THE AMERICAN MINERALOGIST, VOL. 52, SEPTEMBER-OCTOBER, 1967

STRONTIUM AND MANGANESE CONTENT OF SOME COEXISTING CALCITES AND DOLOMITES

D. K. Atwood and H. M. Fry, *Esso Production Research Company, Houston, Texas.*

Various authors have investigated trace element compositions in whole carbonate rocks as possible clues to their diagenetic history. Recently, Stehli and Hower (1961) determined the concentration of magnesium, strontium, manganese and barium in Recent carbonate sediments and environmentally comparable Pleistocene carbonate rocks showing that for each of these elements, diagensis resulted in a marked decrease in concentration. Weber (1964) reported analyses of 300 "primary" and "secondary" dolostones[1] and 150 dolomites for 20 trace elements. Weber reports that rocks he classified as "primary" dolostones had greater abundances of potassium, lithium and barium whereas "secondary" dolomites were enriched in strontium.

Unfortunately, in neither of the above studies nor in any previous work, was the trace element composition of coexisting carbonate phases determined. In ancient limestones these phases consist of only dolomite and calcite and any differences in trace element assemblages between phases are very probably related to the dolomitization process itself. This paper describes an effort to test this hypothesis with regard to two elements (Sr and Mn) by the separation and analysis of 21 dolomitic limestones and dolomites from the Trenton-Black River formation in Michigan.

Sample Source

All samples consisted of core taken from wells penetrating the Trenton-Black River (Middle Ordovician) sequence near the southern margin of the Michigan Basin. In this area, the Trenton-Black River consists of regional dolomitic limestone containing local northwest-southeast oriented trends of dolomite. This dolomite is apparently secondary and localized along fracture zones. Details of the geology are adequately described by Ells (1962). Samples were chosen from wells in and around these dolomitized trends and consisted of rocks containing from 10 to 97 percent dolomite.

Separation and Analysis

Each sample was ground to pass a 200-mesh screen. A portion was then

[1] Weber defines a dolostone as a rock consisting largely of dolomite admixed with clay minerals, pyrite, chert, etc.

mixed with an internal standard (Al powder) and the X-ray diffraction pattern run to determine the position of the d_{112} diffraction peaks for both dolomite and calcite. The sample was then separated and analyzed. The details of analysis are as follows:

Step 1: An aliquot of the ground core sample is treated with 2N HCl dissolving all the carbonates. The calcium and magnesium content of the carbonate fraction is determined by analyzing the resulting solution with versenate and Calver II indicator at pH13 for Ca^{2+} and Erichrome Black T indicator at pH10.5 for Ca^{2+} plus Mg^{2+}.

Step 2: A second aliquot of ground core is pressed into a pellet and the strontium and manganese content determined using an X-ray fluorescence method. Runs on replicate pellets indicate the precision of these determinations to be about ±5 ppm.

Step 3: A third aliquot of ground core is stirred with a 0.5M acetic acid solution, buffered with 0.5M sodium acetate, for approximately 15 minutes. The kinetics of dissolution of dolomite and calcite are such that this treatment dissolves all the calcite and a small amount of dolomite. The sample is then washed, dried, and a portion analyzed by X-ray diffraction to determine whether or not all the calcite has been removed.

Step 4: An aliquot of the residue from Step 3, which consists of dolomite and noncarbonate material, is treated with 2N HCl to dissolve the dolomite. The calcium and magnesium content of the dolomite phase is then determined as in Step 1.

This data is used to:

1. Calculate the Ca/Mg molar ratio of the dolomite.
2. Calculate the amount of dolomite and calcite in the original sample by assuming that all the magnesium found in Step 1 is from dolomite. (This assumption is shown to be reasonable because X-ray diffraction patterns for the original samples showed shifts of <0.01 Å from the ideal position of the calcite d_{112} peak indicating incorporation of less than 2 percent Mg^{2+} in the calcite lattice.)

