We thank Professor U. Franklin, Department of Materials Science, University of Toronto, for helpful comments concerning the interpretation of certain powder patterns. Financial assistance (to SCN and WW-N), from the Natural Sciences and Engineering Research Council of Canada, is gratefully acknowledged.

References

ALLIBERT, C. H. & GIRODIN, D. (1983). To be published.
BAILEY, D. M. & KLINE, G. R. (1971). *Acta Cryst.* **B27**, 650–653.
BUSCHOW, K. H. J. (1970). *Philips Res. Rep.* **25**, 227–230.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1971). *ORXFLS*3, an extensively modified version of the 1962 *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
BYSTRÖM, A., KIERKEGAARD, P. & KNOP, O. (1952). *Acta Chem. Scand.* **6**, 709–719.
CROMER, D. T., LARSON, A. C. & ROOF, R. B. JR (1960). *Acta Cryst.* **13**, 913–918.
DWIGHT, A. E. (1961). *Trans. Am. Soc. Met.* **53**, 479–500.
GABATHULER, J.-P., WHITE, P. & PARTHÉ, E. (1975). *Acta Cryst.* **B31**, 608–610.
HANAMAN, F. (1915). *Int. Z. Metallogr.* **7**, 174–212.
IANDELLI, A. & PALENZONA, A. (1971). *J. Less-Common Met.* **25**, 333–335.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72 *et seq.* Birmingham: Kynoch Press.
LARSON, A. C. & CROMER, D. T. (1961). *Acta Cryst.* **14**, 73–74.
MCMASTERS, O. D., GSCHNEIDER, K. A. JR, BRUZZONE, G. & PALENZONA, A. (1971). *J. Less-Common Met.* **25**, 135–160.
MCMASTERS, O. D., GSCHNEIDER, K. A. JR & VENTEICHER, R. F. (1970). *Acta Cryst.* **B26**, 1224–1229.
RHINEHAMMER, T. B., ETTER, D. E., SELLE, J. E. & TUCKER, P. A. (1964). *Trans. Am. Inst. Min. Metall. Pet. Eng.* **230**, 1193–1198.
SCHILTZ, R. J. JR, STEVENS, E. R. & CARLSON, O. N. (1971). *J. Less-Common Met.* **25**, 175–185.
ZACHARIASEN, W. H. & ELLINGER, F. H. (1977). *Acta Cryst.* **A33**, 155–160.

Acta Cryst. (1984). C**40**, 214–217

Synthetic Phosphorus-Substituted Analcime, $Na_{13}Al_{24}Si_{13}P_{11}O_{96}.16H_2O$, with Ordered Al and Si/P

BY G. ARTIOLI, J. J. PLUTH AND J. V. SMITH

Department of Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, *USA*

(*Received* 28 *February* 1983; *accepted* 13 *October* 1983)

Abstract. $M_r = 3476{\cdot}5$, cubic, $I4_132$, $a = 13{\cdot}7290\,(7)$ Å, $V = 2587{\cdot}7$ Å^3, $D_x = 2{\cdot}23$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 72$ cm^{-1}, $F(000) = 1730$, $T \simeq 295$ K, $R = 0{\cdot}042$ for 242 reflections. The structure has the analcime framework with alternation of 24 Al and (13 Si + 11 P) over tetrahedral sites. No evidence was found for ordering of Si and P.

Introduction. Ordering of Al and Si on tetrahedral nodes of framework structures has been studied extensively, particularly in feldspars (Smith, 1974) and zeolite molecular sieves (Breck, 1974; Rabo, 1976; many recent papers). Alternation of Al and P over tetrahedral nodes was found for the fifth member of a new series of $AlPO_4$ molecular sieves (Bennett, Cohen, Flanigen, Pluth & Smith, 1983). We now return to the problem of ordering of Al, P and Si in the aluminosilicophosphate zeolites synthesized by Flanigen & Grose (1971). X-ray data were collected in 1965 by J. D. Birle, C. R. Knowles, J. V. Smith and L. G. Dowell for an 80 μm cube of zeolite P–C depicted in plate 1 of Flanigen & Grose (1971) and satisfactory refinement was obtained for an average structure of analcime type with space group $Ia3d$. Alternation of (7P + 17Si) and (23Al + 1Si) over the tetrahedral sites was considered, but the X-ray data were inadequate for a valid test. We now report a structural refinement of a trapezohedron of zeolite P–C (Flanigen & Grose, 1971) in space group $I4_132$ which allows ordering between (Si,P) and Al over adjacent tetrahedral nodes.

