

## Synthesis of metastable Ca-Mg carbonates

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### ABSTRACT

Compositional analogues of  $\gamma$ -dolomite,  $\text{Ca}_{0.75}\text{Mg}_{0.25}\text{CO}_3$ , and  $\delta$ -dolomite,  $\text{Ca}_{0.67}\text{Mg}_{0.33}\text{CO}_3$ , were precipitated from homogeneous Ca-Mg formate solutions in the temperature range 145–220 °C over twenty years ago and interpreted to be metastable phases. These experiments confirm the existence of complications in the calcite-dolomite phase diagram due to superstructures with different ordering patterns that have been subsequently observed with the transmission-electron microscope.

### INTRODUCTION

Over twenty years ago, methods were developed to precipitate calcite and dolomite from homogeneous solutions in an effort to determine distribution coefficients for bivalent cations between these carbonates and solutions. Calcium salts of formic, trichloroacetic, trifluoroacetic, propionic, and other organic acids, which hydrolyze slowly in the presence of water at elevated temperatures to yield bicarbonate ions in solution, were found to be satisfactory for the precipitation of calcite (or aragonite) within specific temperature ranges. These methods were later used to determine distribution coefficients of  $\text{Sr}^{2+}$  (Holland et al., 1963),  $\text{Mn}^{2+}$  (Bodine et al., 1965), and  $\text{Zn}^{2+}$  (Tsusue and Holland, 1966) between calcite and solution.

Efforts to coprecipitate calcite and dolomite using this approach resulted in the crystallization of metastable phases with compositions lying between calcite and dolomite. The most consistent results were obtained in experiments using Ca-Mg formate solutions.

Although these, heretofore unreported, experiments were considered to be unsuccessful at the time, synthesis of metastable Ca-Mg carbonates is of current interest because two intermediate phases are similar in composition to those proposed for modulated superstructures with different ordering patterns,  $\gamma$ -dolomite,  $\text{Ca}_{0.75}\text{Mg}_{0.25}\text{CO}_3$ , and  $\delta$ -dolomite,  $\text{Ca}_{0.67}\text{Mg}_{0.33}\text{CO}_3$ , observed recently in natural samples using transmission electron microscopy (TEM) (Wenk and Zhang, 1985; Van Tendeloo et al., 1985). A brief report summarizing these old data would, therefore, appear to be useful and timely.

### PRECIPITATION OF CARBONATES FROM FORMATE SOLUTION

Ca-Mg carbonates were precipitated from 0.1M to 0.2M solutions of calcium and magnesium formate in the temperature range from 145 to 220 °C in 20-mL gasket-seal pressure vessels. About 58 bars of  $\text{CO}_2$  pressure was admitted to the system at the outset of the experiments. Total pressures during the experiments varied between 60 and 250 bars, and the duration of the experiments

ranged from 18 to 144 h. After quenching, the pressure was released and the filtrate was separated from the precipitate.

The compositions of the solid phases were estimated using X-ray diffractometry by careful measurement of  $d_{104}$  spacings against an internal standard,  $\text{CdF}_2$ , which has a conveniently located reflection at  $28.70^\circ 2\theta$   $\text{CuK}\alpha$  (Rosenberg, 1967). The precision of these measurements is  $\pm 0.01^\circ 2\theta$ . This approach to the determination of the chemical composition of rhombohedral carbonates in mixtures of microscopic crystals was conventional in the pre-electron-microprobe era of the early 1960s. Today, compositions determined by this method must be regarded as estimates because coherent intergrowths and other structural heterogeneities may result in strain that could change  $d$  values slightly (Essene, 1983).

### RESULTS

The results of experiments with Ca-Mg formate solutions are summarized in Table 1. Compositions of precipitated phases may be divided into four groups with average  $\text{MgCO}_3$  contents of 10, 22, 34, and 45 mol%; each group apparently represents a discrete phase. Two or three of these phases coexist in the products of each experiment below 220 °C.

