

THE CRYSTALLIZATION OF CALCIUM CARBONATE

IV. The effect of magnesium, strontium and sulfate ions *

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The spontaneous crystallization of calcium carbonate (calcite) from solution at 25°C was studied in the presence of magnesium, strontium, and sulfate ions. Supersaturated solutions containing 10⁻³ M or 10⁻⁴ M sulfate ion, 10⁻⁴ M strontium ion, or 10⁻⁴ M magnesium ion yielded calcite crystals with a morphology identical with that obtained in the absence of these ions. The addition of 10⁻³ M magnesium ion resulted in calcite crystallites with a poorly developed crystal habit which gradually improves with aging. Evidence from X-ray powder diffraction, chemical analysis and scanning electron microscopy of the precipitates formed in the presence of 10⁻³ M magnesium ion indicates that calcium carbonate formation involves an unstable amorphous phase that undergoes subsequent transformation to aragonite and calcite. The crystal growth and morphologic changes of calcite crystals produced by 10⁻³ M magnesium ion can be related to the substitution of magnesium ions for calcium ions in the calcite crystal lattice.

1. Introduction

The precipitation and dissolution of the sparingly soluble carbonates of divalent metal ions, such as calcium carbonate (calcite and aragonite) and calcium magnesium carbonate (dolomite) are of great interest in limnology [1], oceanography [2] and sedimentology [3,4]. Recently the kinetics of crystal growth of calcium carbonate was studied using a reproducible seeded-growth technique [5,6]. The process was found to be one of surface control, and the rate was proportional to the square of the supersaturation. The fact that bulk diffusion in the liquid phase was not the rate-limiting step leads to the important conclusion that the rate of crystal growth of calcite is independent of fluid dynamics [7].

The sensitivity of calcium carbonate crystallization to the presence of magnesium ion has been reported by several investigators [8-17]. Thus Taft [8] suggested that a certain critical magnesium: calcium molar concentration ratio is necessary to retard the transformation of aragonite to calcite. Kitano [9], employing a spontaneous precipitation technique, found that an initial molar concentration ratio greater than 3 yielded a precipitate composed mainly of aragonite. He interpreted this as showing that the presence of magnesium ions in the precipitating solution favored aragonite formation.

Roques and Girou [10] have reported that calcium carbonate precipitation initiated by a sudden change in carbon dioxide partial pressure was markedly reduced in the presence of a narrow range of magnesium ion concentration. By field analyses of cave waters and laboratory experiments with spontaneous precipitation Murray [11] found that the presence of magnesium

* Part III in this series was "Calcite crystal growth inhibition by phosphates", *Desalination* 12 (1973) 61.

ion increases the fraction of aragonite formed during precipitation and that at equal calcium and magnesium solution concentrations aragonite is the major component of the precipitate. Bischoff and Fyfe [12] studied the kinetics of aragonite-to-calcite transformation at elevated temperatures employing an X-ray powder diffraction method and reported that calcite crystallization was strongly inhibited by magnesium ion and less strongly by sulfate. Comparable results have been found with seawater. Pytkowicz [14] has shown in a spontaneous precipitation study that magnesium ion inhibits the formation of calcium carbonate in seawater. Towe and Malone [15] conducted preliminary experiments involving the formation of metastable carbonates from seawater using a vapor diffusion spontaneous precipitation procedure and obtained several metastable carbonates containing significant amounts of magnesium.

Extensive investigations of carbonate reactions in natural waters have attempted to relate these reactions to specific environmental variables such as magnesium ion concentration and solution pH. Calcite occurs in numerous carbonate sediments at concentrations of up to 30 mole% magnesium carbonate [18]. Aragonite, which makes up a large fraction of shallow marine carbonate sediments, exists in a relative pure state but usually contains a small percentage of strontium. Under these conditions aragonite does not transform to calcite, the thermodynamically stable modification, at any measurable rate. Winland has suggested that this apparent persistence of aragonite arises from a decrease in the stability of mixed calcium-magnesium carbonates [18]. In evaporative lakes in South Australia several different $\text{CaCO}_3\text{-MgCO}_3$ salts have been found, and the specific carbonate phase which forms has been correlated with the pH and magnesium concentration of the lake water [19]. Friedman et al. [20] have stressed the importance of organic substances and during carbonate formation reactions. Processes examined by these workers play a role in the cementation of sediments in the Red Sea. Watabe [21] has mentioned the importance of inorganic ions in the formation of calcium carbonate in biological systems.