Refinements of the crystal structure of analcime minerals were made by Calleri & Ferraris (1964), Knowles, Rinaldi & Smith (1965) and Ferraris, Jones & Yerkess (1972). Optical and X-ray anomalies were reported by Coombs (1955), and Mazzi & Galli (1978) showed that tetragonal and orthorhombic varieties resulted from partial Si,Al order over the tetrahedral sites. The ideal topological symmetry of analcime is cubic ($Ia3d$), and a review of known phases related to analcime or leucite is given by Galli, Gottardi & Mazzi (1978).

Experimental. Trapezohedra about 50 μm across, synthesized from gel at 483 K for 160 h, supplied by E. M. Flanigen. Electron-microprobe analyses (ARL-EMX-SM instrument, 15 kV, 1 nA beam current, 10 μm beam diameter, wavelength-dispersive system, Chicago 1976 correction procedure) show less than 0·1 wt%

0108-2701/84/020214-04\$01.50

K_2O and CaO. Al is nearly constant while Si and P vary antithetically by about 10%. Na decreased for successive analyses of a fixed point, but steady readings were obtained for a moving spot. Quantitative analysis is uncertain for adjacent light elements unless standards close to the unknown are available. Amelia albite, Ab30An70 glass, $Ca_2P_2O_7$ and $AlPO_4$-5 were used as standards. Normalized to 48 tetrahedral atoms, the electron-probe analyses (wt%) give a mean of 24·0 ± 0·8 Al, 13·2 ± 0·8 Si, and 10·8 ± 0·8 P, where the error is regarded as an outside limit to the uncertainty in the correction procedure. Moving-spot analyses of Na consistently gave 14·0–15·6 atoms per 24 oxygens when referred to Amelia albite. This range is somewhat higher than the value of 13·2 atoms required to balance the charge difference between the 24·0 Al and 10·8 P for a hydroxyl-free composition, but the excess is comparable to the analytical uncertainty. The electron-microprobe analysis is consistent with the bulk chemical analysis supplied by E. M. Flanigen: $Na_{15\cdot2}(AlO_2)_{23\cdot5}(SiO_2)_{13\cdot1}(PO_2)_{11\cdot5}.\ 24\cdot3H_2O$. A direct analysis of H_2O cannot be obtained with the electron probe, but a low sum of the oxides (~91%) is consistent with presence of H_2O.

Weissenberg photographs demonstrated *I* symmetry but presence of *hhl* diffractions with $2h + l \neq 4n$ ruled out space group *Ia*3*d* of the ideal analcime structure. Refinement of eight measurements for each of 20 diffractions ($29 < \theta < 33°$) for a triclinic cell on an automatic Picker four-circle diffractometer with Krisel automation gave cubic cell dimensions within experimental error [13·7298 (6), 13·7296 (8), 13·7276 (7) Å, 90·007 (5), 90·004 (4), 90·004 (4)°; $\lambda = 1\cdot54178$ Å]. Total of 4792 diffraction intensities collected from one half the sphere of reflection (*h* 0 to 16, *k* −16 to 16, *l* −16 to 16) out to $\sin\theta/\lambda = 0\cdot583$ Å^{-1} with Cu *Kα* radiation and the $\theta/2\theta$ technique. Relative variation of standard reflections remeasured during data collection: 800, 4·0%; 080, 0·8%; 008, 1·0%. *R* for the merging of equivalent reflections 0·032. Averaging for cubic symmetry yielded 246 unique diffraction intensities with 242 above background at the 2σ level. Lorentz and polarization corrections, no absorption correction (crystal small and near-spherical).

