

The crystal structure of chantalite, $\text{CaAl}_2(\text{OH})_4\text{SiO}_4$ *

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Received: November 27, 1978

Abstract. Chantalite, $\text{CaAl}_2(\text{OH})_4\text{SiO}_4$ is tetragonal: $I4_1/a$, $a = 4.952(1)$, $c = 23.275(6)$ Å, $Z = 4$, $D_x = 2.97$ g/cm³, $D_m = 2.9$ g/cm³, $\mu(\text{MoK}\alpha) = 15.9$ cm⁻¹. A structure proposal was obtained by crystal chemical reasoning. From counter diffractometer data the structure was refined anisotropically to a final R value of 0.048 for 357 contributing reflections. Chantalite can be described by the crystal chemical formula $\text{Ca}^{[8]}\text{Al}^{[6]}_2(\text{OH})_4\text{Si}^{[4]}\text{O}_4$. It is characterized by $\text{AlO}_2(\text{OH})_4$ octahedra sharing edges to form chains linked by isolated SiO_4 tetrahedra and $\text{CaO}_4(\text{OH})_4$ polyhedra. Application of the Donnay-Allmann empirical method of recognizing O^{2-} , $(\text{OH})^-$, and H_2O in crystal structures verified the presence of four hydroxyl groups per formula unit.

Chantalite is structurally related to isoelectronic retzian $\text{YMn}_2(\text{OH})_4\text{AsO}_4$ in which the same type of coordination polyhedra are found but with a different type of stacking.

Introduction

Chantalite, $\text{CaAl}_2(\text{OH})_4\text{SiO}_4$ is a new silicate mineral found in rodingitic dykes from an ophiolitic zone in the Taurus Mountains, southwest Turkey. Its mineralogical data have been reported elsewhere [1]. This paper reports its crystal structure with particular emphasis on verifying the role of hydrogen as part of hydroxyl groups in the structure.

Experimental

Single crystals were isolated from crushed rock samples containing mostly prehnite and vuagnatite. Reciprocal-lattice explorer and Weissenberg films

* Dedicated to Prof. W. Nowacki on occasion of his 70th birthday

indicated a tetragonal unit cell with $a = 4.952(1)$ and $c = 23.275(6)$ Å (refined from 2θ values of several high angle reflections using the PARAM program [2]). Laue symmetry and systematic absences of the type $h + k + l \neq 2n$ for hkl , $h \neq 2n$ for $hk0$ and $l \neq 4n$ for $00l$ lead uniquely to space group $I4_1/a$.

Intensities of a plate like crystal ($0.1 \times 0.1 \times 0.02$ mm) were measured on a Philips PW 1100 computer-controlled four-circle diffractometer using graphite-monochromatized $\text{MoK}\alpha$ radiation in the $\theta - 2\theta$ scan mode. A total of 437 non-equivalent reflections was measured out to $\sin \theta/\lambda = 0.96 \text{ \AA}^{-1}$ of which 241 had I_{obs} greater than 2σ . In view of the small μR value, an absorption correction was considered unnecessary.

It was possible to formulate structure proposals by crystal chemical reasoning based on the following considerations: a) the Si–O, Al–O, and Ca–O distances in chantalite should be similar to those found in vuagnatite, $\text{CaAl}(\text{OH})\text{SiO}_4$ [3]; b) the overall chemical formula suggests that chantalite should be a nesosilicate with isolated SiO_4 tetrahedra; c) further and in analogy to vuagnatite, the presence of AlO_6 octahedra and CaO_8 polyhedra could be assumed. Given the unusual cell dimensions and the high symmetry, only two models for the atomic arrangement in the structure are possible of which one was found to be in acceptable agreement with the observed powder diffraction intensities. The Ca, Al, Si, and O atom positions of the acceptable model were used as starting values for a full-matrix refinement of the single crystal data using programs of the X-ray system [2]. The scattering factors of Ca, Al, Si, O [4], and H [5] were used in the refinements. Anomalous dispersion corrections for Ca, Al, and Si [6] were also applied. The system of weights used was $w = 1/\sigma_{\text{F}_{\text{obs}}}^2$.

