

X-ray Diffraction Study of Indiana Limestones¹

BRIAN SNOW,² J. L. WHITE and G. W. BAILEY, Purdue University

The magnesium content of limestone is of considerable interest from an agricultural standpoint. The magnesium and calcium carbonate contents of samples of Indiana limestones from over 80 quarries have been determined (7).

The objective of this study was the determination of the relationships between the d-spacings and x-ray diffraction intensities of the characteristic peaks of dolomite and calcite and the composition of Indiana limestones.

Introduction

Limestones are composed primarily of calcite (CaCO_3) and/or dolomite ($\text{CaMg}(\text{CO}_3)_2$). Calcite consists of alternating layers of Ca^{++} and CO_3^{--} ions (1). In dolomite the Ca^{++} and Mg^{++} ions are present in a 1:1 ratio. Cation planes populated entirely by Ca^{++} alternate with those populated entirely by Mg^{++} ; the CO_3^{--} ions lie between these planes.

Ca^{++} has an ionic radius of 1.06 Å., while Mg^{++} has a radius of 0.78 Å. This sizable difference is reflected in the ordered nature of dolomite and by the fact that only very limited solid solution exists between CaCO_3 and MgCO_3 except at high temperatures (5).

Goldsmith, Graf and Joensuu (2) and Goldsmith and Graf (4) have studied the relationship between the composition of calcite and dolomite and lattice constants and d-spacings. Their work indicates that calcite formed under equilibrium conditions near earth-surface temperatures would be quite low in magnesium. From the earlier work (2) it was concluded that the Ca:Mg ratio of dolomite did not deviate significantly from unity. More recently, however, Goldsmith and Graf (3) have described the occurrence of dolomite fractions that deviate compositionally and structurally from the ideal compound. These were found in Cretaceous and younger rocks and usually have excess CaCO_3 in their structure; some fractions contain approximately 55 mole percent CaCO_3 .

Experimental

Limestone samples having a wide range of MgCO_3 contents were obtained from Dr. Roy D. Bronson of the Purdue Soil Testing Laboratory. These samples had been analyzed chemically for calcium and magnesium carbonates.

The limestone samples were ground for one hour in an automatic grinder having a mullite mortar and pestle. Slurries of the limestones were prepared with a mixture of amyl acetate and collodion (6) and allowed to dry on glass slides. Careful examination of diffractometer tracings revealed no trace of aragonite; it was therefore assumed that

¹ Journal Paper No. 1517, Purdue University Agricultural Experiment Station, Lafayette, Indiana. Contribution from the Department of Agronomy.

² Participant in NSF Program for Superior High School Students, Purdue University, Summer, 1959.

the grinding treatment did not affect the d-spacings of the calcite or dolomite.

X-ray diffractometer tracings of the d_{211} spacings of the samples were made on a General Electric XRD5 diffractometer using Cu radiation. A standard quartz (Novaculite) slide was used to prepare a graph of 2θ versus errors in d-values. This graph was then used to correct observed carbonate d-values.

Diffraction angles were obtained from charts recorded at a rate of $0.2^\circ/\text{min.}$ with a time constant of 2.0 seconds. Intensities were measured as height in millimeters above background.

The mole percent MgCO_3 in the dolomite was estimated from the relationship between d_{211} and composition as given by Goldsmith and Graf (4).

Results and Discussion

The chemical composition and x-ray diffraction data are given in Table 1. The samples are arranged in order of increasing MgCO_3 content. The relationship between MgCO_3 content and intensity of the dolomite line at 2.89 Å. is shown in Fig. 1. It would appear that use of such a curve

