We thank Dr W. B. T. Cruse for growing the crystal used here, Miss K. Hayakawa for drawing some of the diagrams and Mr L. Goulden for the photography. This paper is abstracted from the Ph. D. thesis of G.J.B.W. who thanks the University of Alberta for financial support. The crystallographic computer programs of F. R. Ahmed *et al.*, NRC Ottawa, have been invaluable in this work. Financial support, under grant MA-3406, to M.N.G.J. from the Medical Research Council of Canada is gratefully acknowledged.

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Acta Cryst. (1974). B**30**, 1262

The Crystal Structure of Wenkite

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(*Received* 2 *April* 1973; *accepted* 29 *June* 1973)

The crystal structure of wenkite $(Ba,K)_4(Ca,Na)_6(Si,Al)_{20}O_{41}(OH)_2(SO_4)_3.H_2O$, has interesting relationships with that of the zeolite offretite. Both minerals are characterized by the type of cage found in cancrinite, each cage being joined through bridges of six oxygen atoms to two identical cages, thus building up columns parallel to **c**. In wenkite the columns are interconnected by half-occupied face-sharing tetrahedral pairs. One barium cation is located in the cancrinite cavity enclosed in the columns; the other barium cations, calcium cations and disordered sulphate groups are located in the channels of the structure.

Introduction

Wenkite was found in the marbles of Candoglia, Italy, by Papageorgakis (1959, 1962), who studied its physical and optical properties, determined its hexagonal lattice constants and on the basis of analyses of purified material proposed the following formula: $Ba_{4\cdot5}Ca_{4\cdot5}Al_9Si_{12}O_{42}(OH)_5(SO_4)_2$. Wenk (1966) refined, by least-squares calculations on powder data, the lattice constants, obtaining $a=13\cdot511$ (1), $c=7\cdot462$ (1) Å; he confirmed the diffraction symmetry of wenkite as $6/mmm$ and, by examination of the Harker concentrations on the Patterson map, determined $P\bar{6}2m$ as the most probable space group. Moreover he observed that the formula given by Papageorgakis appeared 'by microprobe analysis to be somewhat inaccurate, mainly because of the fine intergrowth with quartz'.

Experimental

A crystal of wenkite elongated in the **c** direction was reduced to nearly cylindrical shape with cross-sectional radius of 0·095 mm. The intensity data were collected by integrated Weissenberg photographs with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). Seven layers with c as rotation axis ($l = 0$ through 6) were recorded and 482 independent reflexions (423 observed) were collected. The intensities, measured with a Nonius microdensitometer, were reduced to observed structure factors: the absorption correction for cylindrical crystals ($\mu R = 3{\cdot}26$ for Cu $K\alpha$ radiation) was applied.

Structure determination and refinement

The structure was solved by locating barium atoms by examination of the three-dimensional Patterson map and the main features of the structure were established by subsequent electron density maps.*

The refinement was made by alternating cycles of least-squares refinement with three-dimensional electron density and difference syntheses. The maps, together with the least-squares refinement, indicated that each of the four oxygen atoms O(8) through O(11) of the sulphate group is disordered among four positions, related to each other by the two mirror planes which meet along x,0,0 where the sulphur atom is located. Moreover the maps and the least-squares refinement indicated half occupancy for the T(3) cation. This cation occupies a face-sharing pair of tetrahedra related by a mirror plane through the shared face. The possibility of an ordered distribution of cations among these tetrahedral sites, with corresponding lowering of the space-group symmetry to $P321$ or $P31m$, was tested and discarded because of the marked rise in the reliability index. Refinement terminated at the reliability index $R = 0{\cdot}098$ for observed reflexions. Unit weights were attributed to the reflexions and the form factors for the dominant atom in the various structure groups were used. Positional and thermal coordinates are presented in Table 1. Observed and calculated factors are compared in Table 2.

Description and discussion of the structure

The frame structure of wenkite can be conveniently described and understood, by comparison with the zeolite offretite $K_{1\cdot1}Ca_{1\cdot1}Mg_{0\cdot7}Si_{12\cdot8}Al_{5\cdot2}O_{36}.15{\cdot}2H_2O$ (Bennett & Gard, 1967; Gard & Tait, 1972), which also has hexagonal symmetry and cell dimensions $a = 13{\cdot}291$, $c = 7{\cdot}582$ Å comparable with those of wenkite. Both structures are characterized by the polyhedral cages which are formed by five six-membered and six four-membered rings and are also found in cancrinite (Pauling, 1930; Jarchow, 1965), erionite

Table 1. *Positional and thermal parameters for wenkite*

Figures in parentheses signify standard deviations in units of the last significant digit.

