

- QURASHI, M. M. & BARNES, W. H. (1964). *Can. Mineral.* **8**, 23–39.
- ROBERTSON, B. & KOSTINER, E. (1972). *J. Solid State Chem.* **4**, 29–37.
- ROBINSON, K., GIBBS, G. V. & RIBBE, P. H. (1971). *Science*, **172**, 567–570.
- SALMON, R., PARENT, C., LE FLEM, G. & VLASSE, M. (1976). *Acta Cryst.* **B32**, 2799–2802.
- SAUERBREI, E. E., FAGGIANI, R. & CALVO, C. (1973). *Acta Cryst.* **B29**, 2304–2306.
- SAUERBREI, E. E., FAGGIANI, R. & CALVO, C. (1974). *Acta Cryst.* **B30**, 2907–2909.
- SHANNON, R. D. (1971). *Chem. Commun.* pp. 821–822.
- SHANNON, R. D. (1975). Proc. NATO Conf. on Petrophysics, Newcastle-upon-Tyne.
- SHANNON, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- SHANNON, R. D. & CALVO, C. (1972). *Can. J. Chem.* **50**, 3944–3949.
- SHANNON, R. D. & CALVO, C. (1973a). *J. Solid State Chem.* **6**, 538–549.
- SHANNON, R. D. & CALVO, C. (1973b). *Can. J. Chem.* **51**, 70–76.
- SHANNON, R. D. & CALVO, C. (1973c). *Can. J. Chem.* **51**, 265–273.
- SHANNON, R. D. & CALVO, C. (1973d). *Acta Cryst.* **B29**, 1338–1345.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.

Acta Cryst. (1979). **B35**, 720–722

Paradamite

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Abstract. $\text{Zn}_2\text{AsO}_4\text{OH}$, $P\bar{1}$, $Z = 2$, $D_c = 4.595 \text{ Mg m}^{-3}$; cell constants at 293 K: $a = 5.638$ (3), $b = 5.827$ (3), $c = 6.692$ (2) Å, $\alpha = 103.25$ (4), $\beta = 104.37$ (3), $\gamma = 87.72$ (4)°; $\lambda(\text{Mo } K\alpha) = 0.71069$ Å. Paradamite is isostructural with tarbuttite, $\text{Zn}_2\text{PO}_4\text{OH}$.

Introduction. Paradamite is a dimorph of adamite and was first characterized by Switzer (1956). Finney (1966) derived the unit cell and proposed that paradamite is isostructural with tarbuttite, $\text{Zn}_2\text{PO}_4\text{OH}$, and Hawthorne (1976) has discussed the relationship between the adamite and tarbuttite structure types.

Single-crystal precession photographs of paradamite from Mapimi, Mexico, exhibit triclinic symmetry; the unit cell chosen is analogous to that used by Cocco, Fanfani & Zanazzi (1966) for tarbuttite. The unit-cell parameters were derived by least-squares refinement of 15 high-angle reflexions aligned automatically on a four-circle diffractometer. A full set of intensity data (1384 reflexions) was collected over one hemisphere out to a 2θ of 65° from an irregular equidimensional crystal of radius 0.09 mm, following the experimental procedure of Hawthorne & Ferguson (1975). Standard data-reduction procedures with a spherical absorption correction ($\mu = 20.2 \text{ mm}^{-1}$) resulted in 1202 unique reflexions of which 1132 were considered as observed ($I_{\text{net}} > 3\sigma$). Structure refinement was carried out on an IBM 370/158 computer using the program *RFINE*

(Finger, 1969). Scattering factors for neutral atoms were taken from Cromer & Mann (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970). The atomic parameters given by Cocco *et al.* (1966) for tarbuttite, $\text{Zn}_2\text{PO}_4\text{OH}$, were assumed as the starting parameters for paradamite. Several cycles of full-matrix least-squares refinement resulted in convergence (for isotropic temperature factors) at a conventional R of 6.2% (observed reflexions). Conversion to anisotropic temperature factors of the form $\exp(-\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij})$ resulted in convergence (maximum shift/error < 0.01) at an R of 4.8% and an R_w (unit weights) of 5.8%. Final atomic positions and equivalent isotropic temperature factors are given in Table 1. Interatomic distances and angles

