American Mineralogist, Volume 69, pages 186–189, 1984

Willhendersonite, a new zeolite isostructural with chabazite

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Abstract

Willhendersonite ($KCaAl_3Si_3O_{12} \cdot 5H_2O$) is a new zeolite which is isostructural with chabazite, $(Ca,Na_2)[Al_2Si_4O_{12}] \cdot 6H_2O$. It occurs in the San Venanzo Quarry, Terni, Umbria, Italy in cavities of Quaternary lavas as "trellis-like" twinned aggregates, and as tabular crystals in a limestone xenolith from the Ettringer Bellerberg near Mayen, Eifel, Germany. It is triclinic, space group $P\bar{1}$. Single crystals from Mayen have the unit cell parameters $a = 9.23(2)$, $b = 9.21(2)$, $c = 9.52(2)$Å, $\alpha = 92.7(1)$, $\beta = 92.4(1)$, $\gamma = 90.1(1)$, $V = 808$Å^3, Z = 2. Willhendersonite is colorless and transparent, and it has a vitreous luster. The Mohs' hardness is 3. The measured and observed densities are 2.18 and 2.20 g/cm^3, respectively. Willhendersonite is optically biaxial with $\alpha = 1.505(3)$, $\beta = 1.511(3)$, $\gamma = 1.517(3)$ and $2V = 87(3)°$. The strongest lines in the diffraction pattern are: (d, I/I_o) 9.16, 100; 5.18, 30; 4.09, 40; 3.71, 30; 2.907, 60; 2.804, 50.

Introduction

In late 1980, Dr. William A. Henderson, Jr. of Stamford, Connecticut submitted a specimen to P.J.D. that he had obtained several years earlier from Mr. Gianni Porcellini of Rimini, Italy. Dr. Henderson had examined the specimen and had noted that it contained a mineral unknown to him. When this mineral could not be identified following a study of its optical properties, Dr. Henderson made it available for more extensive studies. Preliminary data then indicated that it was indeed a zeolite mineral not correlatable with other known species, and subsequent investigation confirmed this hypothesis. Entirely independently, material was discovered near Mayen, Eifel, Germany by Dr. G. Hentschel of Wiesbaden and its structure and properties were described by Tillmanns and Fischer (1981, 1982). In part with the aid of Dr. Glauco Gottardi (pers. comm.), the specimens from Italy and Germany were found to be of the same mineral. This paper is a description of results independently obtained in the separate investigations.

We are pleased to name this new species willhendersonite in honor of William A. Henderson, Jr. The new mineral and name were approved, prior to publication, by the I. M. A. Commission on New Minerals and Mineral Names. Type specimens of the Italian material are preserved in the Smithsonian Institution under catalog numbers NMNH 148655 (holotype) and NMNH 148656 (cotype).

X-ray crystallography

Single-crystal precession photographs of crystals from near Mayen show that willhendersonite is triclinic, space group $P\bar{1}$ or $P1$, with $a = 9.23(2)$, $b = 9.21(2)$, $c = 9.52(2)$Å, $\alpha = 92.7(1)$, $\beta = 92.4(1)$, and $\gamma = 90.1(1)°$ with Z = 2. $P\bar{1}$ was confirmed as the correct space group on the basis of a refinement of the structure (Tillmanns and Fischer, 1981, 1982). The refinement showed that will-

0003–004X/84/0102–0186$02.00

hendersonite is isostructural with chabazite, with complete Si–Al ordering as indicated by T–O distances; that is, the tektosilicate frameworks of both minerals are topologically similar, and consist in part, of double six-rings of tetrahedra, although the coordinations of Ca are very different.

