Morphological changes in a series of synthetic Mg-calcites

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Abstract

Seven members of the calcite to high Mg-calcite solid solution series were synthesized by mixing calcium and magnesium chloride solutions with a sodium bicarbonate solution at ambient conditions. The synthetic products were found by X-ray diffraction and scanning electron microscopy to be mono-mineralic except for the highest Mg-calcite sample, $(Ca_{0.82}Mg_{0.18})CO_3$, which also contained aragonite. The morphology of the synthetic products ranges from well-developed rhombohedra in the end member calcite and low Mg-calcites to spherical and "peanut-shaped" aggregates in high Mg-calcites.

Introduction

The random substitution of Mg^{2+} for Ca^{2+} in the calcite structure results in a solid solution series ranging from $CaCO_3$ to approximately $(Ca_{0.50}Mg_{0.50})CO_3$. Dolomite expressed by the formula $CaMg(CO_3)_2$ is dissimilar in having an ordered structure with Ca^{2+} ions and Mg^{2+} ions in alternate layers. The solid solution series from pure calcite, through low Mg-calcite to high Mg-calcite at approximately $(Ca_{0.80}Mg_{0.20})CO_3$, is formed in a metastable state at ambient conditions (Goldsmith and Heard, 1961) yet is a common organic carbonate constituent of modern sediments (Bathurst, 1975). Recent work has shown, moreover, that Mg-calcites also form inorganically, particularly as cements, in shallow water environments (Milliman, 1974; Bricker, 1971) but the specific chemical and/or physical conditions causing this precipitation are not well understood.

Laboratory procedures

A series of seven Mg-calcites from the $CaCO_3$ end member to $(Ca_{0.82}Mg_{0.18})CO_3$ were synthesized at 25°C and one atmosphere pressure using the technique of Glover and Sippel (1967). In this procedure, solutions of variable calcium to magnesium chloride ratios are mixed with a sodium bicarbonate solution resulting in the precipitation of Mg-calcites. The pH of the original solution at 8.4 decreases first because of the release of H^+ on precipitation of the crystals, but then increases in response to the loss of CO_2 from the solutions. Because the crystalline precipitate is metastable, the time of the synthesis runs is important. The mixing of the calcium and magnesium chloride with the bicarbonate solutions was done with continuous stirring over a two minute interval. The parent solutions then were allowed to stand unstirred for 150 minutes before the precipitate was filtered out of the parent solution. Allowing the precipitate to remain in contact with the parent solution for longer times resulted in dissolution of the Mg-calcites and precipitation of aragonite crystals.

The Mg^{2+} concentrations were determined by difference using a standard versenate titration or by specific ion electrode for bivalent cation concentration minus the Ca^{2+} concentration. Table 1 summarizes the chemistry of the solutions for each synthetic product. The synthetic products (Table 1) were analyzed with a Philips X-ray diffractometer using CuKα radiation and a quartz internal standard. The analytical curve of Scholle (1978) was used for analysis of the synthetic solid solution members. The samples were analyzed for mineralogic purity using an X-ray diffractometer scan at $2°$ 2θ/min. from 3 to 55°. All samples showed sharp well-developed X-ray lines of Mg-calcites although the pattern for No. 7 (highest Mg^{2+} content) was noticeably less sharp than the diffractograms of other samples.

The yield in the synthetic runs progressively reduced as the Mg^{2+} content increased. Because of the

finely divided nature of the synthetic product and its adherence to the beaker walls, quantification of the product weight was difficult. In approximate terms, the recovered synthetic product for the high Mg-calcites (Nos. 6 and 7) was roughly 10–20% of the recovery for the low Mg-calcites (Nos. 2 and 3).

The scanning electron microscopy was done on an International Scientific Instrument (TV Mini-SEM). The samples, after being washed in distilled water and acetone, were dispersed in distilled water and sedimented onto a one centimeter square glass surface atop the aluminum sample stud. The sample was oven-dried at 75°C for ten minutes and coated for six minutes with gold.