Phases having an  $\text{MgCO}_3$  content less than 15% are magnesian calcites, whereas those with  $\text{MgCO}_3$  contents greater than 40% are considered to be calcian dolomites. Ordering was not observed but is probably present in the  $\text{MgCO}_3$ -rich phase. The compositions of the two intermediate phases correspond closely to those of the metastable superstructures  $\gamma$ -dolomite,  $\text{Ca}_{0.75}\text{Mg}_{0.25}\text{CO}_3$ , and  $\delta$ -dolomite,  $\text{Ca}_{0.67}\text{Mg}_{0.33}\text{CO}_3$ , which have been observed in sedimentary carbonates (Wenk et al., 1983) and interpreted to be metastable phases (Wenk and Zhang, 1985). Van Tendeloo et al. (1985) proposed structural models for these phases;  $\delta$ -dolomite is thought to have a stacking of Mg and Ca layers different from that of dolomite whereas  $\gamma$ -dolomite supposedly has alternating Ca and Mg rows in each cation layer. These structures give rise

TABLE 1. Compositions of phases precipitated from Ca-Mg formate solutions

Temp. (°C)	Time (h)	Solution composition* [Ca/(Ca + Mg)]**	Solid composition (MgCO <sub>3</sub> content, mol%)		
			7	37	45
220	48	0.90	—	—	—
206	144	0.65	13	—	37
205	24	0.82	8	—	34
199	50	0.70	—	—	35
197	22	0.48	—	23	—
186	120	0.65	13	—	35
181	24	0.82	8	—	35
175	48	0.90	3†	—	—
170	18	0.65	14	—	32
145	48	0.48	—	20	33

\* Initial compositions, determined by EDTA titrations (Holland et al., 1963).

\*\* Mole fraction.

† Trace higher-MgCO<sub>3</sub> phase present.

to weak "extra" reflections in electron-diffraction patterns that cannot be observed with X-rays. Thus, all four solid solutions with compositions lying between end-member calcite and dolomite described by Wenk and Zhang (1985) have been synthesized in this study.

Starting solutions with a mole fraction of Ca between 0.90 and 0.60 yield magnesian calcite (composition dependent on the mole fraction of Ca in the starting solution) and the intermediate phase that is higher in MgCO<sub>3</sub> content (Table 1, average 34 mol% MgCO<sub>3</sub>). The appearance of calcian dolomite (Table 1, average 45 mol% MgCO<sub>3</sub>) is time and temperature dependent. With increased duration of experiments and at higher temperatures, the  $d_{104}$  value of the intermediate phase having higher MgCO<sub>3</sub> content shifts slightly toward that of end-member dolomite, and the intensity of its X-ray reflections diminishes. Simultaneously calcian dolomite appears and grows. The intermediate phase with lower MgCO<sub>3</sub> content appears when the mole fraction of Ca in the starting solution is less than 0.50 (Table 1).

#### DISCUSSION AND CONCLUSIONS

There have been a growing number of reports of carbonates with compositions intermediate between calcite and dolomite and superstructures indicative of different ordering patterns. So far all observations have been made on natural samples of sedimentary origin; thus, interpretation has been difficult. The occurrence of similar compositions in experimental samples is potentially significant because correlation of observations on these samples with those on natural samples could provide a deeper insight into structural transformations at low temperatures. Synthesis of modulated microstructures offers many advantages including the possibility that the progress of their crystallization from the disordered structure and their

decomposition to the fully ordered structures could be traced as a function of time and temperature. This will require a detailed structural investigation of experimental products.

Analytical studies using the transmission and analytical electron microscopes are necessary to ascertain whether synthetic phases display superstructures at least on a fine scale, or if they show modulated structures that have been associated with superstructures. Unfortunately, the products of these experiments are not available for further study. Efforts to repeat and extend this study using modern experimental and analytical methods are now underway.

It is interesting to note that intermediate compositions have also been proposed on the basis of model calculations using the cluster-variation method (Burton and Kikuchi, 1984; Burton, 1987). These calculations imply that the compositions Ca<sub>3</sub>Mg(CO<sub>3</sub>)<sub>4</sub> and Ca<sub>5</sub>Mg(CO<sub>3</sub>)<sub>6</sub> may be stable at low temperatures. Thus, studies of natural and synthetic materials as well as theoretical calculations suggest that the calcite-dolomite phase diagram may be much more complicated than is commonly believed.

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