

NOTES ON AN X-RAY DIFFRACTION STUDY OF THE SERIES CALCITE-RHODOCHROSITE

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ABSTRACT

Five analyzed specimens of manganocalcite were studied to determine the relation between the varying per cent of manganese carbonate and the optical, physical, and structural properties of the mineral. These properties were compared with those of the two end members of the group; calcite and rhodochrosite. It was found that as the mineral grades from calcite to rhodochrosite a gradual increase in the indices of refraction and the specific gravity occurs. Charts are shown giving the variation of the indices of refraction, specific gravities, and x -ray diffraction patterns in relation to the per cent of manganese carbonate. The structural relationship, as shown by x -ray diffraction patterns, is such that the variation in the isomorphous constituents can be detected by the diffraction lines representing the interplanar atomic spacing. These patterns show a gradual decrease in the length of the edge of the unit rhombohedron as the mineral grades from calcite to rhodochrosite.

Manganocalcite was first described by Poggendorff¹ as a definite mineral species. It was later found to contain a varying per cent of manganese carbonate which ranged from very small amounts in manganiferous calcite to almost pure manganese carbonate in rhodochrosite. Dana² uses the term, "calciferous manganocalcite," but does not give the material the rank of a definite mineral species.

The relation between the structural and the physical properties, and the variation in the per cent of manganese carbonate in the group calcite-rhodochrosite has always been a matter of much interest. The physical properties of the mineral have been described³ in detail, and it has been shown that in general a uniform rate of variation exists, between the two extremes of the series. The variation in the internal structure, as portrayed by the x -ray diffraction patterns taken in this work, also shows a uniform rate of change. New optical determinations, however, were necessary, because those at present in the literature are limited to a single value for the index of refraction determined by Sundius⁴ on manganocalcite containing 20 molecular per cent manganese carbonate.

In the present work specimens of analyzed manganocalcite have been studied in an attempt to correlate physical, optical, and

¹ Poggendorff, J. C., *Annalen der Physik und Chemie*, vol. 69, p. 429, 1846.

² Dana, E. S., *System of Mineralogy*, 6th Edition, p. 278, 1892,

³ *Op. cit.*

⁴ Sundius, N., *Tsch. Min., Pet. Mit.*, vol. 38, p. 175, 1925.

chemical relationships with x -ray diffraction patterns. The indices of refraction were determined by the immersion method, the specific gravities determined by the use of a pycnometer, and the x -ray diffraction patterns obtained by the powder method of Hull⁵ and Debeye-Scherrer.⁶

The writer is indebted to Dr. Paul F. Kerr, of the Department of Geology and Mineralogy, Columbia University, for suggesting and outlining the problem, and for his advice as the work progressed. The investigation has been greatly aided through the cooperation of Dr. C. S. Ross, of the U. S. Geological Survey, and Mr. L. H. Bauer, of the New Jersey Zinc Co. Through their kindness specimens of manganocalcite have been secured together with accompanying analyses giving the manganese carbonate content. Thanks are also due to Mr. Earl V. Shannon, Mr. J. G. Fairchild, and Mr. J. J. Fahey for analyses of specimens.

The specimen of manganocalcite first described by Poggendorff⁷ in 1846 was thought to be isomorphous with aragonite. Later work by Krenner⁸ in 1884 proved it to be rhombohedral. This work placed it among the group of isomorphous rhombohedral carbonates which includes calcite, rhodochrosite, siderite, smithsonite, and magnesite. The earliest analysis of manganocalcite in the literature was made by Poggendorff in which he obtained 67.48 per cent manganese carbonate. A later analysis of manganocalcite from Franklin, New Jersey, by Roepper⁹ in 1870 gave 43.54 per cent manganese carbonate, while Weibull¹⁰ in 1885 obtained 11.30 per cent and 40.31 per cent manganese carbonate in material from Wester Silfberg. Thus it appears that early analyses of the mineral show considerable variation in the content of manganese carbonate.

