

An X-ray examination of a sample of pure calcite and of solid-solution effects in some natural calcites.

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INTRODUCTION.

IN the course of the routine X-ray examination of a number of low-grade iron ores in order to determine their constitution, it was observed that the calcite phase had varying interplanar spacings. Since these variations could have been due to differing solid-solution contents of other carbonates, further consideration was given to this point. The existence of these generally small amounts of solid solution is of some technological interest.

A sample of 'specpure' calcite, supplied by Messrs. Johnson, Matthey & Co. Ltd., was used to provide accurate lattice parameters and interplanar spacings for pure calcite. There was no satisfactory list of interplanar spacings available with the desired accuracy, although for ordinary identification purposes the values supplied in the 'Index of X-ray diffraction data' (Amer. Soc. Testing Materials) are adequate. Part I of the present paper discusses the results obtained from this 'specpure' calcite in relation to previously reported values of the rhombohedral angles α and α' and the interplanar spacing of the cleavage plane. Part II describes the examination of the solid-solution effects referred to in calcites from seven samples of iron ore and in two other natural calcites. An interpretation of the results is attempted.

PART I. LATTICE PARAMETERS AND INTERPLANAR SPACINGS OF
PURE CALCITE.

A sample of calcite of high purity was obtained from Messrs. Johnson, Matthey & Co. Ltd. The manufacturer's report on this 'specpure' compound is contained in Appendix I together with details of two other calcites. Powder photographs were taken with both Co- $K\alpha$ and Cu- $K\alpha$ radiations in the 19 cm.-diameter camera. The final values for the lattice parameters were obtained from the Cu- $K\alpha$ photograph. The lattice parameters were used in the calculation of accurate interplanar

spacings which are given in table I. These spacings have been submitted for inclusion in a new supplement of the 'Index of X-ray diffraction data' (A.S.T.M.). Hexagonal indices are listed in table I as these are generally more convenient. The pattern obtained with cobalt had lines

TABLE I. Lattice parameters and interplanar spacings of pure calcite.

$a_{rh} 6.3748 \pm 0.0005 \text{ \AA.}$			$a_{hex} 4.9898 \pm 0.0003 \text{ \AA.}$			} at 18° C.
$\alpha 46^\circ 4.8' (46.08^\circ)$			$c_{hex} 17.060 \pm 0.005 \text{ \AA.}$			
d in \AA.	$I.$	$hkil.$	d in \AA.	$I.$	$hkil.$	
3.855	w	10 $\bar{1}2$	0.9897	vw	32 $\bar{5}1$	}
3.035	vs	10 $\bar{1}4$	0.9876		40 $\bar{4}7$	
2.843	vw	0006	0.9848	wm	32 $\bar{5}2$	
2.495	wm	11 $\bar{2}0$	0.9807	w--	31 $\bar{4}10$	
2.285	m	11 $\bar{2}3$	0.9775	wm	10 $\bar{1}17$	}
2.095	m	20 $\bar{2}2$	0.9767		21 $\bar{3}14$	
1.9274	w	20 $\bar{2}4$	0.9656	w+	32 $\bar{5}4$	
1.9123	ms	10 $\bar{1}8$	0.9637	m-	40 $\bar{4}8$	
1.8753	ms	11 $\bar{2}6$	0.9562	vw	20 $\bar{2}16$	
1.6259	w	21 $\bar{3}1$	0.9520	vvw	32 $\bar{5}5$	
1.6042	m	21 $\bar{3}2$	0.9430	m-	41 $\bar{5}0$	
1.5868	vw	10 $\bar{1}10$	0.9377	wm	22 $\bar{4}12$	
1.5253	m-	21 $\bar{3}4$	0.9183	vw	32 $\bar{5}7$	
1.5178	vvw	20 $\bar{2}8$	0.8990	w	32 $\bar{5}8$	
1.5093	w	11 $\bar{2}9$	0.8951	vw	41 $\bar{5}6$	
1.4732	w	21 $\bar{3}5$	0.8928	wm--	21 $\bar{3}16$	}
1.4598	vvw	10 $\bar{1}11$	0.8926		30 $\bar{3}15$	
1.4404	m	3030	0.8865	wm	40 $\bar{4}11$	}
1.4217	wm	00012	0.8860		11 $\bar{2}18$	
1.3568	w	21 $\bar{3}7$	0.8599	vw	50 $\bar{5}2$	
1.3389	w+	20 $\bar{2}10$	0.8572	w-	32 $\bar{5}10$	
1.2967	wm	21 $\bar{3}8$	0.8550	w-	21 $\bar{3}17$	
1.2850	vvw	30 $\bar{3}6$	0.8470	w	50 $\bar{5}4$	
1.2475	w	22 $\bar{4}0$	0.8369	w+	10 $\bar{1}20$	
1.2352	m-	11 $\bar{2}12$	0.8316	w	33 $\bar{6}0$	
1.1798	m-	21 $\bar{3}10$	0.8129	wm	42 $\bar{6}2$	}
1.1538	m+	31 $\bar{4}4$	0.8124		00021	
1.1423	wm	22 $\bar{4}6$	0.8084	vvw	40 $\bar{4}14$	
1.1247	vw	21 $\bar{3}11$	0.8021	w+	42 $\bar{6}4$	}
1.0614	vw	20 $\bar{2}14$	0.8010		50 $\bar{5}8$	
1.0473	wm	40 $\bar{4}4$	0.7982	w	33 $\bar{6}6$	
1.0448	m	31 $\bar{4}8$	0.7966	m-	31 $\bar{4}16$	
1.0352	w-	10 $\bar{1}16$	0.7934	w-	20 $\bar{2}20$	}
1.0349		11 $\bar{2}15$	0.7918	vvw	30 $\bar{3}18$	
1.0230	vvw	21 $\bar{3}13$	0.7910	vvw	32 $\bar{5}13$	
1.0118	m+	30 $\bar{3}12$	0.7858	s	41 $\bar{5}12$	
			0.7753	vw	51 $\bar{6}1$	

