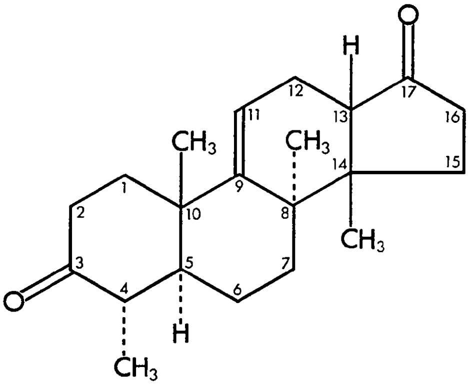

Fig. 1. Structural formula.

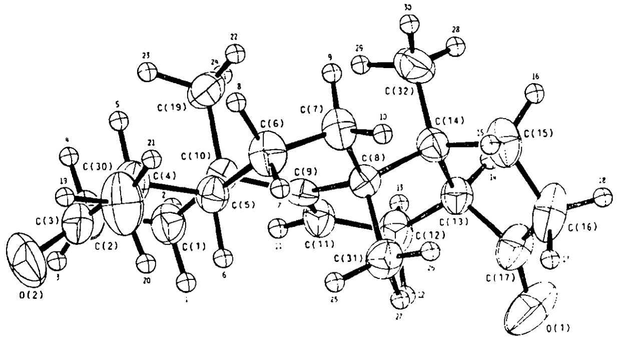

Fig. 2. Molecular structure. Thermal ellipsoids were drawn at the 50% probability level and hydrogen atoms were given an arbitrary temperature parameter.

tion in or adjacent to the rings (see, for example, Geise & Romers, 1966).

The molecules are arranged in the crystal with their longest dimension parallel to **a**, and they are packed side by side in a triangular fashion into layers parallel to **b** and **c**. There are no abnormally close intermolecular contacts. The shortest intermolecular distances between carbon and oxygen atoms are 3·36 Å for C–O, 3·55 Å for C–C, and 4·35 Å for O–O.

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Barium Chloride Silicate with an Open Framework: Verplanckite

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Abstract. Verplanckite is hexagonal, $P6/mmm$, $a=16{\cdot}398\,(10)$, $c=7{\cdot}200\,(4)$ Å, $[(Mn,Ti,Fe)_6(OH,O)_2(Si_4O_{12})_3]Ba_{12}Cl_9\{(OH,H_2O)_7\}$, $Z=1$, $D_x=3{\cdot}33$ g cm^{-3}. Material from the type locality was used, Esquire No. 7 mine, Big Creek, Fresno County, California (Specimen No. M18580, Field Museum of Natural History). The structure is recognized as an example of a new kind of compound which consists of a wide open framework, wholly or partly a silicate, filled by barium and chlorine atoms and OH or H_2O groups. The voids in verplanckite (free diameter 7·2 Å) approach the dimensions of the openings found in the most open zeolites.

Introduction. Two small crystals of verplanckite were isolated from a specimen of sanbornite-bearing rock (Alfors, Stinson, Matthews & Pabst, 1965). One crystal was used to determine by electron microprobe analysis the chemical composition (normalized to 12 for Si) of verplanckite to be $Ba_{11.27}Mn_{4.06}Ti_{1.50}Fe_{0.29}Si_{12}O_{36}O_{2.20}Cl_{8.84}(H_2O)_{7.05}$, where the water content represents the difference between the total weight percents of all other constituents and 100%. The agreement between our analysis and the previous one (Alfors & Putnam, 1965) is fair, except for the water content, which we find to be smaller, and the chlorine content, which we find to be larger.

