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Preliminary X-ray studies of crocidolite and amosite.

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During the course of an investigation into the properties of some fibrous silicates, it became necessary, in the absence of any published information at the time, to determine the unit-cell dimensions and space-group symmetry of crocidolite (ex West Australia) and amosite (ex Transvaal, South Africa), kindly supplied to us by James Hardie & Co. Pty. Ltd. In each material, fibres from the samples were found to consist of bundles of single crystals (individually too small for single-crystal techniques), oriented parallel or nearly so to the common fibre axis, but with random orientation in other directions. The degree of parallelism was found to be much closer for amosite than for crocidolite, which had a larger crystal size. Stationary X-ray photographs, with the incident beam normal to the axis of the fibres in the specimen, therefore approximate to a single-crystal rotation pattern, as found by Warren & Bragg for chrysotile (1930).

The crystal class was found to be monoclinic for both minerals; and, with the aid of a Bunn chart and appropriate reciprocal-lattice constructions, the unit cell dimensions were found to be:

Crocidolite: $a = 9{\cdot}6_5,\ b = 18{\cdot}3,\ c = 5{\cdot}3_0$ Å, $\beta \approx 70°$; axial ratios 0·53:1:0·29.

Amosite: $a = 9{\cdot}89,\ b = 18{\cdot}26,\ c = 5{\cdot}30$ Å, $\beta = 70°$; axial ratios 0·542:1:0·290.

(Owing to the poor parallelism of the crocidolite fibres the parameters for this mineral are approximate only.)

Both structures therefore belong to the monoclinic amphibole group. Absent reflexions are in accordance with the space group $I2/m$.

Shortly after we obtained the results for the West Australian crocidolite, the paper by Whittaker (1949) on the structure of Bolivian crocidolite reached us. In view of the similarity of the results obtained for the unit-cell dimensions, no further analysis on Australian crocidolite has been done.

Subsequent work on amosite has shown the unit cell to contain two molecules, with a formula corresponding to $(\mathrm{Ca\,Na\,Mn\,Fe\,Mg})_{6\cdot09}\,(\mathrm{Si\,Al})_{7\cdot99}\,\mathrm{O}_{22}(\mathrm{OH})_2$ (probable error $\pm 0{\cdot}02$). Preliminary Fourier projections indicate a structure similar to (but differing in certain interesting details from) that proposed by Warren (1930) for tremolite and by Whittaker (1949) for crocidolite. Further refinement is at present in progress.

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The crystal structure of kojic acid.

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The structure of kojic acid, 2 hydroxy 5 hydroxymethyl 1,4 γ-pyrone, has been examined, in continuation of a program for X-ray investigation of sugars and related compounds. Weissenberg photographs were taken with Cu $K\alpha$ radiation. The cell is monoclinic, space-group $P2_1/n$, with

$$a = 3{\cdot}85,\quad b = 18{\cdot}4,\quad c = 8{\cdot}55\ \text{Å},\quad \beta = 84°\ .$$

The measured density of 1·58 g.cm.$^{-3}$ gave $3{\cdot}98 \approx 4$ molecules/cell. These results are in accord with previous measurements by Fox (1945). The molecule contains no asymmetric carbon atoms.

The a-axis periodicity indicated no that overlapping would occur in a projection on (100). The structure was consequently considered a good test subject for several recently-developed analytical methods.

The X-RAC method of approximation via positive kernels, as suggested by one of us (Pepinsky, 1951; Pepinsky & Cochran, 1951) for reduction of terms in the Fourier sum, was successful in giving the orientation of the molecule and its general position in the cell. The approximation technique was not successful in the next stages of the analysis. The application of the non-negativity criterion on X-RAC was useful in all refinements (Eiland & Pepinsky, 1950).

