

CONCLUSION

It appears possible through the use of the method described to extend the observable D.T.A. range beyond the melting point of a mineral without encountering the difficulties noted for analyses made with unprotected thermocouples. This offers the possibility of widespread application of the D.T.A. method to a considerable group of minerals not previously amenable to the method. The few analyses mentioned constitute a small sample of the applications which are conceivable.

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REFINEMENT OF THE CRYSTAL STRUCTURE OF DOLOMITE*

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The mineral dolomite was one of the early substances to be investigated by x-ray diffraction methods (Wyckoff and Merwin, 1924). Dolomite, $\text{CaMg}(\text{CO}_3)_2$, was considered by some to be a solid solution of the simple carbonates calcite and magnesite and by others as a definite compound, distinct from the two simpler carbonates. This early investigation established, with the use of Laue photographs, that the symmetry of the atomic arrangement of dolomite was lower than that of calcite and, therefore, it was a distinct chemical compound. It also established the unit cell dimensions and showed that four atomic parameters needed to be evaluated to determine the structure. At that time no attempt was made to determine the exact positions of the atoms of the carbonate group. The atomic parameters of dolomite were not investigated until Bradley *et al.* (1953) determined the four necessary parameters from powder data. Because the dolomite structure is of such importance in

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mineralogy it was felt that the parameters should be redetermined from single crystal data and that the thermal anisotropy of the atoms should also be investigated.

EXPERIMENTAL

A rhomb of dolomite, 0.12 mm. thick, 0.12 mm. wide, and 0.23 mm. long was rotated about an a axis and three-dimensional data were collected with the Weissenberg camera. Multiple films interleaved with brass foil were taken with Mo $K\alpha$ radiation and the intensities were estimated in the usual way with the aid of a calibrated intensity scale. Equivalent reflections appearing on different films were used to bring all films to the same scale. Altogether 501 reflections were observed. The indices and coordinates used in this investigation refer to the hexagonal unit cell whose lattice constants are $a=4.815$, $c=16.119$ Å. The atoms were placed in space group $R\bar{3}$ as follows: Ca in $3(a)$, Mg in $3(b)$, C in $6(c)$, and O in $18(f)$.

REFINEMENT OF PARAMETERS

Structure factors were first calculated with the parameters given by Bradley *et al.* (1953), and the signs were used to evaluate the bounded projection

$$\rho(xy) = c \int_0^{1/6} \rho(xyz) dz.$$

This projection was refined and backshift corrections on the oxygen parameters were made. The z parameter for the carbon atom was determined from a line synthesis $\rho(00z)$ and the z parameter for the oxygen atom was obtained from a line synthesis passing through the (x, y) coordinates which had been obtained previously from the bounded projection.

The coordinates thus obtained were used as the starting values in a least-squares refinement, making use of all 501 observed reflections. Two iterations on the four coordinate parameters were made using an isotropic temperature factor, and the new atomic coordinates were then used in two separate least-squares iterations which determined anisotropic temperature parameters for each atom in the structure. The available computing equipment limited the evaluation of temperature parameters to two for each atom, one parallel to the c axis and one in the plane perpendicular to the c axis. After the second temperature least-squares iteration the anisotropic parameters together with the previously obtained coordinate parameters were used in another least-squares refinement of the coordinates, and since all changes were smaller than the standard deviations, the refinement was ended. The value of R de-

TABLE 1. PARAMETERS FOR DOLOMITE

	Oxygen	σ	Bradley <i>et al.</i>	Carbon	σ	Bradley <i>et al.</i>
<i>x</i>	0.2374	0.00068	0.257	0	—	0
<i>y</i>	-0.0347	0.00068	-0.028	0	—	0
<i>z</i>	0.2440	0.00017	0.243	0.2435	0.00031	0.243

creased from 0.134 to 0.0925, and $\Sigma\omega(\Delta F)^2$ decreased from 9.986 to 6.270. Table 1 lists the final parameters and their standard deviations and compares the values obtained in this investigation with those reported by Bradley *et al.* (1953).

The temperature factors for the four atoms were obtained by the least-squares refinement of the expression $F(hkl) = \sum_i f_i \exp [-\beta_i r (h^2 + k^2 + l^2) - A_i s l^2]$ where $r = \frac{1}{3}a^2$, $s = \frac{1}{4}c^2$, B_i is the temperature factor of the *i*th atom in the plane perpendicular to the *c* axis and A_i is the temperature factor parallel to the *c* axis. These temperature factors are listed in Table 2.

TABLE 2. TEMPERATURE FACTORS AND RMS DISPLACEMENT OF ATOMS IN DOLOMITE

Atom	<i>B</i>	<i>A</i>	$\bar{\mu}_{\parallel c_0}$	$\bar{\mu}_{\perp c_0}$
Ca	0.37 Å ²	0.30 Å ²	.062 Å	.068 Å
Mg	0.20	0.21	.050	.050
C	0.62	0.36	.067	.088
O	0.59	0.77	.099	.086

DISCUSSION

The parameters of Table 1 lead to the following interatomic distances: C—O = 1.283 Å, Mg—O = 2.095 Å, Ca—O = 2.390 Å, with standard deviations of 0.004 Å. The value of the C—O bond is in good agreement with the predicted length for this bond, 1.288 Å, and with the value 1.294 Å reported by Sass *et al.* (1957) for CaCO₃. The Ca—O bond length is equal to the sum of the ionic radii.

The temperature parameters determined for the cations show that they vibrate isotropically while the atoms of the carbonate group have a considerable anisotropy in their thermal motion. The carbon atom bonded to three oxygen atoms vibrates with a smaller amplitude parallel to the *c* axis than in the (001) plane where the amplitude of vibration is the same as for the three oxygens (Table 2). Thus the carbonate group vibrates as a unit in the plane perpendicular to the *c* axis. The oxygen

atoms are less restricted and their vibrations parallel to the c axis are bigger than those in the (001) plane. Sass *et al.* (1957) reports a rms displacement for oxygen in CaCO_3 of about 0.09 Å parallel to c which is in good agreement with the value reported in this investigation. Their two anisotropic displacements in the (001) plane, 0.06 Å and 0.11 Å, respectively parallel and perpendicular to the a axis, bracket the value of 0.086 Å of Table 2.

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OCCURRENCE OF JORDANITE IN THE OTAVI MOUNTAINS, SOUTH WEST AFRICA

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An interesting occurrence of jordanite ($\text{Pb}_{14}\text{As}_7\text{S}_{24}$?) has recently been found at Kupferberg in the Otavi Mountains of South West Africa. The following brief note describes its mode of occurrence and chemical composition.

The Kupferberg copper prospect lies in the Otavi Valley about 40 miles South West of Grootfontein. Dolomites of the Lower (?) Tsumeb Stage of the Otavi System make up the country rock which is characterised at Kupferberg and elsewhere by widespread and intense calcite replacement. Such calcite may be fine-grained, in which case the original grain size and texture of the dolomite is largely preserved, or coarsely-crystalline with cleavage rhombohedrons up to several centimetres in dimension. Sulphide mineralisation is restricted to the coarse-grained variety of calcite.