

The structure of wenkite¹

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Das Mineral Wenkit $\text{Ba}_4(\text{Ca}_{0,9}\square_{0,1})_6(\text{Al}_{0,4}\text{Si}_{0,6})_{20}\text{O}_{39}(\text{OH})_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ ² wurde von PAPAGEORGAKIS (1962) in den metamorphen Marmoren der Ivreazone (Süd-Alpen) gefunden. Die Strukturverfeinerung ergab eine Symmetrie $P31m$, doch durch submikroskopische Verzwilligung nach (0001) oder durch Lagenunordnung zeigen physikalische Eigenschaften und Röntgenbeugungseffekte $P\bar{6}2m$ -Symmetrie ($a = 13,515 \text{ \AA}$, $c = 7,465 \text{ \AA}$). Wenkit zeigt ein „unterbrochenes“ Al/Si Gerüst mit denselben hexagonalen Bauelementen wie Cancrinit und Gmelinit. Diese Bauelemente sind durch zusätzliche Gerüsttetraeder miteinander verbunden. Zwischen den hexagonalen Einheiten, die Ba(1) enthalten, entstehen große verzerrte Hohlräume mit Ca und Ba(2)SO₄. Eine Kette von BaSO₄-Molekülen erstreckt sich parallel zur z-Achse der Hohlräume, die durch TO₄-Achterringe definiert sind. Das Gerüst enthält auch ein System von Kanälen parallel zur x-Achse mit TO₄-Zehnerringen.

Abstract

The mineral wenkite $\text{Ba}_4(\text{Ca}_{0,9}\square_{0,1})_6(\text{Al}_{0,4}\text{Si}_{0,6})_{20}\text{O}_{39}(\text{OH})_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ ² was found by PAPAGEORGAKIS (1962) in metamorphic marbles of the Ivrea zone (Alps). The structure determination indicated that the basic symmetry is $P31m$, however, by perfect submicroscopical twinning on (0001) or positional disorder, physical properties and diffraction effects show $P\bar{6}2m$ symmetry ($a = 13.515 \text{ \AA}$, $c = 7.465 \text{ \AA}$). This suggests that wenkite might possess a domain structure. Wenkite has an interrupted Al/Si framework with the same hexagonal building units which are found in cancrinite and gmelinite. They are linked through an additional tetrahedron which is only bonded with three corners to the framework. In between these hexagonal cavities, which contain Ba(1), larger highly distorted cavities are formed which contain Ca and Ba(2)SO₄. A chain of BaSO₄ molecules extends parallel to the z axis in the

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¹ The name wenkite was given by J. PAPAGEORGAKIS (1962) in honor of Professor EDUARD WENK (Basel), to whom this paper is dedicated on the occasion of his 65th birthday.

² The symbol \square stands for vacancies.

center of these cavities which are defined by eight-membered TO_4 rings. The framework contains systems of channels parallel to the z axis with 6- and 8-membered rings and a system of kinked channels parallel to the x axis with 10-membered rings.

Introduction

Wenkite is a rock-forming barium aluminosilicate mineral which was found and described by PAPAGEORGAKIS (1959, 1961, 1962) in the highly metamorphic calcite marbles of the Ivrea zone. So far the only locality where this mineral has been found is the abandoned Cava

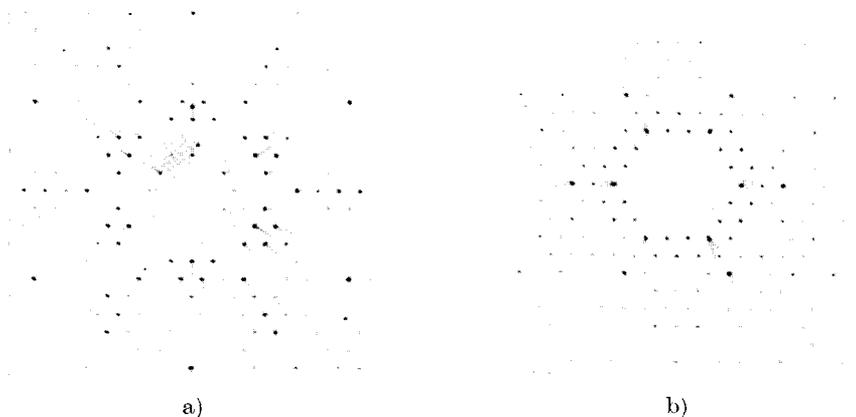


Fig.1. Zero-layer precession photographs of wenkite (Mo radiation, Zr filter) indicating the $P6/mmm$ Laue symmetry. a^* is horizontal. a) $hk0$, b) $hk1$