The positions of Ca, Al, Si, and O were first refined with isotropic and later with anisotropic temperature factors. A difference Fourier map showed a peak position with features characteristic of a hydrogen atom. This hydrogen, bound to O(2), is located as in vuagnatite [3] on oxygens belonging to the edges shared by AlO_6 octahedra.

Attempts at refining the hydrogen position with a fixed isotropic temperature factor produced a small shift in the observed O(2)–H distance from 1.05 to 0.75 Å. For this reason, in the final stage of refinement, the hydrogen was kept fixed in the position observed with an isotropic temperature factor¹.

The final $R(= \Sigma |\Delta F|/\Sigma |F_o|)$ was 0.048 for 357 reflexions with $I \geq 2\sigma_I$ (including those reflexions calculating greater than this less – than threshold). Atomic positional and thermal parameters are given in Table 1. Interatomic distances and angles calculated using the program BONDLA (X-Ray 1976) [2] are given in Tables 2 and 3.

¹ Lists of structure factors obtained during the final refinement have been given to the editor.

Table 1. Atomic positional and thermal parameters for Chantalite. Space group $I4_1/a$ with symmetry center at the origin. Anisotropic temperature factor expressed as $T = \exp(-2\pi^2 \sum_i \sum_j U_{ij} a_i a_j)$ where $a_1 = ha^*$, $a_2 = kb^*$, etc., U_{ij} is $\times 10^3$. Isotropic temperature factor expressed as $T = \exp(-2\pi^2 U s^2)$, where $s = 1/d_{hkl}$, U is $\times 10^3$. E.s.d.'s in parentheses refer to last significant figures

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca (4b)	0	0.25	0.625	10(1)	U_{11}	8(1)	0	0	0
Al (8e)	0	0.25	0.4653(1)	10(1)	6(1)	8(1)	1(1)	0	0
Si (4a)	0	0.25	0.125	6(1)	U_{11}	10(2)	0	0	0
O(1)(16f)	0.1310(6)	0.4967(6)	0.1631(1)	7(2)	10(2)	11(2)	-1(1)	0(1)	5(1)
O(2)(16f)	0.1891(6)	0.9219(6)	0.4703(1)	11(2)	7(2)	5(2)	1(1)	0(1)	1(1)
H (16f)	0.390	0.970	0.460	15					

Table 2. Chantalite. Interatomic distances (Å) within the polyhedra and data for the hydrogen bond. For the notation of the atoms see Fig. 2

Si–O(1) [4 ×]	1.642(3)	Ca–O(1) [4 ×]	2.386(3)
Al–O(1) [2 ×]	1.864(3)	Ca–O(2) [4 ×]	2.554(3)
Al–O(2) [2 ×]	1.960(3)	H–O(2)	1.05
Al–O(2') [2 ×]	1.879(3)	H–O(1)	2.20
		O(1)–O(2)	3.218(4)
		∠ O(2)–H...O(1)	161°

Discussion

As seen in Fig. 1 the chantalite structure is built up of CaO_8 , AlO_6 , and SiO_4 polyhedra. The crystal chemical formula of chantalite is therefore $\text{Ca}^{[8]}\text{Al}^{[6]}\text{Si}^{[4]}\text{O}_4$. Each AlO_6 octahedron shares edges with two neighboring AlO_6 octahedra to form zig-zag chains perpendicular to the *c* axis. Due to the presence of the 4_1 axis, there are four chains in one unit cell, one on top of the other, each being perpendicular to the next. The *z* coordinates for the Al atoms in the octahedron chains are approximately 0, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$. The zig-zag chains are linked by isolated SiO_4 tetrahedra and CaO_8 polyhedra which have their centers at $z = \frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$, and $\frac{7}{8}$. Between parallel AlO_6 zig-zag chains there are channels in which the hydrogen bonds O(2)–H...O(1) are located. Figure 2 shows the individual polyhedra and illustrates the atom notation used. The interatomic distances and angles are listed in Tables 2 and 3.