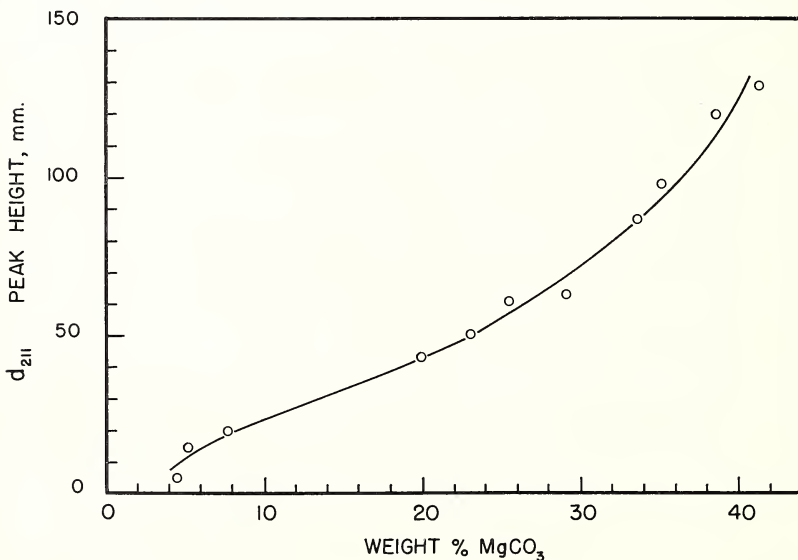


FIG. 1. Variation in the intensity of the d_{211} line of dolomite as a function of the weight percent MgCO_3 in limestone.

would give semiquantitative results for the MgCO_3 content of high purity limestones.

The increase in slope of the curve with increase in MgCO_3 is probably related to the difference in the mass absorption coefficients of Ca and Mg for Cu K α radiation. The mass absorption coefficient of calcium is 172 while that of magnesium is only 41. Thus, as the calcium content of the lime-

TABLE 1. Chemical and x-ray diffraction data for selected limestones.

Lab. No.	Source	County	Percent CaCO ₃	Percent MgCO ₃	A	d ₃₁₁ Dolomite	Int. ¹	Mole Percent MgCO ₃ in Dolomite ²
36	Dunn Limestone Co.	Owen	95.5	0.7	—	—	—	—
54	Calcar Quarries	Orange	90.4	1.4	—	—	—	—
955	Cloverdale Stone Co.	Putnam	93.3	2.4	—	—	—	—
39	Ralph Rogers and Co.	Lawrence	89.9	4.5	2.891	4.5	49.5	49.5
55	William Cave	Orange	87.7	5.1	2.904	14.0	45.5	45.5
43	Hoosier Lime and Stone Co.	Washington	87.6	7.7	2.886	20.0	51.7	51.7
1283	Lynn Stewart	Bartholomew	75.7	19.9	2.888	43.0	51.0	51.0
1281	Paul Frank	Jennings	70.4	23.1	2.886	50.0	51.7	51.7
1261	Standard Materials Corp.	Madison	65.9	25.5	2.884	61.0	52.5	52.5
1282	Lynn Stewart	Bartholomew	62.7	29.1	2.893	63.0	49.3	49.3
100	Francisville Stone Co.	Pulaski	55.5	33.6	2.889	87.0	50.7	50.7
1289	McCorkle Stone Co.	Rush	59.6	35.1	2.884	98.0	52.5	52.5
1051	Erie Stone Co.	Wells	55.2	38.5	2.889	120.0	50.7	50.7
1306	DeKalb County Co-op. (Supplier—Ohio Lime Co.)	Sandusky (Ohio)	56.1	41.3	2.882	129.0	53.0	53.0

¹ Peak height in mm.² Estimated from data of Goldsmith and Graf (4, Fig. 1).

stone decreases the intensity of the dolomite diffraction line will increase disproportionately. Taking the mass absorption coefficient of ideal dolomite

$$\left(\frac{\mu}{\rho}\right) \text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$$

as a base an intensity correction factor for the 2.89 Å. dolomite line may be computed for limestones containing less than 0.50 mole fraction of Mg by determining the ratio of the mass absorption coefficient of the high-calcium limestone to that of the ideal 1:1 dolomite. Thus

$$\frac{\left(\frac{\mu}{\rho}\right) \text{Ca}_{0.8}\text{Mg}_{0.2}\text{CO}_3}{\left(\frac{\mu}{\rho}\right) \text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3} = \frac{65.6}{49.9} = 1.31$$

When these corrections are applied, the relationship between intensity and MgCO_3 content becomes more nearly a linear one. The correlation coefficient for this relationship was 0.980 (Fig. 2).