Crystal morphology

Photomicrographs by SEM (Fig. 1) showed changes in the morphology of the synthetic crystals from the pure calcite end member (Fig. 1-A) to the highest Mg-calcite $(Ca_{0.82}Mg_{0.18})CO_3$ (Fig. 1-F). The pictures shown are crystals and aggregates which are representative of the samples; care was taken not to select bizarre crystals from among the general type. The crystal morphology progressively changes with increasing Mg^{2+} content from well-developed rhombohedra (Fig. 1-A) toward aggregate crystal clusters with little or no suggestion of crystal from (Fig. 1-F).

Figure 2 shows an unusual type of aggregate in the synthetic samples that occurred with some frequency in the high Mg-calcites (> 7 mol % Mg). These "crossed-peanuts" occur frequently enough that a fortuitous juxtaposition of two "peanuts" seems improbable.

Discussion

The synthetic products of the Glover and Sippel (1967) procedure appear to be mono-mineralic except (as noted by them) for the occurrence of aragonite in the high Mg-calcites such as the 18 mol % Mg^{2+} sample. The distinctly different needle morphology observed by SEM only in our 18 mol % Mg^{2+} sample suggests aragonite. It is noted, however, that a needle-like morphology has been shown for Mg-calcite crystals grown in silica gel at pH values above 9.6 (McCauley and Roy, 1974). Although our solutions were aqueous and pH values considerably lower, the identification of the needle-like crystals as aragonite is by inference.

Compositional heterogeneity with a Mg-rich phase, probably nesquehonite, as a nucleus in Mg-calcites was demonstrated by McCauley and Roy

Table 1. Ion concentrations in the solutions used for the seven synthetic runs

Product	Chloride solution		Sodium bicarbonate solution
	Ca^{2+}	Mg^{2+}	HCO_3^{2+}
$CaCO_3$	0.09	0.00	0.60
$(Ca_{0.965}Mg_{0.035})CO_3$	0.09	0.07	0.60
$(Ca_{0.95}Mg_{0.05})CO_3$	0.09	0.11	0.60
$(Ca_{0.94}Mg_{0.06})CO_3$	0.09	0.22	0.60
$(Ca_{0.93}Mg_{0.07})CO_3$	0.09	0.27	0.60
$(Ca_{0.87}Mg_{0.13})CO_3$	0.09	0.73	0.60
$(Ca_{0.82}Mg_{0.18})CO_3$	0.09	0.98	0.60

(1974). The existence of Mg-rich nucleii is possible in our crystals even though the Mg^{2+} concentration did not vary significantly in the solutions during crystallization because of the relatively low yields. Mass calculations indicated less than a 1% reduction in the Mg^{2+} concentration of our solutions during the crystallization process. Large scale compositional zoning also was not indicated because of the sharpness of the X-ray diffraction lines.

The morphologic change from well-developed crystals to microcrystalline aggregates observed in these synthetic samples must be related to the difficulty of crystal growth in the presence of Mg^{2+} impurity ions. Under the experimental conditions of this study, the acceptance of Mg^{2+} ions into the structure is disfavored over Ca^{2+} and only occurs in the synthetic product when Mg^{2+} is present in high relative concentrations. The $Mg^{2+}:Ca^{2+}$ molar ratio in the present solution over the ratio in the crystalline product ranges from approximately 20 for low Mg-calcite to approximately 50 for the high Mg-calcites.