In the present work, precipitation was induced in pure supersaturated solutions of calcium carbonate and in the presence of magnesium, strontium, and sulfate ions. The morphology and polymorphic and chemical composition of the precipitate were examined

in detail to characterize the interaction of inorganic ions with calcium carbonate during precipitation.

2. Experimental

Triply distilled deionized water and analytical-grade reagent chemicals were used. All solutions were filtered through prewashed 0.22 μm Millipore $\text{\textcircled{R}}$ filters. Photomicrographs of crystals obtained were taken with a Unitron Series N microscope and a Mirax camera. X-ray powder diffraction patterns were determined using a Phillips powder diffraction camera and copper $K\alpha$ radiation with a nickel filter.

Samples were coated with 20 nm of gold in a Denton vacuum evaporator with rotating specimen holder and examined with an AMR-1000 or an ETEC Autoscan scanning electron microscope. Calcium analyses were made by atomic absorption spectroscopy (Varian Technon AA 5). Microscopic identification of crystallites was done on a Carl Zeiss RA microscope with a 10X dispersion staining objective (W.A. McCrone Corp.).

Calcium carbonate was precipitated from supersaturated solution by rapidly mixing 10^{-2} M calcium chloride and 10^{-2} M sodium carbonate solutions at 25°C in the presence or absence of added ions. Each solution was mixed within 8 sec and was unstirred thereafter. Precipitation commenced less than 10 sec after mixing, with a rapid onset of turbidity, and the crystals gradually settled out of solution. A sample of the resulting suspension was filtered through a 0.22 μm Millipore $\text{\textcircled{R}}$ filter. The filtrate was analyzed by atomic absorption spectroscopy, and the precipitate retained by the filter was used for characterization of the solid phase. The remainder of the precipitating solution was placed in a glass or polyethylene container which had been cleaned with sulfuric acid-dichromate cleaning solution and dilute nitric acid, and was stored at 25°C until the end of the experiment.

In most experiments the precipitated calcium carbonate adhered tenaciously to the walls and bottom of the reaction cell after several hours of aging. In preliminary experiments conducted with continuous stirring (200 rpm), precipitates were always calcite with an irregular morphology.

3. Results

Results of the precipitation experiments are summarized in table I. Crystals obtained from mixtures

Table I
Calcium carbonate

Experiment

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^a Sodium carbonate

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Table 1
Calcium carbonate spontaneous precipitation at 25°C^a

Experiment	Initial calcium carbonate concn. ($\times 10^{-3}$)	Added ion (M)	Induction time
1A	5	None	< 10 sec
1B	2	None	60 sec
1C	1	None	> 45 min
2	5	SO_4^{2-} (10^{-3})	< 10 sec
3	5	SO_4^{2-} (10^{-4})	< 10 sec
4	5	Sr^{2+} (10^{-4})	< 10 sec
5	5	Mg^{2+} (10^{-3})	< 10 sec
6	5	Mg^{2+} (10^{-4})	< 10 sec

^a Sodium chloride concentration was twice the initial calcium carbonate concentration.

without added ions (expt. 1A) had the characteristic calcite (rhombohedral) morphology (fig. 1). This morphology was independent of solution supersaturation at calcium carbonate concentrations from 1×10^{-3} to 5×10^{-3} M. Crystal size varied slightly with supersaturation, and there was no evidence from X-ray diffraction analysis or scanning electron microscopy of unusual crystal imperfection. Spontaneous precipitation in the presence of 10^{-4} to 10^{-3} M sulfate ion (expts. 2 and 3) and at 10^{-4} M magnesium ion (expt. 6) also resulted in crystals with the characteristic calcite morphology.

The effect of 10^{-4} M strontium ion (expt. 4) was evident (fig. 2). X-ray powder diffraction analysis indicated a mixture of calcite and aragonite, with the

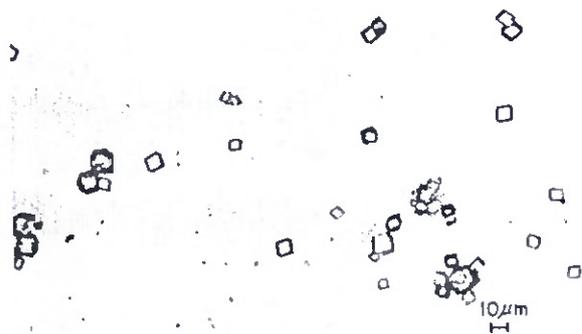


Fig. 1. Calcium carbonate crystals precipitated in the absence of magnesium, strontium and sulfate ions.



Fig. 2. Calcium carbonate crystals precipitated in the presence of 10^{-4} M strontium ion.

calcite fraction having a crystal habit identical to that observed in the absence of strontium ion.