The above spacings are reported in Ångström units, but in the earlier work of Krieger and others the unit is that now referred to as kX. The necessary conversion from the above values to kX units has been effected before using the spacings in fig. 1 and elsewhere.

as far as and including $32\bar{5}7$, but $32\bar{5}8$ may appear on films from some cameras. The actual parameter values obtained were:

$$a_{\text{rh}} 6.3748 \pm 0.0005 \text{ \AA.} = 6.3619 \text{ kX, } \alpha 46^\circ 4.8' (46.08^\circ), \text{ at } 18^\circ \text{ C.}$$

Referred to hexagonal axes, these values correspond to:

$$a_{\text{hex}} 4.9898 \pm 0.0003 \text{ \AA.} = 4.9797 \text{ kX,}$$

$$c_{\text{hex}} 17.060 \pm 0.005 \text{ \AA.} = 17.026 \text{ kX,}$$

with $c/a = 3.4190$.

Dr. A. J. C. Wilson of University College, Cardiff, kindly examined this sample of calcite by the same method and obtained parameter values very close to our own, exact agreement being reached with copper radiation as regards the value of the rhombohedral angle α , although our own photograph with cobalt radiation suggested a slightly lower value.

The new data obtained may be compared with previously reported values for the various lattice parameters and the rhombohedral angle α . It should be mentioned that the X-ray unit cell to which the above measurements refer is the one described by Dana as $M(40\bar{4}1)$, so that his cleavage rhombohedron $r(10\bar{1}1)$ becomes $(10\bar{1}4)$. The angle between two faces of this cleavage rhombohedron, denoted by rr' , is of interest in optical goniometry, and values of this angle have therefore been calculated for comparison with each other, and with the accepted value of $74^\circ 55'$. If the cleavage rhombohedron itself is regarded as a unit cell, the interaxial angle is in the region of $101^\circ 54'$, and values of this angle, which we denote by α' , have been reported by other workers. It is therefore of interest to compare these various angles as well as the corresponding lattice parameters (in kX units). The following values have been obtained:

	$a_{\text{rh.}}$	α .	$a_{\text{hex.}}$	c .	c/a .	α' .	rr' .
Bragg ¹ , 1914 ...	6.361	46° 7'	4.982	17.019	3.417 ₆	101° 55'	74° 55'
Bearden ² , 1931 ...	—	46° 4' 42"	—	—	3.4191	101° 54' 4"	74° 56' 31"
						±10"	
Du Mond & Bollman ³ , 1936 ...	(6.3593)	46° 5'	(4.9871)	(17.019)	3.4186	101° 54' 18"	74° 56' 12"
						±48"	
New data, 1949 ...	6.3619	46° 4' 48"	4.9797	17.026	3.4190	101° 54' 9"	74° 56' 24"

The agreement between the last three sets of values for c/a , α' , and rr' is very close and may be regarded as satisfactory. The present value of 6.3619 kX for the rhombohedral cell edge is not markedly higher

¹ W. L. Bragg, *The atomic structure of minerals*. 1937, p. 114.

² J. H. Bearden, *Phys. Rev.*, 1931, vol. 38, p. 2089.

³ J. W. M. Du Mond and V. L. Bollman, *Phys. Rev.*, 1936, vol. 50, p. 524.

than the early determination of 6.361 by Bragg. The parameter values in brackets from Du Mond and Bollman are calculated from the rather low value of the spacing referred to below.