Since it was quite obvious that the synthetic Al, P, Si material is structurally related to analcime, the major interest was the location of the Al, P and Si atoms on the tetrahedral sites. Of the possible cubic derivatives of *Ia*3*d*, only $I4_132$ proved to be consistent with the observed diffractions and theoretical ordering models. This space group allowed splitting of the 48-fold tetrahedral site of ideal analcime ($\frac{1}{8}$, *x*, $\frac{1}{4}-x$) into two 24-fold sites ($\frac{1}{8}, x, \frac{1}{4}-x$; $\frac{1}{8}, x, \frac{1}{4}+x$). Such a twofold split would allow the 24·0 Al atoms to occupy one site, and the 13·2 Si and 10·8 P atoms to occupy collectively the other site. In spite of the strong correlations and noncentrosymmetric symmetry, refinement of the ordered model (*SHELX*76 program; Sheldrick, 1976) proceeded satisfactorily. $\sum w||F_o|-|F_c||^2$ minimized; $w = \sigma_p^{-2}$. Atomic scattering factors for neutral atoms corrected for anomalous scattering from *International Tables for X-ray Crystallography* (1974).

Framework sites were fixed at full occupancy with 24 Al in one *T* site and 12 Si and 12 P in the other; adjustment to the electron-microprobe composition would cause only trivial changes. The anisotropic displacement factors for the pairs of Na atoms were constrained to be equal because of the strong correlations in the least-squares matrix, and similarly for the two O positions of the water molecules. All other parameters were unconstrained. The populations of the water O atoms [8·5 (3) and 9·1 (3)] are higher than the site multiplicity of 8, perhaps because of neglect of the H atoms. In ideal analcime, $NaAlSi_2O_6.H_2O$, the sixteen Na atoms lie at random in a 24-fold site (Knowles *et al.*, 1965). In the present refinement, the populations of 6·9 and 5·7 for the Na(1) and Na(2) sites are less than the multiplicity of 12, and random occupancy is assumed. The combined total of 12·6 ± 0·4 Na atoms is considerably less than the values of 14·0–15·6 (electron microprobe) and 15·2 (chemical), but is close to the value of 13·2 required to balance the tetrahedral atoms. High and low readings for alkalies in the elctron-probe analysis are probably due to localized electric phenomena [see Ribbe & Smith (1966) for analytical variations in feldspars]. It will be assumed that there are approximately 13 Na atoms in the present crystal.

Final difference map showed random positive and negative peaks of maximum height 0·5 e Å^{-3}, except for weak negative peaks of 0·45 e Å^{-3} displaced from the Si/P site along the twofold axes. Although the water-O positions have large displacements ($U_{11} = 0\cdot11$ corresponds to 0·33 Å root-mean-square displacement), no pattern was found in the difference map.

The final refinement* with anisotropic temperature factors, using symmetry constraints from Trueblood (1956), gave $R = 0\cdot042$, $wR = 0\cdot043$, $S = 2\cdot6$ and $(\Delta/\sigma)_{\max} = 0\cdot05$. For the 59 diffractions inconsistent with *Ia*3*d*, *R* is 0·21.

Discussion. Final atomic coordinates and displacement parameters are given in Table 1 and interatomic distances and angles in Table 2.

The interatomic distances and angles are consistent with the discussion in Knowles *et al.* (1965) when account is taken of the alternation of Al and Si/P on tetrahedral sites. Taken at face value, the mean Al—O

---

* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38912 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distance of 1·729 Å would allow minor substitution of Si or P or both, while the mean Si/P—O distance of 1·571 Å would allow some substitution of Al [*cf.* mean P—O 1·516 Å, mean Al—O 1·739 Å in $AlPO_4$-quartz (berlinite; Thong & Schwarzenbach, 1979), mean Si—O in tetrahedral frameworks near 1·61 Å]. Because refinement of noncentrosymmetric, pseudosymmetric structures is difficult, and because an undetected domain structure might be present, a definite conclusion about the distribution of Al, Si and P between *T* sites cannot be drawn. However, the X-ray data are consistent with nearly complete alternation of Si/P and Al over tetrahedral positions (Fig. 1*a*), and confirm that the ordering scheme is different from those found for natural P-free analcimes (Mazzi & Galli, 1978) in which the Al:Si ratio is close to 1:2.

