

ART. XXIX.—*On Solid Solution in Minerals.* V. *The Isomorphism between Calcite and Dolomite*; by H. W. FOOTE and W. M. BRADLEY.

SOLUTIONS of liquids in liquids may, as is well known, conveniently be divided into two classes depending on whether there is complete or incomplete miscibility in all proportions. In the same way, it is convenient to distinguish two classes of isomorphous mixtures or solid solutions. In one class, isomorphism is complete and solid solutions in any proportions are possible, while in the other, each solid can take up but a limited amount of the other. The alums form solid solutions of the first class, and among minerals, anorthite and albite are similarly capable of mixing in all proportions, forming the plagioclase feldspars. A large number of salts form solid solutions of the second class, each salt taking up only a limited amount of the other, and among minerals, calcite and dolomite belong in this class. In the present investigation, we have endeavored to determine, at least approximately, to what extent solid solution may take place between these two minerals as they occur in nature.

It will be well to consider first the possible effect of temperature on the mixing limits. This influence has very commonly been disregarded in determining to what extent solid solution may take place. For instance, Retgers\* has determined the mixing limits of a large number of salts and has considered the results as representing fixed values without regard to temperature. Van't Hoff,† however, pointed out that the mixing limits of solid solutions, like the composition of partially miscible liquids, should be a function of the temperature and this has been demonstrated experimentally in a number of cases. The determination of mixing limits might, therefore, have little significance unless the temperature were known. However, if the solubility of one solid in another is slight, temperature will have but little influence on the absolute amount dissolved and the mixing limit should be reasonably constant. This is the case, as will be seen below, with calcite saturated with dolomite (or magnesium carbonate). When a solid dissolves a considerable quantity of another, temperature may affect the limit largely and in general a greater absolute change would be expected than where the solubility is slight.

It is evident that for a given temperature each solid will take up the maximum amount of the other when both are

\* A series of eleven articles, *Zeitschr. phys. Chem.*, 1889–1895.

† *Vorlesungen über Chemie*, I, 49.

deposited simultaneously. This is the case, for instance, when solid solutions crystallize as eutectics. If dolomite and calcite could be obtained which had crystallized simultaneously from solution, this material would therefore be ideal for determining the mixing limits of both minerals. A very careful search through the extensive Brush collection has shown no specimen where this condition of affairs was realized, nor have we been able to obtain such a specimen from other sources. This was not unexpected, for it can be shown that at a given temperature, both minerals could be deposited only when the ratio of lime to magnesia in the solution has one fixed value. On the other hand, dolomite or calcite alone could be formed from an infinite number of solutions, with varying proportions of lime and magnesia. Almost the only chance of obtaining such specimens appears to be from the concentration of a large quantity of solution containing salts of both metals, in which case, one mineral would first crystallize to be followed ultimately by the crystallization of both.

There appears to be another way, however, in which crystals of one of the minerals may be obtained saturated with the other. If, for instance, a solution capable of depositing dolomite comes in thorough contact with calcite, the solution should become saturated with the latter and the dolomite resulting should contain the maximum amount of calcium carbonate. A specimen of dolomite, therefore, deposited on calcite, or of calcite on dolomite, may usually be expected to contain the maximum amount of the other salt in solid solution. On the other hand, the calcite or dolomite originally present would not, of necessity, be changed in composition to the limiting value. As will be seen below, one specimen of calcite deposited on a dolomite was apparently not saturated with the latter. In this case, the calcite crystal stood out from the mass of dolomite and the solution from which it formed was probably not saturated with the latter. In general, where the secondary mineral crystallizes in intimate contact with the primary one, the composition should approach closely to the limiting value.

A number of specimens have been obtained showing the associations mentioned above, where either dolomite or calcite has been deposited on the other, and in each case the secondary mineral has been analyzed. In some cases, the material required for analysis was so closely associated with the primary mineral that separation by means of heavy solution was necessary. In the case of one dolomite, No. III, the material was put through the heavy solution twice to remove particles of calcite carried down in the first treatment. Where the specific gravity of the samples is not given in the table, the material was in such good crystals that it could be separated in pure

condition by careful picking. The analyses were made by the usual methods. All the minerals dissolved completely in hydrochloric acid. Iron and manganese were both precipitated by means of bromine and ammonia. Ordinarily, manganese and iron were not both present in appreciable amount and the precipitate, after ignition, was considered either as  $\text{Fe}_2\text{O}_3$  or  $\text{Mn}_2\text{O}_3$ . In the one case necessary, they were separated by the basic acetate method. Calcium was weighed as oxide after a double precipitation as oxalate. We were able to confirm the observation made by Gooch and Austin\* and others that magnesia gives high results when precipitated from a cold solution as ammonium magnesium phosphate in the usual manner. On this account, the precipitate, after standing, was filtered and redissolved in hydrochloric or nitric acid. The solution was heated to boiling, and after adding a small amount of ammonium phosphate, was again made alkaline with ammonia. The precipitate was allowed to stand until cold before filtering. Carbon dioxide was not determined directly.

