Therefore, we conclude that, within the accuracy of this experiment, the structure is centrosymmetric.

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Structure of Bromapatite and the Radius of the Bromide Ion

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Abstract. $Ca_5(PO_4)_3Br$, hexagonal, $P6_3/m$, $a = 9.761$ (1), $c = 6.739$ (1) Å, $V = 556.06$ Å^3, $Z = 2$, $\mu(Mo\ K\alpha) = 6.609$ mm^{-1}, $D_c = 3.374$ Mg m^{-3}. The structure was refined to wR on F^2 of 3.08%. Bromapatite has a typical hexagonal apatite structure with most of the Br$^-$ ions at (0,0,0) and about 2% at (0,0,0·103) (plus equivalent positions). There was no evidence of a Br$^-$ distribution as has been described in non-stoichiometric cadmium bromapatite. The packing of the Br$^-$ ions requires an apparent radius of the Br$^-$ ion of 1·68 Å which is appreciably smaller than the traditional value of 1·95 Å.

Introduction. Calcium bromapatite is of interest because if it is stoichiometric it must contain two Br$^-$ ions along the z axis per unit cell, which is apparently inconsistent with the usual value given for the crystal radius of Br$^-$ of 1·95 Å (Pauling, 1960), so that four times the crystal radius (7·80 Å) is appreciably greater than the c-axis dimension of 6·739 Å (Fig. 1a). The same situation occurs in other apatites, $Cd_5(VO_4)_3I$, $Cd_5(PO_4)_3Br$, $Cd_5(AsO_4)_3Br$ and $Cd_5(VO_4)_3Br$, which contain large halide ions. These compounds have been found to have a halide non-stoichiometry of between 8

and 27% which has been associated with a distribution of the halide ions along the z axis (Fig. 1b) (Sudarsanan, Young & Wilson, 1977; Wilson, Sudarsanan & Young, 1977). Another point of interest is that in some stoichiometric apatites an ordered arrangement of Cl$^-$ or hydroxyl ions occurs which results in a doubling of the b axis and the lowering of the symmetry to the monoclinic space group $P2_1/b$ (Mackie, Elliott & Young, 1972; Elliott, Mackie & Young, 1973).

Crystals of bromapatite were grown by slowly cooling a mixture of powdered bromapatite and $CaBr_2$ in a HBr atmosphere from 1073 to 1013 K at a rate of 0·67 K h^{-1} (Dykes, 1974). A spherical crystal 0·309 mm in diameter was used for X-ray data collection with a Picker FACS-1 diffractometer and Mo $K\alpha$ radiation. A 2θ scan with unfiltered radiation was used for reflections for which there was no interference from $K\beta$ peaks in the range of reflection and background scan. The other reflections were collected by either the balanced-filter ω-scan method or by the single-filter 2θ-scan method (Mackie, 1972). Simultaneous diffraction effects were assessed by a second measurement of each reflection after the specimen had been rotated 1° about the diffraction vector. Those reflections which for

the two settings of the crystal differed by more than three times the standard deviation estimated from counting statistics were rejected. Each reflection was repeatedly scanned up to a maximum of 16 times or until there was 2% statistical precision in the net integrated intensity. 673 reflections were measured, about half of them in a column in reciprocal space parallel to c^* such that $h \leq 4$ and $k \leq 4$, up to $2\theta =$ 120°, and the rest forming a disc perpendicular to c^* such that $l \leq 4$, up to $2\theta = 120°$. Lattice parameters were calculated by least-squares fitting of the positions of 12 reflections determined with the single-crystal diffractometer ($\lambda = 0.70926$ Å).