Table 1. Atomic positions and equivalent isotropic temperature factors (Å²)

	x	y	z	B_{eq}
Zn(1)	0.3928 (2)	0.2498 (2)	0.5008 (2)	0.86 (2)
Zn(2)	0.0214 (2)	0.7355 (2)	0.1867 (1)	0.72 (2)
As	0.8312 (2)	0.2476 (1)	0.2745 (1)	0.49 (2)
O(1)	0.7627 (11)	0.9689 (10)	0.1391 (9)	0.79 (9)
O(2)	0.9421 (12)	0.3885 (11)	0.1233 (9)	0.94 (9)
O(3)	0.5779 (11)	0.3837 (11)	0.3342 (9)	0.85 (9)
O(4)	0.9549 (11)	0.7478 (11)	0.4968 (9)	0.71 (8)
OH	0.3519 (11)	0.8899 (12)	0.2997 (9)	0.89 (9)

were calculated with the program *ERRORS* (L. W. Finger, personal communication) and are given in Table 2.*

* A list of structure factors and details of the anisotropic thermal model have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34097 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected interatomic distances (Å) and angles (°) for paradamite

Zn(1)—O(3)	1.994 (6)	Zn(2)—O(1)	1.972 (6)
Zn(1)—O(3)	2.160 (6)	Zn(2)—O(2)	2.013 (6)
Zn(1)—O(4)	1.965 (6)	Zn(2)—O(2)	2.093 (6)
Zn(1)—OH	2.203 (6)	Zn(2)—O(4)	2.183 (6)
Zn(1)—OH	1.992 (6)	Zn(2)—OH	1.994 (6)
⟨Zn(1)—O⟩	2.063	⟨Zn(2)—O⟩	2.051
As—O(1)	1.676 (6)		
As—O(2)	1.680 (6)		
As—O(3)	1.696 (6)		
As—O(4)	1.693 (6)		
⟨As—O⟩	1.686		
Zn(1) trigonal bipyramid			
O(3)—O(4)	3.627 (9)	O(3)—Zn(1)—O(4)	132.7 (3)
O(3)—OH	3.154 (9)	O(3)—Zn(1)—OH	104.6 (3)
O(4)—OH	3.470 (9)	O(4)—Zn(1)—OH	122.6 (3)
⟨O—O⟩ ^m	3.417	⟨O—Zn(1)—O⟩ ^m	120.0
O(3)—O(3) ^s	2.650 (12)	O(3)—Zn(1)—O(3)	79.2 (3)
O(3)—OH	3.129 (9)	O(3)—Zn(1)—OH	96.3 (2)
O(3)—O(4)	2.891 (9)	O(3)—Zn(1)—O(4)	88.9 (2)
O(3)—OH	3.200 (9)	O(3)—Zn(1)—OH	100.8 (3)
O(4)—OH	2.978 (9)	O(4)—Zn(1)—OH	91.0 (2)
OH—OH ^s	2.828 (12)	OH—Zn(1)—OH	84.6 (2)
⟨O—O⟩ ^a	2.946	⟨O—Zn(1)—O⟩ ^a	90.1
		O(3)—Zn(1)—OH	173.6 (2)
Zn(2) trigonal bipyramid			
O(1)—O(2)	3.477 (9)	O(1)—Zn(2)—O(2)	121.5 (3)
O(1)—OH	3.278 (9)	O(1)—Zn(2)—OH	111.5 (3)
O(2)—OH	3.587 (9)	O(2)—Zn(2)—OH	127.1 (3)
⟨O—O⟩ ^m	3.447	⟨O—Zn(2)—O⟩ ^m	120.0
O(1)—O(2)	3.113 (9)	O(1)—Zn(2)—O(2)	99.9 (3)
O(1)—O(4)	2.928 (8)	O(1)—Zn(2)—O(4)	89.5 (2)
O(2)—O(2) ^s	2.533 (12)	O(2)—Zn(2)—O(2)	76.2 (3)
O(2)—O(4)	2.856 (8)	O(2)—Zn(2)—O(4)	85.7 (2)
O(2)—OH	3.029 (9)	O(2)—Zn(2)—OH	95.6 (3)
O(4)—OH	3.089 (9)	O(4)—Zn(2)—OH	95.3 (2)
⟨O—O⟩ ^a	2.925	⟨O—Zn(2)—O⟩ ^a	90.4
		O(2)—Zn(2)—O(4)	161.9 (2)
As tetrahedron			
O(1)—O(2)	2.715 (8)	O(1)—As—O(2)	108.0 (3)
O(1)—O(3)	2.768 (8)	O(1)—As—O(3)	110.3 (3)
O(1)—O(4)	2.764 (8)	O(1)—As—O(4)	110.3 (3)
O(2)—O(3)	2.769 (9)	O(2)—As—O(3)	110.2 (3)
O(2)—O(4)	2.754 (8)	O(2)—As—O(4)	109.5 (3)
O(3)—O(4)	2.751 (8)	O(3)—As—O(4)	108.5 (3)
⟨O—O⟩	2.754	⟨O—As—O⟩	109.5