*Calcite.*

The specimens used for analysis were the following:

1. Small yellowish scalenohedrons of calcite deposited on well-crystallized dolomite. Locality unknown.
2. Fine crystals of calcite, slightly etched, a combination of prism with rhombohedron, deposited on a crystalline layer of dolomite. This, in turn, was deposited on large scalenohedrons of calcite. The dolomite of this specimen was also analyzed. (See dolomite No. III.) Ouray, Colorado.
3. Small scalenohedrons of calcite deposited on well-crystallized dolomite. Joplin, Missouri (?).
4. Small etched scalenohedrons on a crystalline deposit of dolomite. Guanajuato, Mexico.
5. A single crystal of calcite deposited on a mass of well-crystallized dolomite. Cave of the Winds, Niagara.
6. A large, water-clear crystal of calcite, associated with pink rhombohedral dolomite. Joplin, Mo.

The analyses are given in Table I.

Of the six analyses of calcite, all but one (No. 6) show a reasonably constant amount of magnesium carbonate. The average amount in the five analyses is 0.97 per cent and the greatest deviation from this value amounts to only 0.17 per cent. Coming as the specimens do, from a number of widely separated localities, and varying greatly in habit, it is certain that they were formed under varying conditions. The conclusion appears justified, therefore, that calcite is saturated by

\* This Journal, vii, 187, 1899.

TABLE I.  
*Analyses of Calcite Deposited on Dolomite.*

	1 Sp. gr. 2.713—2.722			2 Sp. gr. undet. Ouray, Colorado.		
	<i>a</i>	<i>b</i>	Average	<i>a</i>	<i>b</i>	Average
	-----	-----	-----	-----	-----	-----
MgCO <sub>3</sub> .....	1.08	0.98	1.03	0.79	0.80	0.80
CaCO <sub>3</sub> .....	99.06	99.08	99.07	96.71	96.48	96.59
MnCO <sub>3</sub> .....	0.12	0.10	0.11	2.92	2.94	2.93
	100.26	100.16	100.21	100.42	100.22	100.32
	3 Sp. gr. undet. Joplin, Mo. ?			4 Sp. gr. 2.741—2.769 Guanajuato, Mexico		
	<i>a</i>	<i>b</i>	Average	<i>a</i>	<i>b</i>	Average
	-----	-----	-----	-----	-----	-----
MgCO <sub>3</sub> .....	1.03	1.06	1.04	1.07	1.12	1.09
CaCO <sub>3</sub> .....	99.26	99.21	99.23	93.05	93.24	93.15
MnCO <sub>3</sub> .....	0.17	0.18	0.18	5.80	5.70	5.75
	100.46	100.45	100.45	99.92	100.06	99.99
	5 Sp. gr. undet. Cave of the Winds, Niagara			6 Sp. gr. undet. Joplin, Mo.		
	<i>a</i>	<i>b</i>	Average	<i>a</i>	<i>b</i>	Average
	-----	-----	-----	-----	-----	-----
MgCO <sub>3</sub> .....		0.87		0.47	0.42	0.44
CaCO <sub>3</sub> .....		99.38		99.65	99.65	99.65
MnCO <sub>3</sub> .....		0.42		0.22	0.22	0.22
		100.67		100.34	100.29	100.31

approximately one per cent of magnesium carbonate at common temperatures of crystallization. As we pointed out before, a nearly constant value is to be expected where the amount of material in solid solution is small, unless, indeed, the temperature variation is great. We know of no reliable data at present to show whether this limit varies appreciably with extreme temperature conditions. An examination of some of the magnesian limestones would probably give information on this point. A number of cases have been reported in which calcites contained more magnesia than has been found by us, but there is no evidence that the material analyzed was homogeneous. Thus, Eisenhuth\* has analyzed two calcites containing respectively 3.01 and 1.52 per cent of magnesium carbonate. Both of his specimens contained insoluble matter, showing the material was not quite homogeneous, and it seems fully as

\*Zeitschr. Kryst., xxxv, 582, 1901.

probable that there may have been a small amount of admixed dolomite as that the calcite itself contained this unusual amount of magnesium carbonate. The magnesium content of our No. 6 is lower than any of the others. In this case, the calcite was probably unsaturated. The crystal was a water-clear specimen projecting two or three centimeters from a mass of dolomite crystals which served as its base. The association was not an intimate one and the solution depositing calcite had evidently not become saturated with magnesium carbonate from the dolomite. The analysis is not given to show the limiting value but to show that fairly intimate association of the minerals is necessary in order that the limiting value may be reached. It is perhaps worth mentioning here that iron in appreciable quantities was not found in any calcite examined. No other samples of calcite were analyzed.