The presence of 10^{-3} M magnesium ion (expt. 5) has a marked effect upon the appearance of the precipitated calcium carbonate. The initial precipitate consisted of small spherulites (fig. 3a) which upon further aging were transformed into crystallites with an irregular crystal habit. The spherulites were of two distinct sizes, approximately 0.5 and 2.5 μm in diameter, with few particles of intermediate size. This distribution may result from a secondary nucleation process. No normal calcite rhombohedra were found in the precipitate. The phase which developed after 72 h (fig. 3b) had an irregular crystal habit. Several crystalline rods were observed (fig. 3b) which appeared to be an extreme example of the dendritic morphology associated with aragonite crystals. Recrystallization processes during extended aging led to a significant increase in size and improvement of habit (fig. 3c) as the calcite crystallites developed. X-ray powder diffraction analyses of a precipitate aged for 3 weeks showed that it consisted of calcite with traces of vaterite and aragonite.

Additional experiments, summarized in table 2, were made using solutions containing 10^{-3} M magnesium ion in order to characterize the initially precipitating calcium carbonate phase and its subsequent transformation to calcite and aragonite. The initial phase was found to be either amorphous (expt. 8A), as indicated by the absence of an X-ray powder diffraction pattern, or largely amorphous (expt. 12A) with traces of calcite and vaterite. The 1% magnesium content of the solid phase

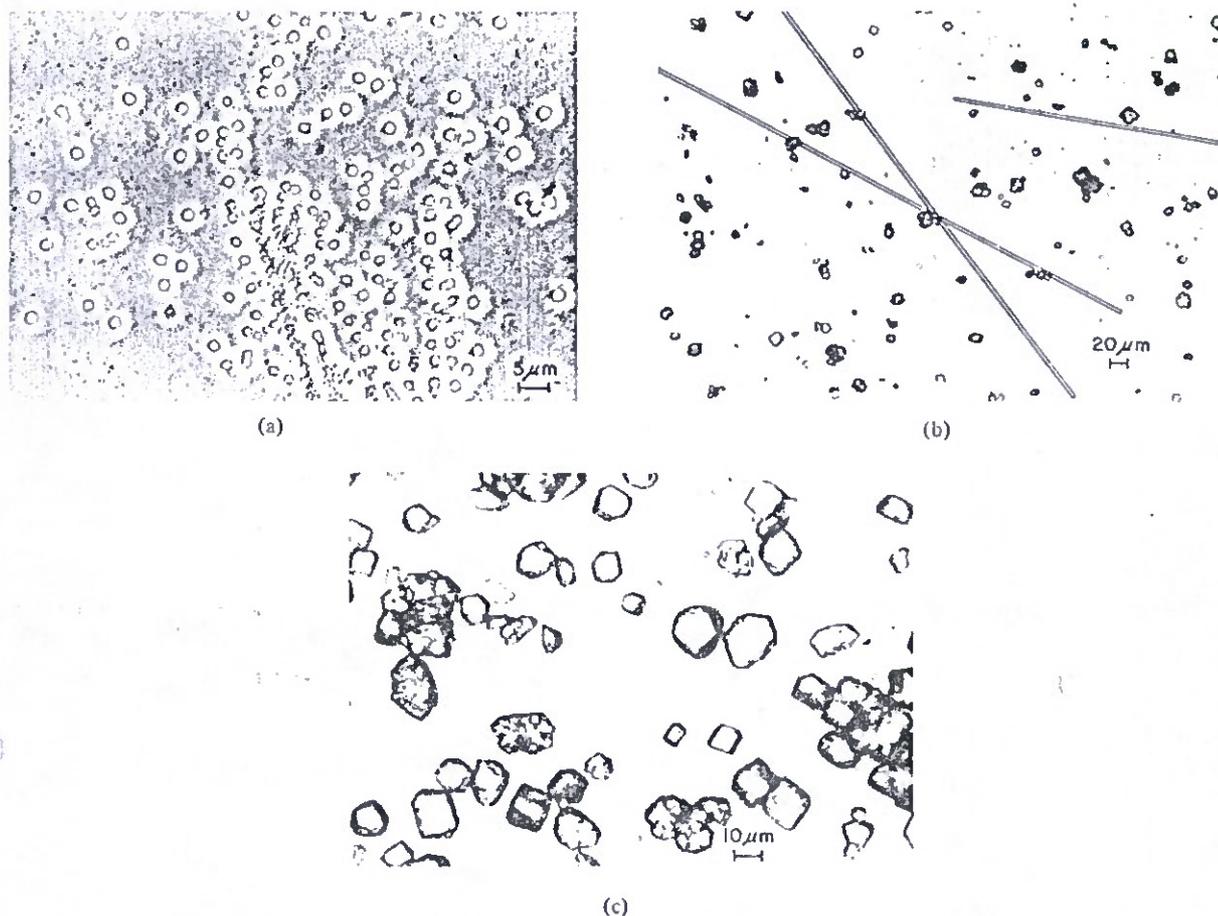


Fig. 3. Calcium carbonate crystals precipitated in the presence of 10^{-3} M magnesium ion. Time after precipitation: (a) 40 min; (b) 72 h; (c) 7 days.