Overexposed Weissenberg photographs did not indicate departure from the usual apatite space group of $P6_3/m$. In particular, there was no evidence for a doubled b axis. The structure was therefore refined in this space group with the full-matrix least-squares program of Busing, Johnson, Ellison, Thiessen & Levy (1973). Atomic scattering factors for Ca^{2+}, P^0 and Br^- were from Doyle & Turner (1968) and for $O^{3/4-}$ a linear interpolation was made from values for O^0 and O^{1-} given in International Tables for X-ray Crystallography (1974). Anomalous-dispersion corrections were made with values given in International Tables for X-ray Crystallography (1974). The observed structure factors were corrected for isotropic secondary extinction (Zachariasen, 1967). 14 reflections had extinction corrections >20%, the largest being 32%. The starting parameters used were those for 'hexagonal' chlorapatite (Mackie, Elliott & Young, 1972) with the Br^- ions slightly displaced from the special positions at (0,0,0) and (0,0,$\frac{1}{2}$). In initial refinements, the Br^- ions always moved to these special positions. In subsequent refinements, all possible multipliers, thermal and positional parameters were varied, except the Br^- ion position which was fixed at (0,0,0). The final weighted residual wR_2 was 4.07%, where $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2]^{1/2}/[\sum w|F_o|^4]^{1/2}$ and w is the reciprocal of the variance for each observation. The strongest peak in the

Table 1. *Comparison between refinements with one, two or six Br^- ions*

All values are multiplied by 10^4. Standard deviations are given in parentheses for parameters varied.

	Occupancy	z	β_{11}	β_{33}
Br	9600 (30)	0	31 (0)	85 (1)
Br(1)	9522 (24)	0	32 (0)	79 (1)
Br(2)	300 (12)	1032 (28)	32	79
Br(1)	9228 (144)	0	32 (0)	70 (5)
Br(2)	342 (174)	500	32	70
Br(3)	192 (54)	1000	32	70
Br(4)	54 (36)	1500	32	70
Br(5)	24 (30)	2000	32	70
Br(6)	3 (18)	2500	32	70

Table 2. *Bromapatite position parameters ($\times 10^4$) and root-mean-square radial thermal displacements, $\langle u^2 \rangle^{1/2}$, calculated with the program of Busing, Martin & Levy (1964)*

Standard deviations of the last figure are given within parentheses for parameters varied.

	Occupancy	x	y	z	$\langle u^2 \rangle^{1/2}$ (Å)
O(1)	9954 (50)	3533 (2)	4972 (2)	$\frac{1}{4}$	0.196 (4)
O(2)	9928 (44)	5954 (2)	4642 (2)	$\frac{1}{4}$	0.176 (4)
O(3)	10052 (38)	3572 (1)	2713 (1)	662 (1)	0.206 (3)
P	9654 (26)	4124 (1)	3785 (1)	$\frac{1}{4}$	0.126 (3)
Ca(1)	9861 (27)	$\frac{1}{3}$	$\frac{2}{3}$	45 (1)	0.163 (2)
Ca(2)	9834 (22)	2672 (1)	121 (1)	$\frac{1}{4}$	0.166 (3)
Br(1)	9522 (24)	0	0	0	0.203 (1)
Br(2)	300 (15)	0	0	1032 (28)	0.203

Table 3. *Bond angles (°) and interatomic distances (Å) for calcium bromapatite*

Standard deviations, in units of the last significant figure, are given in parentheses. $O^1(3)$ is related to $O(3)$ by reflection in m at $z = \frac{1}{4}$. The number of asterisks against a distance indicates the number of times the distance is repeated for symmetry-related sites of the second atom.

PO$_4$ tetrahedra		Environment of Ca atoms	
O(1)—P—O(2)	111.11 (8)	Ca(1) O(1)	2.416 (1)**
O(1)—P—O(3)	112.28 (5)	Ca(1)—O(2)	2.438 (1)**
O(2)—P—O(3)	106.54 (6)	Ca(1)—O(3)	2.809 (1)**
O(3)—P—O^1(3)	107.65 (8)	Ca(2)—O(1)	3.143 (2)
		Ca(2)—O(2)	2.276 (2)
O(1)—P	1.531 (2)	Ca(2)—O(3)	2.344 (1)*
O(2)—P	1.548 (2)	Ca(2)—Br(1)	3.057 (1)
O(3)—P	1.535 (1)*	Ca(2)—Br(2)	2.736 (7)
O(1)—O(2)	2.539 (2)	Br(1)—Br(1)	3.369 (1)
O(2)—O(3)	2.472 (2)*		
O(1)—O(3)	2.546 (2)*		
O(3)—O^1(3)	2.478 (2)		

