

THE CRYSTAL STRUCTURE OF CAVANSITE: LOCATION OF THE H₂O MOLECULES AND HYDROGEN ATOMS IN Ca(VO)(Si₄O₁₀)•4H₂O

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ABSTRACT

Cavansite, Ca(VO)(Si₄O₁₀)•4H₂O, is a novel layer silicate, dimorphous with pentagonite. The earlier determination of its structure did not yield the location of the hydrogen atoms or clear resolution of the oxygen atoms of the H₂O molecules. In this study, structures are reported from data collected at 100(2) and 296(2) K, and they clearly resolve and allow refinement of the position of the H atoms. The 100 K and 296 K structures were refined to *R*1 values of 0.0141 and 0.0389, respectively. Cavansite is orthorhombic with space-group symmetry *Pcmm*, with *a* 9.7518(4), *b* 13.6854(6), and *c* 9.5965(4) Å at 100 K, and *a* 9.7614(7), *b* 13.6666(10), and *c* 9.6049(7) Å at 296 K. Cavansite consists of two layers, a layer of silicate tetrahedra and a layer formed of irregular CaO₄(OH₂)₄ polyhedra and VO₅ square-based pyramids that alternate in ribbons parallel to [100] in (010); the layers join laterally at the four corners of the base of the V pyramid. The silicate layer consists of four- and eight-membered rings of silicate tetrahedra with apices pointing along [010] or [0 $\bar{1}$ 0]. The four oxygen atoms in the Ca polyhedron that are not linked to the V square-based pyramids are part of H₂O molecules. Adjacent ribbons in (010) are linked by hydrogen bonding.

Keywords: cavansite, layer silicate, vanadate, crystal structure.

SOMMAIRE

La cavansite, Ca(VO)(Si₄O₁₀)•4H₂O, est un silicate en couche atypique, dimorphe de la pentagonite. La détermination antérieure de sa structure n'avait pas permis d'en localiser les atomes d'hydrogène et de résoudre clairement les atomes d'oxygène des molécules de H₂O. Ici, nous décrivons les structures affinées à partir de données prélevées à 100(2) et à 296(2) K, et nous avons pu résoudre clairement la position des atomes d'hydrogène. Les structures à 100 K et à 296 K ont été affinées jusqu'à un résidu *R*1 de 0.0141 et 0.0389, respectivement. La cavansite est orthorhombique, groupe spatial *Pcmm*, avec *a* 9.7518(4), *b* 13.6854(6), et *c* 9.5965(4) Å à 100 K, et *a* 9.7614(7), *b* 13.6666(10), et *c* 9.6049(7) Å à 296 K. La cavansite est faite de deux couches, dont un niveau de tétraèdres silicatés et une couche de polyèdres CaO₄(OH₂)₄ irréguliers et de pyramides VO₅ à base carrée qui alternent en rubans parallèles à [100] dans le plan (010); ces couches sont articulées latéralement aux quatre coins de la base de la pyramide V. La couche silicatée est faite d'anneaux de tétraèdres à quatre et huit membres, avec les sommets orientés le long de [010] ou de [0 $\bar{1}$ 0]. Les quatre atomes d'oxygène des polyèdres Ca qui ne font pas partie des pyramides V à base carrée font partie des molécules de H₂O. Les rubans adjacents dans le plan (010) sont interliés par liaisons hydrogène.

(Traduit par la Rédaction)

Mots-clés: cavansite, silicate en couches, vanadate, structure cristalline.

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INTRODUCTION

Cavansite, $\text{Ca}(\text{VO})(\text{Si}_4\text{O}_{10}) \cdot 4\text{H}_2\text{O}$, is a novel layer silicate, dimorphous with pentagonite. The general nature of the atomic arrangement of cavansite was described by Evans (1973), but the poor material from Malheur County, Oregon, used in his study and the nature of the extant diffractometers precluded a detailed refinement of the structure; hydrogen atoms were not located, and the locations of the oxygen atoms of the H_2O molecules were poorly resolved in the refinement, with $R = 0.109$. A subsequent discovery of cavansite of exceptional quality from Pune, India, allows us to describe the details of the atomic arrangement of this rare mineral, including location of the H_2O molecules and the hydrogen atoms. We here report the results of structure refinements at 100(2) and 296(2) K.

As described by Evans (1973), the atomic arrangement in cavansite consists of sheets of SiO_4 tetrahedra that join to form a network of four- and eight-member rings in (010). The sheets are separated by layers formed of ribbons of VO_5 square-based pyramids and irregular CaO_7 polyhedra. We expand upon that description, provide high-quality refinements of the structure, and report the location of the H atoms.