To our knowledge there has not been a previous systematic study of synthetic crystal morphologic changes for this range of Mg-calcites. McCauley and Roy (1974) show photomicrographs which are suggestive of some morphologic features shown by our Mg-calcite spherical aggregates. The small size of our crystals (Fig. 1) relative to theirs, however, makes comparisons difficult. Towe and Malone (1970), show a micrograph of a high Mg-calcite laboratory-precipitated from sea water and describe the finely divided powder as consisting of "individual or interpenetrating wheat-shaped crystals." Certainly, our parent solutions had roughly a ten-fold higher Mg^{2+}/Ca^{2+} ratio than the ratio in the sea water used by Towe and Malone. In comparison, the formation of aggregate crystal shapes that are, in a sense, opposite to ours (wheat-shaped vs. peanut-shaped) is problem-
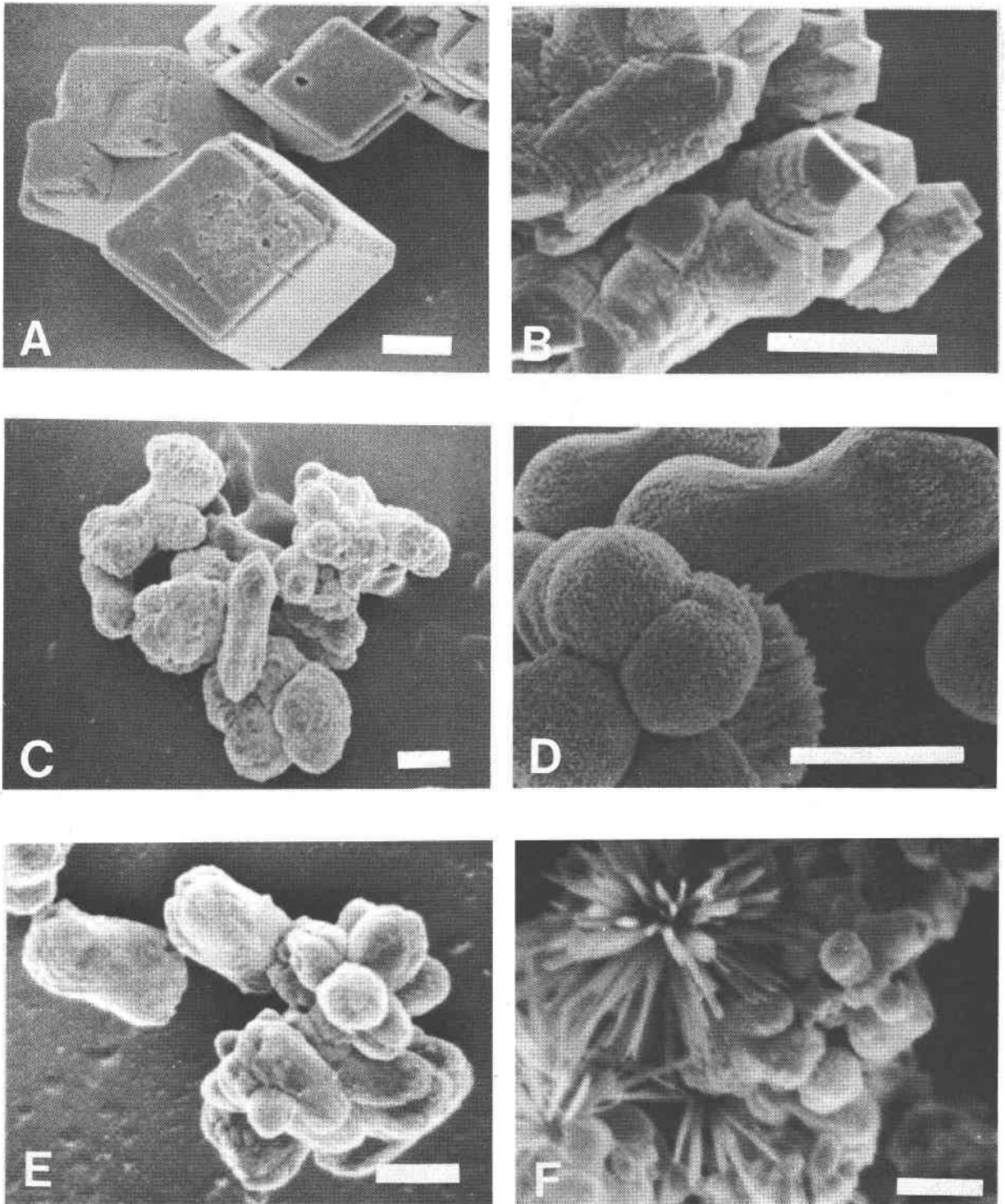
Fig. 1. Scanning electron micrographs of synthetic Mg-calcites. (All bars equal 5 microns): (A) End-member, $CaCO_3$, well-developed rhombohedra; (B) $(Ca_{0.95}Mg_{0.05})CO_3$, "fused" masses terminating in rhombohedron faces; (C) $(Ca_{0.94}Mg_{0.06})CO_3$ "fused" masses entirely with greatly subdued rhombohedron faces; (D) $(Ca_{0.94}Mg_{0.07})CO_3$, spherical and "peanut-shaped" aggregates; (E) $(Ca_{0.87}Mg_{0.13})CO_3$, smaller spherical and less pronounced "peanut-shaped" aggregates; (F) $(Ca_{0.82}Mg_{0.18})CO_3$, spherical aggregates with needles of aragonite.