From the second crystal (approximately cylindrical shape 0·06 × 0·06 × 0·2 mm) we obtained 6557 non-unique intensities on a computer-controlled four-circle diffractometer using crystal-monochromatized Ag $K\alpha$ radiation (wavelength $\lambda=0{\cdot}56083$ Å). The reduction and averaging of the intensity data resulted in 679 unique structure factors (maximum $\sin\theta/\lambda=0{\cdot}60$ Å^{-1}), of which 293 were considered to be of zero intensity. No absorption correction was applied to the observed data (absorption coefficient $\mu=43$ cm^{-1}; μR about 0·13; maximum corrections would have been $\pm 4\%$ on I_{obs}). The absence of systematic extinction of intensities means that space groups $P622$, $P6mm$, $P\bar{6}m2$. $P\bar{6}2m$ and $P6/mmm$ are consistent with the observed diffraction symmetry. The interpretation of the Patterson map allowed an unambiguous assignment of atomic positions in space group $P6/mmm$. A full-matrix least-squares refinement with isotropic temperature factors gave a discrepancy index of $R=0{\cdot}102$ for all observed reflections (Table 1*) and resulted in the parameters listed in Table 2. Attempts to refine the structure in space group $P6mm$ were not successful, therefore $P6/mmm$ has been accepted as the true space group within the limits of accuracy of the determination. The assignment of a statistical occupation of one OH group and one oxygen atom to O(*h*4) is based on the bond strengths (Baur, 1970) received by O(*h*4) and on the fact that X–O(*h*4) and X–O(1) have the same bond lengths. The scattering factor curve used in the refinement for the X site was a weighted combination of the Mn and Ti curves. The occupancy factors of all atomic sites were varied, but only the occupancies of atoms Cl(2) and Cl(3) were found to deviate distinctly and significantly from 1·0 (Table 2). The assignment of chlorine to the Cl(1), Cl(2) and Cl(3) sites was based on the interatomic distances involving these positions and on the microprobe analysis (Table 3).

Discussion. The structure of verplanckite can be described as a three-dimensional framework composed of four-membered rings, $(Si_4O_{12})^{8-}$, of silicate tetrahedra (Fig. 1), and of triple units of square pyramidal coordination polyhedra around the X sites, which are randomly occupied by Mn, Ti and Fe. Three square pyramids are joined at the common apical oxygen atom, O(*h*4). These triple units are connected to each other in the **c** direction by the silicate rings. The chemical composition of this framework is $(Mn,Ti,Fe)_6(O,OH)_2Si_{12}O_{36}$. Each triple unit and the adjoining silicate tetrahedra (halves of three rings) form a slab of triangular cross-section parallel to the **c** direction (Fig. 1). The triangular slabs are arranged in chinese checkerboard fashion thus leaving a void of hexagonal cross-section between them. The walls of the void are lined with Ba atoms which are coordinated to the silicate oxygen atoms and to the Cl(1) atoms which are located halfway between the triple units, and to atoms Cl(2) and Cl(3) in the large hexagonal void. The diameter of the void measures 9·8 Å from the center of one Cl(3) atom to the center of the opposite Cl(3) atom and 8·1 Å from Cl(2) to Cl(2) atom. If we subtract 3·6 Å for the diameter of the Cl atom itself the free diameters would be 6·2 and 4·5 Å respectively. Since, however, both these atomic sites are only statistically occupied the effective free diameter of the hexagonal void is