In principle, the Si and P atoms could order into distinct sites, for which the schemes with highest symmetry have space groups $P4_132$ (Fig. 1*b*) and $P4_12_12$ (Fig. 1*c*). In the former, each four-membered ring has the sequence AlSiAlP whereas there are two types of six-membered rings with sequences AlSiAlSiAlSi and AlPAlPAlP. In the latter, the four-membered rings also have the sequence AlSiAlP but the six-membered rings have sequences AlSiAlSiAlP and AlPAlPAlSi. The tetragonal space group was soon ruled out from the absence of optical or X-ray evidence for non-cubic symmetry. The primitive cubic space group was discarded because all diffractions obey an *I* lattice. Thus the partially ordered model referred to the space group $I4_132$ was assumed and was proved to be the only one satisfying all experimental constraints. Insufficient sample was available to test for short-range ordering by magic-angle nuclear magnetic resonance.

The displacements of the tetrahedral atoms are small and essentially isotropic (Fig. 2), while those of the framework O atoms tend to be elongated in a direction

Table 1. *Atomic coordinates and displacement parameters*

Fractional coordinates are given ×10⁴. U_{eq} (Å²) is the average of the diagonal elements corresponding to the expression:

$$10^4 \exp(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}\, a_i^*\, a_j^*\, h_i\, h_j).$$

	Wyckoff site	Population	*x*	*y*	*z*	U_{eq}
Si/P	24(*h*)	24	3365 (1)	865	3750	186 (9)
Al	24(*g*)	24	1250	1612 (1)	4112	169 (9)
O(1)	48(*i*)	48	3959 (3)	1247 (3)	2853	347 (27)
O(2)	48(*i*)	48	2244 (3)	1033 (3)	3579	344 (27)
W(1)	8(*a*)	8·5 (3)	1250	1250	1250	1101 (58)
W(2)	8(*b*)	9·1 (3)	3750	3750	3750	1101 (58)
Na(1)	12(*c*)	6·9 (2)	1250	0	2500	432 (33)
Na(2)	12(*d*)	5·7 (2)	6250	0	2500	432 (33)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Al—2O(1)	1·717 (4)	Si/P—2O(1)	1·567 (4)
Al—2O(2)	1·741 (4)	Si/P—2O(2)	1·574 (4)
Mean	1·729	Mean	1·571
O(1)—O(1)	2·497 (8)*	O(1)—O(1)	2·707 (8)*
O(1)—2O(2)	2·574 (6)	O(1)—2O(2)	2·850 (6)
O(1)—2O(2)	2·598 (6)	O(1)—2O(2)	2·896 (6)
O(2)—O(2)	2·546 (8)	O(2)—O(2)	2·731 (8)
Na(1)—4O(2)	2·463 (4)	Na(2)—4O(1)	2·553 (4)
Na(1)—2*W*(1)	2·427	Na(2)—2*W*(2)	2·427
W(1)—3Na(1)	2·427	*W*(2)—3Na(2)	2·427
O(1)—Al—O(1)	104·1 (3)	O(1)—Si/P—O(1)	105·6 (3)
2O(1)—Al—O(2)	111·1 (2)	2O(1)—Si/P—O(2)	110·0 (2)
2O(1)—Al—O(2)	113·8 (2)	2O(1)—Si/P—O(2)	111·6 (2)
O(2)—Al—O(2)	103·3 (3)	O(2)—Si/P—O(2)	108·0 (3)
W(1)—Na(1)—*W*(1)	180	*W*(2)—Na(2)—*W*(2)	180
4*W*(1)—Na(1)—O(2)	91·0 (1)	4*W*(2)—Na(2)—O(1)	94·6 (1)
4*W*(1)—Na(1)—O(2)	89·0 (1)	4*W*(2)—Na(2)—O(1)	85·4 (1)
2O(2)—Na(1)—O(2)	177·9 (2)	2O(1)—Na(2)—O(1)	170·8 (2)
2O(2)—Na(1)—O(2)	112·7 (2)	2O(1)—Na(2)—O(1)	122·3 (2)
2O(2)—Na(1)—O(2)	67·3 (2)	2O(1)—Na(2)—O(1)	58·6 (2)

