

## THE PREPARATION OF SYNTHETIC DOLOMITE

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### ABSTRACT

Synthetic dolomite has been formed by precipitation from a solution of  $MgCl_2$ ,  $CaCl_2$ , and urea subjected to elevated temperatures and  $CO_2$  pressures. The  $CO_2$  pressure is not critical above two or three atmospheres but the temperature must be in the range 200° C.–250° C. to obtain dolomite. At lower temperatures basic magnesium carbonate and aragonite are formed, and at higher temperatures the formation of calcite and magnesite is favored. If the temperature is controlled to within  $\pm 10^\circ$  of 220° C., pure dolomite is precipitated.

The presence of NaCl in the solution extends the range of temperatures over which dolomite can be precipitated. Several other salts have the same effect, and the salt concentration influences the relative amounts of calcite, magnesite, dolomite, etc. which are formed in the precipitates. The influence of the salt is believed to be associated with changes in the activities of the various carbonates in solution.

The pH at which the dolomite precipitations occurred was not measured, but the pH's of the solutions which remained after precipitation were measured at ordinary temperature and pressure and found to be in the range 6.5–7.5.

### INTRODUCTION

The synthesis of dolomite has been of interest for many years because of the widespread occurrence of the mineral in nature, both in metamorphic and sedimentary environments. Dolomite has been synthesized by laboratory methods which involve the dry, solid-state, and hydrothermal diffusion of cations in magnesian-calcite mixtures (Graf and Goldsmith, 1955; Graf and Goldsmith, 1956) but there have apparently been no successful attempts to precipitate dolomite directly from solution.\* A study has been made of the problem at this Laboratory in connection with efforts to produce pure samples of carbonate minerals for thermoluminescence studies.

### DOLOMITE PRECIPITATION

It was found that either calcite or magnesite could be crystallized from chloride solutions under the same conditions of temperature and  $CO_2$  pressure (120° C.–350° C. and 60 atmospheres) by a method similar to that described by Jantsch and Zemek (1949) for the synthesis of magnesite. A  $CaCl_2$  or  $MgCl_2$  solution is made slightly acidic (pH = 4–5)

\* A method described by Chillingar (1956) for precipitating dolomite from sea water under 4 atmospheres of  $CO_2$  pressure was duplicated by this author without success. The product obtained by this technique contained mostly calcite with a trace of basic magnesium carbonate ( $5MgO \cdot 4CO_2 \cdot 5H_2O$ ) but there were no traces of dolomite. The x-ray powder pattern for basic magnesium carbonate might be easily mistaken for a poorly crystallized dolomite pattern since two of the principal dolomite peaks nearly coincide with two of the basic magnesium carbonate peaks.

and a suitable quantity of urea is added. The solution is placed in an autoclave and raised to the appropriate temperature under  $\text{CO}_2$  pressure. The hydrolysis of the urea to  $\text{NH}_3$  and  $\text{CO}_2$  at elevated temperatures raises the pH sufficiently to precipitate either calcite or magnesite. The proper alkalinity for the optimum crystallinity of the precipitate can be controlled by adjusting the original pH of the solution and the amount of urea added. At a temperature of  $350^\circ\text{C}$ . magnesite or calcite is completely precipitated in less than an hour. At lower temperatures, the time required for complete precipitation increases and at  $120^\circ\text{C}$ ., 12 to 14 hours are required. At temperatures below  $120^\circ\text{C}$ . the method begins to fail because of the exceedingly slow rates of decomposition of the urea. In general, the crystallinity of the samples prepared in short times at high temperatures is as good or better than those prepared over longer periods at low temperatures. The results of the magnesite and calcite precipitations suggested that a mixture of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  might result in the formation of dolomite under similar conditions.

When the procedure was carried out with a mixed Ca and Mg ion solution dolomite precipitation was found to occur over a narrow range of temperatures near  $220^\circ\text{C}$ . In the temperature range from  $120^\circ\text{C}$ . to  $200^\circ\text{C}$ . poorly crystallized samples of basic magnesium carbonate ( $5\text{MgO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$ ) were obtained, while at temperatures above  $250^\circ\text{C}$ . mixtures of calcite and magnesite precipitated. The precipitation of aragonite was observed in the  $120$ – $150^\circ\text{C}$ . range. At temperatures in the range  $200$ – $250^\circ\text{C}$ . precipitates containing dolomite, magnesite, calcite and basic magnesium carbonate were formed and if the temperature was carefully controlled at  $200^\circ \pm 10^\circ\text{C}$ . precipitates of pure dolomite (cf. Fig. 1) were obtained in about three hours. For precipitates containing pure dolomite the yield was fairly low (5–10 per cent).