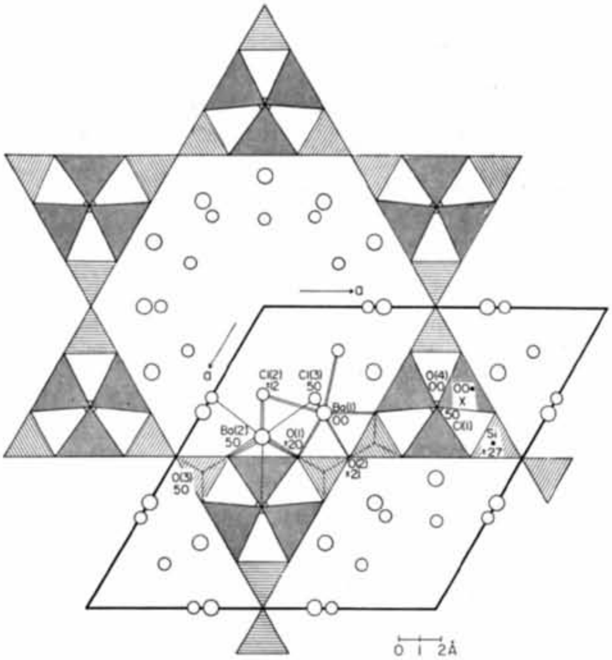

Fig. 1. Crystal structure of verplanckite viewed parallel to the *c* axis. Polyhedral representation for the framework, $X_6(O,OH)_2Si_{12}O_{36}$, where X represents the site occupied by Mn, Ti and Fe. Barium and chlorine atoms are shown as circles and the bonds to the barium atoms are indicated. The heights of the atoms are given as $z \times 100$.

Table 2. *Equipoints* (EP), *coordination numbers* (CN), *positional and thermal parameters for verplanckite* (*estimated standard deviations in units of the least significant digit are given in parentheses*)

	EP	CN	*x*	*y*	*z*	*B* (Å^2)
X(=Mn, Ti, Fe)	6(*l*)	5	0·2606 (4)	0·5212	0	1·0 (2)
Si	12(*o*)	4	0·4440 (4)	0·8880	0·274 (2)	1·2 (2)
O(1)	24(*r*)	4	0·160 (1)	0·499 (1)	0·197 (3)	2·3 (4)
O(2)	6(*i*)	4	$\frac{1}{2}$	0	0·206 (5)	0·9 (8)
O(3)	6(*m*)	4	0·441 (2)	0·882	$\frac{1}{2}$	8 (2)
O(*h*4) (=OH, O)	2(*c*)	3	$\frac{1}{3}$	$\frac{2}{3}$	0	3 (2)
Ba(1)	6(*j*)	8·4	0·3484 (3)	0	0	2·9 (1)
Ba(2)	6(*m*)	8·8	0·2164 (2)	0·4328	$\frac{1}{2}$	2·2 (1)
Cl(1)	2(*d*)	3	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	5 (1)
0·3 × Cl(2)	12(*o*)	3	0·142 (2)	0·284	0·118 (6)	2 (1)
0·6 × Cl(3)	6(*k*)	4	0·301 (2)	0	$\frac{1}{2}$	5 (1)

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* Table 1 has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30132. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Interatomic distances and angles in verplanckite*

SiO_4 group		
Si-O(1)	(2×)	1·59 (2) Å
Si-O(2)		1·66 (2)
Si-O(3)		1·63 (2)
Si-O(2)-Si		146 (3)°
Si-O(3)-Si		175 (5)
(Mn, Ti, Fe) coordination		
X-O(1)	(4×)	2·07 (2) Å
X-O(*h*4)		2·07 (2)
O(*h*4)-X-O(1)		98·8 (6)°
O(1)—X-O(1)		87·0 (6)
O(1)—X-O(1)		90·4 (6)
O(1)—X-O(1)		162·5 (10)
Ba(1) coordination		
Ba(1)-O(1)	(4×)	2·92 (2) Å
Ba(1)-O(2)	(2×)	2·92 (2)
Ba(1)-Cl(2)	(4×)	3·11 (3)
Ba(1)-Cl(3)	(2×)	3·68 (1)
Ba(2) coordination		
Ba(2)-O(1)	(4×)	2·79 (2) Å
Ba(2)-O(3)	(2×)	3·20 (4)
Ba(2)-Cl(1)		3·32 (1)
Ba(2)-Cl(2)	(2×)	3·46 (5)
Ba(2)-Cl(3)	(2×)	3·10 (3)

about 7·2 Å. The highest electron density found in the void in a difference synthesis is 1·9 e $Å^{-3}$, which means that it is not significantly different from zero. The free volume of the void is about 300 $Å^3$ per unit cell (or 18% of the unit cell volume). An opening of this size is large even when compared with a zeolite. Faujasite, which has the most open framework of all the zeolites, has pore openings outlined by 12-membered $(Si,Al)_{12}O_{12}$ rings with a free diameter of about 7·3 Å (Baur, 1964).