The chemical formula of chantalite, first suggested by electron microprobe analysis and later confirmed by the crystal structure determination, indicates a normal valence compound with four OH groups per formula unit. Independent evidence for the presence of these OH groups was given by the

Table 3. Polyhedral edge lengths (Å) and angles (°) in chantalite. For the notation of the atoms see Figure 2

	Distances (Å)	Angles (°)	Edges shared with
O(1)–Si–O(1) } O(1 ¹)–Si–O(1 ¹) }	2.766(4)	114.7(1)	–
O(1)–Si–O(1 ¹) [4 ×]	2.639(4)	106.9(1)	–
	ave. 2.681	ave. 109.5	
O(2) –Al–O(2 ¹) } O(2)* –Al–O(2 ¹)* }	2.452(4)	79.4(1)	AlO ₆
O(2)* –Al–O(2 ¹) } O(2) –Al–O(2 ¹)* }	2.835(4)	95.2(1)	–
O(1) –Al–O(2) } O(1)* –Al–O(2)* }	2.744(4)	94.3(1)	CaO ₈
O(1)* –Al–O(2) } O(1) –Al–O(2)* }	2.655(4)	90.3(1)	–
O(1) –Al–O(2 ¹) } O(1)* –Al–O(2 ¹)* }	2.740(4)	91.5(1)	–
O(2 ¹) –Al–O(2 ¹)*	2.531(4)	80.4(1)	CaO ₈
O(1) –Al–O(1)*	2.766(4)	98.5(2)	–
	ave. 2.679	ave. 90.0	
O(2) –Ca–O(2)* } O(2 ¹) –Ca–O(2 ¹)* }	2.531(4)	59.9(1)	AlO ₆
O(1) –Ca–O(2) } O(1)* –Ca–O(2)* }	2.744(4)	67.4(1)	AlO ₆
O(1 ¹) –Ca–O(2 ¹)* } O(1 ¹)* –Ca–O(2 ¹) }			
O(1) –Ca–O(1 ¹) } O(1) –Ca–O(1 ¹)* }	3.600(4)	97.9(1)	–
O(1)* –Ca–O(1 ¹) } O(1)* –Ca–O(1 ¹)* }			
O(1) –Ca–O(2)* } O(1)* –Ca–O(2) }	3.008(4)	74.9(1)	–
O(1 ¹) –Ca–O(2 ¹)* } O(1 ¹)* –Ca–O(2 ¹) }			
O(1) –Ca–O(2 ¹) } O(1)* –Ca–O(2 ¹)* }	3.255(4)	82.3(1)	–
O(1 ¹) –Ca–O(2) } O(1 ¹)* –Ca–O(2)* }			
	ave. 3.083	ave. 78.3	