Mergozzoni, part of the large quarry system of Candoglia (Novara, Italy) which supplied the marble for the cathedral of Milan. Wenkite coexists with calcite, barite and hyalophane. Crystals are prismatic up to 3 cm long, with striations. The mineral is optically uniaxial negative $n_x = 1.589$, $n_y = 1.595$). The symmetry, determined on Laue and precession photographs is $P6/mmm$ with no systematic extinctions (Fig.1). Lattice constants have been refined from Guinier photographs [WENK (1966): $a = 13.515(2) \text{ \AA}$ $c = 7.465(2) \text{ \AA}$, $V = 1180.7(3) \text{ \AA}^3$]. When exposed to x-rays, wenkite changes color from colorless-yellowish to purple.

The exact chemical composition is rather uncertain and no definite formula was available for the structure determination. Some chemical formulae are listed in Table 1. For the structure determination, it

³ Standard deviations are given in parentheses.

Table 1. *The chemical composition of wenkite*
 Microprobe analyses are normalized for 20 (Al, Si)

From structure	Ba ₄ (Ca _{0.9} □ _{0.1}) ₆	(Al, Si) ₂₀ O ₃₉ (OH) ₂	· (SO ₄) ₃	· $\frac{1}{2}$ H ₂ O
PAPAGEORGAKIS (1959)	Ba _{4.5} Ca _{4.4}	Al ₉ Si ₁₂ O ₄₂ (OH) ₅	· (SO ₄) ₂	· —
GUBSER, Zurich (microprobe)*, 1964 **	Ba _{3.4} Ca _{4.5}	Al _{8.3} Si _{11.7}	— · (SO ₄) _{2.5}	· —
SCHWANDER, Basel (microprobe)*, 1964 **	Ba _{2.9} Ca _{5.5}	Al _{7.5} Si _{12.5}	— · (SO ₄) _{3.4}	· —
SCHWANDER, Basel (microprobe), 1972 **	Ba _{3.96} (Ca _{4.89} Na _{0.68} K _{0.14})Al _{8.64} Si _{11.36}	—	· (SO ₄) _{2.61}	· —

* Both analyses are done on the same crystal. The fairly poor determinations are mainly due to the difficulty of finding adequate standards for this mineral.

** Personal communication.

was assumed that the elements Si, O, Ba (possibly in solid solution with Ca and vacancies) and an unknown amount of S are present. Quantitative values were only obtained during the refinement.

Structure determination

X-ray diffraction intensities were measured with Mo radiation and balanced-filter technique by Dr. M. FEHLMANN on a Hilger-Watts diffractometer at Monsanto in Zurich in 1964 on a prismatic crystal ($0.10 \times 0.12 \times 0.30$ mm). The data were corrected for Lorentz and polarization effects. 5,700 measured reflections were averaged to 568 independent reflections in the Laue group $P6/mmm$. Since equivalent reflections gave more or less the same intensity, no absorption correction was made ($\mu = 46 \text{ cm}^{-1}$). Unfortunately only the 568 averaged structure amplitudes were available when the structure was determined in winter, 1972. Thus anomalous absorption could not be used to reveal the true noncentric space group and it was not possible to determine meaningful standard deviations from counting statistics. Nevertheless, the data were good enough to determine all the main features of the structure. On account of the uncertainties in the intensity data, and because of the small number of independent reflections, the resolution of site occupancies and anisotropic temperature factors was relatively poor, even though refinement led to an R value of 4.6%.

The structure was determined using a combination of Patterson, Fourier (program FORDAP, ZALKIN, personal communication 1972) and least-squares (program NUCLS6, BUSING, MARTIN and LEVY, 1962; modified by IBERS and RAYMOND) techniques. Scattering-factor tables of CROMER and MANN (1968) interpolated for 0.1 electron formal charge were used for all atoms. Anomalous scattering was applied to Ba and Ca (CROMER, 1965). In the three-dimensional Patterson map the main concentrations were in the plane $w = 0$ (Fig. 2) and $w = 0.5$, suggesting a concentration of atoms in the basal planes. The peak at $u = 0.2$, $v = -0.4$, $w = 0$ was interpreted as a Ba—Ba Harker peak of the position $x = 0.4$, $y = 0$, $z = 0$ in the space group $P\bar{6}2m$ (Fig. 3). With this position a structure-factor calculation was made ($R = 50\%$) and a three-dimensional Fourier synthesis was calculated in which seven atoms were well resolved. A new Fourier synthesis, phased with seven atoms, was calculated first with the assumption that all atoms were Ba and Si ($R = 45\%$), then refining in one least-squares cycle the occupancies and positions of the seven

