

## The crystal structure of dundasite

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**SUMMARY.** The crystal structure of dundasite from Gonnese (Italy) was solved by a three-dimensional Patterson function computed using intensity data collected photographically by the Weissenberg method, and refined by successive Fourier maps and least-squares cycles to an  $R$  index 0.066 for 505 independent observed reflections.

The chemical formula resulting from the structural analysis is  $\text{PbAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$ . The mineral is orthorhombic, space group  $Pbmm$ , with  $a$  9.08 Å,  $b$  16.37 Å,  $c$  5.62 Å. The dundasite structure consists of a three-dimensional framework of coordination polyhedra around Pb and Al. Pb ions are coordinated by nine oxygen atoms with distances ranging from 2.53 to 2.91 Å. Al ions show the usual octahedral coordination with average Al-O distance 1.90 Å. C-O mean distances are 1.28 and 1.27 Å for the two non-equivalent  $\text{CO}_3$  groups. The water molecules are not coordinated by the cations.

**DUNDASITE**, a basic hydrated carbonate of Al and Pb, is a rare mineral found originally in Dundas, Tasmania, by Petterd (1893). The present X-ray investigation concerns crystals from the locality of Gonnese, Sardinia (Italy), where the mineral is associated with cerussite. The occurrence of dundasite in Gonnese was first mentioned by Beaumont and Guillemin (1960), who determined the chemical and physical properties of the crystals from this locality. Recently Jambor, Fong, and Sabina (1969) discovered a new mineral, named dresserite, in Quebec, Canada, which chemical analyses and comparison of X-ray powder patterns proves to be the barium analogue of dundasite.

*Lattice constants and space group determination.* As Beaumont and Guillemin (1960) pointed out, dundasite from Gonnese occurs as spherical clusters of radiating acicular crystals. A preliminary optical investigation showed that the crystals probably belong to the orthorhombic system and that very thin needles of the mineral are not single crystals but subparallel aggregates. The optical sign of the elongation of these needles is positive and the birefringence is high, as observed by Beaumont and Guillemin (1960).

Because of the impossibility of selecting a single crystal, the X-ray study was performed on a very thin needle built up by a few parallel single crystals; therefore the appearance of the photographs was rather poor but a careful examination of the films allowed us to recognize the reciprocal lattice points of a larger single individual among those due to the satellites present in the fibre. Rotation and Weissenberg equi-inclination photographs were collected with the elongation axis as rotation axis, employing Cu- $K\alpha$  radiation. Dundasite proved to be orthorhombic in agreement with optical observations and as required by the analogy with dresserite. The unit-cell

parameters are:  $a$   $9.08 \pm 0.01$ ,  $b$   $16.37 \pm 0.02$ ,  $c$   $5.62 \pm 0.01$  Å, in close agreement with those employed by Jambor *et al.* (1969) for indexing the powder pattern of dundasite. The crystals are elongated, like those of dresserite, along [001]. Systematic absences are *hol* reflections for  $h+l$  odd and *okl* reflections for  $k$  odd, whence the possible space-groups are *Pbnm* and *Pbn2<sub>1</sub>*. These space-groups are consistent with those suggested by Jambor *et al.* for dresserite, assuming that the latter lacks the *n*-glide. The structure investigation below showed that the space-group of dundasite is in fact *Pbnm*.

*Chemical formula and cell content.* All the available analyses of dundasite agree with the formula  $\text{PbAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot n\text{H}_2\text{O}$ . Prior (1966) finds a  $\text{H}_2\text{O}$  content of 15.1 % and suggests  $n = 2$ , while Beaumont and Guillemin (1960) with a lower amount of water (13.2 %) propose  $n = 1.5$ .

Assuming that the metal ions are completely ordered and taking into account that both the possible space-groups do not allow lower multiplicity than four, the cell content of dundasite is  $4[\text{PbAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot n\text{H}_2\text{O}]$ , with a calculated density of  $3.573 + 0.143n$  g.cm<sup>-3</sup>, which is higher than all the experimental values. However, all these values are scattered over a large range: 3.25 g.cm<sup>-3</sup> (Prior, 1966) on Trefriw material; 3.41 g.cm<sup>-3</sup> (Beaumont and Guillemin, 1960) on crystals from Gonnessa; 3.10 g.cm<sup>-3</sup> and 3.55 g.cm<sup>-3</sup> (Jambor *et al.*, 1969) on crystals from Gonnessa and Dundas respectively. These notably low densities are presumably due to the finely fibrous nature of the material and to the appreciable content of adsorbed water, and cannot be of any help in order to determine the number of water molecules in the unit-cell. The detailed structure showed only one 4-fold water position and dundasite is therefore assigned the formula  $\text{PbAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$ .