There have been a number of reported values for the interplanar spacing of the $10\bar{1}4$ planes, referred to above, as corresponding to the faces of the cleavage rhombohedron. This distance was of great importance in the determination of standard X-ray wave-lengths. As explained by Compton and Allison,¹ if the diminishing effect of refractive index with increasing order of diffraction is taken into account, Siegbahn's value of 3.02904 kX (at 18° C.) approaches a true value of 3.02945 kX. Our own value is 3.0294₁ kX and would, as it is uncorrected for refraction, approximately correspond to the value given by Compton and Allison for the fourth order, viz. $d_4 = 3.02942$. Y. C. Tu² obtained 3.0294 for this spacing, although Du Mond and Bollman, using a powder method, obtained 3.02923 kX. It is not easy to account for this last-named result being relatively lower than the others, but it should be noted that the three values of α' which were determined showed a rather wide scatter, which gives a correspondingly marked \pm error on the value of d . Again, these authors used a sample of natural calcite which could conceivably be affected by very slight traces of solid-solution elements as suggested below.

PART II. SOLID-SOLUTION EFFECTS IN SOME NATURAL CALCITES.

Description of samples examined.—The calcites examined are listed in table II. No. 1 is a fine-grained limestone and no. 2 a large crystal obtained from a lead mine in North Wales. Nos. 3 to 6 are calcites separated from certain low-grade iron ores by a simple gravity-settling method. The separation was not expected to be complete and, as suggested in table IIb, there are small amounts of chalybite and goethite, and occasionally other constituents. These do not affect the measurements of the calcite lines on the X-ray powder photographs except for one or two instances of overlapping lines. The small amounts of sample normally produced were not sufficient for a complete chemical analysis and a choice had to be made as to the most desirable quantities to determine. As a consequence some uncertainties arose, e.g. in regard to the amount of calcium present as calcium phosphate. In the case of the samples nos. 7 and 8 the calcite spacings were measured on

¹ A. H. Compton and S. K. Allison, X-rays in theory and experiment. 1936, pp. 680–682.

² Y. C. Tu, Phys. Rev., 1932, vol. 40, p. 662.

TABLE IIa. Chemical data for calcites and ores.
Weight percentages.

Ref. No.	Description of Material.	CaO.	CO ₂ .	total Fe.		MnO.	MgO.	P ₂ O ₅ .	CaO.	MnO.	MgO.	Molecular ratios		wt. % × 100 molecular wt. CO ₂ .	P ₂ O ₅ .	Ca ₃ P ₂ O ₆ .
				FeO.	Fe ₂ O ₃ .							FeO.	MgO.			
1.	Limestone from Hope (Derbyshire) ...	53.95	42.2	0.31	0.01	1.12	—	—	96.19	0.014	2.78	>0.55	96.0	—	—	—
2.	Calcite from North Wales ...	55.7	43.7	0.19 ₆	0.10	0.60	—	—	99.31	0.141	1.49	>0.35	99.0	—	—	—
3.	Calcite from Frodingham ironstone (a) ...	24.7	21.2	33.0	1.13	4.68	—	—	44.04	1.59	11.61	>2.37 (?)	48.0	—	—	—
4.	Calcite from Frodingham ironstone (b) ...	37.05	38.7	14.6	1.55	3.81	—	—	65.97	2.19	9.45	10.4 (?)	88.0	—	—	—
5.	Calcite from Yarboro' (Lincs.) (a) ...	41.55	33.4	8.57	0.60	2.42	—	—	74.08	0.85	6.00	>1.07 (?)	76.0	—	—	—
6.	Calcite from Yarboro' (b) ...	41.55	30.75	13.0	0.59	5.32	—	—	74.08	0.83	13.2	(?)	70.0	—	—	—
7.	Ore from Scunthorpe (a)	30.16	26.10	FeO 3.89	0.89	1.08	0.77	0.77	53.77	1.25	2.7	5.4	59.0	0.54	—	52.15
8.	Ore from Scunthorpe (b)	14.0	18.26	FeO 14.33	0.87	2.06	0.99	0.99	24.96	1.23	5.11	19.9	41.5	0.67	—	22.95
9.	Raw Trent ore (Lincs.) (Calcite separated for photograph) ...	22.32	22.27	FeO 9.13	2.06	2.43	1.03	1.03	39.79	2.90	6.03	12.7	50.5	0.72	—	37.63

TABLE IIb. X-ray results and data deduced from Table IIa.