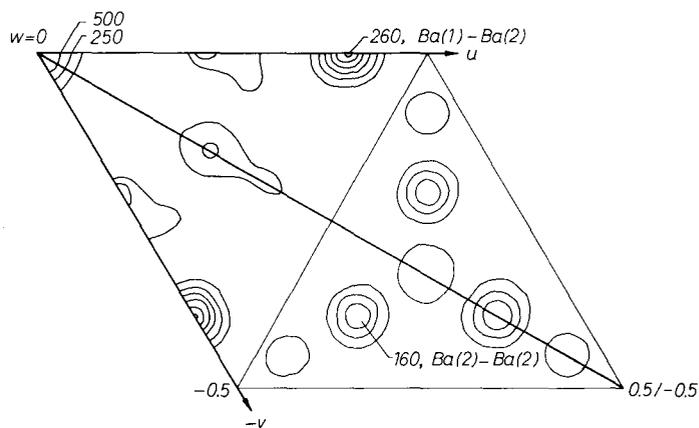


Fig.2. $uv0$ section of the Patterson synthesis ($P6/mmm$). The map is normalized such that the peak in the origin is 999. Contours are at 50 units intervals

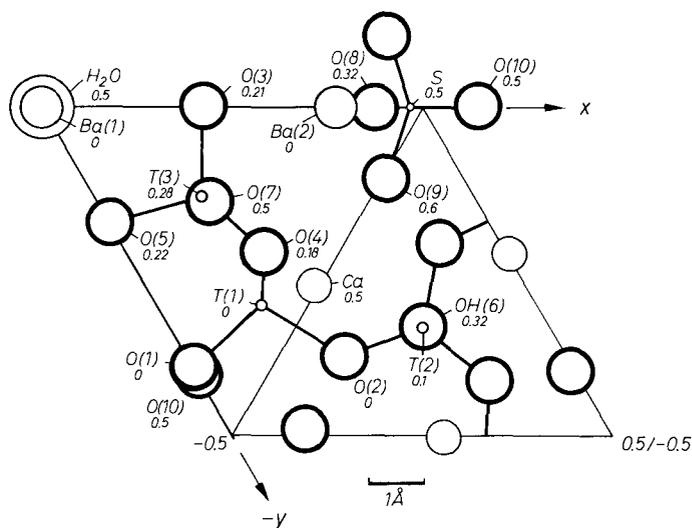


Fig.3. Atomic positions in the structure of wenkite ($P\bar{6}2m$). Illustrated is a projection on to the xy plane of the unit $0 < x < 0.5$ and $0 > y > -0.5$, which has been chosen because the asymmetric unit can be represented compactly and is easy to visualize. The radii of the atoms are drawn proportionally to the ionic radii

atoms ($R = 35^0/0$) before calculating the Fourier summation. All these Fourier syntheses indicated that there was another heavy atom in the origin. Adding a second barium at $x = 0, y = 0, z = 0$, brought the

Table 2. *Structural parameters of wenkite refined with isotropic temperature factors ($R = 5.2\%$)*In parentheses rounded up standard deviations of the last digit of the refined parameters. Space group $P\bar{6}2m$

Atom	Wyckoff symbol	multi- plicity	occu- pancy	x	y	z	B
Ba(1)	e	2	0.48(1)	0	0	0.015(1)	1.2(1) Å ²
Ba(2)	i	6	1/2	0.3927(1)	0	0.0212(4)	1.05(4)
Ca	l	12	0.41(1)	0.2243(5)	-0.2753(5)	0.488(3)	1.8(2)
T(1)	j	6	1	0.1378(4)	-0.3006(4)	0	0.67(8)
T(2)	h	4	1/2	1/3	-1/3	0.103(2)	0.4(2)
T(3)	l	12	1	0.1333(3)	-0.1335(3)	0.2820(4)	0.75(5)
O(1)	f	3	1	0	-0.400(2)	0	1.9(4)
O(2)	j	6	1	0.207(1)	-0.376(1)	0	1.4(3)
O(3)	i	6	1	0.216(1)	0	0.208(2)	1.4(2)
O(4)	l	12	1	0.179(1)	-0.215(1)	0.182(1)	1.8(2)
O(5)	i	6	1	0	-0.171(1)	0.219(2)	1.5(2)
OH(6)	h	4	1/2	1/3	-1/3	0.320(4)	1.0(4)
O(7)	k	6	1	0.150(1)	-0.144(1)	1/2	1.3(2)
S	g	3	1	0.4831(5)	0	1/2	1.5(1)
O(8)	i	6	1/2	0.430(4)	0	0.327(8)	6.9(1.3)
O(9)	l	12	1/2	0.493(3)	-0.406(3)	0.394(5)	5.8(7)
O(10)	g	3	1/2	0	-0.408(3)	1/2	5.0(6)
H ₂ O?	b	1	0.24(6)	0	0	1/2	—