Five samples of the mineral from four different localities, each with a different per cent of manganese carbonate, have been examined in this work. These, with the two end members of the group, calcite and rhodochrosite, are listed in Table I, together with the locality and analysis of each. The range from zero per cent manganese carbonate to 42.17 per cent is fairly well covered by the analyses. No material was secured, however, with a man-

⁵ Hull, A. W., *Physical Review*, vol. 10, pp. 661-669, 1917.

⁶ Debeye, P., and Scherrer, P., *Phys. Zeitsch.*, vol. 17, p. 277, 1916.

⁷ *Op. Cit.*

⁸ Krenner, J. A., *Zeit. f. Kryst.*, Vol. 8, p. 242, 1884.

⁹ Roepper, W. T., *Amer. Jour. Science*, vol. 50, p. 37, 1870.

¹⁰ Weibull, Mats., *Min. und Pet. Mitt.*, vol. 7, p. 111, 1885-1886.

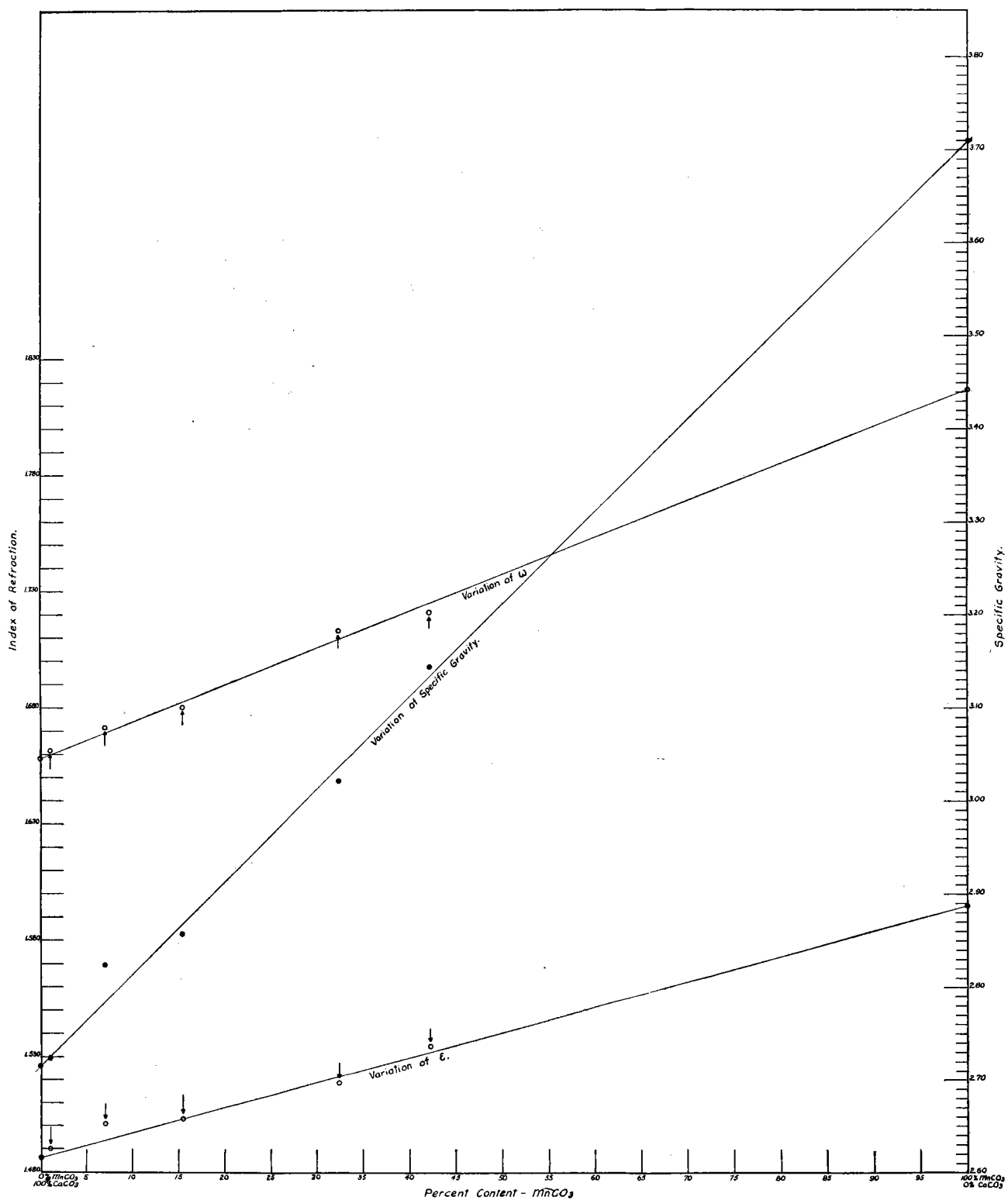


FIG. 1.

