

The Crystal Structure of Brazilianite, $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4$

BY B. M. GATEHOUSE AND B. K. MISKIN

Chemistry Department, Monash University, Clayton, Victoria, Australia 3168

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The mineral brazilianite, $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4$, is monoclinic, space group $P2_1/n$, with $a=11.233$ (6), $b=10.142$ (5), $c=7.097$ (4) Å and $\beta=97.37$ (2) Å. With $Z=4$ the calculated density, 2.998 (4), compares well with the measured density, 2.98 (1) g cm^{-3} . The structure was solved by direct phasing and Fourier techniques. Of the 2276 unique reflexions collected by counter methods, 2033 with $I > 3\sigma(I)$ were used in the least-squares refinement to $R=0.030$ ($wR=0.050$). Brazilianite is composed of chains of edge-sharing Al–O octahedra linked by P–O tetrahedra, with Na located in cavities in the framework.

Introduction

The Corrego Frio pegmatite, Minas Gerais, Brazil has yielded a number of phosphate minerals. Among these is the anhydrous sodium aluminum phosphate, brazilianite, the mineralogy of which was described by Tavora (1945), Pough & Henderson (1945), and Hurlbut & Weichel (1946), with some additional data published by Pecora & Fahey (1949). A second occurrence of this mineral in the Palermo pegmatite was described by Frondel & Lindberg (1948).

We report here the structure of brazilianite. A preliminary report (Finney & Eggleton, 1967) was brought to our attention after the completion of this work. The non-hydrogen atom positions refined to $R=0.12$ by Finney & Eggleton were kindly supplied by Dr Eggleton and agree with those reported here.

Experimental

The crystals used in this study were cleaved from a small fragment of brazilianite from the Corrego Frio pegmatite. The sample was supplied by Dr P. Phakey, Physics Department, Monash University, and came from the Mineral Collection, Department of Geology, University of California, Los Angeles. The crystal used for data collection was irregular with maximum and minimum thicknesses of about 0.28 and 0.23 mm ($\mu R \approx 0.13$). A preliminary microscopic investigation of the crystal with polarized light showed no indication of twinning or other defects.

The specimen was mounted on a Philips PW1100 four-circle automatic diffractometer in an arbitrary orientation. With the automatic peak-hunting routine, a standard program in the PW1100 software, a chosen area of reciprocal space was scanned until 25 unique reflexions had been found. As each peak was located its centre was determined and its coordinates in reciprocal space calculated. All vectors between these 25 lattice points were then calculated and the three shortest, non-coplanar vectors were chosen as the basis of a primitive unit cell. The 25 reflexions were then indexed on this basis and used in a least-squares routine

to refine the cell and orientation parameters. No reduction or transformation of this cell was necessary since the primitive unit cell chosen was the Dirichlet reduced cell and corresponded to that reported by Hurlbut & Weichel (1946). An examination of the six independent scalar products of pairs of a^* , b^* and c^* showed no indication of a centred cell or an alternative crystal system, and subsequent examination of the data confirmed that the space group was $P2_1/n$.

The density obtained by flotation in Clerici's solution, 2.98 (1) g cm^{-3} , compares well with those reported previously by Frondel & Lindberg (1948), and Hurlbut & Weichel (1946), 2.980 (5) and 2.976 g cm^{-3} respectively.

Accurate lattice parameters were obtained by two methods. The first was a least-squares refinement of cell and orientation parameters from 25 medium to high-angle peaks obtained with Mo $K\alpha_1$ radiation ($\lambda=0.70926$ Å). The second was measurement of the reciprocal lattice spacings for the $h00$, $0k0$, $00l$, $h0h$ and $h0\bar{h}$ zones of reflexions using the four highest weight reflexions for each zone and their anti-reflexions in a least-squares refinement of that particular lattice spacing. (The weight of a reflexion is given by the product of the peak intensity and $\tan \theta$, where θ is the Bragg angle.) The results of both these methods agree

Table 1. Crystallographic data for brazilianite

a (Å)*	11.233 (6)	11.229 (6)
b (Å)	10.142 (5)	10.142 (5)
c (Å)	7.097 (4)	7.098 (4)
β (°)	97.37 (2)	97.41 (2)
U (Å ³)	802 (1)	802 (1)
Z	4	
D_{calc} (g cm^{-3})	2.998 (4)	
D_{meas} (g cm^{-3})	2.98 (1)	
$\mu_{\text{Mo } K\alpha}$ (cm^{-1})	10.34	
Space group	$P2_1/n$	
Equivalent positions	(i) x y z (ii) \bar{x} \bar{y} \bar{z} (iii) $\frac{1}{2} + x$ $\frac{1}{2} - y$ $\frac{1}{2} + z$ (iv) $\frac{1}{2} - x$ $\frac{1}{2} + y$ $\frac{1}{2} - z$	

* The first set of parameters was obtained from the refinement of lattice spacings and the second from the refinement of cell and orientation parameters using 25 peaks (see text).