### Dolomite.

The specimens of dolomite deposited on calcite were the following:

I. A crystalline layer of dolomite deposited on massive calcite. Guanajuato, Mexico.

II. Small rhombohedral crystals of dolomite deposited as a crust on scalenohedrons of calcite. Guanajuato, Mexico.

III. An occurrence similar to that of No. II. On the dolomite, calcite was subsequently deposited (see calcite No. 2). Ouray, Colorado.

The analyses are given in Table II.

TABLE II.  
*Analyses of Dolomite deposited on Calcite.*

	I			II		
	Sp. gr. 2·865—2·914			Sp. gr. 2·891—2·907		
	Guanajuato, Mexico			Guanajuato, Mexico		
	<i>a</i>	<i>b</i>	Average	<i>a</i>	<i>b</i>	Average
MgCO <sub>3</sub> .....	33·52	33·48	33·50	31·50	31·45	31·48
FeCO <sub>3</sub> .....	6·14	5·95	6·05	8·43	8·49	8·46
CaCO <sub>3</sub> .....	60·68	60·61	60·64	60·67	60·76	60·71
	100·34	100·04	100·19	100·60	100·70	100·65

  

III			
Sp. gr. 2·887—2·860			
Ouray, Colorado			
	<i>a</i>	<i>b</i>	Average
MgCO <sub>3</sub> .....	30·57	30·85	30·71
FeCO <sub>3</sub> .....	3·45	3·40	3·43
MnCO <sub>3</sub> .....	3·41	3·07	3·24
CaCO <sub>3</sub> .....	63·03	63·04	63·03
	100·46	100·36	100·41

The analyses show that all specimens contained more or less ferrous carbonate, and one, manganese carbonate also. We consider that these components replace magnesium carbonate. The ratios are as follows :

	I	II	III
MgCO <sub>3</sub> .....	·397	·373	·364
FeCO <sub>3</sub> .....	·052	·073	·030
MnCO <sub>3</sub> .....	-----	-----	·028
CaCO <sub>3</sub> .....	·606	·607	·630

The ratios  $\frac{\text{CaCO}_3}{(\text{Mg,Mn,Fe})\text{CO}_3}$  calculated from these results are :

I	II	III
1·349	1·361	1·492

These ratios show a somewhat surprising excess of calcium above the dolomite ratio, and the excess is variable. Since the material was homogeneous, but deposited directly on calcite, we see no reason why the ratios do not represent approximately limiting values for calcium carbonate in dolomite. From the fact that dolomite occurs so generally in the 1:1 ratio, Retgers\* assumed that this ratio could not be much exceeded, but this appears not to be the case. The variable ratio is not unexpected and should be due in large part to the influence of temperature at the time of formation. These were all the specimens analyzed, in which dolomite was clearly the secondary mineral. One specimen was obtained in which there was primary formation of dolomite followed by the formation of a single large calcite crystal. (See calcite anal. No. 6.) About the base of the calcite, a small quantity of dolomite had subsequently formed. Both deposits were similar in appearance and could not be separated. A sample, chipped off near the base of the calcite crystal and containing some of each deposit, gave the following results on analysis :

Sp. gr. 2·834–2·868

Joplin, Mo.      •

	<i>a</i>	<i>b</i>	Average
MgCO <sub>3</sub> .....	40·31	40·13	40·22
FeCO <sub>3</sub> .....	1·91	1·93	1·92
CaCO <sub>3</sub> .....	58·19	58·13	58·16
	<hr/> 100·41	<hr/> 100·19	<hr/> 100·30

The ratio  $\frac{\text{CaCO}_3}{(\text{MgFe})\text{CO}_3}$  calculated from these results is 1·176.

\* Loc. cit., vi, 227, 1890.

The proportion of calcium in this case is much larger than is commonly found in a dolomite, but it cannot be regarded as a limiting ratio, as some of the primary dolomite was present.

Our results do not show whether the effect of increased temperature will be to increase or diminish the proportion of lime at the mixing limit. In this case, as in that of calcite, it is probable that the investigation of limestones containing magnesia would give some information.

In conclusion; we wish to call attention to the fact that the quantitative isomorphous relations between other mineral carbonates are quite unknown. To what extent, for instance, siderite or rhodochrosite can take up calcium carbonate has not been determined. It seems not unlikely that some of these problems, at least, may be settled by artificial preparations, and this method would have the very great advantage of working under known temperature conditions.

Chemical and Mineralogical Laboratories  
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