Chart showing the variation in the indices of refraction and specific gravity of manganocalcite as the per cent of manganese carbonate increases from calcite to rhodochrosite.

ganes carbonate content between the 42.17 per cent of the Sparta, N. C., specimen and the 95.72 per cent of the Lake County, Colo., rhodochrosite. The samples were not entirely free from magnesium carbonate and iron carbonate, which in some places may account for slightly discordant results.

TABLE I

%	%	%	%	%	%	%	Analyzed by
MnCO ₃	CaCO ₃	MgCO ₃	FeCO ₃	ZnCO ₃	SrCO ₃	Insol.	
—	100.00	—	—	—	—	—	—
1.09	95.32	1.34	0.09	—	—	2.48	J. J. Fahey.
7.00	86.90	2.57	3.50	—	0.24	—	J. G. Fairchild.
15.40	—	—	—	—	—	—	N. J. Zinc Co.
32.34	65.98	Trace	Trace	0.69	—	—	N. J. Zinc Co.
42.17	56.31	1.71	0.08	—	—	0.25	E. V. Shannon.
95.72	0.50	0.68	1.87	—	—	—	E. T. Wherry ¹¹

As the mineral grades from calcite to rhodochrosite, increasing in the per cent of manganese carbonate, the indices of refraction, as generally supposed, grow correspondingly larger. A chart, (Fig. D), gives the variation in indices of refraction and specific gravities found in the five samples, compared with those determined for calcite and rhodochrosite. The data for calcite has been taken from Hastings,¹² and the indices of refraction for rhodochrosite were determined by Larsen¹³ for the Lake County variety. With a small per cent of manganese carbonate, as in the sample from Kings Mt., N. C., which contained 1.09 per cent, the increase in ϵ and ω from that of calcite was very small; $\epsilon=1.490 \pm .003$; $\omega=1.662 \pm .003$. This is but slightly higher than calcite; $\epsilon=1.486$; $\omega=1.658$; the increase in both ϵ and ω being .004. In the sample from Ore Knob, N. C., which contained 7.00 per cent manganese carbonate, a slightly greater increase was noticed, particularly in ϵ . This greater increase is probably due to the presence of other isomorphous constituents which would have a tendency to increase the indices of refraction. This sample contained 3.50 per cent iron carbonate and 2.57 per cent magnesium carbonate. The two samples from Franklin, N. J., and the one from Sparta, N. C., each with a greater per cent of manganese carbonate, showed

¹¹ Wherry, E. T., *Wash. Acad. Science*, vol. 7, p. 365, 1917.

¹² Hastings, C. S., *Amer. Jour. Science*, 3rd Ser., vol. 35, p. 73, 1888.

¹³ Larsen, E. S., *Wash. Acad. Science*, vol. 7, p. 365, 1917.

a gradual increase in the indices of refraction corresponding closely to the theoretical values which might be expected between calcite and rhodochrosite.

The specific gravity variations were observed to correspond; namely, as the calcium carbonate is replaced by manganese carbonate a gradual increase in the specific gravity takes place. The sample from Ore Knob, N. C., showed a greater increase in specific gravity than the 7.00 per cent manganese carbonate would warrant. The presence of iron and magnesium carbonates would easily account for this higher value. The values obtained for the remaining samples correspond closely to the theoretical values as shown on the chart in figure I. The figures obtained for the indices of refraction and the specific gravities are shown in Table 2.