No.	Description of Material.	MnO × 100		MnO × 100		Mean % change in calcite =		MgO.	CO ₂ - 2MgO.	100 × Δd/d.	Constituents other than calcite.
		CaO + MnO.	CaO + MnO + FeO.	CaO + MnO.	CO ₂ .	MnO × 100	CO ₂ - 2MgO.				
1.	Limestone from Hope (Derbyshire)	0.014	0.015	0.015	0.015	0.085	—	—	—	—	FeCO ₃ & goethite, small amount; dolomite, possible small amount
2.	Calcite from North Wales ...	0.14	0.14	0.147	0.147	0.13	—	—	—	—	dolomite, possible small amount
3.	Calcite from Frodingham ironstone (a)	3.61	3.30	3.54	3.54	0.30	—	—	—	—	FeCO ₃ , med./small amount; dolomite, ? very small amount
4.	Calcite from Frodingham ironstone (b)	3.20	2.49	2.49	3.17	0.24	—	—	—	—	FeCO ₃ & goethite, traces; dolomite, very small amount
5.	Calcite from Yarboro' (Lincs.) (a)	1.12	1.12	1.12	1.32	0.20	—	—	—	—	FeCO ₃ , very small amount
6.	Calcite from Yarboro' (b)	1.11	1.19 (max.)	1.18	1.91	0.15	—	—	—	—	FeCO ₃ & goethite, traces; dolomite, very small amount
7.	Ore from Scunthorpe (a)	2.33	2.07	2.12	2.33	0.30	—	—	—	—	FeCO ₃ , very small amount; goethite, small + amount
8.	Ore from Scunthorpe (b)	5.07	2.73	2.96	3.93	0.40	—	—	—	—	FeCO ₃ , medium amount; goethite, small/med. amount; Chamosite, possible small amount
9.	Raw Trent ore (Lincs.) (Calcite separated for photograph)	7.12	5.24	5.74	7.54	0.32	—	—	—	—	FeCO ₃ , small + amount; goethite, small + amount

photographs of the original iron ores for which more complete chemical analyses were available. In the last iron ore in the list, no. 9, the same analytical details were available, but the calcite from which the spacing measurements were taken was again largely separated from the other constituents. Further samples showing the same effect have been examined but are not reported as no chemical data is available.

In addition to the chemical analyses (weight percentages) table IIa also records the values of the 'molecular ratios' $\frac{(\text{weight percentage} \times 100)}{(\text{molecular weight})}$ of the various components. It was not possible in every case to decide how much of the 'total Fe' should be allocated to FeO, but in some instances this cannot be very much, whilst for nos. 7, 8, and 9, FeO was determined directly.

X-ray examination of calcite phase.—In considering the relation of the solid-solution effects observed in the calcite phase to the amounts of manganous oxide and other components it was necessary to measure the change in interplanar spacings themselves, since extrapolated values of the lattice parameters could not have been obtained in most of the cases examined owing to the weakness and diffuseness of the 'high angle' lines. A quantity representing the average decrease in interplanar spacings and thus of the lattice parameters was derived as explained in Appendix II. This was expressed as a percentage and represented by $\Delta d_2/d \times 100$. Thus, the standard interplanar spacings in table I were taken as correct and the effect of solid solution in the natural calcites was to lower the interplanar spacings by amounts which in proportion to the actual value of the spacing should have been more or less equal, assuming the axial ratio change to be negligible over the relatively small range of composition involved. The simple method of Appendix II gives the mean value of $\Delta d_2/d \times 100$ and allows for the absorption of the specimen in the powder camera. The quantity obtained is a measure of the amount of other carbonates in solid solution, and the actual values are recorded in table IIb.

Consideration of the available data.—The most probable elements replacing calcium in calcite solid solutions are manganese, iron, or magnesium. No X-ray data on the solid solutions formed between the various carbonates of these elements appear to have been reported apart from the work of Krieger¹ who tabulated interplanar spacings, densities, and also refractive indices of solid solutions between manganese and calcium carbonates, referred to as manganocalcites. Wayland, using optical and

¹ P. Krieger, Amer. Min., 1930, vol. 15, p. 23. [M.A. 4-274.]

density methods, reported complete solid solutions between these two end members.¹ Earlier, Ford had carried out an extensive study of minerals in the calcite group, and related densities and refractive indices to the composition of the various mineral samples examined.² This author suggested that manganese carbonate would be expected to dissolve to the largest extent, iron carbonate next, and magnesium carbonate the least, and that the solid solutions would probably be restricted. No extensive solid solutions of FeCO_3 or MgCO_3 in CaCO_3 have in fact been reported. Hawkes and Smythe³ reported three calcites which appear to contain FeCO_3 , MgCO_3 , and MnCO_3 in solid solution. Smythe and Dunham⁴ fitted these results into a ternary system $\text{CaCO}_3\text{-MgCO}_3\text{-(Fe,Mn)CO}_3$, but no other samples indicating a wide range of solid solutions in calcite were reported.

The small amounts of solid solution observed in the nine samples listed in table II could therefore probably be accounted for as being due to one or more of the three carbonates MnCO_3 , FeCO_3 , and MgCO_3 . The samples did not lend themselves to density or to refractive-index measurements (apart from no. 2, which showed a very slightly higher value of ω than for pure calcite—the difference being too small to be definitely related to the minor constituents). Consequently, the only standard of comparison from other work is the X-ray data of Krieger referred to above. These data are therefore taken as the basis on which the values of $\Delta d_2/d$ are related to the percentage solid solution of MnCO_3 , assuming this is the main constituent in solid solution. This assumption may not be completely justified, but a good correlation with Krieger's work would tend to support it, and as suggested below this is in fact the case, although there is also some indication of the other possible solid-solution constituents.