Table 2. Final positional parameters ($\times 10^4$) and temperature factors

The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*) \times 10^{-4}]$. B is the Debye-Waller temperature factor. Hydrogen positional parameters are $\times 10^3$; the error was taken to be the maximum error associated with the estimation of the centre of the peak on the difference electron density map. Estimated standard deviations are in parentheses.

(a) Parameters for anisotropic atoms

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	1804 (1)	3122 (1)	2375 (2)	32 (4)	37 (4)	37 (4)	0 (3)	3 (3)	6 (3)
P(2)	3124 (1)	3279 (1)	7538 (2)	33 (4)	31 (4)	40 (4)	-2 (3)	7 (4)	-4 (3)
Al(1)	432 (2)	2204 (1)	5614 (2)	52 (5)	47 (5)	49 (5)	5 (4)	15 (5)	-4 (4)
Al(2)	2630 (1)	673 (1)	5082 (2)	35 (5)	48 (5)	59 (5)	3 (4)	7 (4)	-6 (4)
Al(3)	4594 (1)	2545 (1)	4328 (2)	48 (5)	46 (5)	43 (5)	-1 (4)	11 (4)	2 (4)
Na	3036 (3)	751 (2)	350 (3)	369 (12)	144 (9)	173 (10)	-49 (9)	61 (9)	5 (7)

(b) Parameters for isotropic atoms

	x/a	y/b	z/c	$B(\times 10^3)$		x/a	y/b	z/c	$B(\times 10^3)$
O(1)	1035 (3)	794 (3)	4498 (4)	53 (4)	O(9)	1000 (3)	3403 (3)	3935 (4)	61 (4)
O(2)	4238 (3)	1010 (3)	5620 (4)	56 (4)	O(14)	3917 (3)	3673 (3)	6014 (4)	61 (4)
O(3)	30 (3)	3496 (3)	7243 (4)	54 (4)	O(11)	2259 (3)	4468 (3)	1822 (4)	69 (4)
O(4)	4974 (3)	3860 (3)	2698 (4)	55 (4)	O(12)	2355 (3)	4487 (3)	7907 (4)	61 (4)
O(5)	1145 (3)	2392 (3)	664 (4)	66 (4)	H(1)	62 (10)	3 (10)	372 (10)	100
O(6)	2878 (3)	2219 (3)	3187 (4)	53 (4)	H(2)	464 (10)	98 (10)	680 (10)	100
O(7)	2260 (3)	2135 (3)	6811 (4)	55 (4)	H(3)	73 (10)	408 (10)	748 (10)	100
O(8)	3878 (3)	2806 (3)	9348 (4)	62 (4)	H(4)	46 (10)	58 (10)	840 (10)	100

Table 3. Observed and calculated structure factors ($\times 10$) for brazilianite

Statistically unreliable reflexions which were not included in the refinement are marked with an asterisk. Reflexions marked with an 'E' were considered to be extinction-affected and were not included in the later stages of the refinement.