The square pyramidal coordination around the X sites is an extremely rare coordination for both Mn^{2+} and Ti. Divalent manganese in square-pyramidal five coordination has been reported previously only in diphenyl methyl arsine perchlorate, $Mn(Ph_2MeAsO)_4(ClO_4)_2$ (Lewis, Nyholm & Rodley, 1965). We can exclude that manganese is in the three-valent state in verplanckite because the bond length X–O would then have to be about 1·95 Å. The coordination around Ba(1) is formally twelvefold and around Ba(2) elevenfold. However, since the Cl(2) and Cl(3) sites are only partially occupied the effective coordination numbers are smaller (Table 2).

The chemical analysis as based on the microprobe data can be reconciled with the structure determination if written

$$(Mn_{4.06},Ti_{1.50},Fe_{0.29})(OH,O)_2Si_{12}O_{36}Ba_{11.27}Cl_{8.84}\{(OH)_{1.40}(H_2O)_{5.85}\}.$$

The OH and H_2O content written in brackets could not be placed in any of the equipoints listed in Table 1 and must be assumed to be distributed over the free volume of the void, either statistically over many positions with very small occupancy factors, or freely floating through the framework the way it is likely to occur in faujasite (Baur, 1964). Only 7·25 oxygen atoms have to be placed, while the free volume is sufficient to accommodate 10 oxygen atoms. The chemical analysis as based on the crystal structure determination differs slightly from the microprobe result

$$(Mn_{4.06},Ti_{1.50},Fe_{0.29})(OH,O)_2Si_{12}O_{36}Ba_{12}Cl_{9.2}\{(OH)_{2.50}(H_2O)_{4.75}\}.$$

The difference in Cl content is not significant. The deficiency in Ba content could not be confirmed by a refinement of the occupancy factors of the Ba atoms. The discrepancy could be removed by recalculating the microprobe analysis on the basis of 12 Ba atoms. But this would result in an Si content of 12·8 atoms and there are no likely sites for the excess silicon. Keeping these limitations in mind, a likely formulation for verplanckite is

$[(Mn,Ti,Fe)_6(OH,O)_2(Si_4O_{12})_3]Ba_{12}Cl_9\{(OH,H_2O)_7\}$,

where the part in square brackets corresponds to the framework which is filled by Ba, Cl, OH and H_2O. The structure possesses a large degree of disorder: some of the atoms cannot be located at all, other atoms show partial occupation of equipoints, other atomic kinds occupy statistically one equipoint. There is also evidence in the Fourier synthesis for positional disorder of several atoms, as shown by their high temperature factors: Ba(1), O(3), Cl(3) (Table 2).

Verplanckite is the third example of a new kind of silicate which can be called a barium chloride silicate. The other two known examples are muirite, $[(Ca,Mn,Ti)_4(OH,O)_4Si_8O_{24}]Ba_{10}Cl_8(H_2O)_4$ (Khan & Baur, 1971), and the synthetic compound $[(Si,Al)_8O_{16}]Ba_3Cl_2(OH,Cl)$ (Solov'eva, Borisov & Bakakin, 1972). The three structures have in common: an open framework which accommodates barium, chlorine and hydroxyl or water groups; a highly symmetrical structure; local disorder as evidenced by high temperature factors and statistical occupation of equipoints. Because of the porous open frameworks these compounds are likely candidates for having zeolitic properties. However, we were not able to investigate the ion exchange (or molecular sieve) properties of verplanckite because of the minuteness of our sample. Such studies will have to wait until verplanckite can be synthesized.

Another mineral which could be a barium chloride silicate is traskite (Alfors *et al.*, 1965).

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