		Equipoint	x	y	z	B(Å^2)
Ba(1)	(=Ba, K)	1(b)	0	0	$\frac{1}{2}$	
Ba(2)	(=Ba, K)	3(g)	0·3932 (3)	0	$\frac{1}{2}$	
Ca	(=Ca, Na)	6(j)	0·4988 (12)	0·2743 (11)	0	
T(1)	(=Si, Al)	12(l)	0·2666 (7)	0·1336 (8)	0·2178 (11)	0·8 (1)
T(2)	(=Si, Al)	6(k)	0·4380 (9)	0·3008 (9)	$\frac{1}{2}$	0·4 (1)
0·5 × T(3)	(=Al, Si)	4(h)	$\frac{2}{3}$	$\frac{1}{3}$	0·3970 (40)	0·4 (2)
S		3(f)	0·5200 (14)	x	0	1·3 (3)
O(1)		6(j)	0·296 (2)	0·145 (2)	0	0·2 (4)
O(2)		12(l)	0·392 (2)	0·215 (2)	0·317 (3)	1·4 (4)
O(3)		6(i)	0·216 (2)	0	0·294 (4)	0·8 (4)
O(4)		6(i)	0·170 (2)	x	0·275 (4)	1·0 (5)
O(5)		3(g)	0·399 (4)	x	$\frac{1}{2}$	2·2 (9)
O(6)		6(k)	0·580 (3)	0·378 (3)	$\frac{1}{2}$	1·3 (6)
O(7)	(=O, OH)	4(h)	$\frac{2}{3}$	$\frac{1}{3}$	0·170 (7)	3·0 (9)
0·25 × O(8)		12(l)	0·421 (6)	0·402 (6)	−0·049 (7)	0·9 (15)
0·25 × O(9)		12(l)	0·492 (13)	0·606 (12)	0·074 (17)	2·6 (25)
0·25 × O(10)		12(l)	0·599 (8)	0·553 (9)	−0·158 (15)	1·6 (15)
0·25 × O(11)		12(l)	0·591 (9)	0·499 (12)	0·154 (19)	2·9 (18)

Anisotropic thermal parameters in the form

$$\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\}.$$

Values are multiplied by 10^4.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba(1)	42 (5)	β_{11}	68 (23)	$\beta_{11}/2$	0	0
Ba(2)	15 (2)	24 (3)	136 (18)	$\beta_{11}/2$	0	0
Ca	25 (6)	37 (8)	155 (28)	10 (6)	0	0

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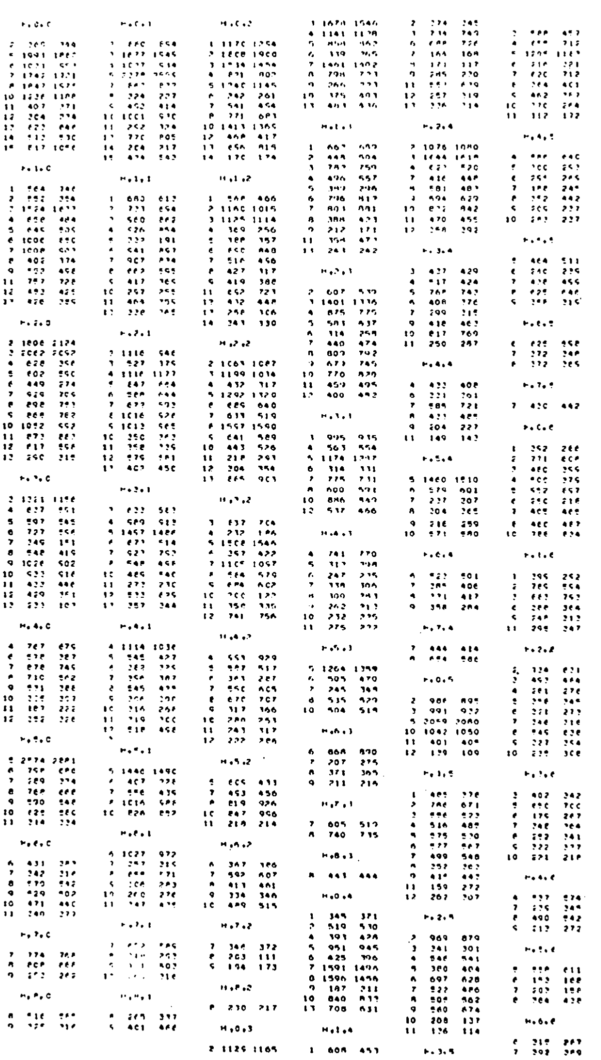
* Since this paper was submitted the author's attention has been drawn to an earlier determination of the structure (Wenk & Lee, 1972; Wenk, 1973).