* Shared edge between tetrahedron and NaO_6 polyhedron.

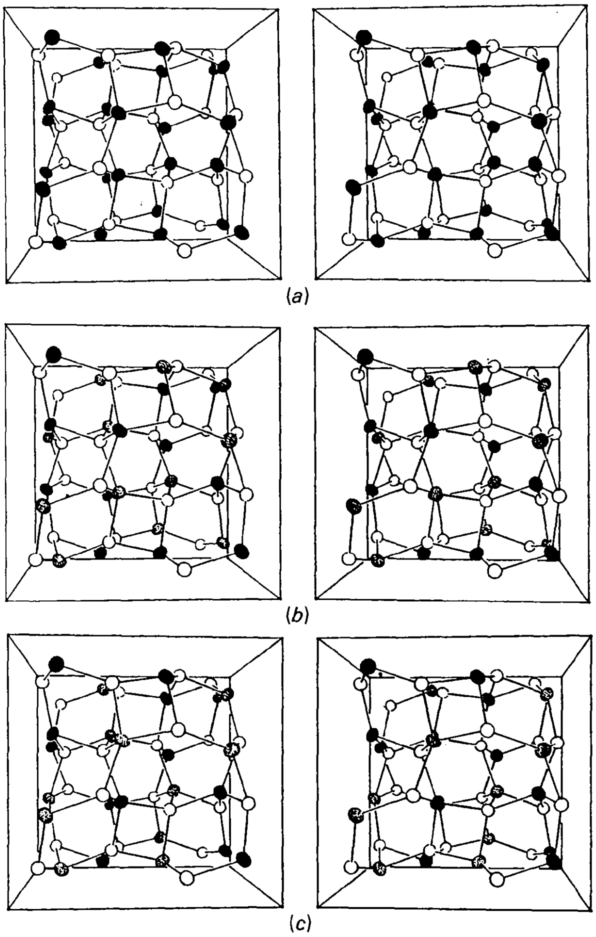

Fig. 1. Ordering schemes in analcime-type zeolite P–C: (*a*) partially ordered model as determined in this study, Al (open circle) and Si/P (solid circle); (*b*),(*c*) two possible schemes for ordering of Si (solid circle) and P (stippled circle) over the Si/P sites in (*a*). *ORTEP* plot (Johnson, 1965). Outline of unit cell shown. Tetragonal *c* axis in (*c*) is vertical in the plane of the drawing.

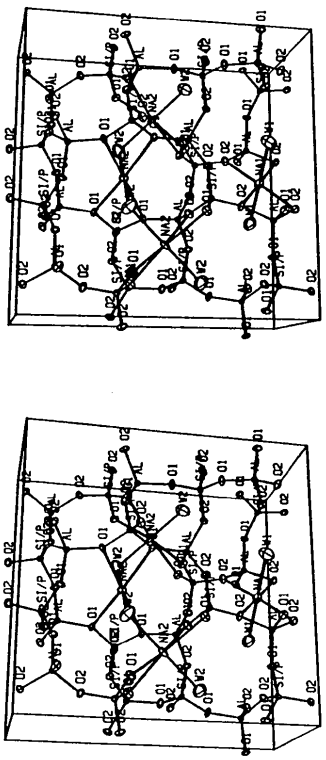

Fig. 2. Stereoplot of atomic positions and ellipsoidal approximation to the displacements in one half of unit cell (30% probability level).

perpendicular to the tetrahedral atoms. Because only half of the Na sites are occupied, the Na—O and Na—*W* distances in Table 2 are probably longer than the actual bonding distances. Some of the displacement of the water O atoms probably results from unbalance of electrostatic forces from Na atoms. In principle, such Na vacancies and H_2O displacements might become ordered, but no evidence was found. Data collection at low temperature could help clarify this point. Protons were not located from the X-ray refinement.