*Structure determination and refinement.* 815 independent diffraction effects were collected on the reciprocal lattice layers from *hko* to *hk4*; of these, 310 were too weak to be observed and were given an intensity value just below the minimum observed one. The intensity data were measured with a microdensitometer and different layers were put approximately on the same scale, taking into account their exposure time. The usual geometrical corrections were made. Absorption corrections were calculated assuming the crystal to have a cylindrical shape (0.013 mm in diameter;  $\mu R = 0.27$ ).

The crystal structure was solved in the centrosymmetric space group *Pbnm*. Interpretation of the Patterson function allowed us to locate Pb atoms in the unit cell. Then the structural model was developed by successive Fourier syntheses combined with stereochemical considerations. The positions of carbon atoms were found by a difference synthesis. At this stage the *R* factor, defined as  $\sum ||F_o| - |F_c|| / \sum |F_o|$ , was 0.15. The refinement of the structure was performed by the least-squares method, using a block-diagonal program written by Albano *et al.* (1963). The following weighting scheme was employed: reflections with intensities up to 4 times the minimum observable value ( $F_{\text{min}}$ ) were assigned unit weight; more intense reflections were given a weight  $w = (4F_{\text{min}}/F_o)^2$ . Unobserved reflections were excluded from the refinement. After five cycles of calculations employing individual isotropic temperature factors,

when the shifts in the atomic parameters were less than the estimated standard deviations, the refinement was stopped. The  $R$  value was 0.066 for all observed reflections. Finally, a three-dimensional difference synthesis was computed in order to check the possible presence of additional water molecules, but it did not show any significant amount of residual localized electron density. Final atomic coordinates and individual thermal parameters with standard deviations are listed in table I. The distinction

TABLE I. Fractional atomic coordinates and isotropic thermal parameters with their standard deviations in parentheses

Atom	$x/a$	$y/b$	$z/c$	$B (\text{\AA})^2$
Pb	0.5131 (2)	0.4117 (1)	3/4	2.4 (0.1)
Al	0.3338 (8)	0.1998 (5)	0.9980 (20)	2.3 (0.2)
C (1)	0.4172 (46)	0.3506 (26)	1/4	2.5 (1.3)
C (2)	0.7599 (49)	0.4502 (29)	1/4	2.8 (1.4)
O (1)	0.4027 (21)	0.3097 (12)	0.0521 (45)	2.7 (0.7)
O (2)	0.4599 (26)	0.4224 (15)	1/4	2.1 (0.8)
O (3)	0.7737 (18)	0.4112 (13)	0.0506 (38)	2.5 (0.5)
O (4)	0.7399 (33)	0.5242 (18)	1/4	2.8 (0.9)
OH (1)	0.1969 (26)	0.2076 (15)	1/4	1.9 (0.7)
OH (2)	0.4705 (25)	0.1856 (14)	3/4	1.9 (0.7)
OH (3)	0.4619 (31)	0.1668 (18)	1/4	2.4 (1.0)
OH (4)	0.2182 (29)	0.2375 (17)	3/4	2.4 (0.9)
H <sub>2</sub> O	0.1085 (36)	0.4576 (21)	1/4	3.9 (1.1)

between oxygen atoms, hydroxyl groups, and water molecules is made on the basis of Pauling's electrostatic valence rule. A table of observed and calculated structure factors is deposited in the library of the Department of Mineralogy, British Museum (Natural History). The atomic scattering factors of Cromer and Weber (1965) for the Pb<sup>2+</sup> ion, and of the International Tables (1962) for Al, C, and O were used for the calculations. Contributions of the real component of the anomalous dispersion to the scattering factors of Pb and Al were taken into account: correction was applied with the values  $\Delta f'$  determined for Cu- $K\alpha$  radiation by Cromer (1965).

*Discussion of the structure.* A clinographic view of the crystal structure of dundasite is shown in fig. 1. The lists of bond lengths and bond angles with their standard deviations are included in table II.