Table 2
Calcium carbonate spontaneous precipitation in the presence of 1×10^{-3} M magnesium ion at 25°C ^a

Experiment	Length of experiment	Polymorphic composition	Magnesium content of solid phase (%)
8A	3 min	Amorphous	1.0
12A	3 min	Amorphous, with traces of calcite and vaterite	1.0
15A	6 days 20 days	Calcite and aragonite	2.5

^a Initial concentrations were: calcium carbonate, 5×10^{-3} M, sodium chloride, 1×10^{-2} M.

was similar to that of a low-magnesium calcite. The initially precipitating phase was composed of aggregates of small spherulitic particles approximately $0.25 \mu\text{m}$ in diameter (fig. 4a); the lack of crystal habit is consistent with the absence of an X-ray powder diffraction pattern. During longer aging (expt. 15A) the average solid-phase magnesium ion content increased to about 2.5% (table 2), and two types of particles formed: crystallites (fig. 4b), with either dendritic (fig. 4c) or irregular morphology (fig. 4d). Refractive index measurements showed that crystals with irregular morphology were low-magnesium calcite and the dendritic aggregates were aragonite. X-ray powder diffraction analysis of the precipitate, which contained crystals of both morphologies, showed both calcite and aragonite.

Fig.
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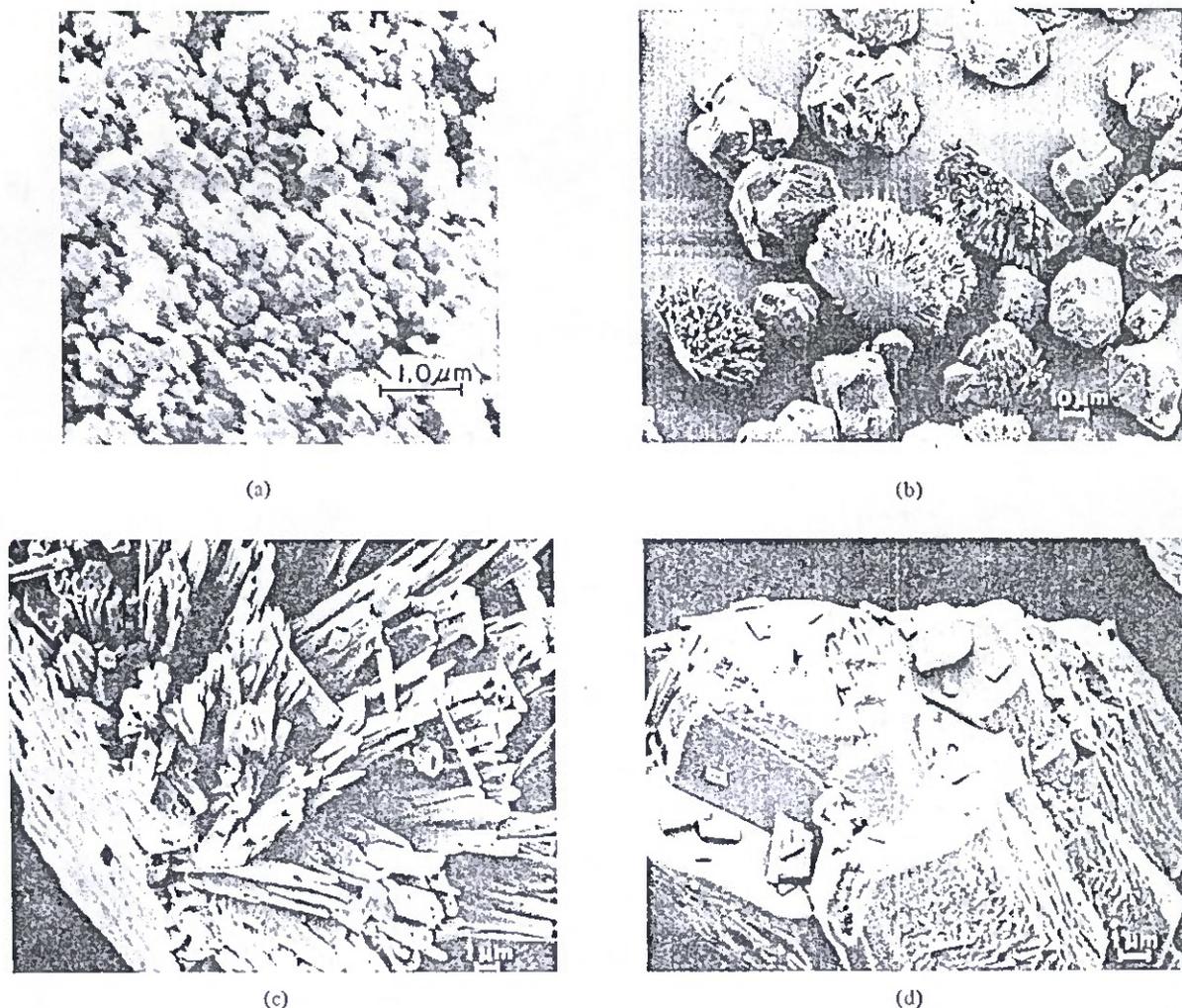