Step 5: A second aliquot of the residue from Step 3 is pressed into a pellet and strontium and manganese determined as in Step 2. Runs on replicate pellets again indicated the precision of these determinations to be about ±5 ppm. Both here, and in Step 4, the assumption is made that the dolomite dissolved in Step 3 is essentially the same as that left in the residue. Some error is introduced due to preferential dissolution of the more Ca-rich dolomites as noted by Peterson *et al.* (1966) and as evidenced by comparing the position of the d_{112} diffraction peak for dolomite in the leached and unleached samples. Some shifting in peak position was noted, but, these shifts were generally less than 0.01 Å which would represent a difference of <0.1 in the molar Ca/Mg ratio.

Step 6: A third aliquot of the residue from Step 3 is reacted with 2N HCl to remove the dolomite.

Step 7: The residue from Step 6, which consists of non-carbonate material, is mixed with a standard carbonate matrix and strontium and manganese determined as in Step 2.

Using the strontium and manganese concentrations from Steps 2, 5, and 7, along with the concentrations of dolomite, calcite and non-carbonate material determined in Steps 1 and 4, the strontium and manganese content of each phase is calculated. Taking into account the precision of the Sr and Mn determinations, as well as the assumptions made, the error limits for both the Sr and Mn data on each phase is considered to be in the order of ±20 ppm.

RESULTS

Strontium. The range of concentrations and average concentration for strontium in each phase are shown in Table 1. As can be seen, a range of data exists for each phase with some overlap, however, it is quite clear that the strontium is concentrated in the calcite phase of the rocks, with the dolomite phase containing about a third as much. Due to the range of the data, and the fact that the dolomite is apparently secondary, no attempt was made to calculate a distribution coefficient for strontium between the calcite and dolomite phases. However, it is quite interesting to consider the Sr content of the dolomite as a function of the molar Ca/Mg ratio of dolomite. Goldsmith *et al.*, (1955), as well as Füchtbauer and Goldschmidt (1966), have demonstrated that the position of the d_{112} diffraction peak for dolomite is a direct indication of its molar Ca/Mg ratio with dolomites of high Ca/Mg ratios having low d_{112} diffraction angles.[1] Ideal dolomite *i.e.*, dolomite with a molar Ca/Mg ratio of 1.0 has a d_{112} angle of 30.96° 2θ when CuKα radiation is used. Thus, dolomites with d_{112} diffraction angles lower than 30.96° 2θ are Ca-rich in composition. Such Ca-rich dolomites can be considered as "incomplete" and result from some "diagenetic restraint" during their formation.

TABLE 1. RANGE AND AVERAGE STRONTIUM CONCENTRATIONS FOR TRENTON-BLACK RIVER LIMESTONES

Phase	Range ppm	Average ppm
Calcite	154–459	302
Dolomite	37–266	88
Non-Carbonate	3–55	29

The dolomite present in the Trenton-Black River samples used in this study had d_{112} diffraction angles varying from 30.67 to 30.96° 2θ. This represents a compositional variation of from $Ca_{58}Mg_{42}$ (58 mole% $CaCO_3$ and 42 mole % $MgCO_3$) to $Ca_{50}Mg_{50}$ for the dolomite.

Figure 1 shows the strontium content of the dolomite phase plotted versus the dolomite $2\theta(112)$ angle. A definite correlation is indicated with the low $2\theta(112)$ angle Ca-rich dolomites containing more strontium. The linear correlation coefficient for the data as plotted is -0.79 with the

---

[1] The incorporation of large amounts of other elements in the dolomite lattice also affects d_{112}. However, in this case no other elements (not even Mn^{2+} or Sr^{2+}) were shown to be present in sufficient quantity to cause extensive lattice distortions. Thus, all variations in the d_{112} angle are attributed to variations in the Ca^{2+} and Mg^{2+} content.