Pb ions lie on the mirror planes and are coordinated by nine oxygen atoms according to irregular polyhedra (each of them shares four vertices and two edges with six different CO<sub>3</sub> groups, the ninth oxygen atom belonging to an hydroxyl group). Pb-O distances range from 2.53 to 2.91 Å with a mean value of 2.73 Å. This average distance is slightly shorter than those recently reported for Pb in ninefold coordination: Pb<sup>[9]</sup>-O mean distances are 2.77 and 2.78 Å in fornacite (Cocco, Fanfani, and Zanazzi, 1967), 2.778 and 2.818 Å in hemihedrite (McLean and Anthony, 1970).

Four hydroxyl groups and two oxygen atoms belonging to different carbonate groups surround each Al ion in an octahedral trans-configuration. Al-O distances

in the  $\text{Al}(\text{OH})_2\text{O}_2$  octahedra range from 1.85 to 1.93 Å (mean value 1.90 Å) in agreement with the values reported in the literature for aluminum in sixfold coordination.

The carbonate anions have the usual triangular shape. C-O average distances are 1.28 and 1.27 Å for the two non-equivalent groups. Water molecules are not coordinated by the cations, and are hydrogen-bonded to the framework. Distances

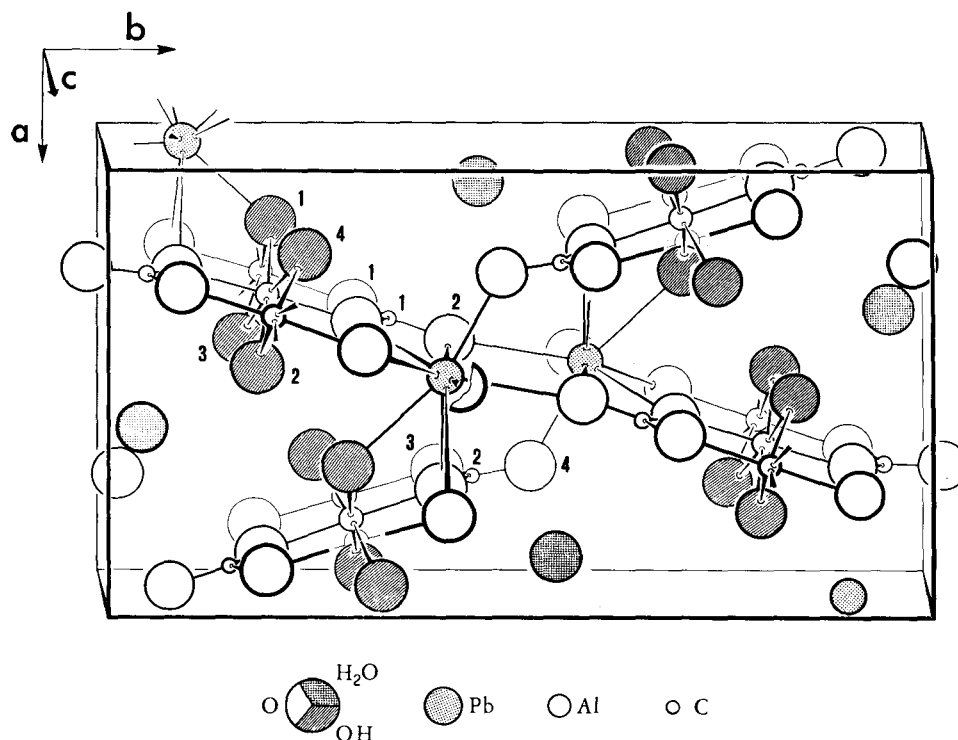


FIG. 1. Clinographic view of the dundasite structure.

less than 3 Å between oxygen atoms not belonging to the same coordination polyhedron and ascribable to hydrogen bonds are listed in table III.

The crystal structure of dundasite consists of a three-dimensional framework of coordination polyhedra around Pb and Al. Pb ions in the same unit cell are coupled by an edge through the inversion centre at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  and equivalent centres. Each Pb ion shares an oxygen atom with each of the two Pb ions of the adjacent unit-cells in the *c* direction, so that the Pb-coordination motif results in columns parallel to the *c* axis. Each of these columns is connected to the four nearest ones by four chains running in the *c* direction too, and built up by Al octahedra sharing opposite edges. Carbonate groups connect adjacent Al-octahedra in the same chain sharing an edge of the triangle. Linkages through carbonate groups occur also between different Pb ions of the same columns and between lead and aluminum coordination polyhedra. A view

TABLE II. Bond lengths and angles in *dundasite*. (I) =  $x, y, z$ ; (II) =  $x, y, 1+z$ ; (III) =  $1-x, 1-y, 1-z$ ; (IV) =  $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$ ; (V) =  $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$ ; (VI) =  $x, y, \frac{1}{2}-z$ ; (VII) =  $1-x, 1-y, -z$ ; (VIII) =  $\frac{1}{2}-x, \frac{1}{2}+y, z$ .