Table 2. *Observed and calculated structure factors* (× 10)



(Staples & Gard 1959; Kawahara & Curien, 1969), synthetic zeolites *L* (Barrer & Villiger, 1969) and (K, Ba)–G, *L* (Baerlocher & Barrer, 1972). The cages are linked in the **c** direction through their two planar six-membered rings, thus building up columns parallel to **c**. Two types of cavity are present in the columns, one in each cancrinite cage and the other, which is referred to as the hexagonal prism, between two successive cages. The former is occupied by potassium cations in offretite and by Ba(1) cations, located in 1(*b*) at $0,0,\frac{1}{2}$ in wenkite. The columns, which are the common feature of the two minerals, have point-group symmetry $\bar{6}2m$; the differences arise from the different positioning of the columns in the unit cell, because whereas in offretite the vertical mirror planes are parallel to $\{11\bar{2}0\}$ (space group $P\bar{6}m2$), in wenkite these mirror planes are parallel to $\{10\bar{1}0\}$ (space group $P\bar{6}2m$) (Fig. 1). Consequently whereas in offretite each column is cross-linked to three others, forming single rings of six tetrahedra, in wenkite the interconnexion of the columns is assured by the two half-occupied face-sharing tetrahedral pairs located along the threefold axes at $\frac{1}{3},\frac{2}{3},z$ and $\frac{2}{3},\frac{1}{3},z$ with the shared faces on the horizontal symmetry plane at $z=\frac{1}{2}$. The large cavities with their axes on $\frac{1}{3},\frac{2}{3},z$ and the very wide channels with their axes along $\frac{2}{3},\frac{1}{3},z$, which in offretite contain the exchangeable cations and a large number of water molecules, are absent in wenkite; this mineral presents smaller channels with elliptic cross-section. In these channels the sulphate groups and the cations Ba(2) and Ca are located: the sulphate group is disordered among four symmetry-related positions, with the sulphur atom located at the special position $x,0,0$ with threefold multiplicity, Ba(2) and Ca are located at special positions $x,0,\frac{1}{2}$ with threefold multiplicity and $x,y,0$ with sixfold multiplicity, respectively. The cations are firmly bound to the oxygen anions of the framework

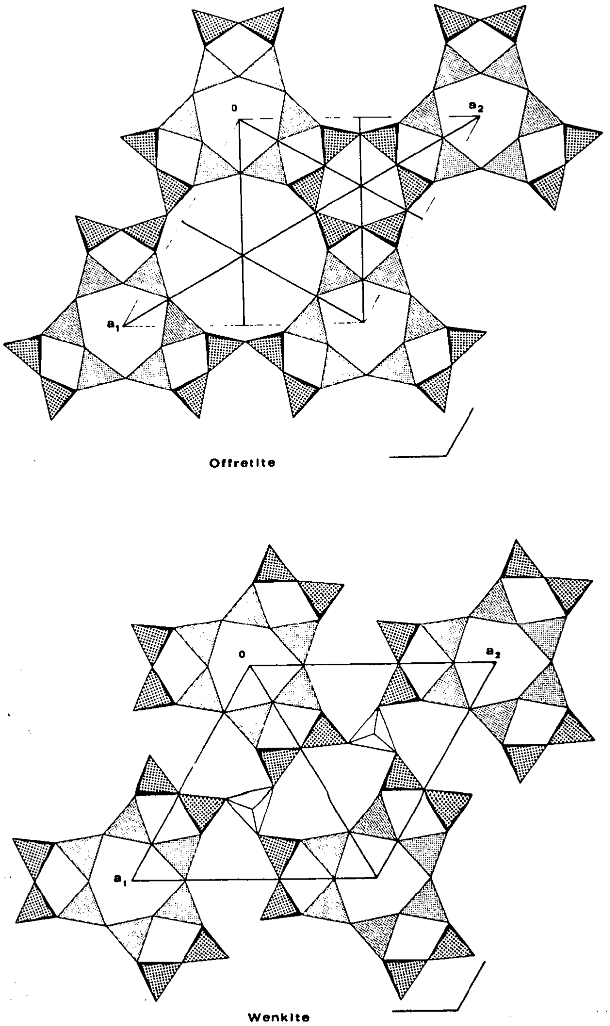


Fig. 1. Frame structures of offretite and wenkite. The positions of the mirror planes in the two space groups are indicated. The half-occupied tetrahedral pairs in wenkite are drawn unshaded.

and thus the structure has no zeolitic character (Fig. 2).