R value down to 23%, indicating that the structure was basically solved. The use of the least-squares technique with site-occupancy refinement in the early stages of the structure determination proved to be a powerful method in assigning an atomic species to a given site. Other space groups in the Laue group $P6/mmm$ have been tested, but none of them gave satisfactory results, which was an empirical confirmation that $P\bar{6}2m$ was the right choice.

At an R value of 15%, the framework was determined. The position of Si(2) was anomalous, with only half the occupancy for the site and very close to the $xy0$ mirror plane in the space group $P\bar{6}2m$. The distinction between Ca and S, and O, OH and H₂O was more difficult because of vacancies. The oxygen atoms O(8), O(9), and O(10) of the sulfate group were only found in the last stages of the refinement. Similarly to Si(2) the sulfate group was found to be close to the $xy0$ mirror plane and the positions were only half occupied. All oxygen atoms of the sulfate group showed very large temperature factors.

Table 3. *Anisotropic temperature factors for Ba(1), Ba(2), Ca, assuming that these atoms are on the basal mirror plane*They are of the form $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Atom	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} = \beta_{23} = 0$
Ba(1)	21(3)	β_{11}	104(6)	$\beta_{11}/2$	
Ba(2)	20(1)	β_{11}	149(4)	$\beta_{11}/2$	
Ca	50(5)	33(4)	110(11)	30(4)	

The refinement with isotropic temperature factors but splitting the Ba(1), Ba(2) and Ca positions into two positions symmetrically related by the $xy0$ mirror plane, was straightforward and reached $R = 5.1\%$. The results are listed in Table 2. Refining Ba(1), Ba(2) and Ca on the mirror plane but with anisotropic temperature factors for these atoms produced a thermal ellipsoid which was strongly elongated parallel to z . R reached 4.9% . An anisotropic refinement of all atoms gave an R value of 4.6% . Positional parameters in the various refinements agreed within a standard deviation and only those of the isotropic refinement are listed in Table 2. The results of the anisotropic refinement (Table 3) were used for the ORTEP stereodrawings (Fig. 8–11) mainly as an aid in visualizing the stereoscopic effect, but the anisotropy apart from Ba and Ca is barely significant and may be mainly due to positional disorder. Seventeen sites were determined with certainty. The H_2O site at $00\frac{1}{2}$ refined to a very small temperature factor and may be partially occupied by a heavier atom. No other water could be determined although the chemical analyses and infra-red data (PAPAGEORGAKIS, 1962) suggest that there is considerable H_2O present in the structure.

The last difference Fourier synthesis showed a very steep and rugged topography of equally intense positive and negative peaks distributed randomly over the unit cell.

Discussion of the structure

The structure of wenkite (Fig. 3, 4) resembles that of zeolites (SMITH, 1963; FISCHER and MEIER, 1965). It is an open framework with large channels which contain the cations and the sulfate group.

Framework (Fig. 4–7)

The building unit of the Si/Al framework is the same hexagonal cavity which is found in gmelinite (FISCHER, 1960), cancrinite (JAR-

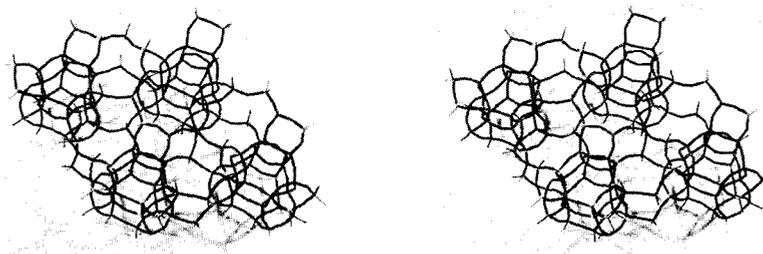


Fig. 4. Stereoscopic pair of photographs of the Al-Si framework of wenkite. A unit cell of the ordered basic structure ($P31m$) is shown