Variations in the  $\text{CO}_2$  pressure had very little effect on the quality (purity, crystallinity, etc.) of the dolomite obtained. Precipitates of well crystallized, pure dolomite were obtained at  $\text{CO}_2$  pressures as low as 2 atmospheres and as high as 60 atmospheres.

The composition and crystallinity of all of the precipitates were determined on the basis of their  $x$ -ray powder diffraction patterns.

#### EFFECTS OF $\text{NaCl}$ AND OTHER SALTS

To determine what effect the presence of  $\text{NaCl}$  might have on the dolomite precipitation various concentrations of the salt were added to the initial solution. In general, the effect was to improve the quality of the dolomite crystals and to extend the range of temperatures over which they could be formed. In very dilute and very concentrated salt solutions the precipitation of calcite and magnesite was enhanced.

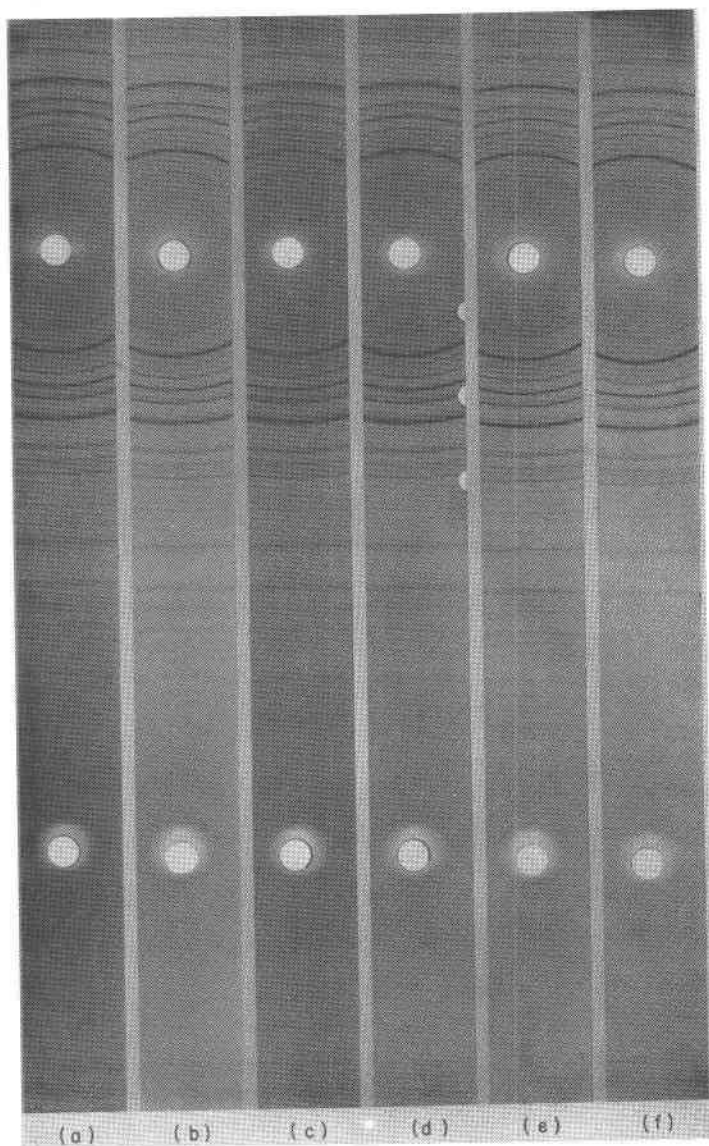


FIG. 1. X-ray powder diffraction patterns for synthetic and natural dolomite samples. All patterns were made with a 4.6 mm. Phillips camera using  $\text{CuK}\alpha$  radiation.