TABLE II

	% MnCO ₃	Indices of Refraction		Specific Gravities
		ϵ	ω	
Calcite, C. P.	00.00	1.486	1.658	2.715
Manganocalcite Kings Mt., N. C.	1.09	1.490	1.662	2.724
Manganocalcite Ore Knob, N. C.	7.00	1.501	1.672	2.824
Manganocalcite Franklin, N. J.	15.40	1.503	1.680	2.856
Manganocalcite Franklin, N. J.	32.34	1.519	1.713	3.021
Manganocalcite Sparta, N. C.	42.17	1.534	1.721	3.143
Rhodochrosite Lake Co., Colo.	95.72	1.595	1.817	3.710

Isomorphous variation in the structure is illustrated by the *x*-ray diffraction patterns reproduced in Figure 2. All of the patterns have the same arrangement of lines with approximately the same variation in intensity. As the calcium carbonate is replaced by manganese carbonate, however, the distance of a certain line from the

undeviated, or zero beam becomes greater until it reaches a maximum in rhodochrosite. The distances from the zero beam are measured in millimeters, and the interplanar spacings are computed according to the well-known formula of Bragg,¹⁴ $n\lambda = 2d \sin\theta$. The interplanar spacings are given above each line in Figure 2, in Ångstrom Units ($\times 10^{-8}$ cm.) and represent the distances between the atomic planes within the mineral. A few of the less intense lines, due to the decrease in reticular density with higher indices and consequent weakened reflecting power, could not be observed in all of the films. These have been put in as dotted lines and marked "unobserved" on the chart in approximately the position in which they should occur. These lines were observed in other films.

A decrease in the size of the unit rhombohedron, $2d_{(100)}$ occurs throughout the series as the calcium atoms are replaced by the manganese atoms. The first line on the left of each x -ray diffraction pattern (Fig. 2) is produced by reflection from the atomic planes whose spacing varies from 3.075 Ångstrom units in calcite to 2.850 Ångstrom units in rhodochrosite. In the manganese mineral, therefore, these atomic planes are more closely spaced, and consequently some of the atomic diameters are smaller. Since the manganese and calcium atoms provide the only variables in the series it is to be inferred that the variation is due to the replacement of the calcium atoms by manganese atoms in the atomic structure.

The variation is not limited to the first planes, but occurs throughout the whole group of lines in each diffraction pattern. Table 3 shows all of the variations compared with x -ray diffraction measurements for calcium carbonate given by Harrington.¹⁵

The difference between calcite and rhodochrosite can be readily seen in Figure 3, which shows the actual photographs of the diffraction patterns, and where calcite has been placed next to rhodochrosite for comparison.

The structure of the group has not been considered, having been previously determined by the Braggs¹⁶ from x -ray spectrometer measurements, and by Wyckoff¹⁷ from Laue photographs.

¹⁴ Bragg, W. H. and W. L., *X-rays and Crystal Structure*, G. Bell and Sons, London, p. 106, 1924.

¹⁵ Harrington, E. A., *Amer. Jour. Sci.*, 5th Series, vol. 13, p. 477, 1927.

¹⁶ *Op. cit.*

¹⁷ Wyckoff, R. G. W., *Amer. Jour. Sci.*, 4th Series, vol. 50, p. 317, 1920.