Pb (I)	$\left\{ \begin{array}{l} \text{—O(1) (II)} \quad 2.58 \pm 0.02 \text{ \AA} \\ \text{—O(1) (VI)} \quad 2.58 \quad 0.02 \\ \text{—O(2) (I)} \quad 2.86 \quad 0.01 \\ \text{—O(2) (II)} \quad 2.86 \quad 0.01 \\ \text{—O(2) (III)} \quad 2.73 \quad 0.02 \\ \text{—O(3) (II)} \quad 2.91 \quad 0.02 \\ \text{—O(3) (VI)} \quad 2.91 \quad 0.02 \\ \text{—O(4) (III)} \quad 2.53 \quad 0.03 \\ \text{—OH(1) (IV)} \quad 2.57 \quad 0.02 \end{array} \right.$	O(1) (II)—Pb (I)	$\left\{ \begin{array}{l} \text{—O(1) (VI)} \quad 82.2^\circ \pm 0.7^\circ \\ \text{—O(2) (I)} \quad 128.3^\circ \quad 0.7^\circ \\ \text{—O(2) (II)} \quad 47.7^\circ \quad 0.7^\circ \\ \text{—O(2) (III)} \quad 132.7^\circ \quad 0.5^\circ \\ \text{—O(3) (II)} \quad 86.1^\circ \quad 0.6^\circ \\ \text{—O(3) (VI)} \quad 134.1^\circ \quad 0.6^\circ \\ \text{—O(4) (III)} \quad 85.2^\circ \quad 0.7^\circ \\ \text{—OH(1) (IV)} \quad 76.2^\circ \quad 0.6^\circ \end{array} \right.$
Al (I)	$\left\{ \begin{array}{l} \text{—O(1) (II)} \quad 1.93 \pm 0.02 \text{ \AA} \\ \text{—O(3) (V)} \quad 1.92 \quad 0.02 \\ \text{—OH(1) (II)} \quad 1.89 \quad 0.02 \\ \text{—OH(2) (I)} \quad 1.88 \quad 0.02 \\ \text{—OH(3) (II)} \quad 1.91 \quad 0.02 \\ \text{—OH(4) (I)} \quad 1.85 \quad 0.02 \end{array} \right.$	O(2) (I)—Pb (I)	$\left\{ \begin{array}{l} \text{—O(2) (II)} \quad 159.3^\circ \quad 0.7^\circ \\ \text{—O(2) (III)} \quad 87.4^\circ \quad 0.5^\circ \\ \text{—O(3) (II)} \quad 135.2^\circ \quad 0.6^\circ \\ \text{—O(3) (VI)} \quad 64.3^\circ \quad 0.6^\circ \\ \text{—O(4) (III)} \quad 79.7^\circ \quad 0.5^\circ \\ \text{—O(1) (IV)} \quad 99.0^\circ \quad 0.5^\circ \end{array} \right.$
C(1) (I)	$\left\{ \begin{array}{l} \text{—O(1) (I)} \quad 1.30 \pm 0.03 \text{ \AA} \\ \text{—O(1) (VI)} \quad 1.30 \quad 0.03 \\ \text{—O(2) (I)} \quad 1.24 \quad 0.05 \end{array} \right.$	O(2) (III)—Pb (I)	$\left\{ \begin{array}{l} \text{—O(3) (II)} \quad 86.0^\circ \quad 0.6^\circ \\ \text{—O(4) (III)} \quad 70.6^\circ \quad 0.8^\circ \\ \text{—OH(1) (IV)} \quad 134.3^\circ \quad 0.7^\circ \\ \text{—O(3) (VI)} \quad 71.0^\circ \quad 0.6^\circ \\ \text{—O(4) (III)} \quad 137.9^\circ \quad 0.5^\circ \\ \text{—OH(1) (IV)} \quad 57.9^\circ \quad 0.6^\circ \\ \text{—OH(1) (IV)} \quad 155.1^\circ \quad 0.9^\circ \end{array} \right.$
C(2) (I)	$\left\{ \begin{array}{l} \text{—O(3) (I)} \quad 1.30 \pm 0.03 \text{ \AA} \\ \text{—O(3) (VI)} \quad 1.30 \quad 0.03 \\ \text{—O(4) (I)} \quad 1.22 \quad 0.06 \end{array} \right.$	O(3) (II)—Pb (I)	
		O(4) (III)—Pb (I)	
		O(1) (II)—Al (I)	$\left\{ \begin{array}{l} \text{—O(3) (V)} \quad 177.4^\circ \pm 0.9^\circ \\ \text{—OH(1) (II)} \quad 91.8^\circ \quad 1.1^\circ \\ \text{—OH(2) (I)} \quad 91.0^\circ \quad 1.0^\circ \\ \text{—OH(3) (II)} \quad 87.1^\circ \quad 1.2^\circ \\ \text{—OH(4) (I)} \quad 89.5^\circ \quad 1.1^\circ \end{array} \right.$
		O(3) (V)—Al (I)	$\left\{ \begin{array}{l} \text{—OH(1) (II)} \quad 89.1^\circ \quad 1.0^\circ \\ \text{—OH(2) (I)} \quad 88.0^\circ \quad 1.0^\circ \\ \text{—OH(3) (II)} \quad 90.6^\circ \quad 1.1^\circ \\ \text{—OH(4) (I)} \quad 92.7^\circ \quad 1.1^\circ \end{array} \right.$
		OH(1) (II)—Al (I)	$\left\{ \begin{array}{l} \text{—OH(2) (I)} \quad 176.8^\circ \quad 1.1^\circ \\ \text{—OH(3) (II)} \quad 82.2^\circ \quad 1.0^\circ \\ \text{—OH(4) (I)} \quad 99.7^\circ \quad 0.9^\circ \end{array} \right.$
		OH(2) (I)—Al (I)	$\left\{ \begin{array}{l} \text{—OH(3) (II)} \quad 96.5^\circ \quad 0.9^\circ \\ \text{—OH(4) (I)} \quad 81.8^\circ \quad 0.9^\circ \end{array} \right.$
		OH(3) (II)—Al (I)	$\left\{ \begin{array}{l} \text{—OH(4) (I)} \quad 176.2^\circ \quad 1.3^\circ \end{array} \right.$
		O(1) (I)—C(1) (I)	$\left\{ \begin{array}{l} \text{—O(1) (VI)} \quad 117.0^\circ \pm 3.4^\circ \\ \text{—O(2) (I)} \quad 121.3^\circ \quad 1.9^\circ \end{array} \right.$
		O(3) (I)—C(2) (I)	$\left\{ \begin{array}{l} \text{—O(3) (VI)} \quad 119.7^\circ \pm 3.9^\circ \\ \text{—O(4) (I)} \quad 120.1^\circ \quad 2.0^\circ \end{array} \right.$