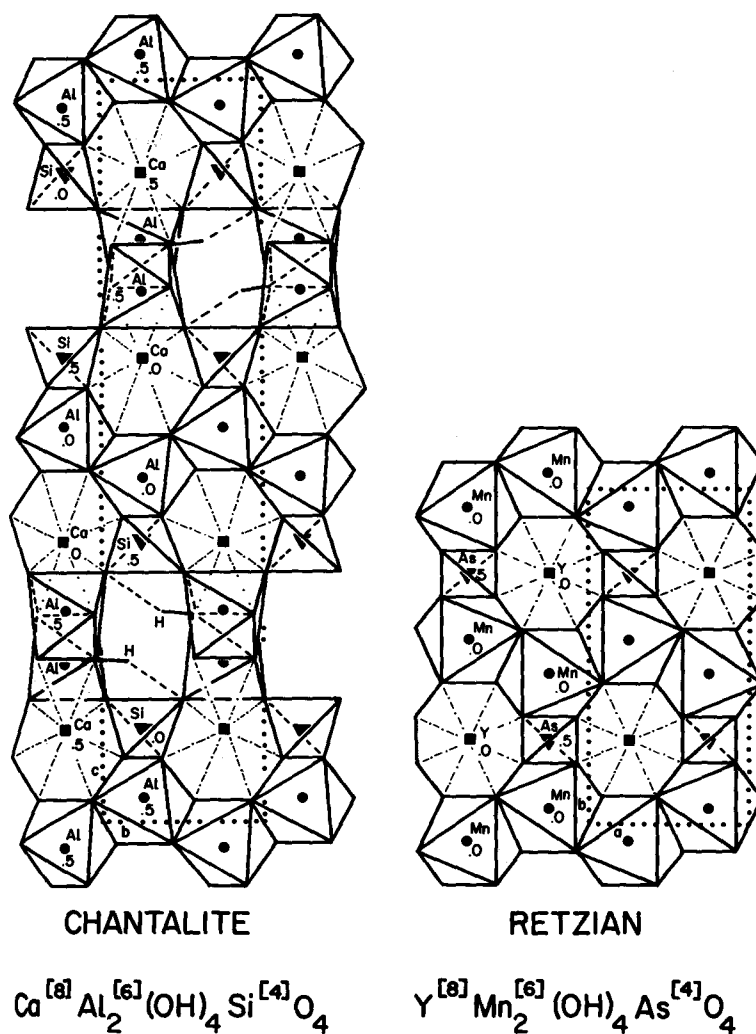


Fig. 1. The structure of chantalite as compared with the structure of isoelectronic retzian built up of polyhedra of the same kind

valence summation procedure proposed by Donnay and Allmann [7]. The results of this procedure, shown in Table 4, indicate that the hydrogen atom is closer to O(2) than to O(1) and that the hydrogen bond extends to O(1) with values Σv_{cation} for O^{2-} and $(\text{OH})^{1-}$ of 1.89 and 1.11 respectively. This result for chantalite is in agreement with those for other hydroxo-aluminosilicates where the $-\text{OH}$ group is always bound to Al.

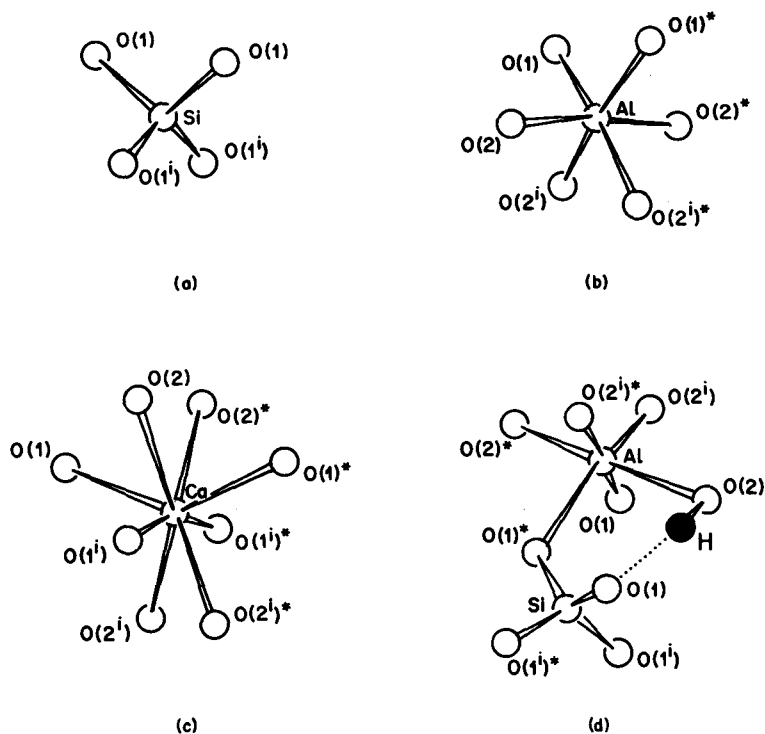


Fig. 2 a—d. Schematic representation of the a Si tetrahedron b Al octahedron, c Ca polyhedron and d hydrogen bond present in chantalite

The numerical data for the hydrogen bond are given in Table 2. Oxygen in these type of compounds prefers a tetrahedral environment. Considering the H atom as forming part of a coordination polyhedra, one may describe the coordination of O(2) as tetrahedral (2 Al, 1 Ca, and 1 H). O(1) in general is also surrounded by a tetrahedron (Ca, Al, Si and H), but this is strongly elongated in the direction of the H atom ($d_{O(1)...H} = 2.20 \text{ \AA}$) and should be better described as a trigonal pyramid. The O(1) atoms shift toward the plane formed by Ca, Al, and Si (average value for $M-O-M$ angle is 118.3°).