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	0	0	100	100	0	0	0	100	100	0	0	0	100	100	0	0	0	100	100
1	0	0	34	29*	1	0	0	34	29*	1	0	0	34	29*	1	0	0	34	29*
2	0	0	68	58*	2	0	0	68	58*	2	0	0	68	58*	2	0	0	68	58*
3	0	0	102	87*	3	0	0	102	87*	3	0	0	102	87*	3	0	0	102	87*
4	0	0	136	116*	4	0	0	136	116*	4	0	0	136	116*	4	0	0	136	116*
5	0	0	170	145*	5	0	0	170	145*	5	0	0	170	145*	5	0	0	170	145*
6	0	0	204	174*	6	0	0	204	174*	6	0	0	204	174*	6	0	0	204	174*
7	0	0	238	203*	7	0	0	238	203*	7	0	0	238	203*	7	0	0	238	203*
8	0	0	272	232*	8	0	0	272	232*	8	0	0	272	232*	8	0	0	272	232*
9	0	0	306	261*	9	0	0	306	261*	9	0	0	306	261*	9	0	0	306	261*
10	0	0	340	290*	10	0	0	340	290*	10	0	0	340	290*	10	0	0	340	290*
11	0	0	374	319*	11	0	0	374	319*	11	0	0	374	319*	11	0	0	374	319*
12	0	0	408	348*	12	0	0	408	348*	12	0	0	408	348*	12	0	0	408	348*
13	0	0	442	377*	13	0	0	442	377*	13	0	0	442	377*	13	0	0	442	377*
14	0	0	476	406*	14	0	0	476	406*	14	0	0	476	406*	14	0	0	476	406*
15	0	0	510	435*	15	0	0	510	435*	15	0	0	510	435*	15	0	0	510	435*
16	0	0	544	464*	16	0	0	544	464*	16	0	0	544	464*	16	0	0	544	464*
17	0	0	578	493*	17	0	0	578	493*	17	0	0	578	493*	17	0	0	578	493*
18	0	0	612	522*	18	0	0	612	522*	18	0	0	612	522*	18	0	0	612	522*
19	0	0	646	551*	19	0	0	646	551*	19	0	0	646	551*	19	0	0	646	551*
20	0	0	680	580*	20	0	0	680	580*	20	0	0	680	580*	20	0	0	680	580*
21	0	0	714	609*	21	0	0	714	609*	21	0	0	714	609*	21	0	0	714	609*
22	0	0	748	638*	22	0	0	748	638*	22	0	0	748	638*	22	0	0	748	638*
23	0	0	782	667*	23	0	0	782	667*	23	0	0	782	667*	23	0	0	782	667*
24	0	0	816	696*	24	0	0	816	696*	24	0	0	816	696*	24	0	0	816	696*
25	0	0	850	725*	25	0	0	850	725*	25	0	0	850	725*	25	0	0	850	725*
26	0	0	884	754*	26	0	0	884	754*	26	0	0	884	754*	26	0	0	884	754*
27	0	0	918	783*	27	0	0	918	783*	27	0	0	918	783*	27	0	0	918	783*
28	0	0	952	812*	28	0	0	952	812*	28	0	0	952	812*	28	0	0	952	812*
29	0	0	986	841*	29	0	0	986	841*	29	0	0	986	841*	29	0	0	986	841*
30	0	0	1020	870*	30	0	0	1020	870*	30	0	0	1020	870*	30	0	0	1020	870*
31	0	0	1054	899*	31	0	0	1054	899*	31	0	0	1054	899*	31	0	0	1054	899*
32	0	0	1088	928*	32	0	0	1088	928*	32	0	0	1088	928*	32	0	0	1088	928*
33	0	0	1122	957*	33	0	0	1122	957*	33	0	0	1122	957*	33	0	0	1122	957*
34	0	0	1156	986*	34	0	0	1156	986*	34	0	0	1156	986*	34	0	0	1156	986*
35	0	0	1190	1015*	35	0	0	1190	1015*	35	0	0	1190	1015*	35	0	0	1190	1015*
36	0	0	1224	1044*	36	0	0	1224	1044*	36	0	0	1224	1044*	36	0	0	1224	1044*
37	0	0	1258	1073*	37	0	0	1258	1073*	37	0	0	1258	1073*	37	0	0	1258	1073*
38	0	0	1292	1102*	38	0	0	1292	1102*	38	0	0	1292	1102*	38	0	0	1292	1102*
39	0	0	1326	1131*	39	0	0	1326	1131*	39	0	0	1326	1131*	39	0	0	1326	1131*
40	0	0	1360	1160*	40	0	0	1360	1160*	40	0	0	1360	1160*	40	0	0	1360	1160*
41	0	0	1394	1189*	41	0	0	1394	1189*	41	0	0	1394	1189*	41	0	0	1394	1189*
42	0	0	1428	1218*	42	0	0	1428	1218*	42	0	0	1428	1218*	42	0	0	1428	1218*
43	0	0	1462	1247*	43	0	0	1462	1247*	43	0	0	1462	1247*	43	0	0	1462	1247*
44	0	0	1496	1276*	44	0	0	1496	1276*	44	0	0	1496	1276*	44	0	0	1496	1276*
45	0	0	1530	1305*	45	0	0	1530	1305*	45	0	0	1530	1305*	45	0	0	1530	1305*
46	0	0	1564	1334*	46	0	0	1564	1334*	46	0	0	1564	1334*	46	0	0	1564	1334*
47	0	0	1598	1363*	47	0	0	1598	1363*	47	0	0	1598	1363*	47	0	0	1598	1363*
48	0	0	1632	1392*	48	0	0	1632	1392*	48	0	0	1632	1392*	48	0	0	1632	1392*
49	0	0	1666	1421*	49	0	0	1666	1421*	49	0	0	1666	1421*	49	0	0	1666	1421*
50	0	0	1700	1450*	50	0	0	1700	1450*	50	0	0	1700	1450*	50	0	0	1700	1450*
51	0	0	1734	1479*	51	0	0	1734	1479*	51	0	0	1734	1479*	51	0	0	1734	1479*
52	0	0	1768	1508*	52	0	0	1768	1508*	52	0	0	1768	1508*	52	0	0	1768	1508*
53	0	0	1802	1537*	53	0	0	1802	1537*	53	0	0	1802	1537*	53	0	0	1802	1537*
54	0	0	1836	1566*	54	0	0	1836	1566*	54	0	0	1836	1566*	54	0	0	1836	1566*
55	0	0	1870	1595*	55	0	0	1870	1595*	55	0	0	1870	1595*	55	0	0	1870	1595*
56	0	0	1904	1624*	56	0	0	1904	1624*	56	0	0	1904	1624*					