TABLE III. Distances ascribable to hydrogen-bonds in *dundasite* (Notation as in table II)

H <sub>2</sub> O (I)	$\left\{ \begin{array}{l} \text{—OH(2) (V)} \quad 2.66 \text{ \AA} \\ \text{—O(3) (VIII)} \quad 2.93 \end{array} \right.$	OH(1) (VIII)—OH(2) (III)	2.70 \AA
		OH(4) (VIII)—OH(3) (III)	2.81

of these columns and chains and of the triangular carbonate groups is shown in fig. 2.

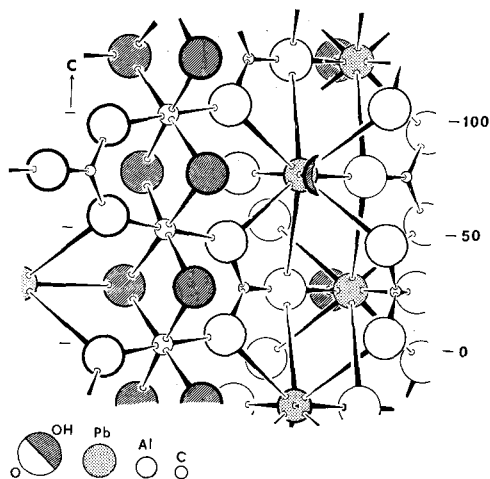


FIG. 2. Partial view of the dundasite structure projected along  $[110]$ .

In the crystal structure there are empty channels along the  $c$  axis, where the water molecules are located. The observed  $\{010\}$  cleavage may be explained considering that a weak point in the framework is represented by the channels containing the water molecules and by the Pb–O–Pb linkages.

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