TABLE III

Harrington		Manganocalcite					Rhodochrosite
CaCO ₃	CaCO ₃	1.09	7.00	%MnCO ₃		42.17	95.72% MnCO ₃
A.U.	A.U.	A.U.	A.U.	A.U.	A.U.	A.U.	A.U.
3.03	3.075	3.055	3.020	3.005	2.975	2.948	2.850
2.49	2.522	2.500	2.491	2.472	2.455	2.400	2.389
2.28	2.300	2.297	2.268	2.257	2.250	2.235	2.180
2.10	2.110	2.105	2.085	2.070	2.060	2.038	1.990
1.920	1.935	1.925	1.903	1.883	1.866	1.850	1.809
1.870	1.880	1.875	1.862	1.845	1.833	1.808	1.762
1.602	1.613	1.608	1.599	1.589	1.575	1.561	1.540
1.520	1.525	1.513	1.515	1.505	1.486	1.480	1.457
1.437	1.450	1.438	1.435	1.425	1.413	1.402	1.378
1.355				1.394	1.378	1.370	1.309
	1.347	1.337	1.325	1.320	1.306	1.296	1.258
1.295	1.306	1.300	1.285	1.275	1.267	1.253	1.222
			1.248	1.239	1.233	1.217	1.197
1.235	1.242	1.233	1.223	1.214	1.200	1.191	
1.178	1.190	1.181	1.168	1.158	1.144	1.140	1.128
1.149	1.156	1.145	1.138	1.130	1.125	1.123	1.100
1.044	1.045	1.042	1.037	1.028	1.023	1.010	0.985
1.014	1.017	1.015	1.000	0.995	0.985	0.980	0.943
0.984	0.988	0.985	0.973	0.969	0.961	0.960	
0.965	0.970	0.965	0.960	0.951	0.942	0.938	0.900
0.943	0.945	0.940	0.934	0.929	0.920	0.918	0.880
	0.895	0.890	0.885	0.880	0.875	0.869	0.850
	0.854	0.850	0.844	0.839	0.835	0.929	0.812
	0.836	0.833		0.819	0.810	0.805	
	0.799	0.797	0.790			0.780	0.760
	0.790	0.786	0.780	0.774	0.768	0.761	