The high symmetry of the crystal structure of chantalite is partly reflected in the symmetry of the SiO_4 , AlO_6 , and CaO_8 polyhedra shown in Figs 2 and 3. The SiO_4 tetrahedra are characterized by 4 point symmetry and have accordingly equal Si—O(1) distances and only 2 types of O(1)—Si—O(1) angles (Tables 1 and 2).

The AlO_6 octahedra are centered on the 2-fold axis along c giving three pairs of different Al—O distances. Further as shown in Table 3 the 12 edges

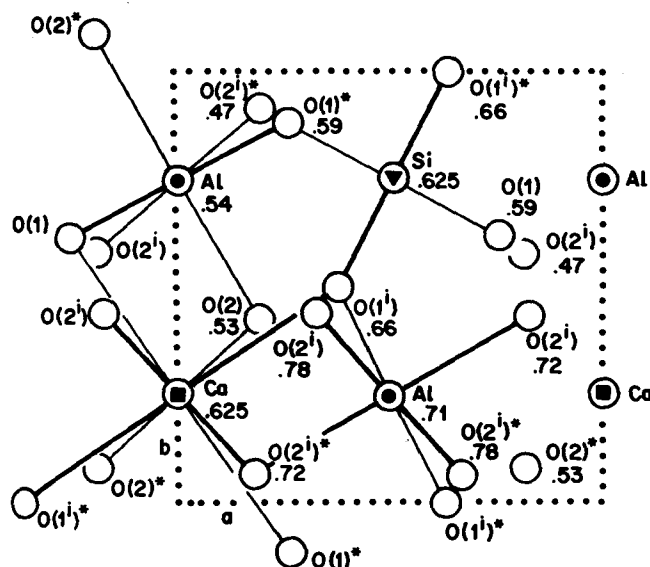


Fig. 3. Projection along the c axis of chantalite. Only atoms with $0.47 \leq z \leq 0.78$ are shown. Heavy lines indicate oxygen-metal bonds where $z_O > z_M$ and thin lines where $z_O < z_M$.

of the octahedron can be divided into 5 pairs and two additional edges with distinct values.

The CaO_8 bisdisphenoidal dodecahedron formed by O(1) and O(2), has also $\bar{4}$ symmetry. The eight Ca–O distances can be divided into 2 groups of equal distances (Figs. 2 and 3).

From the crystal chemical point of view chantalite $\text{CaAl}_2(\text{OH})_4\text{SiO}_4$ may be compared with vuagnatite $\text{CaAl}(\text{OH})\text{SiO}_4$. Both are normal valence compounds with structures which in principle could be formed as well with compounds having other tetrahedral anion complexes. The formulae of possible isoelectronic² sulphates and phosphates (or arsenates) are listed in Table 5. Those for which compounds are actually known have been framed. The crystal structures of these compounds can be classified according to the kinds of cation-oxygen coordination. In the ideal case where there are no deformations one should expect tetrahedra with 4 coordination, trigonal bipyramids with 5 coordination, octahedra with 6 coordination, and square antiprisms with 8 coordination. The kind of polyhedra formed depends on

² Here isoelectronic compounds are defined as those having the same number of valence electrons. Cu atoms in octahedral surroundings always provide two valence electrons. In the case of transition elements the number of valence electrons is determined from the formal cation charges according to Table 5.

Table 4. Donnay-Allmann valence summation procedure applied to chantalite

	Ca		Al		Si		Σv_{cation}	Σv_{cation} corrected for H-bonding*	Anion chemistry
	Measured bond length	Modified bond valence	Measured bond length	Modified bond valence	Measured bond length	Modified bond valence			
O(1)	4 × 2.386	0.279	2 × 1.864	0.555	4 × 1.642	1.0	1.834	1.89	O ²⁻
O(2)	4 × 2.554	0.223	2 × 1.879 2 × 1.960	0.532 0.418			1.173	1.11	(OH) ¹⁻
Σv_{anions} Cation chemistry	2.008		2.010		4.0				
\bar{L}	2.470		1.901		1.642				sum of bond valences emanating from surrounding cations and anions
L_{max}	3.25		2.26		2.13				average of measured bond length
$p = \frac{\bar{L}}{L_{\text{max}} - \bar{L}}$	3.17		5.29		3.36				theoretical maximum bond length
v_i	$\frac{2}{6}$		$\frac{3}{6}$		$\frac{4}{4}$				ideal bond valence according to the Pauling concept