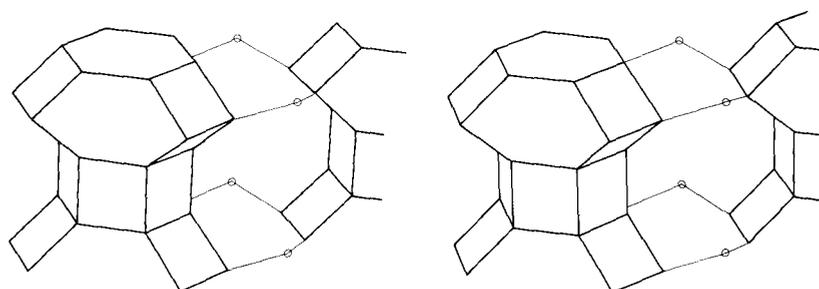


Fig. 5. The framework of wenkite represented as T polyhedron. Notice the hexagonal building unit which is also found in gmelinite and cancrinite

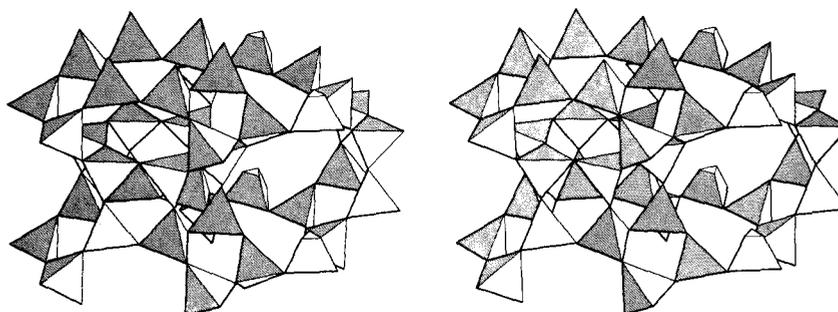


Fig. 6. Stereoscopic pair of drawings of the tetrahedral interrupted framework of wenkite. The truncated corners indicate oxygen atoms which are not bonded in the framework [T(2)]

CHOW, 1965) or in the synthetic zeolite L (BARRER and VILLIGER, 1969). Six-membered rings of tetrahedra are connected in alternate layers directly and through insertion of six additional bridging tetrahedra, causing a trigonal distortion of those channels which extend parallel

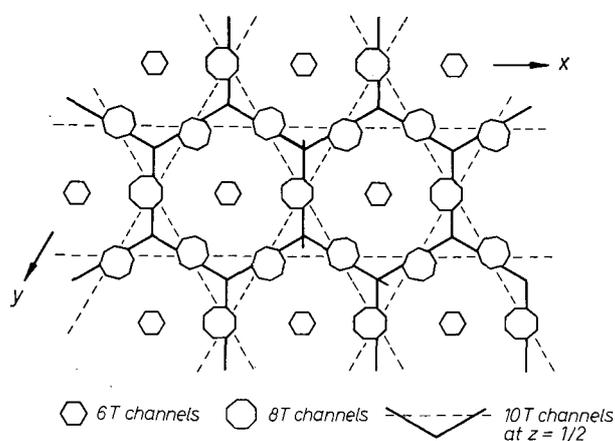


Fig. 7. Schematic representation of the three channel systems

Table 4. Selected interatomic distances assuming that Ba(1), Ba(2), Ca, S and T(1) are on basal mirror planes

Atoms	distance	multiplicity	atoms	distance	multiplicity
Ba(1)—O(3)	3.313(12) Å	6	T(1)—O(1)	1.665(7) Å	1
—O(5)	2.838(13)	6	—O(2)	1.693(14)	1
			—O(4)	1.684(10)	2
			average	1.682	
Ba(2)—O(1)	2.793(12)	1	T(2)—O(2)	1.688(13)	3
—O(2)	2.975(13)	2	—OH(6)	1.633(27)	1
—O(3)	2.846(12)	2	average	1.674	
—O(4)	3.201(9)	4	T(3)—O(3)	1.671(6)	1
—O(8)	2.51(6)	1	—O(4)	1.691(10)	1
Ca—O(4)	2.68(10)	2	—O(5)	1.674(6)	1
—OH(6)	2.39(2)	1	—O(7)	1.660(7)	1
—O(7)	2.43(2)	1	average	1.674	
—O(9) ₁	2.57(4)	1			
—O(9) ₂	2.72(4)	1			
—O(10)	2.64(7)	1			
S—O(8)	1.46(6)	1			
—O(9)	1.45(3)	2			
—O(10)	1.42(3)	1			
average	1.44(4)				

to the z axis. The repeat period of the building unit in the channels is $7.5 \text{ \AA} = c$ and the diameter of the six-membered rings is about 5 \AA . These hexagonal channels are linked in none of the ways which have

been discussed by BARRER and VILLIGER (1969) but by insertion of an additional tetrahedron T(2). Only three corners of this tetrahedron are linked in the framework, the fourth one is free and probably occupied by an OH group. The free corner is pointing upwards and downwards randomly, thus producing a $P\bar{6}2m$ symmetry from a $P31m$ basic structure. Because of this partially bonded tetrahedron, wenkite possesses an *interrupted framework* with very large additional cavities between the hexagonal channels.