Crystals from Terni were also studied using single-crystal techniques. Initial results appeared to indicate that the space group is *C2/m*, *C2*, or *Cm* with cell parameters $a = 12.95(4)$, $b = 12.96(3)$, $c = 9.45(2)$Å, and $\beta = 93.6(2)°$. Subsequent detailed examination of photographs of carefully selected, relatively perfect crystals showed that high-theta reflections on upper-level Weissenberg photographs are doubled. This confirmed that the crystals are triclinic, but twinned so as to give a diffraction pattern nearly identical to that of a monoclinic phase. Lattice parameters could not be directly measured for the triclinic unit cell because of complete overlap of most reflections. Cell parameters were obtained by transforming those of the monoclinic cell of the twins, yielding the parameters $a \simeq b = 9.16$, $c = 9.45$Å, $\alpha \simeq \beta = 92.5$, and $\gamma = 90.0°$. These parameters are very similar to those determined for the Mayen crystals although the cell translations are slightly smaller. The angles $\alpha = \beta$ are precisely the average of α and β for the Mayen crystals. The cell parameters are similar to those for chabazite which is apparently rhombohedral, with a $\simeq$ 9.40Å and $\alpha \simeq 92°$.

Table 1. X-ray powder diffraction data for willhendersonite. The *d*-values are calculated using triclinic unit cell parameters as transformed from refined, pseudomonoclinic parameters: a = b = 9.16, c = 9.45Å, $\alpha = \beta = 92.5$, $\gamma = 90.0°$.

d (Obs.)	d (Calc.)	hkl[1]	I/I_0[2]	d (Obs.)	I/I_0
9.16	9.15	100	100	2.429	10
5.18	5.18	111	30	2.264	15
4.71	4.72	002	5	2.209	1
4.57	4.58	200	5	2.163	15
4.27	4.27	$10\bar{2}$	2	2.078	10
4.09	4.09	210	40	2.042	10
	4.10	$1\bar{2}0$		2.004	5
3.93	3.93	$11\bar{2}$	20	1.979	5
3.82	3.84	$12\bar{1}$	20	1.875	5
	3.81	$1\bar{1}2$		1.845	15
3.71	3.73	$2\bar{1}1$	30	1.819	5
	3.70	112		1.794	15
3.06	3.06	$2\bar{1}2$	10	1.738	2
	3.05	300		1.692	20
3.01	3.02	$01\bar{3}$	10	1.570	5
	3.00	122			
	3.00	221		1.552	2
				1.515	2
2.907	2.900	$11\bar{3}$	60	1.489	2
	2.896	$3\bar{1}0$		1.459	2
2.804	2.809	$13\bar{1}$	50	1.426	1
	2.791	$1\bar{3}1$			
2.746	2.747	$1\bar{3}\bar{1}$	2	1.408	5
	2.747	$22\bar{2}$		1.387	2
				1.370	1
2.674	2.670	$2\bar{2}2$	1	1.314	2
2.538	2.541	$2\bar{3}0$	20	1.279	2
	2.539	203			
2.508	2.511	032	20	1.260	1
				1.220	1
				1.206	2
				1.191	1
				1.142	1

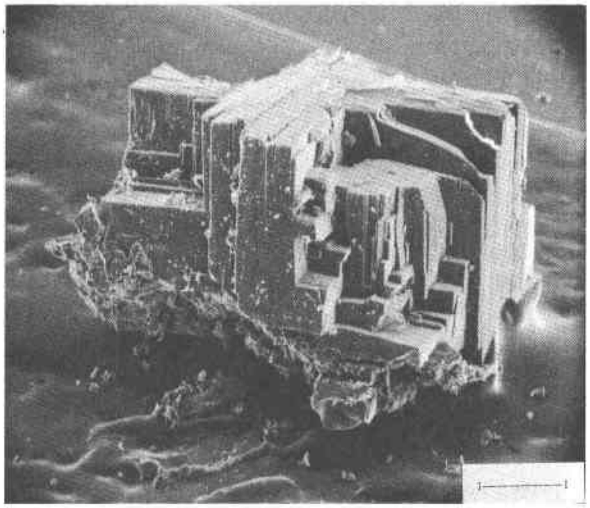

Fig. 1. SEM photomicrograph of willhendersonite twinned-crystal aggregate from Terni. Scale bar is 0.1 mm. NMNH #148655. The crystals are flattened on {001}, the narrow faces; each approximately perpendicular to {001}, are {100} and {010}.