* considering the valence correction corresponding to an O(1)...O(2) distance equal to 3.2 Å

Table 5. Formulae of isoelectronic normal valence compounds of the type $M_2(OH)XO_4$ and $M_3(OH)_4XO_4$. Formulae for which compounds are known have been framed. The roman numerals correspond to the formal charges of the cations

	$M_2(OH)XO_4$	$M_3(OH)_4XO_4$
Silicate	$M^II M^{III}(OH)SiO_4$	$M^II M_2^{III}(OH)_4SiO_4$
Phosphate or Arsenate	$M^I M^{III}(OH)PO_4$	$M^I M_2^{III}(OH)_4PO_4$
	$M_2^{II}(OH)PO_4$	$M_2^{II} M^{III}(OH)_4AsO_4$
Sulfate	$M^I M^{II}(OH)SO_4$	$M_3^{II}(OH)_4SO_4$
		$M^I M^II M^{III}(OH)_4SO_4$

the cation-oxygen radius ratio according to Pauling's first rule [8]. The known structure types for $M_2(XO_4)(OH)$ and $M_3(XO_4)(OH)_4$ compounds together with isotypic compounds are given in Table 6. The structure types are arranged according to the cation coordinations. The polyhedra are nearly always distorted, in particular, polyhedra with high coordination. For the $M_2(XO_4)(OH)$ compounds eight structure types are known, one or two possibilities for nearly every choice of cation coordination. With the $M_3(XO_4)(OH)_4$ compounds only five structure types are known. Still missing is a structure type containing only 6- and 4-coordinated cations which could, for example, occur with (hypothetical) $BeAl_2SiO_4(OH)_4$.

For $M_3(OH)_4XO_4$ compounds with cations in 8 and 6 coordination there are two entries: chantalite and retzian $YMn_2(OH)_4AsO_4$. From Fig. 1 it can be seen that both structures may be considered as stacking variations of a particular kind. One may consider the chantalite structure as consisting of four identical segments which are stacked, one on top of the other along the c axis according to the symmetry requirements of the 4_1 symmetry axis. Each segment consists of AlO_6 zig-zag chains linked to SiO_4 and CaO_8 polyhedra. In retzian there are only two such segments of the same construction along the b axis; however, the upper one is a mirror image of the lower one.

One may also compare chantalite with the structure of prosopite $CaAl_2(OH)_4F_4$ [25] where the SiO_4 tetrahedron is replaced by four F^- . The structure of prosopite differs from chantalite in that there are now not only AlO_6 zig-zag chains (linked in a different way) but also chains of CaO_8 polyhedra.

We wish to thank Prof. K. Yvon and Dr. M. G. Vincent for valuable discussions and Mrs. K. Cenzał for building a model of chantalite.

Table 6. Types and isotypes of $M_2(XO_4)OH$ and $M_3(XO_4)(OH)_4$ compounds, only those with tetrahedral anions XO_4 and hydroxyl groups (OH) being considered. The structure types are classified according to the coordinations of the cations