Table 3 (cont.)

Table 3 (cont.)

Table 3 (cont.) data grid with columns H, K, FO, FC and rows of numerical values.

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within the errors and are reported in the summary of crystallographic data, Table 1.

Intensities were collected with Mo Kα radiation monochromated by a flat graphite monochromator (2θ=11.87°). A θ-2θ scan mode was used with a scan width (Δθ) of 1.4° and scan speed, 0.075° s⁻¹. At a limit of the scan range a background count was measured for half the scan time. Three non-coplanar reflexions were measured every two hours and their intensities and positions showed no systematic variations. All 2276 unique reflexions with positive h and k indices, and 3.00° ≤ θ ≤ 30.00° were measured, of which 243 with intensity I ≤ 3σ(I) were not used in the refinement. In addition, the systematically absent reflexions, 0k0 with k odd and h0l with h+l odd, were measured to verify the choice of space group.

The intensities were reduced to structure amplitudes after the application of the normal Lorentz and polarization corrections. Since the plane of reflexion of the graphite monochromator was perpendicular to that of the specimen crystal, the Lorentz-polarization correction was:

(Lp)⁻¹ = sin 2θ(1 + cos² 2θₘ)/(cos² 2θ + cos² 2θₘ)

where θₘ is the Bragg angle of the monochromator. The variance of the intensity was calculated as the sum of the variance due to counting statistics and the square

of 0.04 I where the 4% uncertainty was introduced to allow for other error sources. The variance of the structure amplitude was then:

$$\sigma^2(F) = \sigma^2(I) (\text{Lp})^{-2} / 4F^2.$$

The atomic scattering factors used were those of Cromer & Waber (1965) for P^0 , Al^0 , Al^{3+} , Na^+ and O^0 while the curve for H^0 was from Ibers (1962). All computing was performed on the Monash University CDC 3200 computer, the major programs used being *MONLS*, a modified version of the full-matrix least-squares program of Busing, Martin & Levy (1962), *MONDLS*, a block-diagonal least-squares program adapted from the 'SF series' of Shiono (1968), the Fourier summation program, *MONFR* (White, 1965), the direct phasing methods programs of Hall (1968) for the calculation of normalized structure factors and the *MULTAN* system of Germain, Main & Woolfson (1970) for the calculation of sets of phases. *ORTEP*, the thermal-ellipsoid plot program of Johnson (1965), was used to produce the diagrams which appear in this paper.

Structure solution and refinement

The absolute scale and the overall temperature factor were determined by the method of Wilson (1942). A set of normalized structure factors (Karle & Hauptman, 1956) were calculated and the 331 with values greater than 1.5 were used as input to the *MULTAN* series of programs. Of the eight sets of phases output, that with the highest internal consistency was used in the calculation of an E map.

All non-hydrogen positions could be unambiguously located with the exception of a possible sodium position for which a choice between two parts of a bifurcated peak was not made at this stage.

The positions for the three Al^0 , two P^0 and twelve O^0 atoms were included in a structure-factor calculation which, after variation of the scale, resulted in $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.399$. A difference synthesis showed that the sodium atom was located at the greater of the two maxima observed in the E map. One cycle of refinement of positional parameters followed by four cycles refining the positions and temperature factors by the full-matrix least-squares technique with unit weights for all reflexions gave $R = 0.055$. A further two cycles of refinement, with reflexions weighted according to the inverse of the variance of the observed structure amplitude, reduced R to 0.050 and $wR = \sqrt{[\sum w(|F_o| - |F_c|)^2] / \sum wF_o^2}$, from 0.074 to 0.067. The temperature factors of all the non-oxygen atoms were then allowed to vary anisotropically. Successive cycles of block-diagonal least-squares refinement of all positional and thermal parameters reduced R to 0.037 and wR to 0.054.