- (a) Synthetic sample precipitated without salt.
- (b) Synthetic sample precipitated in presence of  $\text{NaCl}$ .
- (c) Synthetic sample precipitated in presence of  $\text{CdCl}_2$ .
- (d) Synthetic sample precipitated in presence of  $\text{BaCl}_2$ .
- (e) Natural dolomite from Ellenburger formation (Texas).
- (f) Natural dolomite from Edwards formation (Texas).

In samples which contained no NaCl, dolomite precipitation was only observed over a range of temperatures between 210° C. and 230° C. At NaCl concentrations of 6–7 per cent, dolomite precipitation was observed over the range 150°–350° C. Below 150° C. the formation of aragonite and basic magnesium carbonate was still observed and there was again no trace of dolomite. The high temperature precipitates (230°–350° C.) contained magnesite, calcite and dolomite, and the low temperature precipitates (150–210° C.) contained dolomite and traces of basic magnesium carbonate. Pure dolomite could be precipitated only at or near 220° C. Temperatures above 350° C. were not investigated. The time required for complete precipitation at 220° C. was 6–8 hours.

In order to obtain a better understanding of the observed effects of NaCl the precipitations were carried out in the presence of other salts. Dolomite was obtained in the presence of LiCl, KCl, CsCl, CuCl<sub>2</sub>, BaCl<sub>2</sub>, CdCl<sub>2</sub>, ZnCl<sub>2</sub>, NaNO<sub>3</sub>, NaBr, and Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> but could not be precipitated in the presence of MnCl<sub>2</sub>, SrCl<sub>2</sub>, NaI, and CdI<sub>2</sub>. To avoid the confusion of mixed ion effects the magnesium and calcium ions were put into solution by dissolving their carbonates in the acid corresponding to the anion of the salt used; for example, when NaBr was used CaCO<sub>3</sub> and MgCO<sub>3</sub> were dissolved in HBr to form MgBr<sub>2</sub> and CaBr<sub>2</sub> in solution.

In most cases the salts which prevented dolomite precipitation also prevented the formation of calcite or magnesite; the precipitates obtained were usually poorly crystallized forms of basic magnesium carbonate (5MgO·4CO<sub>2</sub>·xH<sub>2</sub>O). Apparently the effects produced by these salts are not associated with the crystal structure favored by the salt since NaCl and NaI both have cubic structures, for example, and NaNO<sub>3</sub> has a rhombohedral structure like dolomite. Moreover, neither the type of salt added (i.e., uni-univalent, uni-divalent, etc.) nor the size of the cation and anion involved appear to be important in influencing the identity of the precipitation products.

The most reasonable explanation for these variations in composition of the precipitate seems to be that they are associated with the changes, caused by the presence of the added salt in the activities (and hence the solubilities) of the various carbonates (calcite, dolomite, magnesite, etc.) in the solution. For it was observed that the composition of the precipitates varied not only with the kind of salt present but also with its concentration. For example, in a group of samples precipitated at 270° C., a solution containing 1.5 per cent NaCl resulted in a precipitate of basic magnesium carbonate; a solution containing 3 per cent NaCl yielded a mixture of the basic magnesium carbonate, calcite and dolomite, while a 7 per cent NaCl solution resulted in a similar mixture with a much greater abundance of dolomite. A solution saturated with NaCl resulted in a mixture of dolomite and magnesite.

The results obtained in NaCl solutions indicate that other salts or salt mixtures might improve the conditions for dolomite precipitation even more. This possibility has not been investigated but it has been observed that of the few salts mentioned above, both BaCl<sub>2</sub> and CdCl<sub>2</sub> improve the quality of the dolomite precipitate a little more effectively than NaCl. Figure 1 compares the x-ray diffraction patterns of dolomite prepared in a solution free of added salts with those for samples obtained in NaCl, BaCl<sub>2</sub>, and CdCl<sub>2</sub> solutions. Patterns for two natural dolomites are also shown.