Powder X-ray diffraction data are listed in Table 1. They were obtained using a polycrystalline sample of Terni crystal fragments mounted in a Gandolfi camera (114.6 mm diameter), with silicon as an internal standard. Because reflections related by the pseudomonoclinic symmetry could not be resolved, and because the unit cell is almost perfectly metrically monoclinic, the diffraction pattern was indexed using the pseudomonoclinic C-centered unit cell and a least-squares refinement was carried out leading to the cell parameters for the pseudomonoclinic unit cell as given above. The triclinic lattice parameters for the Terni material as listed above were obtained by transformation of those parameters.

Morphology and twinning

Willhendersonite from Terni occurs only in very characteristic twinned specimens which have a very striking appearance. As illustrated in Figure 1, the twinned aggregates (which are less than 1.0 mm in diameter) consist of crystals in three different orientations, each with faces approximately perpendicular to those of the others, and arranged in most specimens to have a "trellis-like" appearance. The faces of individual crystals are indexable using the triclinic cell as {100}, {010} and {001}. The crystals are tabular, flattened on {001}. (Crystals from Mayen display the same forms.) The twinning is apparently by rotation about [111], a pseudo three-fold axis in willhendersonite which is supposedly a three-fold axis or psuedo three-fold axis in other members of the chabazite group.

Additional complex twinning of two types was observed within each individual of the twins related by rotation around [111]. The single-crystal diffraction patterns clearly showed twinning by reflection across (001). In addition they demonstrated twinning either by reflection across $(1\bar{1}0)$ or rotation around $[1\bar{1}0]$ (referred to the triclinic cell). This plane and axis are the pseudosymmetry elements of the pseudomonoclinic cell which was referred to above, as compatible with a twinning relation consistent with Mallard's law. Because the twinned lattice displays only subtle differences from that of a monoclinic lattice, the twin law could not be distinguished between $(1\bar{1}0)$ or $[1\bar{1}0]$. However, this twinning was also observed optically as polysynthetically twinned lamellae with approximate composition plane $(1\bar{1}0)$.

Chemistry

Willhendersonite from Terni was chemically analyzed utilizing an ARL-SEMQ electron microprobe using an operating voltage of 15 kV and a beam current of 0.15 μA. Standards used were microcline (K), and bytownite (An_{80}) (Ca, Al, Si). The data were corrected using standard Bence–Albee correction factors. Elements analyzed for but not detected included Fe, Mg, Ti, Mn, Sr, Ba and F. Potassium determinations were made with a 40 μm beam spot to minimize volatilization. There was inadequate material for the direct determination of water. A microprobe scan indicated the absence of any other elements with atomic number greater than 9, except those reported herein. The resultant analysis is presented in Table 2. The data yield the empirical formula, based on 12 oxygens in the anhydrous part, of: $K_{0.90}Ca_{1.01}Al_{2.93}Si_{3.08}O_{12} \cdot 5.43H_2O$, which compares favorably with the ideal formula $KCaAl_3Si_3O_{12} \cdot 5H_2O$ (Z = 2), assuming some loss of K in analysis. The value for H_2O as determined by difference must of course be subject to a larger error than would be the case if it could have been determined directly. Because the amount of H_2O in zeolites may be variable and not consistent with space group equipoint requirements, this calculation of H_2O content is simply the best possible under the circumstances, and may be subject to change when samples large enough for water analysis are found.

Table 2. Microprobe analyses of willhendersonite.