(*m*) Meridional parameters. (*a*) Axial parameters. (*s*) Shared edges.

Discussion. Cocco *et al.* (1966) indicate that the H atom is strongly bonded to the O atom designated OH. Difference Fourier maps in the vicinity of the OH anion showed a slight rather smeared peak between OH and O(1) that was assumed to be the H atom. However, the H position was not incorporated into the refinement as H positions derived from X-ray crystal structure refinement are usually significantly in error due to bonding effects. Examination of the empirical bond-strength table for paradamite (Table 3) shows a bond-strength excess around OH and a bond-strength deficiency around O(1). This together with the OH—O(1) distance of 2.877 (9) Å suggests significant hydrogen bonding between OH and O(1) (Fig. 1). Comparison of the bond-strength tables for adamite (Hawthorne, 1976) and paradamite suggests that the hydrogen bonding in paradamite is significantly stronger than in adamite. Unfortunately there was insufficient material available to record an infrared spectrum of paradamite. However, comparison of the principal OH stretching frequencies in adamite (358.0 mm⁻¹) and tarbuttite (344.0 mm⁻¹) indicates that hydrogen bonding is

Table 3. Empirical bond-strength table for paradamite

Calculated from the curves of Brown & Shannon (1973).

	Zn(1)	Zn(2)	As	H	Σ	Σ*
O(1)		0.469	1.265	(0.213)	1.734	(1.947)
O(2)		0.423	1.253		2.024	
		0.348				
O(3)	{ 0.444		1.205		1.947	
	{ 0.298					
O(4)	{ 0.478	0.282	1.214		1.974	
	{ 0.270					
OH	{ 0.446	0.444	(0.787)	1.160	(1.947)	
Σ	1.936	1.966	4.937	(1.000)		

* Hydrogen-bond strengths estimated (values in parentheses) by minimization of deviation from ideality of sums around the anions.

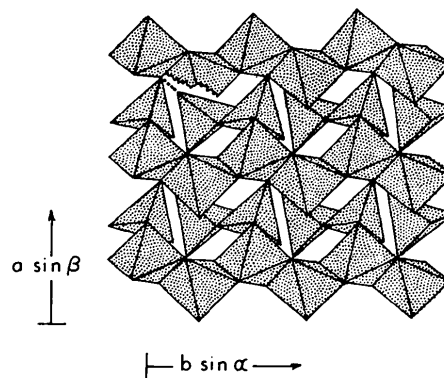


Fig. 1. Polyhedral representation of the paradamite structure. The hydrogen bond is indicated by the broken line.

stronger in tarbuttite than in adamite, and lends support to the contention that it is also stronger in paradamite than in adamite.