#### EFFECT OF VARIATIONS IN THE CA:Mg RATIO IN SOLUTION

It was found that the relative concentrations of calcium and magnesium ions in the original solutions had important effects on the products obtained. The Ca:Mg ratio in solutions which yielded the best dolomite varied with the temperature and the kind of salt present, but was independent of the CO<sub>2</sub> pressure over the range studied. For example, at 220° C. in the presence of NaCl the optimum Ca:Mg ratio (by weight) in solution was 1.4. The Ca:Mg ratio in the best synthetic dolomite samples prepared here was 1.67 (as determined by thermogravimetric analysis) in agreement with the theoretical value, but in the presence of NaNO<sub>3</sub> it was 1.9. At 300° C. with NaCl present the optimum ratio was 2.1 but it was only 1.2 at 170° C. At temperatures above 200° C. the formation of calcite was observed when the Ca:Mg ratio was greater than optimum and magnesite was found when the ratio was less than this. Below 220° C., Ca:Mg ratios greater than optimum favored the formation of basic magnesium carbonate rather than calcite, and Ca:Mg ratios less than optimum favored the formation of both magnesite and basic magnesium carbonate. At 220° C. variations in the Ca:Mg ratio over a fairly wide range did not appreciably affect the quality of the product obtained, which was pure dolomite. These results add significance to the fact that dolomite was obtained at temperatures near 220° C. whether NaCl was present or not, and indicate that the changes in the activities of the carbonates in solution resulting from the different CaCl<sub>2</sub> and MgCl<sub>2</sub> concentrations might be more important than the relative amounts of calcium and magnesium ions in solution.

It was observed from the powder patterns that the *d*-spacings for the calcite and magnesite in high-temperature precipitates were appreciably different from their normal values. These shifts in the *d*-spacings (to smaller values for calcite and larger values for magnesite) are probably the result of magnesium substitution in the calcite lattice and calcium substitution in the magnesite lattice (Goldsmith and Graf, 1958). However, there was very little correlation between shifts in the calcite and magnesite spacings and the Ca:Mg ratio in the original solution. In

general, the shifts in the calcite spacings were greater than those in magnesite and the precipitates in which dolomite was found exhibited smaller shifts in the calcite and magnesite *d*-spacings than those which contained only calcite and magnesite (obtained by precipitation at high temperatures without the addition of NaCl).

#### EFFECT OF UREA CONCENTRATION

The quality of the dolomite was found to be a rather critical function of the amount of urea added to the system. The optimum urea concentration varied with CO<sub>2</sub> pressure (increased with increasing pressure) but not with temperature. It was not possible to measure the pH of the solutions during precipitation in the autoclave, and the pH of the solution which remained after precipitation (measured at room temperature and pressure with a Beckman pH meter) was probably a very poor indication of the pH which existed in the autoclave under high CO<sub>2</sub> and NH<sub>3</sub> pressures.

The final pH values of all of the solutions which contained the best dolomite precipitates were in the range 6.5–7.5. Final pH values which fell within this range were observed over a wide range of original urea concentrations and original acidities, but for a given CO<sub>2</sub> pressure the best dolomite samples were always found in solutions of the same urea concentration. For example, at 60 atmospheres CO<sub>2</sub> pressure the best dolomite precipitates were obtained from solutions containing 3 per cent urea with final pH values in the 6.5–7.5 range. Solutions containing as little as 1 per cent or as much as 6 per cent urea yielded final pH values in this same range (perhaps due to the buffering action of CaCO<sub>3</sub> in the presence of ammonium chloride), but the dolomite in these samples was of much poorer quality and contained other products.

To illustrate the effects of variations in the temperature, salt concentration, Ca:Mg ratio, and urea concentration, some representative results have been selected from the 200 samples which were prepared and these are presented in Table 1. The relative amounts of each product in the precipitate have been roughly estimated from the *x*-ray powder patterns. The Ca<sup>++</sup> concentration (0.023 g./ml.) and the total volumes (35 ml.) of the original solutions were constant for the samples shown in Table 1.