The Harker–Kasper inequalities were inapplicable because of the low values of the unitary structure factors. There were sets of related factors large enough, and the cell was sufficiently thin, to suggest that the squared-crystal method (Sayre, 1951, 1952), and, in particular, the

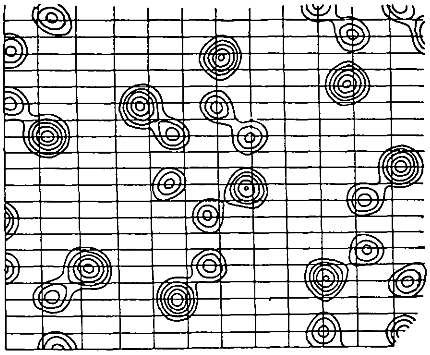

Fig. 1. Kojic acid: projection on (100).

modification suggested by Pepinsky & Cochran (1951), should be useful. However, the amplitudes were so distributed that the latter modification failed entirely, and the equations relating the Fourier coefficients of the squared and unsquared density functions gave correct sign relationships only when the *full* set of coefficients was used in each equation. As a consequence, these methods were not useful at all in the early, critical stages.

The vector convergence density (VCD) method (Buerger, 1950; Beevers & Robertson, 1950) for interpretation of the Patterson diagram was first tried unsuccessfully. It was later discovered that a computational error (human, not machine!) was responsible for the failure. The *a*-axis projection was actually first solved by the very classical use of Bragg–Lipson charts and packing considerations. Subsequent application of the VCD method showed that this led directly to the correct projection on (100).

The *a*-axis projection is shown in Fig. 1, as photographed from X-RAC. The correctness ratio, $R = \Sigma|F_o - F_c| \div \Sigma|F_o|$, for this projection is 0·20. The structural formula is shown in Fig. 2.

A projection on (010) was computed in order to determine the *x* coordinates. All coordinate assignments to date are presented in Table 1. A full three-dimensional analysis is in progress and will be reported subsequently.

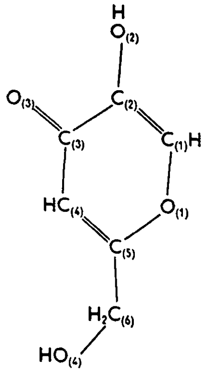

Fig. 2. Structural formula for kojic acid.

Table 1. *Coordinates for kojic acid*

	x	*y*	*z*
C_1	0·14	0·047	0·300
C_2	0·00	0·099	0·393
C_3	0·04	0·165	0·313
C_4	0·22	0·170	0·159
C_5	0·29	0·114	0·059
C_6	0·26	0·091	0·902
O_1	0·36	0·057	0·140
O_2	0·12	0·091	0·545
O_3	0·86	0·210	0·393
O_4	0·16	0·162	0·799

A projection on (010) is now in progress, to determine the *x* coordinates. Full details of the structure will be published upon completion of this phase of the analysis.

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The crystal structure of artinite, $Mg_2(OH)_2CO_3 . 3H_2O$.

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A trial structure of artinite has been derived from (*a*) unit-cell parameters (see below); (*b*) the presumed analogy to certain magnesium oxychlorides (de Wolff & Walter-Levy, to be published) involving infinite bands $||b$ with a brucite structure; (*c*) the outstanding strength of the (203) reflexion, indicating the azimuth of the bands; (*d*) Heritsch's (1948) conclusion (optical) that CO_3 ions lie in planes $||b$, and his value for their azimuth; (*e*) Fenoglio's (1942) conclusion from etching figures, that the space group is probably *C*2.

The value of F_c were compared with $|F_o|$ values of the 34 ($h0l$) reflexions with $(\sin\theta)/\lambda < 0{\cdot}32$, obtained from the photometer record of a powder pattern (sample kindly submitted by Dr de Jong, with $a = 16{\cdot}56$, $b = 3{\cdot}15$, $c = 6{\cdot}22$ Å, $\beta = 99° 9'$) and completed for some coincident reflexions by using Heritsch's qualitative single-crystal data. Slight parameter changes led to a satisfactory agreement. The final projection (Fig. 1, Table 1) shows the bands consisting of two rows of

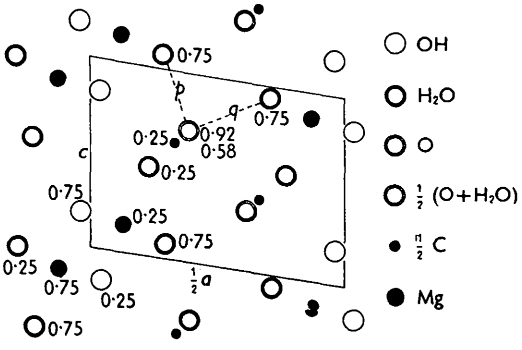

Fig. 1. (010) projection.