

THE AMERICAN MINERALOGIST, VOL. 47, NOVEMBER-DECEMBER, 1962

## THE ACTION OF WATER ON CALCITE, MAGNESITE AND DOLOMITE

GEORGE W. MOREY,<sup>1</sup> *Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.*

The experiments described in this paper were performed at the Geophysical Laboratory of the Carnegie Institution of Washington in 1956 and reported at the Minneapolis, Minnesota, meeting of the Geological Society of America in 1956 (Morey, 1956). The apparatus used was described by Morey and Fournier (1961). It consisted essentially of a stainless steel reaction tube, 10 ml capacity, closed at each end by a porous stainless steel filter. This tube was placed in a furnace, and pure water, freed from CO<sub>2</sub> by passing over a suitable ion-exchange resin, was pumped through the tube. The rate of flow was controlled by a throttling valve at the exit end, and the pressure was maintained at 200 atmospheres. This was well above the vapor pressure of water at the highest temperature used, so that the water remained liquid.

The calcite, magnesite and dolomite used were from S. W. Africa, Brazil and Maryland, respectively, and were selected by the late Dr. W. F. Foshag, Head Curator, Department of Geology, U. S. National Museum, to whom I express my gratitude. The samples were crushed, sieved through 24 mesh per inch, caught on 48 mesh, worked and placed in the reaction tube. Analyses were made by the versene titration method.

The effect of rate of flow of the H<sub>2</sub>O was determined with calcite at 250° C. Table 1 shows that an eight-fold increase in rate of flow did not affect the results within experimental error, and the flow was kept below 1 ml per minute.

Calcite, CaCO<sub>3</sub>, was dissolved without decomposition by water, as shown by the x-ray pattern of the material remaining unchanged. Some material was deposited on the stainless steel filter at the exit end of the

TABLE 1. EFFECT OF RATE OF FLOW ON THE AMOUNT OF CaCO<sub>3</sub> DISSOLVED

Rate of flow, ml per min.	Weight CaCO <sub>3</sub> , ppm
0.16	15.06
0.31	15.74
0.47	15.37
0.61	15.41
1.2	15.40

<sup>1</sup> Present address: U. S. Geological Survey, Washington, D. C.

TABLE 2. THE SOLUBILITY OF  $\text{CaCO}_3$  IN  $\text{CO}_2$ -FREE WATER

Temperature, ° C.	25	65	95	120	165	180	220	250	300	350
Solubility, ppm	20	20	21	21	20	19	17.5	15	12	7

reactor, which proved to be calcite. The results are in Table 2 and Fig. 1. These appear to be the only studies made on  $\text{CaCO}_3$  in which  $\text{CO}_2$ -free water was used. Wells (1915*a*) used air containing about 3.2 ppm of  $\text{CO}_2$ , and the higher results he obtained at lower temperature may be due to the  $\text{CO}_2$ . At 50° C., the highest temperature at which Wells worked, the results were about the same. Schloemer (1952) found the much greater value of 390 ppm at 374° C.

Magnesite,  $\text{MgCO}_3$ : An *x*-ray study made after a series of runs at 25° to 350° C. showed that above 150° C. the  $\text{MgCO}_3$  had been entirely changed to brucite,  $\text{Mg}(\text{OH})_2$ . Some snowy white crystals of sepiolite,  $2\text{MgO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , identified by *x*-rays were found, especially on the stainless steel filter at the outlet end of the reactor, as well as some dolomite. Both extraneous phases doubtless were the result of impurities in the magnesite. The solubility of  $\text{MgCO}_3$  is congruent up as high as 150° C., above that it is incongruent. Analyses made to determine the presence of  $\text{CO}_2$  in the exit water by titration with N/44 NaOH, using phenolphthalein as indicator, showed no free  $\text{CO}_2$  below 150°, 0.5 ppm at 154°, 1 ppm at 165°, 3 ppm at 167°, and 7 ppm at 184° C. The results are presented in Table 3 and Fig. 2. The congruent solubility of  $\text{MgCO}_3$  increases to a maximum of 13 ppm at 150°, then decreases. Above 150° the water is

TABLE 3. THE ACTION OF  $\text{CO}_2$ -FREE WATER ON MAGNESITE,  $\text{MgCO}_3$ 

Temp., ° C.	MgO in Solution, in ppm	
	Calc. as $\text{MgCO}_3$	Calc. as $\text{Mg}(\text{OH})_2$
25	4.2	
60	8.2	
100	11.8	
130	12.8	
160	12.5	
180	11.2	
200	8.0	
210		17
240		14
250		13
240		9
290		3