In the conventional classification of silicates developed by Bragg, wenkite should take its place among the framework silicates, with a sharing coefficient 1·975 according to Zoltai (1960), or 3·90 according to a modified definition by Coda (1969). The tetrahedral framework is interrupted in only 2 out of 41 oxygen atoms: they are the apical oxygen atoms of the two occupied T(3) tetrahedra in the unit cell. These tetrahedra can point up or down with equal probability. A similar situation was observed by Townes, Fang & Perrotta (1967) in a ferrimagnetic barium ferrite; in its structure they found two half-occupied face-sharing FeO_4 tetrahedra, with the Fe^{3+} cation statistically distributed on two sites displaced 0·156 Å from the mirror plane which relates the two tetrahedra. In the present case, however, the occupancy in the T(3) site also affects the O(7) position, making it necessary for O(7) to be an OH^- ion when the T(3) position is vacant and an oxygen atom when the T(3) position is occupied. Thus, taking account of the fact that the chemical analyses indicated the presence of sodium and potassium, the results of the structural investigation can be summarized in the following formula for wenkite:

$$(Ba,K)_4(Ca,Na)_6(Si,Al)_{20}O_{41}(OH)_2(SO_4)_3.$$

The interatomic distances are given in Table 3. The average T–O distances in the three independent T sites are T(1)–O 1·66$_8$ Å, T(2)–O 1·67$_5$ Å and T(3)–O 1·72$_8$ Å. From these values, making use of the determinative curve derived by Jones (1968) on the basis of 19 non-feldspar framework structures, the aluminum contents 0·40, 0·44 and 0·78 in T(1), T(2) and T(3), respectively, were obtained. The calculated content of 9·00 aluminum atoms in the unit cell is in agreement with the value obtained by the chemical analyses. Brown & Gibbs (1970) proposed that in framework silicates, silicon should prefer those tetrahedral sites involved in the widest average T–O–T angles, while Al, B, Be or Mg those involved in the narrowest T–O–T angles. The average values for T(1)–O–T, T(2)–O–T and T(3)–O–T angles are, respectively, 141, 136 and 123°: the aluminum distribution in wenkite is thus consistent with the proposal by Brown & Gibbs. If we take account of the Loewenstein's (1954) rule that AlO_4 tetrahedra avoid being linked together, as far as possible, in aluminosilicate framework structures, we have to admit a high degree of ordering in the tetrahedral columns parallel to **c**, with a point symmetry for each column lower than $\bar{6}2m$. The space group $P\bar{6}2m$ is therefore probably an average one, resulting from a different aluminum ordering in the different columns. The coordination polyhedra around Ba(1) and Ba(2) cations are normal, both with regard to coordination number and interatomic distances. Ba(1) has coordination number 12 with mean bond length Ba(1)–O 3·07 Å; the potassium cation is similarly coordinated in offretite with bond distances K–O(2) 2·96 (3) Å and