difference Fourier map (Zalkin, 1973) was 0.76 e Å^{-3} at (0,0,0.1375). Therefore, further refinements were undertaken with a second Br^- at this position with its thermal parameters constrained to be equal to those of the Br^- at (0,0,0) but with its z parameter and multiplier being allowed to vary. The value of wR_2 fell to 3.08%. The strongest peak in the Fourier difference map was now 0.526 e Å^{-3} at (0.0375, 0.2875, 0.2500) and the largest peak on the z axis was 0.324 e Å^{-3} at (0,0,0.1875). In order to make comparisons with the work of Sudarsanan, Young & Wilson (1977), refinements were undertaken with six fixed, equally spaced Br^- ions whose multipliers were varied individually but whose thermal parameters were constrained to vary together. With this model, the value of wR_2 was 3.03%. The results for the Br^- ion for the three different models are summarized in Table 1. There is no evidence that the model with six equally spaced Br^- ions is significantly better than that with two Br^- ions, and therefore the list of parameters for the structure (Table

2) is given only for the two Br⁻ model. In Table 2 root-mean-square thermal displacements are given, but the anisotropic temperature factors* were very similar to those for 'hexagonal' chlorapatite. Various bond angles and interatomic distances, calculated with the program of Busing, Martin & Levy (1964), are given in Table 3.

Discussion. The positions of most of the Br⁻ ions at (0,0,0) are consistent with the finding that the b axis is not doubled. In hydroxyapatite (Elliott, Mackie & Young, 1973) and chlorapatite (Mackie, Elliott & Young, 1972) which have a doubled b axis, the doubling is associated with an ordered arrangement of the OH⁻ or Cl⁻ ions above or below the positions $(0,0,\frac{1}{4})$ or (0,0,0) respectively. In bromapatite this is clearly not possible.

The formula derived from the site occupancies (Table 2) is $Ca_{10.20}P_6O_{24.87}Br_{2.04}$ and therefore, within the standard deviations in Table 2, the crystal is almost stoichiometric. This result agrees with the chemical analysis of Br of 14·06% (stoichiometric value 14·14%) on the same sample (Dykes, 1974). The small amount of Br⁻ displaced 0·695 Å from (0,0,0) probably arises because these Br⁻ ions are adjacent to a Br⁻ vacancy (Fig. 1c), which suggests that the crystal was

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35723 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
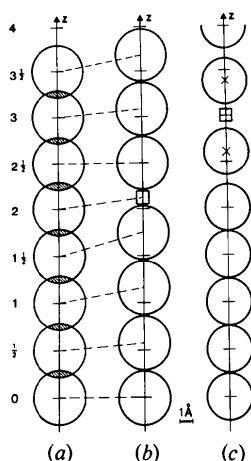

Fig. 1. Packing of bromide ions along the z axis in bromapatite. (a) The overpacking that results when ions with the traditional crystal radius (1·95 Å) are placed at $z = 0, \frac{1}{2}, 1, 1\frac{1}{2}$ etc. (b) A possible solution to this overpacking requiring non-stoichiometry of the type proposed by Wilson, Sudarsanan & Young (1977) for cadmium apatites in which successive ions are displaced by increasing amounts, for example from $z = 0, \frac{1}{2}, 1, 1\frac{1}{2}$, until the increasing strain is relieved by a vacancy. (c) An alternative solution in which smaller bromide ions ($r = 1·68$ Å) are located at $z = 0, \frac{1}{2}, 1$, etc. If there is a vacancy (say at $z = 3$), adjacent ions will be slightly displaced.