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References

BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst. A* **29**, 266–282.

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Refinement of 3C Pyrrhotite, Fe₇S₈

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Abstract. A metastable form of Fe₇S₈, trigonal, *P*3₁21, *a* = 6.8652 (6), *c* = 17.046 (2) Å, *Z* = 3, *D*_x = 4.59 Mg m⁻³. The crystal structure was refined to *R* = 0.043 for 1026 reflections. The apparent space group *P*6₂22 is explained by the twin-related domains with trigonal symmetry. The supercell contains ordered vacancies in alternating Fe layers normal to the *c* direction. The Fe atom is octahedrally coordinated with a mean Fe–S distance of 2.445 Å.

Introduction. Fleet (1971) determined the structure of 3C Fe₇S₈ assuming the twin-related domains with space group *P*3₁. The structural study of synthetic 3C Fe₇S₈ was made by Nishiguchi (1977), also based on *P*3₁. Their structures are essentially the same as that of 3C Fe₇Se₈ reported by Okazaki & Hirakawa (1956) which has the symmetry *P*3₁21. However, Fleet and Nishiguchi did not examine the possibility of *P*3₁21. This study has been carried out to obtain the true symmetry and to determine precisely the actual displacements of atoms from the ideal structure.

The 3C Fe₇S₈ was prepared by the dry method and quenched from 973 K into ice water. A spherical crystal, 140 μm in diameter, was used for data collection on an automatic four-circle diffractometer, using the ω–2θ scan technique (2θ_{max} = 65°) with Mo

COCCO, G., FANFANI, L. & ZANAZZI, P. F. (1966). *Z. Kristallogr.* **123**, 321–329.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

FINGER, L. W. (1969). *RFINE. A Fortran IV Computer Program for Structure Factor Calculation and Least-Squares Refinement of Crystal Structures*. Geophysics Laboratory, Carnegie Institute, Washington (unpublished).

FINNEY, J. J. (1966). *Am. Mineral.* **51**, 1218–1220.

HAWTHORNE, F. C. (1976). *Can. Mineral.* **14**, 143–148.

HAWTHORNE, F. C. & FERGUSON, R. B. (1975). *Acta Cryst.* **B31**, 1753–1755.

SWITZER, G. (1956). *Science*, **123**, 1039.

*K*α radiation (λ = 0.71069 Å), monochromatized by pyrolytic graphite. The observed Laue symmetry (6/*mmm*) and the systematic absences (00*l* with *l* ≠ 3*n*) indicate an apparent space group *P*6₂22 or *P*6₄22. Because the ordered 3C type of Okazaki & Hirakawa's (1956) model must have a trigonal symmetry of *P*3₁21 (*P*3₂21) or *P*3₁ (or *P*3₂), the apparent *P*6₂22 (and/or *P*6₄22) symmetry of the specimen has been explained by many small domains related by 180° rotation about [001] and/or by reflection across (100) in the specimen.

Observed structure factors, *F*_o(*hkl*), were calculated from the observed intensities, *I*_o(*hkl*), by the following relation:

$$|F_o(hkl)|^2 = (Lp)^{-1} AE_s I_o(hkl) I_c(hkl) / [I_c(hkl) + I_c(khl)].$$

*F*_o(*hkl*) were corrected for the usual Lorentz and polarization factors (*Lp*), absorption [*A*, μ(Mo *K*α) = 12.8 mm⁻¹, transmission factors between 0.27 and 0.33] and isotropic secondary extinction [*E*_s, *c* = 0.59 (1) × 10⁻⁵; Zachariasen, 1963]. *I*_c(*hkl*) and *I*_c(*khl*) were calculated at each cycle of the least-squares refinements, and the computing program *ORFLS* (Busing, Martin & Levy, 1962) was modified for this purpose. The scattering factors for neutral