These cavities are strongly distorted. They connect to form a set of channels with eight-membered rings parallel to the z axis (at $x = \frac{1}{2}$, $y = 0$) and a set of channels with slightly kinked ten-membered rings parallel to the x axis (at $y = \frac{1}{2}$, $z = \frac{1}{2}$). The three channel systems are shown schematically in Fig. 7. The structure is open with large spaces for cations. The diameter of the six-membered rings is about 5 Å, of the eight-membered rings $6\frac{1}{2}$ Å and of the ten-membered rings 8 Å. Thus the wenkite framework should have excellent ion-exchange properties.

All T—O distances of this interrupted framework are similar and average to 1.675 Å (Table 4). This suggests disorder of the 8 Al and 12 Si atoms on all three T positions.

Cations

The *cations and the sulfate group* occupy positions in the channels. The channel with six-membered rings is highly symmetrical (approaching $6/mmm$) and Ba(1) occupies the largest cage in it at 000. It has a twelfold coordination (Fig. 8), with an average Ba(1)—O distance of 3.07 Å and a shortest Ba(1)—O(5) distance of 2.84 Å. Ba(1) is

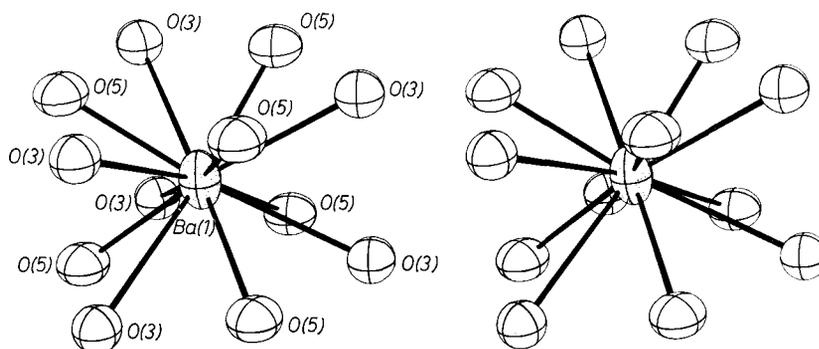


Fig. 8. Stereoscopic pair of ORTEP drawings showing the coordination of Ba(1). The ellipsoids give probability contours of 98%

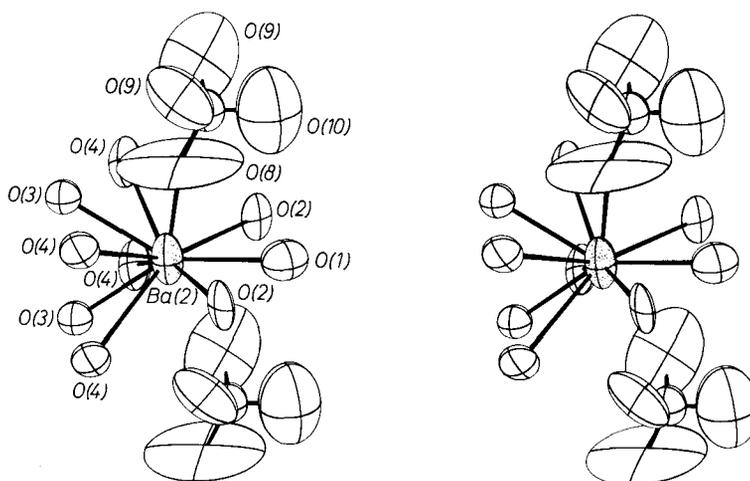


Fig. 9. Stereoscopic pair of drawings showing the coordination of Ba(2) and the BaSO₄ chain extending parallel to the *z* axis. 98% probability contours

