Ca ratio and of the rate of growth upon the morphology of the crystals. The precipitates were examined using the Scanning Electron Microscope (SEM).

Results and Discussion

The addition of Na₂CO₃ to varying amounts of magnesium leads to the formation of carbonate minerals (Table 1). The amounts of magnesium added are shown as (Mg²⁺):(Ca²⁺) ratios, where the Ca²⁺ concentration was 0.00993 mole 1⁻¹ in all cases.

X-ray diffraction results of the precipitates (Table 1) show three different calcium carbonate minerals: pure calcite (at zero Mg²⁺ ions in solution), mixture of magnesium calcite and aragonite, and pure aragonite alone. The mole % MgCO₃ in calcite increases with (Mg²⁺):(Ca²⁺) concentration ratio in solution, as well as the increase of degree of saturation. Table 1 shows that high Na₂CO₃ added in the presence of
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TABLE 2. Effect of the degree of saturation and Mg$^{2+}$ concentration upon the transformation of calcium carbonate mineralogy.

\[
\text{(Mg}^{2+} : \text{Ca}^{2+}) = 2 : 1
\]

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>mole% MgCO$_3$</th>
<th>wt% calcite</th>
<th>I$<em>{arag}$ (I$</em>{arag} + I_{vatr}$)</th>
<th>Time (days)</th>
<th>mole% MgCO$_3$</th>
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\[
\text{(Mg}^{2+} : \text{Ca}^{2+}) = 3 : 1
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<th>wt% calcite</th>
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<th>Time (days)</th>
<th>mole% MgCO$_3$</th>
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N.V. = No Vaterite.

results showed that the mineral compositions depend upon the initial supersaturation of the magnesium content and tended to approach a steady-state equilibrium. The dissolution of high magnesian calcite and the precipitation of calcite with lower MgCO$_3$ content and aragonite obviously occurred. These precipitates have stabilities which depend upon the activities of the ions in solution and the composition of the mineral itself.

The crystal forms which were precipitated at different (Mg$^{2+} : \text{Ca}^{2+}$) concentration ratios and different ionic products in artificial seawater were acicular (needle-like in form). The images of carbonate minerals precipitated from Mg-free artificial seawater showed equant (same diameter in all directions) in shape (Fig. 2). Some
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FIG. 2. SEM images of equant pure calcite precipitated from artificial seawater at addition of 1.48 mmolel⁻¹ Na₂CO₃.

Characteristics of the surface of the crystals also appeared to be affected by the rate of the reaction and the (Mg²⁺):(Ca²⁺) concentration ratio. In the presence of magnesium ions in solution, the crystals appeared in the forms of bundles of fibrous or needle-like aggregates.

Furthermore, the experimental results showed that the presence of Mg²⁺ in solution was one of the parameters that controlled the morphology of calcium carbonate. At zero magnesium concentration in solution the crystal morphology was equant (Fig. 2) both at high and low concentration of carbonates and, thus, at fast and low reaction. Therefore, one would expect that the reaction rate of precipitation was not the main control in determining the morphological feature of calcium carbonate crystals but rather the presence of different ions in the solutions, especially the magnesium ions.

Conclusion

The mineralogy of inorganic homogeneous precipitation is a results of the Mg²⁺ ion concentration and rate of the reaction at constant T and P conditions. Pure calcite is favored in Mg-free solution; low-magnesian calcite is favored at Mg:Ca ratio <
**FIG. 4.** SEM images of acicular aragonite at $(\text{Mg}^{2+}) : (\text{Ca}^{2+})$ ratio of 5:1 in artificial seawater (a) by adding 1.44 mmole$^{-1}$ Na$_2$CO$_3$ and (b) by adding 4.64 mmole$^{-1}$ Na$_2$CO$_3$. 