The structure factors for a number of high-intensity reflexions calculated on the basis of this model were somewhat higher than the corresponding observed values, the worst being the 020 reflexion with a cal-

culated value 41% too high. A difference synthesis showed corresponding areas of negative density with quite broad minima at the heavy-atom positions and smaller negative areas at the oxygen positions. The minimum densities ranged from about 0 to $-0.8 \text{ e } \text{\AA}^{-3}$ at the O^0 positions, -1.0 to $-1.4 \text{ e } \text{\AA}^{-3}$ at the three Al^0 positions, $-1.0 \text{ e } \text{\AA}^{-3}$ for both P^0 positions and $-0.4 \text{ e } \text{\AA}^{-3}$ at the Na^+ position. The most significant areas of positive density were three peaks with maximum densities of about $1.0 \text{ e } \text{\AA}^{-3}$ which were close to O(1), O(3) and O(4), and a bifurcated peak close to O(2) with both maxima about $0.6 \text{ e } \text{\AA}^{-3}$ but with one maximum somewhat broader than the other. Before proceeding, the 16 reflexions which calculated more than 10% higher than the observed values were excluded from the refinement. These reflexions were probably extinction-affected.

Another data set was collected from a very small crystal (approximately $0.05 \times 0.05 \times 0.05 \text{ mm}$) which had been subjected to thermal and mechanical shock. Relative to a set of randomly chosen, medium-intensity reflexions, the intensities of the reflexions which were excluded from the first data set all showed significant increases. Unfortunately the statistics of this second set of data prevented it from refining to better than $R = 0.044$ ($wR = 0.052$).

The original data set, minus the 16 extinction-affected reflexions, converged at $R = 0.032$, $wR = 0.050$. The use of an Al^{3+} curve in place of Al^0 caused wR to drop marginally to 0.049. A difference synthesis cal-

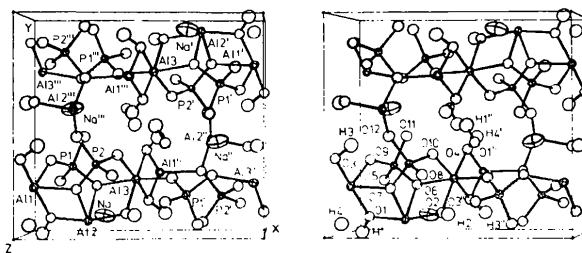


Fig. 1. The cell contents of brazilianite. The labelling of the atoms is consistent with that in Table 4. Thermal ellipsoids are drawn at 90% probability.

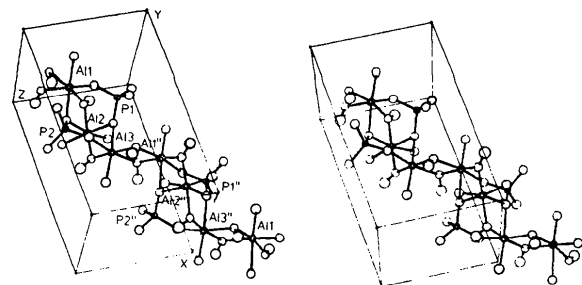


Fig. 2. The basic chain of edge-sharing Al-O octahedra with associated P-O tetrahedra. Only those P-O tetrahedra which share two vertices with the same Al-O chain are shown. The remaining two vertices of these tetrahedra are connected to different chains.

culated at this stage was basically unchanged from that mentioned above. The three largest peaks were in chemically reasonable positions for hydrogen atoms and the inclusion of these three positions, H(1), H(3) and H(4), in a block-diagonal least-squares refinement of all non-hydrogen positional and thermal parameters reduced R to 0.030 and wR to 0.048. The remaining hydrogen was more difficult to place. Both parts of the bifurcated peak were about 0.9 Å from O(2). When the position of the larger part of the peak was included in the parameter list wR decreased to 0.046, a significant drop. However the distance between this position and

that related to it by a centre of symmetry was only 1.3 Å which is impossibly small (Baur, 1972). When the alternative position was used wR increased from 0.048 to 0.050 but the position was far more sensible from a chemical point of view and was therefore taken to be the position of the fourth hydrogen, H(2). Without corrections for extinction, the data set was probably not sufficiently accurate to allow unambiguous location of the fourth hydrogen. Since the authors did not wish to embark on an expensive and time consuming treatment for extinction, the refinement was terminated at this point.