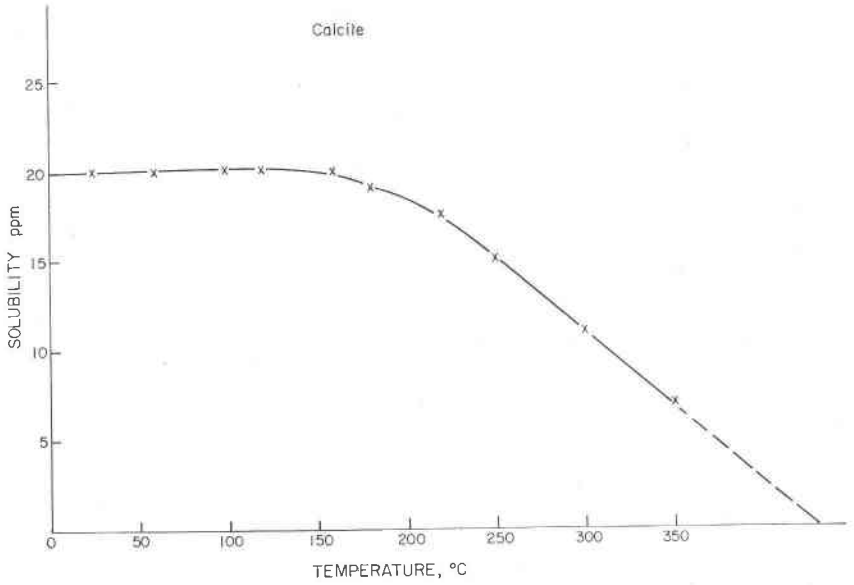


FIG. 1. The solubility of  $\text{CaCO}_3$  in  $\text{CO}_2$ -free water. The solubility remained practically unchanged up to about  $150^\circ\text{C}$ ., after which it fell off rapidly. It probably would be about zero at the critical temperature of water.

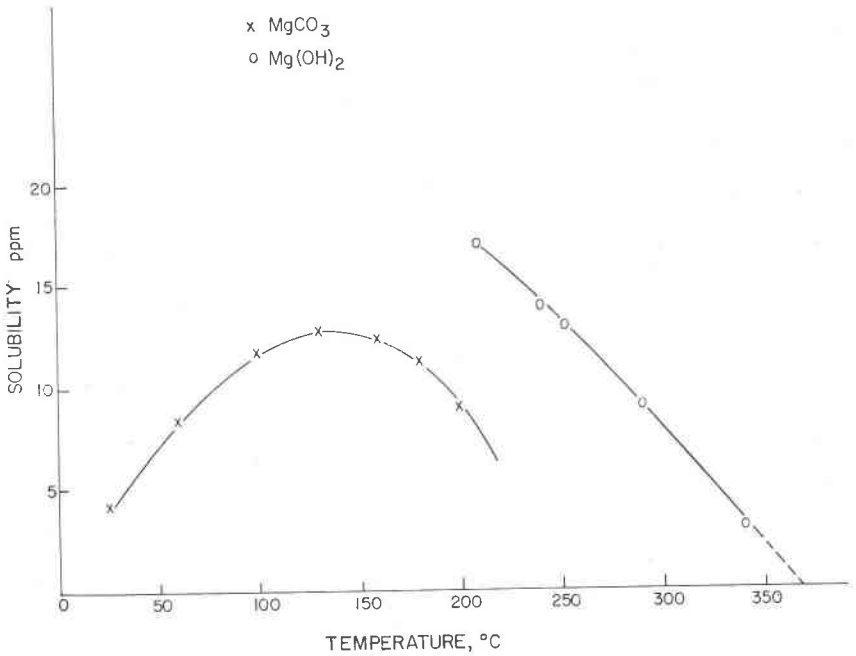


FIG. 2. The action of  $\text{CO}_2$ -free water on magnesite,  $\text{MgCO}_3$ .