		$M_2(XO_4)(OH)$	
Cation coordina- tions	Types	Isotypes	
[8] [6]	$Ca^{II}Cu^{II}(AsO_4)(OH)$	conichalcite [9]	$CaAl(SiO_4)(OH)$ [3] vuagnatite [3]
[8] [4]	$Ca^{II}Be^{IV}(PO_4)(OH)$	herderite [10, 11]	$CaB(SiO_4)(OH)$ [10] datolite [10]
[6] [5]	$Zn^{II}Zn^{II}(AsO_4)(OH)$	adamite [12]	$Cu_2(PO_4)(OH)$ [13] libethenite [13] $Cu_2(AsO_4)(OH)$ [14] oliveneite [14] $Mn_2(AsO_4)(OH)$ [15] eveite [15] $Co_2(AsO_4)(OH)$ [16] – [16]
[6] [4~5]	$(Mn, Fe)_2^{II}(PO_4)(OH)$	triploidite [17]	$Mn_2(AsO_4)(OH)$ [18] sarkinite [18]
[6] [4~5]	$Li^{I(4-5)}Al^{IV}(PO_4)(OH,F)$	amblygonite [19]	
[6] [4]	$Be^{IV}(Mn, Fe)^{II}(PO_4)(OH)$ $Be^{IV}Al^{IV}(SiO_4)(OH)$	väyrynenite [20] euclase [20]	
[5] [5]	$Zn^{II}_2(PO_4)(OH)$	tarbuttite [21]	
		$M_3(XO_4)(OH)_4$	
[8] [6]	$Y^{III}Mn_2^{II}(AsO_4)(OH)_4$ $Ca^{II}Al^{IV}(SiO_4)(OH)_4$	retzian [22] chantalite [22]	
[8] [4]	$Ca^{II}_2B^{IV}(AsO_4)(OH)_4$	cahnite [23]	
[6] [6]	$Cu_3^{II}(SO_4)(OH)_4$ $Mn_3^{II}(AsO_4)(OH)_4$	antlerite [24] flinkite [22]	

References

1. Sarp, H., Deferne, J., Liebich, B. W.: *Bull. Suisse Minéral. Pétrogr.* **57**, 149–156 (1977)
2. X-Ray System: Techn. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland 1976
3. McNear, E., Vincent, M. G., Parthé, E.: *Amer. Min.* **61**, 831–838 (1976)
4. Cromer, D. T., Mann, J. B.: *Acta Crystallogr.* **A24**, 321–324 (1968)
5. Stewart, R. F., Davidson, E. R., Simpson, W. T.: *J. Chem. Phys.* **42**, 3175–3187 (1965)
6. *International Tables for X-Ray Crystallography*. Vol. IV, p. 149. Birmingham: Kynoch Press 1974
7. Donnay, G., Allmann, R.: *Amer. Min.* **55**, 1003–1015 (1970)
8. Pauling, L.: *The Nature of the Chemical Bond*. Third Ed., p. 545. Ithaca: Cornell University Press 1960
9. Qurashi, M. M., Barnes, W. H.: *Can. Min.* **7**, 561–577 (1963)
10. Pavlov, P. V., Belov, N. V.: *Sov. Phys. Crystallogr.* **4**, 300–314 (1960)
11. Lager, G. A., Gibbs, G. V.: *Amer. Min.* **59**, 919–925 (1974)
12. Kokkoros, P.: *Z. Kristallogr.* **96A**, 417–434 (1937)
13. Walitzi, E. M.: *Miner. (Tschermaks) Petrogr. Mitt. Österr.* **8**, 614–624 (1963)
14. Toman, K.: *Acta Crystallogr.* **B33**, 2628–2631 (1977)
15. Moore, P. B., Smyth, J. R.: *Amer. Min.* **53**, 1841–1845 (1968)
16. Riffel, H., Zettler, F., Hess, H.: *Neues Jb. Miner., Mh.*, 514–517 (1975)
17. Waldrop, L.: *Z. Kristallogr.* **131**, 1–20 (1970)
18. Dalnegro, A., Giuseppetti, G., Martin Pozas, J. M.: *Miner. (Tschermaks) Petrogr. Mitt.* **21**, 246–260 (1971)
19. Baur, W. H.: *Acta Crystallogr.* **12**, 988–995 (1959)
20. Mrose, M. E., Appleman, D. E.: *Z. Kristallogr.* **117**, 16–36 (1962)
21. Cocco, G., Fanfani, L., Zanazzi, P. F.: *Z. Kristallogr.* **123**, 321–329 (1966)
22. Moore, P. B.: *Amer. Min.* **52**, 1603–1613 (1967)
23. Prewitt, C. T., Buerger, M. J.: *Amer. Min.* **46**, 1077–1085 (1961)
24. Finney, J. J., Araki, T.: *Nature* **197**, 70–71 (1963)
25. Pudovkina, Z. V., Pyatenko, Yu. A.: *Dokl. Akad. Nauk SSSR, Earth Sciences* **190**, 130–133 (1970)