	Willhendersonite Mayen		Willhendersonite Terni		$KCaAl_3Si_3O_{12} \cdot 5H_2O$
	wt %	atoms**	wt %	atoms**	wt %
K_2O	6.8	0.74	8.0	0.90	8.95
Na_2O	n.d.	--	tr.	--	0.00
CaO	11.6	1.06	10.7	1.01	10.65
Al_2O_3	30.1	3.02	28.1	2.93	29.05
SiO_2	35.5	3.02	34.8	3.08	34.26
H_2O	16.0*	4.54	18.4*	5.43	17.09
Total	100.0		100.0		100.0

*water by difference.

**number of atoms per 12 framework oxygen atoms.

Accuracy of data: ±3% of the amount present for Na, Ca, Al and Si
±10% of the amount present for K.

Material from Mayen was analyzed using energy dispersive techniques (15kV, 0.007 μA). Standards were Al_2O_3 for Al, SiO_2 for Si, wollastonite for Ca and a glass with the composition 35% $KAlSi_2O_6$ and 65% $MgCaSi_2O_6$ for K. ZAF corrections were applied with the program MAGIC by Colby (1980). The results of the analysis are also listed in Table 2. Water content was calculated by difference leading to the formula $K_{0.73}Ca_{1.03}Si_3Al_3O_{12} \cdot 4.5H_2O$. Some loss of potassium was observed in subsequent analyses of the same specimen. The crystal structure analysis (Tillmanns and Fischer, 1981, 1982) confirms the ordering of Al and Si, and K and Ca which is implied by this formula. A difference Fourier synthesis suggests that there are one potassium atom and five water molecules per formula unit. Thus the composition of willhendersonite from both occurrences is very close to the ideal one, $KCaSi_3Al_3O_{12} \cdot 5H_2O$. For comparison, the formula of chabazite is $(Ca, Na_2)[Al_2Si_4O_{12}] \cdot 6H_2O$.

Physical properties

Willhendersonite is colorless with vitreous luster on both crystal faces and cleavage fragments. The cleavages are perfect, parallel to {100},{010} and {001}, as indexed on the triclinic cell, and easily produced. These three cleavages are equivalent to the rhombohedral cleavage of rhombohedral and isostructural chabazite. The Mohs' hardness is approximately 3. Willhendersonite is quite brittle. The density, for Terni material, determined using heavy liquid techniques, is 2.18 g/cm^3, in excellent agreement with the density of 2.1(2)g/cm^3 measured for the Mayen material and with the calculated value of 2.20 g/cm^3. Willhendersonite is non-fluorescent in ultraviolet radiation.

Optically, willhendersonite is biaxial, but neither the optic sign nor the value of $2V$ could be accurately measured due to the complex polysynthetic twinning, small size and complex mosaic structure of the crystals from Terni. An attempt to measure $2V$ with the universal stage was made with fragments from a small twinned crystal. The results were ambiguous, giving two sets of data, one optically positive the other negative. One group yielded a $2V$ around Z of approximately 80°. The other group yielded a $2V$ around X of about 60°. These data imply that, like chabazite, the optical properties of willhendersonite may be nonuniform, or that perhaps the crystals examined were zoned in some unknown fashion. The measured indices of refraction are $\alpha = 1.507(2)$ and $\gamma = 1.517(2)$. The calculated value of β for these indices and a $2V$ of $+80°$ is 1.511, and for a $2V$ of $-60°$ is 1.514.

Complete optical properties could be determined on the

Mayen material, as it is untwinned. Measurements were made utilizing a spindle stage with internal refractometer (Medenbach, unpublished) by the double variation method, resulting in the values $\alpha = 1.505(3)$, $\beta = 1.511(3)$, $\gamma = 1.517(3)$, $2V = 87(3)°$ at 5920Å. These values are very close to those measured for crystals from Terni for $2V = 80°$. The orientation of the indicatrix relative to the crystal faces, is shown in a stereographic projection in Figure 2.