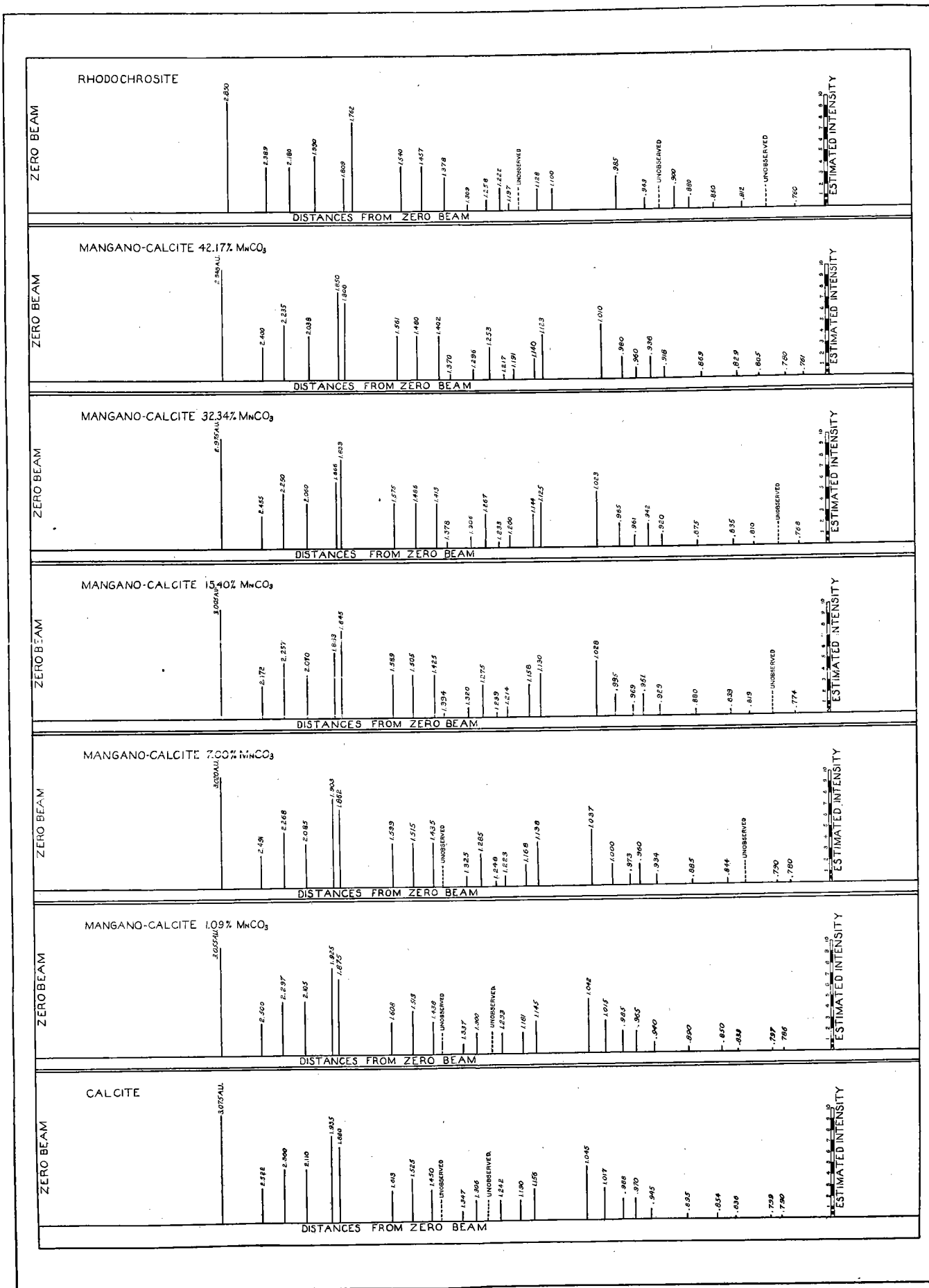


FIG. 2.

Diagrams illustrating x-ray diffraction patterns of the isomorphous series calcite-rhodochrosite. Calcite is placed at the bottom of the figure, rhodochrosite at the top, and between the two are five x-ray diffraction patterns of manganocalcite arranged in the order of increasing manganese carbonate content. The height of each line represents estimated intensities; the figure above the line, the interplanar atomic spacing in Ångstrom Units ($\times 10^{-8}$ cm.) and the distance of each line from the zero beam, a measure of the arc of reflection.

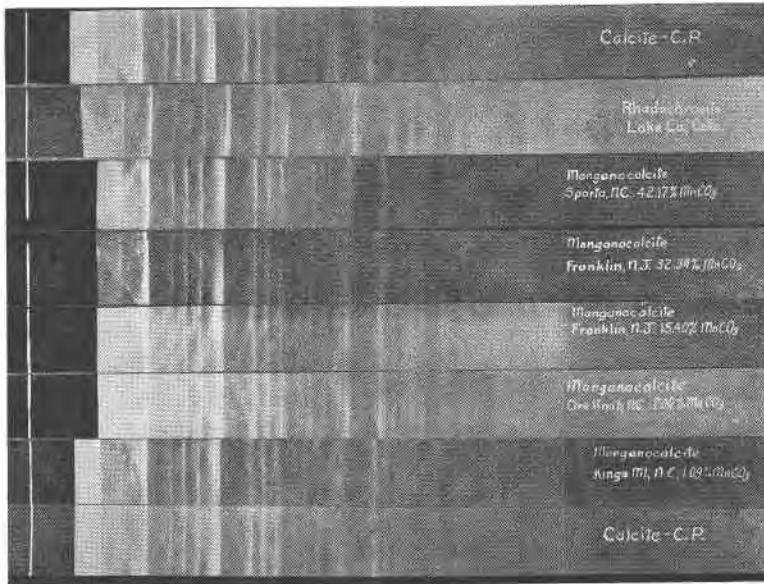


FIG. 3. Reproduction of x -ray diffraction patterns arranged in the order of increasing manganese carbonate content. A calcite pattern is placed above the one of rhodochrosite for comparison. See Figure 2 for interpretation of patterns.

CONCLUSION

Data obtained by a study of the indices of refraction, specific gravities, and x -ray diffraction patterns of manganocalcite show a uniform variation within experimental limits depending upon the chemical composition. A study of five specimens of manganocalcite shows a definite relationship between the per cent of manganese carbonate and the physical or structural, and optical properties. The relation of the manganese carbonate content to the specific gravity is indicated by a gradual rise in value as the calcium carbonate is replaced by manganese carbonate until the composition of rhodochrosite is reached. The indices of refraction show an increase in both ϵ and ω as the per cent of manganese carbonate increases, approaching those of rhodochrosite as a limit. The first line of the diffraction patterns varies from 3.075 Ångstrom units in calcite to 2.850 Ångstrom units in rhodochrosite.