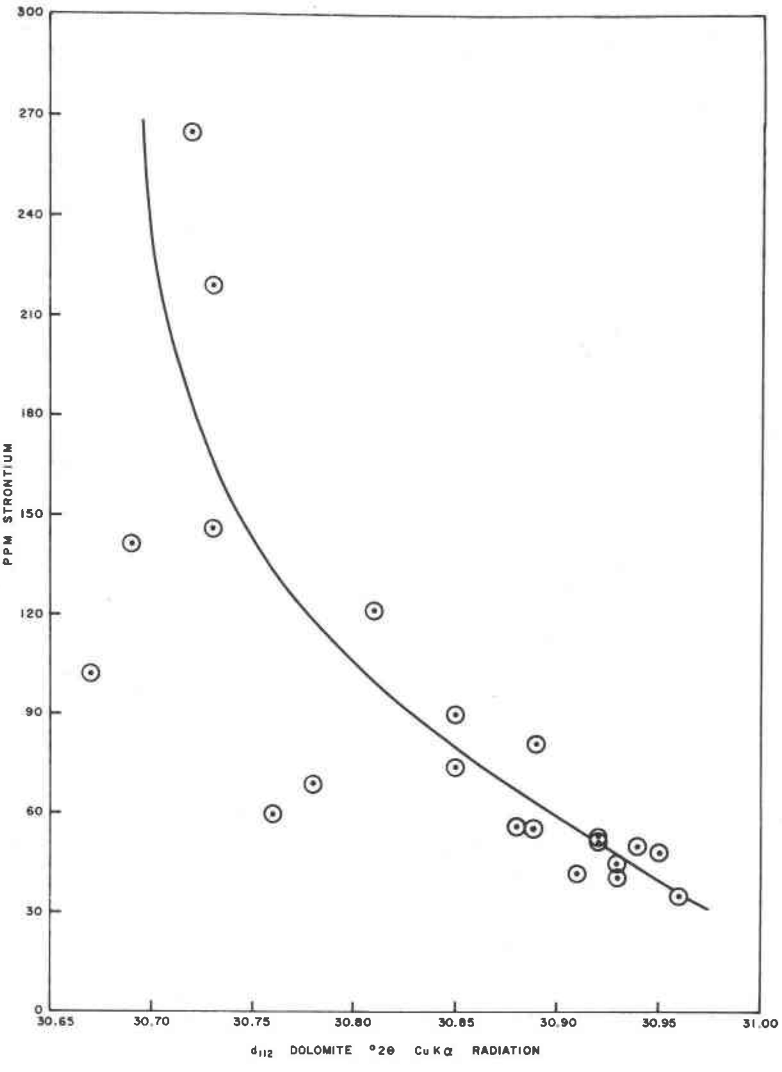

FIG. 1. Sr Concentration versus $2\theta(112)$ of dolomite phase.

probability of a random distribution giving such a coefficient being <0.001. There is also evidence of a discontinuity in the data at the low angle (Ca-rich) end. This correlation suggests that during dolomitization the Sr present in the parent calcite is excluded from the smaller dolomite lattice due to its large size. As the reaction proceeds, converting the incomplete Ca-rich dolomite to ideal dolomite, more and more strontium seems to be excluded until a final value of about fifty ppm is reached as compared to an average value of 300 ppm for the original calcite.

Manganese: The range of concentrations and average concentrations for manganese in each phase are shown in Table 2. As in the case of strontium, a range of data exists for each phase precluding any calculation of meaningful distribution coefficients. It is apparent, however, that the manganese present in the Trenton-Black River samples analyzed is concentrated in the dolomite fraction. It is also quite obvious from these data that the Mn^{2+} in the dolomite could not have come from the parent calcite, and, therefore, was probably present in the dolomitizing solution. Since Mn^{2+} is quite similar to Mg^{2+} in ionic size and electronegativity, this incorporation of Mn^{2+} in the dolomite lattice during dolomitization should occur quite readily.