in fact very slightly non-stoichiometric. This interpretation is made by analogy with melt-grown chlorapatite in which the halide deficiency is much larger (10–15%) so that the situation is clearer (Elliott, Young, Mackie & Dykes, 1975). In this case, there was a Cl⁻ ion displaced 0·867 Å from (0,0,0) and a Ca^{II} correspondingly displaced 0·385 Å towards the z axis. In bromapatite, there was some evidence of a displaced Ca^{II} in the final difference Fourier maps, but it was not possible to refine the structure with an additional Ca^{II} as was done for non-stoichiometric chlorapatite. It would seem that the appearance of a displaced Br⁻ ion is a more sensitive indicator of non-stoichiometry than either the chemical analysis or multipliers of the atoms.

The Br–Br distance of 3·37 Å in bromapatite is at variance with the traditional value of the crystal radius of the Br⁻ ion, 1·95 Å, which gives a closest approach distance of 3·9 Å. The traditional values of the ionic radii were determined from interionic distances in simple ionic structures; however, an additional criterion is required to determine the relative sizes of the anions and cations because only the sums of radii are known. The various criteria that have been used have been critically discussed by Fumi & Tosi (1964a,b) who concluded that they all had objectionable features. They calculated the absolute sizes of the alkali and halide ions in individual alkali halides with the NaCl structure from parameters entering expressions for the first- and second-neighbour contributions to the Huggins–Mayer form of the Born repulsive energy. The calculated values agreed, within the expected errors, with radii determined by other workers from electron density maps of NaCl and LiF for which the criterion used to define the limit of an ion was the minimum in the electron density map along the nearest-neighbour line. Fumi & Tosi concluded that the crystal radii of the alkali and halogen ions in the NaCl structure are, respectively, larger and smaller than the traditional crystal radii by about 0·2 Å. The average values of the crystal radii of Cl⁻, Br⁻ and I⁻ were calculated as 1·62, 1·76 and 1·97 Å respectively with an estimated uncertainty of about 0·05 Å. This value for Br⁻ also agrees with the 1·73 ± 0·07 Å later determined experimentally from electron density maps by Meisalo & Inkinen (1967). The apparent radius of the Br⁻ ion in bromapatite is 1·68 Å which agrees with the value determined by Meisalo & Inkinen, but is just outside the lower limit of the calculated value of Fumi & Tosi.

The values of the Br–Br distances found in non-stoichiometric $Cd_5(PO_4)_3Br$, $Cd_5(AsO_4)_3Br$ and $Cd_5(VO_4)_3Br$ by Wilson, Sudarsanan & Young (1977) were 3·65, 3·36 and 3·36 Å, which give effective radii of the Br⁻ ion of 1·82, 1·68 and 1·68 Å respectively. These values are consistent with the apparent radius in bromapatite of 1·68 Å. Looked at another way, given the Br–Br distances found by Wilson, Sudarsanan & Young and the value of the c axis of bromapatite, it

would be anticipated that this compound could be stoichiometric and without a distribution of Br^- ions, as indeed was found in this work. The value of 1.82 Å found for the effective radius of the Br^- ion in $Cd_5(PO_4)_3Br$ suggests that this compound could probably accommodate more Br^- ions than the 0.83 per half unit cell found by Wilson, Sudarsanan & Young.

The above discussion on the radius of the Br^- ion can be compared with Cl^- ions in apatite. Engel, Pretzsch, Gramlich & Baur (1975) determined the Cl—Cl distance in stoichiometric $Mn_5(PO_4)_3Cl$ to be 3.1 Å, which gives an effective Cl^- ionic radius of 1.55 Å. They reconciled this with the traditional value of the radius of 1.8 Å by assuming that the short Cl—Cl distance could be caused by a compression forced upon the ions by the whole apatite structure. However, 1.55 Å is only just outside the lower limit of 1.62 ± 0.05 Å calculated for the radius by Fumi & Tosi (1964a,b), a situation which is directly comparable to that found here in bromapatite. Therefore, although the halide ions in apatite sometimes might suffer a slight compression, there seems no reason to believe that it is as extensive as the traditional values of the ionic radii would require.

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