Table 4. Selected interatomic distances (Å) and angles (°) in brazilianite

The symmetry transformations (ii), (iii) and (iv) (Table 1) are indicated by ', '' and ''' respectively. The superscripts indicate that the atom is in an adjacent unit cell, the relationship of which to the primary unit cell is given by: (a) (-, 0, 0); (b) (0, -, 0); (c) (0, 0, -); (d) (0, -, -); (e) (-, -, 0).

Distances and Angles in the Al-O Octahedra and P-O Tetrahedra								
Al(1) - O(1)	1.808(3)	Al(2) - O(1)	1.790(3)	Al(3) - O(4)	1.851(4)	P(1) - O(11)	1.527(3)	
- O(3)	1.841(3)	- O(2)	1.829(3)	- O(5'')	1.875(3)	- O(5)	1.529(3)	
- O(8'')	1.859(3)	- O(11''')	1.838(3)	- O(2)	1.876(3)	- O(9)	1.543(3)	
- O(9)	1.871(3)	- O(12''')	1.865(3)	- O(10)	1.885(3)	- O(6)	1.564(3)	
- O(4'')	1.953(3)	- O(7)	2.002(4)	- O(3'')	1.931(3)	O(11) - P(1) - O(5)	111.9(2)	
- O(7)	2.119(3)	- O(6)	2.107(3)	- O(6)	2.021(3)	- O(9)	105.3(2)	
O(1) - Al(1) - O(3)	166.8(2)	O(1) - Al(2) - O(2)	165.3(2)	O(4) - Al(3) - O(5'')	91.0(2)	- O(6)	110.6(2)	
- O(8'')	99.5(1)	- O(11''')	92.0(2)	- O(2)	169.8(2)	O(5) - P(1) - O(9)	113.0(2)	
- O(9)	93.3(1)	- O(12''')	97.6(1)	- O(10)	95.9(2)	- O(6)	106.3(2)	
- O(4'')	92.6(2)	- O(7)	79.1(1)	- O(3'')	79.2(2)	O(9) - P(1) - O(6)	109.8(2)	
- O(7)	75.6(1)	- O(6)	90.7(2)	- O(6)	98.7(2)			
O(3) - Al(1) - O(8'')	90.9(2)	O(2) - Al(2) - O(11''')	96.8(2)	O(5'') - Al(3) - O(2)	91.4(2)	P(2) - O(8)	1.523(3)	
- O(9)	93.9(2)	- O(12''')	92.8(1)	- O(10)	94.8(2)	- O(12)	1.540(3)	
- O(4'')	78.9(1)	- O(7)	90.6(2)	- O(3'')	95.5(1)	- O(10)	1.540(3)	
- O(7)	94.3(2)	- O(6)	77.7(1)	- O(6)	170.2(1)	- O(7)	1.558(3)	
O(8'')	Al(1) - O(9)	O(11''')	Al(2) - O(12''')	O(2) - Al(3) - O(10)	93.7(2)	O(8) - P(2) - O(12)	111.7(2)	
- O(4'')	92.3(1)	- O(7)	169.1(2)	- O(3'')	90.7(2)	- O(10)	111.4(2)	
- O(7)	174.3(1)	- O(6)	89.9(1)	- O(6)	78.9(1)	- O(7)	107.5(2)	
O(9) - Al(1) - O(4'')	170.5(1)	O(12''')	Al(2) - O(7)	O(10) - Al(3) - O(3'')	168.7(2)	O(12) - P(2) - O(10)	107.5(2)	
- O(7)	83.4(1)	- O(6)	168.4(2)	- O(6)	84.9(2)	- O(7)	108.0(2)	
O(4'')	Al(1) - O(7)	O(7) - Al(2) - O(6)	84.0(1)	O(3'')	Al(3) - O(6)	85.8(2)	O(10) - P(2) - O(7)	110.7(2)
Na - O distances ≤ 3.1 Å		Distances and Angles associated with the Hydrogen Bonding Schemes (Fig. 4)						
Na - O(8) ^c	2.433(4)	H(1) - O(1)	1.03(10)	O(1) - O(4''')	2.667(4)	H(2) - O(2) - Al(2)	123(6)	
- O(11''')	2.450(4)	- O(4''')	1.64(9)	O(2) - O(9'')	2.935(4)	- Al(3)	112(6)	
- O(6)	2.529(4)	O(1) - H(1) - O(4''')	174(9)	O(3) - O(12)	2.782(4)	- H(3''')	58(7)	
- O(3'')	2.576(4)			- O(2'')	3.026(4)	Al(2) - O(2) - Al(3)	108.6(2)	
- O(12''')	2.630(4)	H(2) - O(2)	0.90(8)	O(4'')	O(10''')	- H(3''')	85(3)	
- O(9'')	2.638(3)	- O(9'')	2.11(9)			Al(3) - O(2) - H(3''')	167(3)	
- O(5)	2.730(4)	O(2) - H(2) - O(9'')	153(9)					
- O(7) ^c	2.912(4)							
- O(10''')	3.105(3)	H(3) - O(3)	0.98(11)			H(4'')	O(4) - H(1''')	93(7)
		- O(12)	1.86(11)			- Al(3)	106(7)	
		- O(2'')	2.37(10)	H(1) - O(1) - Al(2)	116(6)	- Al(1'')	125(6)	
H - H distances ≤ 2.5 Å		O(3) - H(3) - O(12)	156(9)	- Al(1)	131(6)	H(1'')	O(4) - Al(3)	143(4)
H(1) - H(4) ^e	1.91(12)	- O(2'')	123(7)	Al(2) - O(1) - Al(1)	111.9(2)	- Al(1'')	93(4)	
- H(1') ^e	2.43(14)	O(12) - H(3) - O(2'')	77(4)			Al(3) - O(4) - Al(1'')	100.3(2)	
H(2) - H(3''')	2.04(15)			H(3) - O(3) - Al(1)	106(6)			
		H(4) - O(4'')	0.89(10)	- Al(3''')	118(6)			
		- O(10''')	2.08(10)	Al(1) - O(3) - Al(3'')	101.5(2)			
		O(4'')	H(4) - O(10''')	150(9)				