TABLE 2. RANGE AND AVERAGE MANGANESE CONCENTRATIONS FOR TRENTON-BLACK RIVER LIMESTONES

Phase	Range ppm	Average ppm
Calcite	0–255	55
Dolomite	333–3207	1221
Non-Carbonate	48–709	169

Table 3 is a compilation of the results of all analyses.

CONCLUSIONS

1. The strontium and manganese content of coexisting calcite and dolomite can be quite different.
2. In Trenton-Black River dolomites and dolomitic limestones strontium is concentrated in the calcite and Ca-rich dolomites and manganese is concentrated in the dolomite phase.
3. Conclusions 1 and 2 suggest that strontium is excluded from the crystal lattice during dolomitization of calcite. As dolomitization proceeds from Ca-rich to ideal dolomites, this exclusion seems to become even more pronounced.
4. Manganese is concentrated in the dolomite phase, suggesting that it was incorporated from the dolomitizing solution rather than the parent calcite.

REFERENCES

ELLS, G. D. (1962) *Structures associated with the Albion-Scipio oilfield trend.* Mich. Dept. Conserv. Lansing, Mich, 86 p.

FÜCHTBAUER, H. AND H. GOLDSCHMIDT (1966) Beziehungan zwischen Kalzium Gehalt und Bildungsbedingungen der Dolomite. *Geol. Rundsch.* **55,** 29–40.

TABLE 3. SR AND MN CONTENT OF TRENTON-BLACK RIVER CALCITES AND DOLOMITES

Sample No.	% Dolomite ±5	% Calcite ±5	% Non-Carbonate ±2	Total Sample		Non-Carbonate		Dolomite		Calcite	
				ppm Sr ±20	ppm Mn ±20	ppm Sr ±20	ppm Mn ±20	ppm Sr ±20	ppm Mn ±20	ppm Sr ±20	ppm Mn ±20
1	20	67	13	229	520	29	134	142	2608	292	0
2	74	17	9	97	1200	28	92	59	1588	300	71
3	97	0	3	40	900	40	48	40	924	—	—
4	93	1	6	45	—	26	—	42	—	341	—
5	22	74	4	340	90	48	86	82	376	433	3
6	62	33	5	107	475	30	104	57	693	211	129
7	96	0	4	52	1410	23	93	53	1471	—	—
8	10	77	13	302	90	33	183	266	362	354	39
9	82	0	18	44	1180	44	77	44	1424	—	—
10	93	0	7	48	909	15	86	50	966	—	—
11	81	0	19	51	1980	27	171	57	2417	—	—
12	36	53	11	210	800	3	159	102	3207	—	—
13	14	78	8	260	280	15	142	218	1680	292	40
14	14	83	3	250	288	38	208	146	1634	272	59
15	29	67	4	210	410	32	82	76	1395	279	0
16	66	30	4	83	673	55	709	52	968	154	30
17	19	79	2	237	168	14	231	122	764	270	20
18	16	80	4	380	264	19	189	68	333	459	255
19	5	92	3	256	42	23	95	89	495	271	16
20	95	0	5	38	540	54	225	37	557	—	—
21	95	0	5	46	540	9	279	48	554	—	—

GOLDSMITH, J. R., D. L. GRAF, AND O. I. JOENSUU (1955) The occurrence of magnesian calcites in nature. *Geochim. Cosmochim. Acta* **7,** 212–230.

PETERSON, M. N. A., C. C. VON DER BORCH, AND G. S. BIEN (1966) Growth of dolomite crystals. *Amer. J. Sci.* **264,** 257–272.

STEHLI, F. G. AND J. HOWER (1961) Mineralogy and early diagenesis of carbonate sediments. *J. Sed. Petrology* **31,** 358–371.

WEBER, J. N., (1964) Trace element composition of dolostones and dolomites and its bearing on the dolomite problem. *Geochim. Cosmochim. Acta* **28,** 1817–1886.