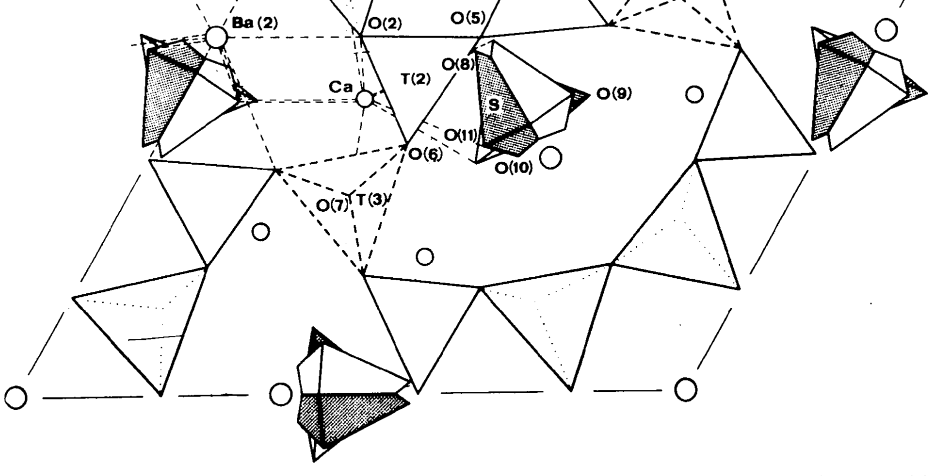


Fig. 2. Crystal structure of wenkite viewed parallel to the **c** direction. One pair of symmetry-related positions for the sulphate group is represented; the other pair is obtained by reflexion in the horizontal mirror plane. The half-occupied face-sharing tetrahedral pairs T(3) are dashed. The bonds to barium and calcium cations are indicated by broken lines.

K–O(3) 3·33 (3) Å (Gard & Tait, 1972). Ba(2) has coordination number 11, with mean bond length Ba(2)–O 2·98 Å. As regards the calcium cation, if we take account only of oxygen atoms at distances less than 3·00 Å, its coordination number is 8. Table 2 lists two more Ca–O distances of 3·03 Å, referring to the O(10) atom which has occupancy 0·25. Thus calcium cations can have coordination 8 or 9, with mean bond lengths 2·55 and 2·60 Å, respectively, which compare well with the values 2·52 and 2·58 Å given by Shannon & Prewitt (1969).

Table 3. *Interatomic distances in wenkite*

A prime is used to distinguish equivalent atoms.

T(1)–O(1)	1·66 (1) Å	Ba(1)–O(3)[×6]	3·30 (3) Å
T(1)–O(2)	1·67 (2)	Ba(1)–O(4)[×6]	2·84 (3)
T(1)–O(3)	1·68 (1)	Ba(2)–O(2)[×4]	3·22 (3)
T(1)–O(4)	1·66 (4)	Ba(2)–O(3)[×2]	2·84 (3)
		Ba(2)–O(5′)	2·81 (6)
T(2)–O(2)[×2]	1·69 (2)	Ba(2)–O(6′)[×2]	2·93 (3)
T(2)–O(5)	1·66 (5)	Ba(2)–O(10′)[×4]	2·64 (11)
T(2)–O(6)	1·66 (4)	Ba(2)–O(11′)[×4]	2·92 (13)
		Ca—O(1)	2·40 (3)
T(3)–O(6)[×3]	1·74 (5)	Ca—O(2)[×2]	2·68 (3)
T(3)–O(7)	1·69 (6)	Ca—O(7)[×2]	2·36 (3)
		Ca—O(8)[×2]	2·45 (11)
S–O(8)	1·53 (9)	Ca—O(8′)[×2]	2·89 (11)
S–O(9)	1·50 (6)	Ca—O(9)[×2]	2·29 (10)
S–O(10)	1·50 (11)	Ca—O(9′)[×2]	2·61 (15)
S–O(11)	1·61 (11)	Ca– O(10)[×2]	3·03 (11)
		Ca—O(11)[×2]	2·73 (10)
		Ca—O(11′)[×2]	2·88 (15)

The bond valence sums are satisfactory and indicate, as was previously reported, the presence of two hydroxyl anions in the unit cell at O(7) positions. Chemical analyses however gave a higher water content; moreover infrared spectra (Papageorgakis, 1962) indicated the presence both of hydroxyl ions and water molecules in the structure of wenkite. A possible site for a water molecule is inside the hexagonal prism, where it should be randomly distributed. Thus the crystallochemical formula which corresponds better to the data of the chemical analyses and the results of the structural investigation is:

$$(Ba_{3\cdot5}K_{0\cdot5})\,(Ca_{5\cdot5}Na_{0\cdot5})\,(Si_{11\cdot0}Al_{9\cdot0})O_{41}(OH)_2(SO_4)_3\,.\,H_2O\,.$$

The calculated density corresponding to this formula is 3·21 g cm^{-3}, which compares well with the observed value of 3·19 ± 0·01 g cm^{-3} (Papageorgakis, 1962).

Thanks are due to Professor Roggiani, who supplied a specimen of wenkite.

This work was supported by the Consiglio Nazionale delle Ricerche, Roma. All the calculations were performed on the I.B.M. 360/67 Computer of the 'Centro Nazionale Universitario di Calcolo Elettronico,' Pisa.

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