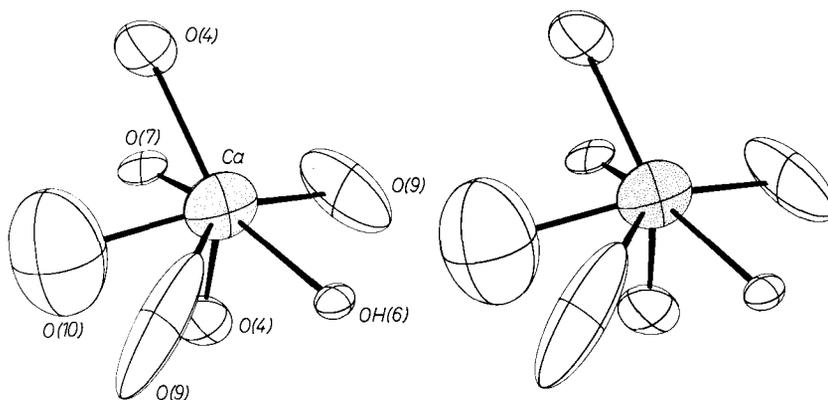


Fig. 10. Stereoscopic pair of drawings showing the irregular coordination of Ca. 98% probability contours

either vibrating strongly along the channel axis (*z*) or statistically occupying two positions close to the mirror plane. A water molecule is probably located at $00\frac{1}{2}$. The channels with eight-membered rings have a much lower symmetry ($2/m$), and atoms in them [Ba(2), Ca, SO₄] have an irregular coordination (Figs. 9 and 10).

At least some of the Ba—O and Ca—O distances [from Table 4: Ba(2)—O(1) = 2.79 Å, Ba(2)—O(8) = 2.50 Å, Ca—OH(6) = 2.39 Å, Ca—O(7) = 2.43 Å] are shorter than we would expect from published

average ionic radii (SHANNON and PREWITT, 1969) indicating strong bonds and polarization. Ba(2) is most closely bonded to the SO_4 tetrahedron, thus producing BaSO_4 molecules (Fig. 9) slightly resembling the barite structure (SAHL, 1963). Interestingly enough, part of the barium in the only other known Ba- SO_4 silicate innelite is also closely associated with the sulfate group (CHERNOV *et al.*, 1971). A bent chain of BaSO_4 molecules extends parallel to the z axis (at $x = 0$, $y = \frac{1}{2}$) in the center of the channels with 8-membered rings. SO_4 tetrahedra are randomly pointing upwards and downwards like the T(2) tetrahedron. The oxygen atoms of the SO_4 groups have much larger temperature factors than the framework oxygen, indicating a rather loose connection in the structure. These large BaSO_4 molecules and the Ba(1) atoms plug the channels. Thus, although the framework contains three systems of very large channels, it is unlikely that wenkite will show the exchange properties of zeolites. No exchange experiments have been done, but PAPAGEORGAKIS (1962) showed that no water is lost in heating to 500°C but a slow and gradual loss occurs at higher temperatures (up to 1100°C). It would be interesting to investigate the properties of the wenkite framework which is not filled with barium.

Symmetry⁴

The true symmetry of wenkite is $P31m$. The structure has been refined with averaged $P6/mmm$ diffraction data in the $P\bar{6}2m$ space group. Neither physical properties nor diffraction effects indicate any deviation from this pseudosymmetry. The true symmetry is only revealed by large anisotropic temperature factors of atoms on the basal mirror plane which is probably due to positional disorder, by Si(2), which is close to the mirror plane, and by the T(2) and SO_4 tetrahedra which point in half occupancy upwards and downwards. Thus, although even small fragments exhibit $P\bar{6}2m$ symmetry, on a submicroscopic scale wenkite consists of small domains which are in a (0001) twin relation. If these domains are of the size of the unit cell, we would call it disorder on two separate sites, each one-half occupied. If the domains are larger, then they should be called submicroscopical twins. The hexagonal and the tetragonal systems seem to favor such twinning because the lattices of host and twin coincide. Twinning does not affect the framework and thus leaves the lattice constants unchanged.

⁴ Compare also note at the end of the paper.

Chemical formula

The formula which is suggested from the x-ray structure refinement is $\text{Ba}_4(\text{Ca}_{0.9}\square_{0.1})_6 \cdot (\text{Al, Si})_{20}\text{O}_{39}(\text{OH})_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$. In Table 1 it is compared with formulas derived from chemical analyses and appears to be an average. The Ba(2) and the SO_4 sites are fully occupied; the Ca site contains considerable vacancies or substitution by K and Na (see new analysis: Table 1, SCHWANDER, 1972), and so probably does the Ba(1) site. A small amount of water may be on the partially occupied $00\frac{1}{2}$ site and in other positions, but its determination was beyond the resolution of the data. The density which has been calculated from the structural formula (without water) is $3.16 \text{ g} \cdot \text{cm}^{-3}$ which agrees well with the experimentally determined value of $3.10 \text{ g} \cdot \text{cm}^{-3}$. The positive charge of +4.8 in the structural formula can be balanced either by adding OH, which could not be located, through substitution of Ca by Na or K or by adjusting the rather uncertain Si/Al ratio.