The final positional and thermal parameters are listed in Table 2 and the structure factors in Table 3.

Discussion of the structure

Brazilianite is a pseudo-*A*-centred structure composed of chains of edge-sharing Al–O octahedra linked by P–O tetrahedra, with sodium atoms located in holes in this three-dimensional network. A stereoscopic diagram of the structure, viewed perpendicular to (001), is presented in Fig. 1. Apart from the coordination around aluminum and phosphorus, the structure has little relationship to that of wardite, $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (Fanfani, Nunzi & Zanazzi, 1970) where P–O tetrahedra join the sheets of corner-linked octahedra which form the Al–O framework. In wardite the H_2O is coordinated to aluminum, while in brazilianite the edge-sharing of Al–O octahedra partly compensates for the lack of this H_2O .

In the structure there are two types of octahedral coordination around aluminum; *trans*- $\text{AlO}_4(\text{OH})_2$ around Al(2) and *trans*- $\text{AlO}_3(\text{OH})_3$ about Al(1) and Al(3). The coordination octahedron of Al(1) shares the edge formed by O(7) and the hydroxyl O(1) with the Al(2) octahedron, which in turn shares an edge with the Al(3) octahedron through O(6) and hydroxyl O(2). The Al–O chain is completed by the coupling of the octahedra around Al(3) and Al(1') through the common edge, hydroxyls O(3') and O(4) (Fig. 2). The average Al–O distances are 1.909, 1.905 and 1.906 Å for the octahedra around Al(1), Al(2) and Al(3) respectively. These distances lie in the range 1.790 to 2.119 Å, the distances between Al and the two *trans*-hydroxyls being the shortest in all cases, although the Al(3)–O(5'') distance is also very short (Table 4). The distances between the oxygens which form unshared edges of octahedra vary from 2.611 to 2.940 Å with an average of 2.742 Å. The three shared edges are somewhat shorter; 2.413, 2.420 and 2.478 Å. These short distances are reflected in the angles subtended at the central cations by the edges of the coordination octahedra; the smallest O–Al–O angles, 75.6° to 79.2°, are invariably those which involve the two oxygens of a shared edge, while the remaining angles lie between 83.4° and 99.5°.

Each of the two phosphorus atoms in the asymmetric unit is tetrahedrally coordinated by four crystallographically independent oxygen atoms, of which none is a hydroxyl oxygen. Therefore the 12 independent oxygen atoms in the structure form two mutually exclusive sets; eight oxygens form tetrahedra about the two phosphorus atoms and the remaining four are hydroxyl oxygens. Each phosphorus tetrahedron shares two vertices with the three independent Al–O octahedra of the basic Al–O chain to form the arrangement shown in Fig. 2. P(1) shares O(9) with Al(1), and O(6) with both Al(2) and Al(3), while O(10) is common to the polyhedra around P(2) and Al(3), and O(7) is shared by P(2), Al(1) and Al(2). The remaining two oxygens associated with each phosphorus are both