Fig. 1 shows the variation with composition of Krieger's interplanar spacings for the first eight principal lines having the hexagonal indices shown. These points do not lie as consistently close to the straight lines drawn as might have been expected. The percentage of MnCO_3 in solid solution is taken direct in each case from the analysis given by Krieger, but there are also small amounts of MgCO_3 and FeCO_3 , also in one sample ZnCO_3 and in another SrCO_3 . If these minor constituents are allowed for the points are displaced slightly to the right, but by

¹ R. G. Wayland, *Amer. Min.*, 1942, vol. 27, p. 614. [M.A. 9-124.]

² W. E. Ford, *Trans. Connecticut Acad. Arts & Sci.*, 1917, vol. 22, p. 211. [M.A. 1-10.]

³ L. Hawkes and J. A. Smythe, *Min. Mag.*, 1935, vol. 24, p. 65.

⁴ J. A. Smythe and K. C. Dunham, *Min. Mag.*, 1947, vol. 28, p. 53.

amounts that are unimportant. The scatter of some of the points must be attributed to experimental error and, although straight-line variation is not necessarily followed, there is no reason for attempting to draw curves through the points available. These lines cut the vertical axis for zero MnCO_3 very near to the values for pure calcite from table I,

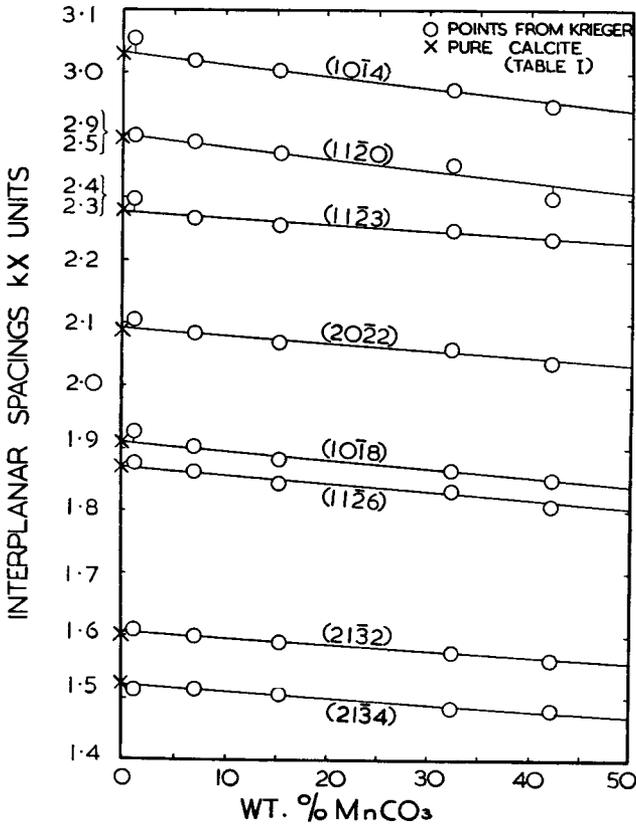


FIG. 1. Variation of interplanar spacings with composition for CaCO_3 - MnCO_3 solid solutions. (Plotted from P. Krieger's data, 1930.)

converted to kX units, although it is noted that the first of Krieger's points (1.09 % MnCO_3) for several lines is somewhat high. Thus the value 3.055 kX for the 1014 line is very unlikely to be correct, as accurate values for pure calcite itself are all reported near to 3.03 kX.

The relative slopes of the lines in fig. 1 are different for different indices, but there is an average decrease of 3.15 % in terms of the

spacings for pure calcite on going from 0 to 50 % MnCO_3 by weight. This would correspond to 3.3 % decrease for a 50 atomic per cent. solid solution of MnCO_3 . Thus our own average spacing decreases for solid solutions in calcite might be expected to lie near to a line of this slope