Acknowledgements

We thank Dr. M. FEHLMANN for collecting the intensity data on the Hilger-Watts diffractometer at Monsanto (Zurich). Stimulating discussions with Professors W. MEIER, A. NIGGLI, ADOLF PABST and Dr. S. GHOSE, support from the Miller Institute for Basic Research and from the Computer Center at Berkeley are gratefully acknowledged.

Note added in proofs. Since the manuscript was submitted the domain structure of wenkite has been further investigated. The possibility of submicroscopic domains which was suggested on structural grounds has been confirmed experimentally with transmission electron microscopy. High-voltage dark-field electron micrographs display smoothly curved boundaries resembling APB's about 50–100 Å apart and polysynthetic lamellae resembling twins spaced about 100 Å (LEE, 1973; WENK and LEE, 1972). The antiphase domains could only be imaged with the weak super reflections h , k , and l uneven which were observed in electron-diffraction patterns and in extremely strongly exposed precession photographs. The superreflections, which were not noticed before, show hexagonal $P6/mmm$ symmetry and double x and z axes.

References

- R. M. BARRER and H. VILLIGER (1969), The crystal structure of the synthetic zeolite L. *Z. Kristallogr.* **128**, 352–370.
W. R. BUSING, K. O. MARTIN and H. A. LEVY (1962), A FORTRAN crystallographic function and error program. ORNL-TM-305.
A. N. CHERNOV, V. V. ILYOKHIN, B. A. MAKSIMOV, and N. V. BELOV (1971), Crystal structure of innelite $\text{Na}_2\text{Ba}_3(\text{Ba, K, Mn})(\text{Ca, Na})\text{Ti}(\text{TiO}_2)_2[\text{Si}_2\text{O}_7]_2$

- (SO₄)₂. *Kristallografiya* **16**, 87–92; *Soviet Physics—Crystallography* **16**, 65–69.
- D. T. CROMER (1965), Anomalous dispersion corrections computed from self-consistent field relativistic Dirac-Slater wave functions. *Acta Crystallogr.* **18**, 17–23.
- D. T. CROMER and J. MANN (1968), X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr. A* **24**, 321–324.
- K. F. FISCHER (1960), Strukturuntersuchung von Gmelinit. *Fortschr. Miner.* **38**, 201.
- K. F. FISCHER und W. M. MEIER (1965), Kristallchemie der Zeolithe, eine Zusammenfassung neuerer Ergebnisse. *Fortschr. Miner.* **42**, 50–86.
- O. JARCHOW (1965), Atomanordnung und Strukturverfeinerung von Cancrinit. *Z. Kristallogr.* **122**, 407–421.
- FLORENCE LEE (1973), The submicroscopic structure of wenkite (an electron microscopy study). M. A. thesis Univ. of California, Berkeley.
- J. PAPAGEORGAKIS (1959), Ein neues Bariummineral des Marmors von Candoglia in der unteren Val d'Ossola. *Schweiz. Mineral. Petrogr. Mitt.* **39**, 333–335.
- J. PAPAGEORGAKIS (1961), Marmore und Kalksilikatfelse der Zone Ivrea-Verbano zwischen Ascona und Candoglia. *Schweiz. Mineral. Petrogr. Mitt.* **41**, 157–254.
- J. PAPAGEORGAKIS (1962), Wenkit, ein neues Mineral von Candoglia. *Schweiz. Mineral. Petrogr. Mitt.* **42**, 269–274.
- K. SAHL (1963), Die Verfeinerung der Kristallstrukturen von PbCl₂ (Cotunnit), BaCl₂, PbSO₄ (Anglesit) und BaSO₄ (Baryt). *Beitr. Mineral. Petrogr.* **9**, 111–132.
- R. D. SHANNON and C. T. PREWITT (1969), Effective ionic radii in oxides and fluorides. *Acta Crystallogr. B* **25**, 925–946.
- J. V. SMITH (1963), Structural classification of zeolites. *Mineral. Soc. America Spec. Paper* **1**, 281–290.
- H.-R. WENK (1966), New x-ray data for wenkite. *Schweiz. Mineral. Petrogr. Mitt.* **46**, 85–88.
- H. R. WENK and FLORENCE LEE (1972), Wenkite, an interrupted framework silicate with domain structure. *Geol. Soc. Amer. abstr.* **417**, 703–704.