shared with the Al–O octahedra of separate, symmetry-related chains. Al(2'') is linked to P(1) and P(2) by O(11) and O(12) respectively, O(5) is common to P(1) and Al(3'), and O(8) is shared by P(2) and Al(1'). The tetrahedra have average P–O distances of 1.541 Å and 1.540 Å (1.523 to 1.564 Å) which compare favourably with the data presented by Shannon & Calvo (1973) who found that the weighted average tetrahedral P–O distance for a number of different phosphates was 1.537 Å. The longest P–O distance in each tetrahedron is to the oxygen which is shared by the phosphorus and two aluminum atoms. These distances, 1.564 Å [P(1)–O(6)] and 1.558 Å [P(2)–O(7)], are considerably longer than 1.543 Å which is the maximum separation between phosphorus and any oxygen shared with only one aluminum. Both P–O tetrahedra have the same average edge length, 2.515 Å (2.441 to 2.562 Å). The tetrahedral angles at the phosphorus lie between 105.3° and 113.0°.

The sodium atom is located in a large, irregular cavity within the framework of P–O and Al–O polyhedra. The coordination around the sodium is difficult to describe. The shortest Na–O distance is 2.433 Å (Table 4) and there are an additional eight distances with values up to 3.105 Å, the next distance being 3.700 Å [Na–O(9'')]. The situation is somewhat complicated by the presence of H(4) which projects into the cavity occupied by the sodium. Mutual repulsion forces the sodium to one side of the cavity so that it is more heavily coordinated by oxygen on one side than on the other. Apart from the positions of the hydrogen atoms, it is this displacement of the sodium atom which is the major departure of the structure from true *A*-centring. The coordination of the sodium is probably best described as irregular seven-coordination (Fig. 3); the Na–O(7) and Na–O(10'') distances (2.912 and

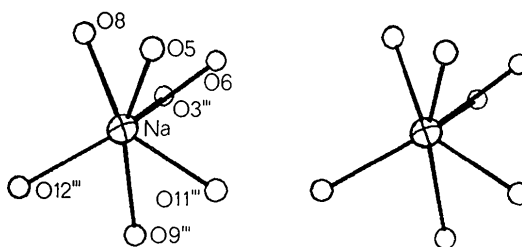


Fig. 3. The sodium coordination in brazilianite. The seven shortest Na–O contacts are shown.

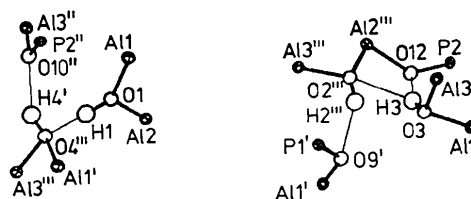


Fig. 4. Hydrogen-bonding schemes in brazilianite. Single lines indicate possible hydrogen-bonding interactions (see text).

3.105 Å) are probably too long for reasonable Na–O contacts.

Hydrogen bonding

All four hydrogen atoms appear to be involved in interchain hydrogen bonding and hence contribute to the cohesion of the structure. Diagrams of the hydrogen-bonding schemes are given in Fig. 4 and some pertinent distances and angles are listed in Table 4.

The shortest hydrogen bond is O(1)–H(1)···O(4'''). The hydroxyl bond length is 1.0 Å and the acceptor–hydrogen distance [O(4''')–H(1)] is 1.6 Å, with an O–H–O angle of 174°. The close approach of O(1) and O(4''') (2.667 Å) is indicative of a strong interaction. O(4''') is also a hydroxyl with an O(4''')–H(4') bond length of 0.9 Å. This hydrogen atom almost certainly interacts with O(10'') which is located at a distance of 2.1 Å from it. The short distance between H(1) and H(4') (1.9 Å) arises because O(4''') acts as both a donor and acceptor atom.

Another reasonably strong interaction is O(3)–H(3)···O(12). The hydroxyl bond length is 1.0 Å, the H(3)–O(12) distance is 1.9 Å and the donor–acceptor distance is 2.782 Å with an O–H–O angle of 156°. In addition, H(3) may also interact with O(2''') at a distance of 2.4 Å in which case O(2''') would act as both a donor [to H(2''')] and an acceptor [H(3)]. The close approach of these two hydrogens (2.0 Å) may be indicative of a weak H(3)–O(2''') interaction or simply a result of the close packing of the hydroxyls in the oxygen array. The long donor–acceptor distance (3.026 Å) and the uncomfortably small H(3)–O(2''')–H(2''') angle (58°) would tend to suggest that the second of these alternatives is probably closer to the truth. The remaining hydrogen bonding interaction is O(2''')–H(2''')–O(9') where the donor–hydrogen bond length is 0.9 Å, the hydrogen–acceptor distance is 2.1 Å and the angle at the hydrogen is 153°.

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