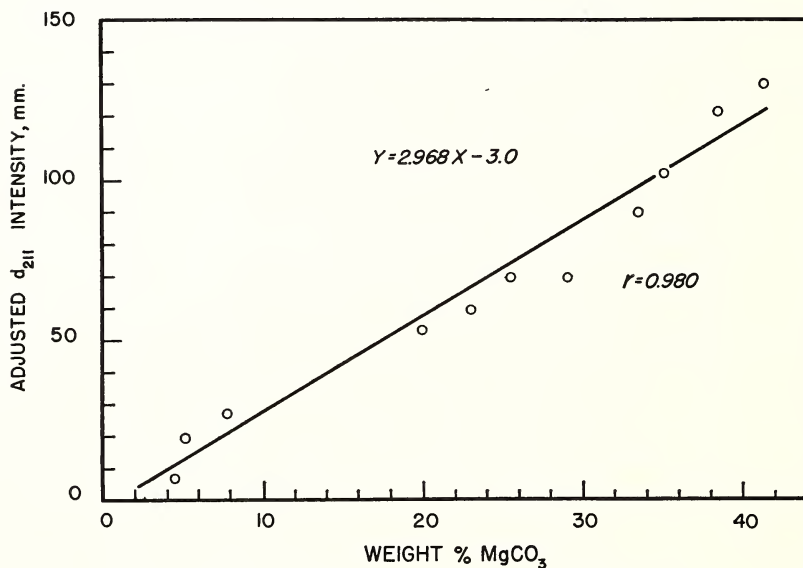


FIG. 2. Relationship between the adjusted intensity of the d_{211} line of dolomite and the weight percent MgCO_3 in limestone.

The mole percent MgCO_3 in the dolomite, as estimated from the d_{211} value (4), varies from 45.5 to 53 percent. That this is a real difference is illustrated in Fig. 3 in which the d_{211} peaks of two dolomites show a difference of 0.020 Å. The d_{211} for sample No. 55, which contains 5.1 per-

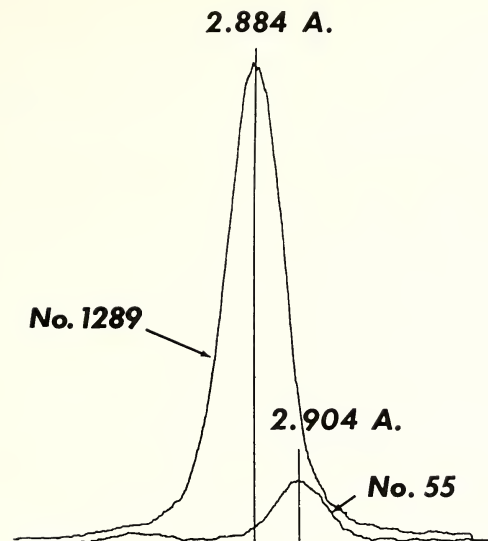


FIG. 3. A portion of the diffractometer tracing for samples No. 55 and No. 1289 showing a difference of 0.02 A. in the d_{211} values.

cent MgCO_3 , is 2.904 A., indicating the presence of Ca^{++} ions in the planes of Mg^{++} ions.

The d_{211} values for calcite indicate a maximum of 3 to 3.5 mole percent MgCO_3 . This is in agreement with the results of Goldsmith, Graf and Joensuu (2).

Literature Cited

1. BRAGG, W. L. 1937. Atomic structure of minerals. Cornell University Press, Ithaca, New York. pp. 115-116.
2. GOLDSMITH, J. R., GRAF, D. L., and JOENSUU, O. I. 1955. The occurrence of magnesian calcites in nature. *Geochim. et Cosmochim. Acta* 7:212-230.
3. GOLDSMITH, J. R., and GRAF, D. L. 1957. Structural and compositional variation in some natural dolomites (Abstract). *Bull. Geol. Soc. Amer.* 68:1735-1736.
4. GOLDSMITH, J. R., and GRAF, D. L. 1958. Relation between lattice constants and composition of the Ca-Mg carbonates. *Amer. Mineralogist* 43:84-101.
5. GOLDSMITH, J. R. 1959. Some aspects of the geochemistry of carbonates; in *Researches in geochemistry*, Edited by P. H. Abelson. John Wiley and Sons, Inc., New York. pp. 336-358.
6. JEFFRIES, C. D. 1947. The use of the x-ray spectrometer in the determination of the essential minerals in soils. *Soil Sci. Soc. Amer. Proc.* 12:135-140.
7. Purdue University, Agricultural Extension Service. 1954. Agronomy Mimeograph AY 23a. Lafayette, Indiana.