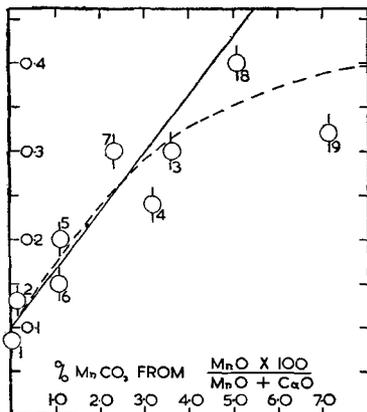


FIG. 2

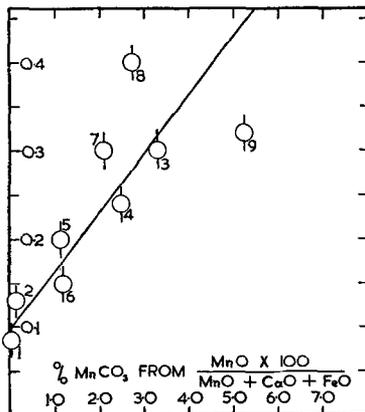


FIG. 3

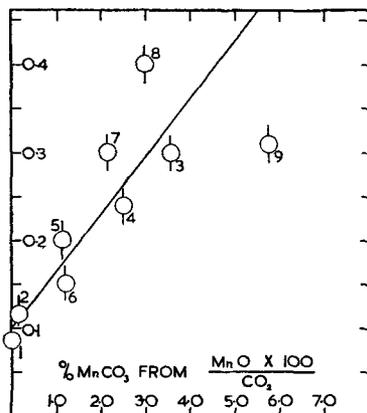


FIG. 4

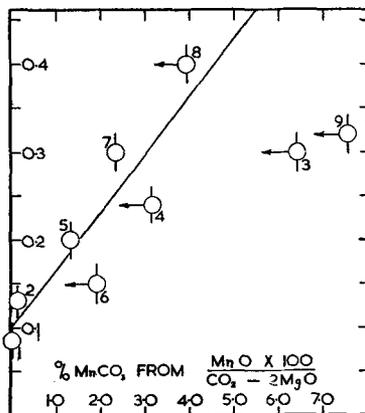


FIG. 5

FIGS. 2-5. Percentage decrease in interplanar spacings (ordinates) for calcite solid solutions. (The straight line on each figure has a slope equal to the average from Krieger's data.)

when plotted against some suitable quantity to represent % MnCO_3 , providing that it is correct to account for most of the solid solution effect in this way.

In fig. 2 the % MnCO_3 is represented by $(\text{MnO} \times 100)/(\text{CaO} + \text{MnO})$.

This ratio implies the assumption that all the CaO and MnO are combined as carbonate. Some of the samples, however, contained chalybite which may also have dissolved manganese carbonate, and in some cases the 'molecular ratio' for CO₂ table IIa is less than for the sum of the basic oxides (apart from MgO). Thus, some uncertainty in the use of the analytical data is bound to arise. In fig. 2 the points are scattered approximately on either side of the broken curve. A line of slope equal to 3.3% decrease in 50 atomic % MnCO₃ is drawn to show how near the points correspond to this slope, which is suggested by Krieger's work.

Fig. 3 has a similar significance to fig. 2, but in cases where the FeO content is highest the points are shifted to the left. Thus, if the samples which contain a marked amount of chalybite also have some manganese carbonate dissolved in this constituent, it cannot be decided with certainty how much is so accounted for. The abscissae in fig. 3 are given by $(\text{MnO} \times 100)/(\text{MnO} + \text{CaO} + \text{FeO})$, which divides the MnO in proportion to the relative amounts of the two carbonates where both are present. Some spacing changes in the chalybite constituent were in fact observed, but it was not possible to make any reliable quantitative estimates as for the calcite constituent, since iron was present only as a minor impurity in most cases.

In view of the inequality of the sum $\text{MnO} + \text{CaO} + \text{FeO}$, to which MgO may also be added, with the CO₂ content, it might seem better to express the % MnCO₃ in terms of the total carbonate, $(\text{MnO} \times 100)/\text{CO}_2$, as in fig. 4. If, however, the magnesium oxide is taken into consideration, the method of plotting must allow for its combination in the form of dolomite. This reduces the amount of carbonate as calcite. It is unlikely that all the MgO is combined as dolomite especially in those cases where the amount of MgO is highest. Fig. 5, therefore, which assumes all MgO as dolomite, has placed certain points too far to the right, the abscissae being $(\text{MnO} \times 100)/(\text{CO}_2 - 2\text{MgO})$.

It is suggested that the best representation would lie between fig. 4 and fig. 5, but nearer the former. The points for nos. 7, 8, and 9 would be expected to be most affected in any of the methods of representation as the analyses are taken for the whole of the ore. In no. 5 the separation of the calcite has evidently not been as successful as for some of the others, but it falls very well in line with them, except in fig. 5 where the MgO content is effective in displacing it to the right. It is apparent that in all the four ways of representation the points are not widely scattered from a line of the slope suggested by the work of Krieger. This line does not, however, appear to pass through the origin—that

is assuming that it does not depart markedly from a straight line. The intercept may be significant, as it seems to suggest a small residual solid-solution content in natural calcites due to traces of some element or elements other than manganese.

The above results are based on the assumption that the 'specpure' calcite spacings are themselves the most correct available for the pure compound CaCO_3 . The spectrographic examination of this calcite as carried out by the manufacturers is compared in Appendix I with a similar examination in our own laboratory of the calcite from North Wales, no. 2 in table II, and with a sample of 'A.R.' quality supplied as a laboratory chemical. The last of these is not referred to in table II as it is not a natural calcite and no ordinary analysis could be satisfactorily obtained. It is interesting, however, to observe that the percentage decrease in spacing is here 0.5. Thus, we have a chemically prepared pure calcite which appears to fall half-way between 'specpure' and the natural calcites examined as regards traces of solid-solution elements other than manganese. This intermediate position is obviously reflected in the results of spectrographic examination and it is significant that the elements chiefly concerned are iron and magnesium.