#### TEMPERATURE EFFECTS

Fairly conclusive evidence is provided by these experiments that elevated temperatures are necessary for dolomite to be the thermodynamically stable product in the system used here. The lowest temperature at which dolomite could be precipitated was approximately 150° C. and

TABLE 1

Original Solution					Precipitate				
Sample	Ca:Mg	% NaCl	% Urea	Temp.	Dolomite	Calcite	Magnesianite	5MgO·4CO <sub>2</sub> ·×H <sub>2</sub> O	Aragonite
154	1.4	0	2.9	125° C	0	0	0	30%	70%
129	1.4	0	2.9	180° C	0	0	0	100%	0
139	1.4	0	2.9	230° C	100%	0	0	0	0
176	1.4	0	2.9	270° C	30%	0	60%	10%	0
1	2.6	0	2.9	295° C	0	50%	30%	20%	0
19	2.1	1.5	2.9	270° C	0	trace	0	100%	0
20	2.1	3.0	2.9	270° C	20%	20%	0	60%	0
21	2.1	14.0	2.9	270° C	75%	20%	0	5%	0
22	2.1	sat.	2.9	270° C	80%	0	20%	0	0
177	1.4	1.5	2.9	220° C	100%	0	0	trace	0
178	1.4	3.0	2.9	220° C	100%	0	0	0	0
179	1.4	7.1	2.9	220° C	90%	0	0	10%	0
181	1.4	sat.	2.9	220° C	80%	0	0	20%	0
33	2.4	7.1	2.9	220° C	90%	0	10%	0	0
48	1.7	7.1	2.9	220° C	100%	0	trace	0	0
50	1.4	7.1	2.9	220° C	100%	0	0	0	0
52	1.2	7.1	2.9	220° C	80%	0	20%	0	0
59	1.4	7.1	1.4	220° C	50%	0	0	50%	0
60	1.4	7.1	2.9	220° C	100%	0	0	trace	0
61	1.4	7.1	5.7	220° C	60%	0	30%	10%	0
62	1.4	7.1	14.0	220° C	0	40%	40%	20%	0

this lower limit appears to be independent of the CO<sub>2</sub> pressure in the system. This is well above the temperature required for the complete hydrolysis of urea (in the times involved here) at atmospheric pressure and it has been demonstrated by at least two authors (Krase, 1930 and Kawasumi, 1955) that increased CO<sub>2</sub> pressures do not affect the hydrolysis rate.

This point is of interest in connection with attempts to precipitate dolomite under conditions which might have existed during its natural formation in sedimentary environments. The failure to observe its precipitation at temperatures below 150° C. in these experiments does not provide conclusive evidence that it could not be formed at lower temperatures in a different system or over much longer periods of time in this system. The formation of dolomitic sediments in a number of saline lakes

has recently been reported by Alderman and Skinner (1957) in southeast Australia. An investigation of the thermodynamic equilibrium constants associated with the various components of the present system might suggest means of precipitating dolomite in the laboratory at temperatures and pressures more similar to earth-surface conditions.

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#### REFERENCES

1. ALDERMAN, A. R. AND SKINNER, H. C. W. (1957), "Dolomite Sedimentation in the South-East of South Australia," *Amer. Jour. Sci.*, **225**, 561-567.
2. CHILLINGAR, G. V. (1956), "Relationship Between Ca/Mg Ratio and Geologic Age," *Bull. AAPG*, **40**, 2256-2266.
3. GOLDSMITH, J. R. AND GRAF, D. L. (1958), "Relations Between Lattice Constants and Composition of the Ca-Mg Carbonates," *Am. Mineral.*, **43**, 84-101.
4. GRAF, D. L. AND GOLDSMITH, J. R. (1955), "Dolomite-Magnesian Calcite Relations at Elevated Temperatures and CO<sub>2</sub> Pressures," *Geochim. et Cosmochim. Acta*, **7**, 109-128.
5. GRAF, D. L. AND GOLDSMITH, J. R. (1956), "Some Hydrothermal Syntheses of Dolomite and Proto-Dolomite," *Jour. Geol.*, **64**, 173-186.
6. JANTSCH, G. AND ZEMEK, F. (1949), "Preparation of Synthetic Crystalline Magnesium Carbonate," *Radex-Rundschau*, **3**, 110-111.
7. KAWASUMI, SCHOHACHI (1955), "Equilibrium of the CO<sub>2</sub>-NH<sub>3</sub>-Urea-H<sub>2</sub>O System under High Temperature and Pressure," *Bull. Chem. Soc. Japan*, **26**, 218-227.
8. KRASE, H. J. (1930), "Equilibria in the Ammonium Carbonate-Urea-Water-Ammonia System," *J. Am. Chem. Soc.*, **52**, 3088.

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