Fig. 4. Calcium carbonate crystals precipitated in the presence of 10^{-3} M magnesium ion. Time after precipitation: (a) 3 min; (b,c,d) 20 days.

The aragonite aggregates (fig. 4c) exhibited a characteristic mosaic structure; their appearance was quite different from the single aragonite crystals observed in expt. 5 (fig. 3b). This may reflect nucleation and growth of aragonite on the walls of the reaction vessel in expt. 15a. The aragonite crystallites apparently form by transformation of the initial amorphous phase, with vaterite as a possible intermediate. Low magnesium calcite crystals produced during extended aging exhibit both low-index faces, typical of calcite precipitated in pure solutions, and high-index faces, which are not commonly seen. The irregular texture of some crystal faces (fig. 4d) indicates

that the crystals were formed by aggregation as well as by transformation.

4. Discussion

The results of the present study indicate that sulfate ion does not interact with calcite surfaces sufficiently to retard their growth rate or alter their morphology development. In the presence of magnesium ion at concentrations greater than 10^{-3} M, the initial precipitate contains varying amounts of amorphous calcium carbonate,

which eventually recrystallizes to yield aragonite and a low-magnesium calcite with a distorted morphology. These changes probably arise because of incorporation of the magnesium ion in specific high-index calcium carbonate crystal faces. This inhibits nucleation and subsequent growth and leads to a modification of the characteristic rhombohedral morphology of the calcite crystallites. Although magnesium ion may substitute for calcium ion in the calcite lattice with little distortion, the rate of dehydration of magnesium ions at growth sites on the crystal surface prior to incorporation into the lattice may significantly reduce the overall growth rate. The relatively low level of magnesium ion incorporation in the solid phase indicates that the effect arises at the crystal solution interface. An interfacial reaction has been shown to be rate determining in calcium carbonate crystal growth [6].

Several studies have been made of the interaction of magnesium with calcium carbonate surfaces [13-17]. A radioisotopic investigation [16] of the magnesium content of calcite surfaces showed that at low magnesium ion concentrations the magnesium:calcium surface ratio is directly proportional to the solution concentration ratio. The extent of magnesium ion substitution in the calcite surface, calculated from these data, is not more than 10% in the initial stages of spontaneous precipitation experiments using 10^{-3} M magnesium ion. The dehydration energy difference between calcium ion and magnesium ion has been suggested as responsible for the inhibition of the precipitation of calcium carbonate in sea water by magnesium ion, often cited as the cause of the persistent supersaturation of surface sea water with calcium carbonate [14]. Bischoff [13] examined the role of magnesium ion in the aragonite-to-calcite phase transformation and showed that the magnesium ion reduced the nucleation rate of calcite and, in so doing, was incorporated into the crystal nuclei. Möller [17] attributed magnesium ion inhibition of calcium carbonate nucleation to destabilization of calcite critical nuclei by the magnesium ion. All these findings are consistent with the results of the present work with magnesium ion retarding crystallization by incorporation at crystal growth sites.

It is interesting to note that amorphous calcium carbonate, observed in the initial precipitates in the presence of 10^{-3} M magnesium ion, has also been observed in solutions containing other crystal growth inhibitors. Brooks et al. [22] reported that polyphosphate ions

caused reduction in the growth rate and marked changes in morphology of the calcite crystals. We are now conducting seeded crystal growth experiments to further characterize the mechanism of inhibition of calcium carbonate crystal growth by magnesium ion.

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