The intercept in figs. 2-5 which corresponds to a 0.1% contraction of the lattice may thus be due to solid solution of traces of the elements iron and magnesium. The data in Appendix I suggest that iron is likely to be mainly responsible, as the 'A.R.' calcite shows considerably more iron relative to 'specpure', whereas the magnesium content, although greater than in 'specpure', has not increased so markedly. It must, however, be admitted that the presence of greater amounts of iron or magnesium in solid solution in some of the other samples is not ruled out. It can only be claimed that the above interpretation suggests that manganese is mainly responsible for the solid-solution effects observed in the natural calcites examined.

Finally, it is interesting to observe that the ionic diameter of manganese is nearest to that of calcium, and, as reported above, this is the only element whose carbonate seems to form a complete series of solid solutions with calcite. In contrast, both of the elements magnesium and iron appear to form a double carbonate in which the ions of calcium on the one hand and magnesium or iron on the other occupy, in an ordered arrangement, the lattice sites which in calcite solid solutions would be occupied in a random manner.¹ This does not exclude a limited mutual solid solution between chalybite or magnesite and calcite. It should be

¹ cf. W. L. Bragg, *The atomic structure of minerals*. 1937, p. 116.

added that Smythe and Dunham (*loc. cit.*) have pointed out that the solid-solution series between dolomite and ferrodolomite, in which some of the iron may be replaced by manganese, seems to terminate at about 75 % (Fe,Mn)Ca(CO₃)₂. It may be correct to suggest that complete solid solutions are favoured by ionic diameters which are not greatly different, whilst the dolomite type of compound is preferred if the difference becomes more marked.

Conclusions.—1. Accurate lattice parameters and interplanar spacings are given for a very pure sample of chemically prepared calcium carbonate. The values of the lattice parameters and of the rhombohedral angles α and α' , the angle rr' , and the $10\bar{1}4$ spacing (corresponding to the faces of the cleavage rhombohedron) are discussed in relation to previously published values, and agreement with the more recent determinations is considered to be very satisfactory.

2. X-ray examination of nine natural calcites of which seven are present in low-grade iron ores reveals changes in interplanar spacings which may be largely accounted for as being due to solid solution replacement of calcium by manganese. Four different methods of relating the X-ray measurements to the chemical data available all give general support to this view, although they are not all equally satisfactory representations, and there is no means of allowing for the fact that the calcite constituent could not be completely separated from other constituents. The results are in general agreement with the work of Krieger (*loc. cit.*) on manganocalcites. The amounts of other elements in solid solution may, however, be greater than implied by this agreement.

3. The presence of some iron and magnesium in solid solution as well as manganese is indicated, and there is evidence that the chemically pure calcite and a calcite of 'analytical reagent' quality are purer than any natural calcites. The natural calcites, including those listed by Krieger, suggest that, even with no manganese carbonate in solid solution, there is still a residual solid-solution content of some other carbonate or carbonates. This conclusion is supported by a spectrographic examination in which the calcite of 'A.R.' quality definitely falls between 'specpure' calcite and the naturally occurring calcites, especially as regards the iron and magnesium contents.

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APPENDIX I. Spectrographic examination of calcites.

The following table summarizes the data for 'specpure' calcite as reported by the manufacturer, and the corresponding data for two samples of calcite referred to in the text. The conditions of the tests for the two calcites were slightly different and so a pilot test on the 'specpure' was also carried out in our own laboratory.

Elements.	Lines detected.	'Specpure' manufacturer's report.	'Specpure' pilot test.	'A.R.' calcite.	North Wales calcite (no. 2 in table II).
Lead	2833-069 2802-003 2614-178	Faintly visible	{ Not detected	Barely visible	Barely visible
Strontium	4607-331 4077-714 3464-57				
Aluminium	3961-527 3944-032 3092-713 3082-155	Faintly visible	{ Faintly visible	Visible, slightly fainter than in N. Wales calcite	Visible, slightly fainter than in 'specpure'
Copper	3273-962 3247-540				
Iron	3020-640 2599-396 2488-148 2483-270 2395-625 2382-039	Very faintly visible	{ Very faintly visible	The Fe lines detected too numerous to record individually, but all these lines were fainter than in N. Wales calcite	Fe lines too numerous to record individually
Silicon	2881-578 2516-123 2514-331 2506-899				
Magnesium	3838-258 3829-350 2852-129 2802-695 2795-53 3096-899	Faintly visible	{ Faintly visible	Visible, stronger than in 'specpure'	Strongly visible
Silver	3382-891 3280-683				
Sodium	5895-923 5889-953 3302-988 3302-323	Very faintly visible (fainter than in graphite blank)	{ Faintly visible	Visible, stronger than in 'specpure'	Faintly visible
Manganese	4034-490 4033-073 4030-755 2949-205 2939-304 2933-063				
No lines of these elements were detected	—	As, Au, E, Ba, Be, Bi, Cd, Co, Cr, Ga, Ge, Hg, In, K, Li, Mn, Mo, Ni, Pt, Sb, Sc, Sn, Ti, Tl, V, W, Zn, Zr.	—	As, Bi, Be, Co, Cr, Cd, Mn, Mo, Ni, Sn, Sb, Ti, V, W, Zr, Zn.	As, Bi, Be, Co, Cr, Cd, Mo, Ni, Sn, Sr, Sb, Ti, V, W, Zr, Zn.