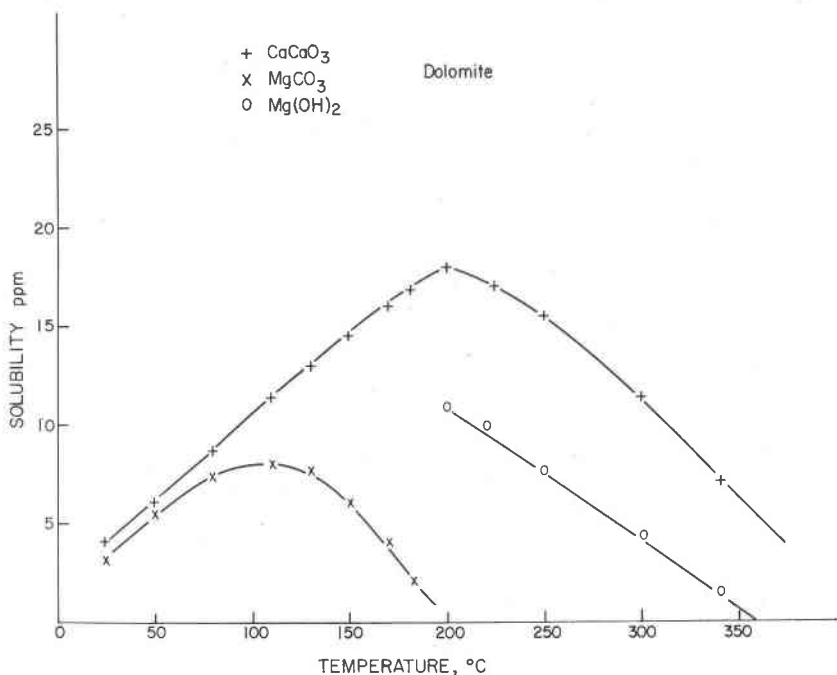


FIG. 3. The action of CO<sub>2</sub>-free water on dolomite, CaCO<sub>3</sub>·MgCO<sub>3</sub>.

passing over a mixture of MgCO<sub>3</sub> and Mg(OH)<sub>2</sub>, and if the run were continued long enough at that temperature the MgCO<sub>3</sub> would be entirely replaced by Mg(OH)<sub>2</sub>. The only comparable results are those of Wells (1915*b*), who used air containing the normal amount of CO<sub>2</sub>. With nesquehonite (MgCO<sub>3</sub>·3H<sub>2</sub>O) he found 0.36 g Mg and 1.01 g CO<sub>2</sub> per liter at 20° C. With MgCO<sub>3</sub> he found the much smaller value of 0.02 g Mg and 0.07 g CO<sub>2</sub> per liter. Schloemer (1952) also found that MgCO<sub>3</sub> was decomposed to brucite by water.

Dolomite, CaCO<sub>3</sub>·MgCO<sub>3</sub>: In the runs with dolomite both MgO and CaO were determined, and calculated to MgCO<sub>3</sub> and CaCO<sub>3</sub>. The amount of calcite increased linearly with temperature up to 200° C., then decreased sharply (Fig. 3). The amount dissolved at 200° C., 18 ppm, is the same as was found for *calcite*. The amount of MgCO<sub>3</sub> increased up to 100° C., then decreased. There appeared to be a break a little below 200° C., after which the MgO content abruptly increased. This is interpreted as indicating the formation of brucite. The *x*-ray determinations showed that the finer-grained material was calcite and brucite, but the coarser grains had a core of dolomite. No free CO<sub>2</sub> was found below 180° C., but at that temperature there was 3 ppm of free CO<sub>2</sub>. With magnesite the reaction

TABLE 4. THE ACTION OF CO<sub>2</sub>-FREE WATER ON DOLOMITE, CaCO<sub>3</sub>·MgCO<sub>3</sub>

Temp., ° C.	CaCO <sub>3</sub> , ppm	MgCO <sub>3</sub> , ppm	Mg(OH) <sub>2</sub> , ppm
25	4	3	
50	6	5.5	
80	8.6	7.3	
110	11	8	
130	13	7.8	
150	14.5	6	
200	18		11
225	17		10
250	15.5		8
300	12.5		4
340	7		1.5

MgCO<sub>3</sub>+H<sub>2</sub>O⇌Mg(OH)<sub>2</sub>+CO<sub>2</sub> began at about 150° C.; with dolomite it began a little higher, at 180° C. X-ray studies below 209° C. of material from the top of the reaction tube show only the dolomite patterns, but at 209° C. the pattern was of calcite and brucite. The results are in Table 4 and Fig. 3.

## REFERENCES

- MOREY, GEORGE W. (1956) Action of hot water on some carbonates. *Geol. Soc. Am. Bull.* **67**, 1721-1722.
- AND R. O. FOURNIER (1961) The decomposition of microcline, albite, and nepheline in hot water. *Am. Mineral.* **46**, 688-699.
- SCHLOEMER, H. (1952) Hydrothermal studies in the system CaO-MgO-CO<sub>2</sub>-H<sub>2</sub>O. *Neues Jahrb. Mineral., Monatshefte*, 129-135.
- WELLS, R. C. (1915a) The solubility of calcite in water in contact with the atmosphere and its variation with temperature. *Jour. Wash. Acad. Sci.*, **5**, 617-622.
- (1915b), The solubility of magnesium carbonate in natural waters. *Jour. Am. Chem. Soc.*, **37**, 1704-1707.

THE AMERICAN MINERALOGIST, VOL. 47, NOVEMBER-DECEMBER, 1962

## SOME ALKALI ALUMINATE CRYSTALS AND POTASSIUM FERRITE

GEORGE W. MOREY,<sup>1</sup> *Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.*

The following alkali aluminate crystals were found in a study started about 1940 at the Geophysical Laboratory of the Carnegie Institution of Washington, but never completed.

At 130° C. the solid phase in equilibrium with a solution of the composi-

<sup>1</sup> Present address: U. S. Geological Survey, Washington, D. C.