In conclusion, the present study demonstrates that P is substituted in the zeolites synthesized by Flanigen & Grose (1971), and implies that the relative substitutions of P, Al and Si in tetrahedral frameworks are limited by a strong tendency for Al to be ordered with respect to P and Si. This is consistent with the two limiting models in their Table XI.

We thank J. D. Birle, C. R. Knowles and L. G. Dowell for access to their unpublished manuscript, and E. M. Flanigen and R. W. Grose for the specimen, chemical analysis, and discussion. Financial support from NSF-CHE 80-23444 and Union Carbide Corporation is appreciated. E. M. Flanigen and J. M. Bennett reviewed the manuscript.

References

Bennett, J. M., Cohen, J. P., Flanigen, E. M., Pluth, J. J. & Smith, J. V. (1983). *Intrazeolite Chemistry. ACS Symp. Ser.* 218, pp. 109–118. American Chemical Society, Washington, DC.

Breck, D. W. (1974). *Zeolite Molecular Sieves.* New York: John Wiley.

Calleri, M. & Ferraris, G. (1964). *Atti Accad. Sci. Torino,* **98**, 821–846.

Coombs, D. S. (1955). *Mineral. Mag.* **30**, 699–708.

Ferraris, G., Jones, D. W. & Yerkess, J. (1972). *Z. Kristallogr.* **135**, 240–252.

Flanigen, E. M. & Grose, R. W. (1971). *Molecular Sieve Zeolites,* Vol. 1. *Adv. Chem. Ser.* 101, pp. 76–101. American Chemical Society, Washington, DC.

Galli, E., Gottardi, G. & Mazzi, F. (1978). *Mineral. Petrogr. Acta,* **22**, 185–193.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Knowles, C. R., Rinaldi, F. F. & Smith, J. V. (1965). *Indian Miner.* **6**, 127–140.

Mazzi, F. & Galli, E. (1978). *Am. Mineral.* **63**, 448–460.

Rabo, J. (1976). *Zeolite Chemistry and Catalysis. ACS Monogr.* 171, American Chemical Society, Washington, DC.

Ribbe, P. H. & Smith, J. V. (1966). *J. Geol.* **74**, 217–233.

Sheldrick, G. M. (1976). *SHELX76.* A program for crystal structure determination. Univ. of Cambridge, England.

Smith, J. V. (1974). *Feldspar Minerals.* Heidelberg: Springer.

Thong, N. & Schwarzenbach, D. (1979). *Acta Cryst.* A**35**, 658–664.

Trueblood, K. N. (1956). *Acta Cryst.* **9**, 359–361.

Acta Cryst. (1984). C**40**, 217–220

Rubidium Pentaborate Tetrahydrate, $Rb[B_5O_6(OH)_4].2H_2O$

By Helmut Behm

Institut für Kristallographie der Universität Karlsruhe (TH), Kaiserstrasse 12, POB 6380, D-7500 Karlsruhe, Federal Republic of Germany

(*Received 22 July 1983; accepted 3 October 1983*)

Abstract. $M_r = 339{\cdot}6$, orthorhombic, space group *Aba*2, $a = 11{\cdot}302\,(2)$, $b = 10{\cdot}962\,(2)$, $c = 9{\cdot}335\,(1)$ Å, $V = 1156{\cdot}6\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}95$, $D_m = 1{\cdot}91$ g cm^{-3} (flotation method), $\mu(\text{Mo }K\alpha) = 42{\cdot}15$ cm^{-1}, $F(000) = 663{\cdot}85$, room temperature, $R = 0{\cdot}033$ for 1623 reflections. The absolute configuration has been determined. The structure belongs to the class of soroborates and contains isolated pentaborate