Conditions of test:

(a) 'Specpure' manufacturer's report:

A spectrographic examination was made by means of (i) an intermittent A.C. arc taking 7 amps., and (ii) a constant-current D.C. arc taking 5.6 amps., between pure graphite electrodes. In each case duplicate spectra of the sample and a comparison blank of the graphite were photographed with a flat-field medium-size spectrograph, on an Ilford long-range spectrum plate, the time of exposure being one minute.

(b) 'A.R.' (analytical reagent) calcite, North Wales calcite, and 'specpure' pilot test:

The spectrographic examination was made by means of an intermittent A.C. arc taking 6.5 amps., between pure graphite electrodes. The three spectra were photographed on to the same plate under the same conditions. (The wave-lengths are those listed in the Massachusetts Institute of Technology Wavelength Tables, 1939.)

Conclusions.—The 'A.R.' quality CaCO_3 appears to be slightly more impure than 'specpure', major differences being in Cu, Mg, Na, and most of all in Fe. The North Wales calcite contains Mg, Mn, and Fe as the chief impurity elements whilst there are also traces of Pb, Al, Cu, Si, Ag, and Na. The Mg and Fe contents both increase on going from 'specpure' to 'A.R.' and again on going from 'A.R.' to the North Wales calcite, whilst the last is the only one in which Mn has been detected. These conclusions are referred to in the text.

APPENDIX II. A method of obtaining the average lattice-spacing change for a non-cubic substance.

In cases where small solid-solution effects do not cause any marked axial ratio change the average change in interplanar spacings can be used to estimate the lattice-spacing change and hence the overall effect of the solid-solution replacement.

In our own practice the specimen in the powder camera is made large enough (corresponding to the absorption properties of the material) to ensure that most of the diffracted beam comes from the outer layers of the specimen. Under these conditions Jay¹ showed that a cubic substance would give an approximately linear extrapolation if lattice spacing is plotted against $\cos^2\theta/\sin\theta$. This function does, in fact, give points, very near indeed to the function $\frac{1}{2} \left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta} \right)$ proposed by Taylor and Sinclair,² and by Nelson and Riley³ for general use, and the extrapolated value is practically identical.

For a cubic substance we may write: $\Delta a/a = \text{const.} \times \cos^2\theta/\sin\theta$.

For a non-cubic substance the same kind of relationship must apply, and in this case the relative interplanar spacing difference $\Delta d/d$ is given by $\text{const.} \times \cos^2\theta/\sin\theta$. Thus $\Delta d/d \times \sin\theta$ gives a linear, or very nearly linear plot against $\cos^2\theta$. This method of plotting has the advantage that the quantity $\Delta d/d \sin\theta$ varies from zero to a finite value and $\cos^2\theta$ varies from 0 to 1, whereas if $\Delta d/d$ is plotted against $\cos^2\theta/\sin\theta$ both quantities increase indefinitely for $\theta \rightarrow 0$.

The straight line, or curve, obtained by plotting $\Delta d/d \sin\theta$ against $\cos^2\theta$ should pass through the origin for both quantities equal to zero. For the naturally occurring calcites examined this is not the case. The intercept from $\cos^2\theta = 0$ (i.e. $\sin\theta = 1$) gives a positive value for $\Delta d/d \sin\theta$. This implies that all the interplanar spacings

¹ A. H. Jay, Unpublished work. Referred to at conference of the X-ray Analysis Group (Institute of Physics) in 1942 and again in 1948.

² A. Taylor and H. Sinclair, Proc. Phys. Soc. London, 1945, vol. 57, p. 126.

³ J. B. Nelson and D. P. Riley, Proc. Phys. Soc. London, 1945, vol. 57, p. 160.

have, in addition to the variable absorption (and eccentricity) correction a further difference relative to the standard interplanar spacings for the pure calcite: i.e.

$$\Delta d = \Delta d_1 + \Delta d_2,$$

where Δd_1 = variable correction due to absorption, &c.

Δd_2 = spacing change due to solid solution.

$\frac{\Delta d - \Delta d_2}{d}$ would now give an almost linear plot against $\cos^2\theta$ passing through the origin.

$\frac{\Delta d_2}{d}$ (expressed as a percentage) gives the relative change in spacings due to elements replacing calcium in solid solutions. Since the values are all 'positive', the true interplanar spacings have decreased, suggesting the presence of ions of smaller size than calcium (of which manganese, iron, and magnesium are examples).