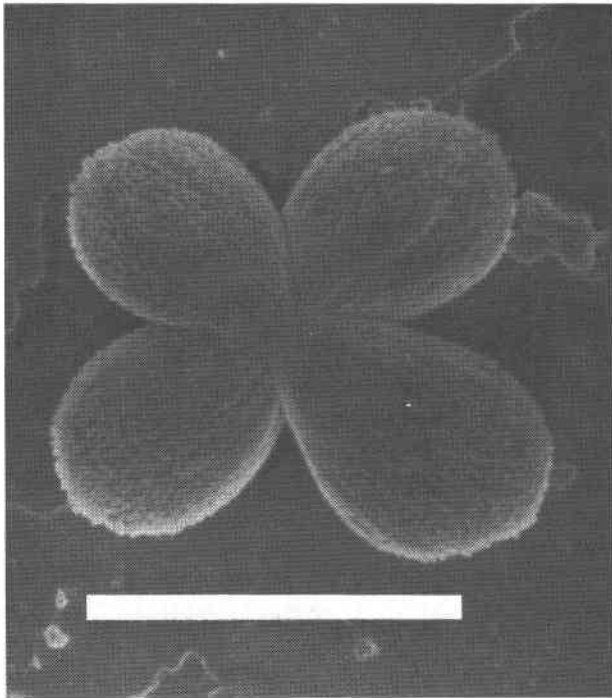
Fig. 2. Scanning electron micrograph of "crossed-peanuts" found occurring in high Mg-calcites with 7–13 mol % Mg^{2+}. (Bar equals 5 microns).

atic. The closest crystal aggregate shape found in the literature shows aragonite forming "sheaves and bundles" occasionally occurring as crossed pairs, thereby giving a "Maltese cross effect" (Oppenheimer, 1961). Apparently the same aggregate shapes of our Mg-calcite occur for aragonite when it is grown from sea water devoid of bacteria as shown by Oppenheimer.

Application of our experimental findings to natural occurrences is difficult. Although there are described occurrences of high Mg-calcite cements which are not obviously biogenic (Alexandersson, 1978; Macintyre, 1977; Milliman, 1974; Bricker, 1971), these generally occur lining walls of cavities in near-shore environments. To the extent that some of the high Mg-calcites occur as "peloids (or globules, pellet-like bodies, knobs, bumps, clots, or whatever)" (Alexandersson, 1978), morphological similarity with the synthetic products is suggested. This suggests the possibility that some Mg-calcite cements form by rapid changes in CO$_2$ content of the parent solutions (Hanor, 1978) and/or by mixing waters (Schmalz, 1971), both conditions which parallel the synthetic conditions used in the Glover and Sippel procedure.

Acknowledgments

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