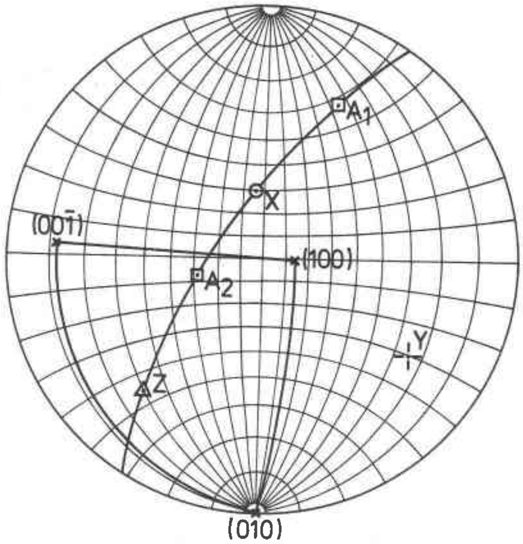

Fig. 2. Stereographic projection of relative positions of the crystal faces and optical indicatrix.

Occurrence

The type specimens of willhendersonite were found in 1979 by Mr. Gianni Porcellini of Rimini, Italy, and were called to our attention by Dr. William Henderson, for whom this species is named. The specimens were found in the "Vispi" Quarry, near the town of San Venanzo, in the Province of Terni, Umbria, Italy. The quarry, which is in Quaternary basic potassic lavas, was used for the procurement of road-building stone but it is now closed.

The surface of the holotype specimen is covered with microcrystals of zeolites and related species. The most dominant of these is phillipsite, which occurs as radiating sprays of colorless crystals formed contemporaneously with willhendersonite. The two minerals are intergrown, but without any obvious mutual orientation. Colorless spherules of thomsonite and white, frosted, translucent, anhedral blebs of apophyllite also occur, having formed subsequent to the willhendersonite and phillipsite. On an additional specimen, herein designated cotype, the surface of the matrix is coated with brown phlogopite, upon which occur crystals of phillipsite, thomsonite, melilite and willhendersonite. The sequence of formation is not clear except that melilite is the youngest phase.

Optical examination of thin sections produced from the matrices of these two specimens showed that they consist of forsterite, (15%) and clinopyroxene (30%) in a fine-grained groundmass of melilite, nepheline or kalsilite (50%) with 1% phlogopite marginal to the olivine, and 4% opaques. Also present are traces of perovskite, apatite and a zeolite. Mittempergher (1965) has described the petrology of so-called "venanzite". Although it is not entirely clear that the rocks from the San Venanzo quarry in which willhendersonite occurs are the same as those described by Mittempergher, we tentatively assume that they are. He described lavas from the San Venanzo volcano with the minerals: forsterite (15), diopside (10), melilite (30), leucite (20), kalsilite (10), phlogopite (5–10), opaques (1–5), fluorapatite (1), perovskite (1) and carbonate (1–5%). Although somewhat different than we have observed for the matrix of the willhendersonite samples, the two descriptions are similar enough for us to conclude that the two lavas are at least closely related.

The Mayen material has a related, but different paragenesis. It is found as clear well-formed crystals averaging 60 × 30 × 10 μm in dimensions in cavities in a limestone xenolith from a basalt. The locality is from the Ettringer Bellerberg near Mayen, Eifel, Germany. Associated minerals include gismondine, chabazite, phillipsite, thomsonite, ettringite and thaumasite. A detailed description of the altered limestone inclusions from different parts of the lava flows of the Ettringer Bellerberg has been given by Jasmund and Hentschel (1964).

Acknowledgments

The authors thank Mr. Gianni Porcellini for providing information about the occurrence and generously contributing specimens for study. Specimens of willhendersonite from the Ettringer Bellerberg were kindly provided by Mr. H. Schäfer, Mr. T. Ternes, and Dr. G. Hentschel to whom E.T. and R.X.F. are also indebted for interesting and helpful discussions. The latter authors thank Dr. K. Abraham for the microprobe analysis of the Mayen material, Dr. O. Medenbach for an introduction into the use of the Medenbach spindle stage and the Deutsche Forschungsgemeinschaft for financial support.

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Manuscript received, April 6, 1982;
accepted for publication, May 26, 1983.