CRYSTAL STRUCTURE

Experimental

A blue-green gem-quality crystal of cavansite from Pune, India, was isolated for our structure study. Chemical data were gathered on a JEOL 6060 Scanning Electron Microscope with an Oxford Instruments INCA 50 mm^2 XMAX energy-dispersive spectrometer. The only elements detected in energy-dispersive analyses on ten spots were Ca, V, Si and O. A crystal of approximate dimensions $0.21 \times 0.24 \times 0.37$ mm was used for the X-ray structure analysis. The X-ray intensity data were measured on a Bruker APEX II CCD system equipped with a Triumph curved crystal monochromator and a Mo fine-focus tube. The structure was solved and refined using the Bruker SHELXTL software package (Sheldrick 2008), with anisotropic full-matrix least-squares refinement on F^2 . In the 100 K refinement, the H atoms were located in difference-Fourier maps, and their positions and isotropic displacement parameters were refined. In the 296 K refinement, the positions of the H atoms were constrained (AFIX 3) with tetrahedral H–O–H angles. Table 1 contains details of the data collection and results of the refinement, and Table 2 offers the coordinates and equivalent isotropic displacement parameters of the atoms in cavansite. Table 3 (on

deposit) lists the anisotropic displacement parameters for the non-hydrogen atoms in cavansite, and Table 4 contains selected bond-distances and bond-valence sums for atoms in cavansite. Table 5 (on deposit) contains observed and calculated structure-factors for the two refinements of the cavansite structure. Copies of Tables 3 and 5 and the CIF files are available from the Depository of Unpublished Data on the Mineralogical Association of Canada website [document Cavansite CM49_1267].

Description of the structure

We describe cavansite as a layer silicate structure. The atomic arrangement of cavansite is formed of two alternating layers, a silicate layer and a vanadium–calcium layer. The silicate layer consists of tetrahedra that link three bridging oxygen atoms in (010); the tetrahedra are oriented with tetrahedron apices pointing along [010] or $[0\bar{1}0]$. The vanadium–calcium layer is formed of [001] chains of alternating V^{4+}O_5 square

TABLE 1. CAVANSITE: DETAILS ON DATA COLLECTION AND STRUCTURE REFINEMENT

Diffractometer	Bruker APEX II CCD	
X-ray radiation	MoK α ($\lambda = 0.71073$ Å)	
Temperature	100(2) K	296(2) K
Structural formula	$\text{Ca}(\text{VO})(\text{Si}_4\text{O}_{10}) \cdot 4\text{H}_2\text{O}$	
Space group	<i>Pcmm</i>	
Unit-cell dimensions		
<i>a</i> (Å)	9.7518(4)	9.7614(7)
<i>b</i> (Å)	13.6854(6)	13.6666(10)
<i>c</i> (Å)	9.5965(4)	9.6049(7)
<i>V</i> (Å ³)	1280.72(9)	1281.34(16)
<i>Z</i>	4	
Absorption coefficient	1.631 mm^{-1}	
<i>F</i> (000)	908	
Crystal size	0.21 × 0.24 × 0.37 mm	
θ range (°)	2.56 to 52.16	2.56 to 47.83
Index ranges	$-21 \leq h \leq 21$, $-29 \leq k \leq 30$, $-19 \leq l \leq 21$	$-20 \leq h \leq 20$, $-28 \leq k \leq 28$, $-18 \leq l \leq 20$
Reflections collected	98017	91723
Unique reflections	7499	6242
R^2_{int}	0.0177	0.0445
Reflections with $F_o > 4\sigma F$	7,130	1,928
Maximum transmission	0.7257	0.7258
Minimum transmission	0.5867	0.5868
Refinement method	Full-matrix least-squares on F^2	
Parameters refined	121	103
GoF	1.133	1.094
Final <i>R</i> indices [$I > 2\sigma(I)$]		
R_1	0.0141	0.0367
wR_2	0.0341	0.0987
<i>R</i> indices (all data)		
R_1	0.0154	0.0389
wR_2	0.0347	0.1000
Largest diff. peak	1.605 $\text{e}\text{Å}^{-3}$	1.826 $\text{e}\text{Å}^{-3}$
Largest diff. hole	-0.827 $\text{e}\text{Å}^{-3}$	-1.587 $\text{e}\text{Å}^{-3}$

based pyramids and irregular $\text{CaO}_4(\text{OH}_2)_4$ polyhedra. Rinaldi *et al.* (1975) noted that cavansite can be considered a framework structure consisting of silicate layers that are connected along **b** by V^{4+} square-based pyramids, yielding a framework composition of $[(\text{VO})(\text{Si}_4\text{O}_{10})]^{2-}$.

The silicate layer

The silicate layer in cavansite consists of Si1 and Si2 tetrahedra that join together to form four-membered rings of tetrahedra, each with two Si1 and two Si2 tetrahedra (Fig. 1). Each tetrahedron links two of its oxygen atoms with adjacent members of the ring, and a third oxygen atom with a tetrahedron of an adjacent ring, forming a two-dimensional (010) sheet of tetrahedra. Throughout the four-membered ring and sheet, the tetrahedra alternate in a *UUDD* manner (Smith 1978), with each Si1 tetrahedron linking in (010) to three Si2 tetrahedra, and each Si2 tetrahedron linking to three Si1 tetrahedra in (010); nowhere does a tetrahedron link to a like tetrahedron.

The four-membered rings in cavansite link together to form eight-membered rings (Fig. 1). The eight-membered rings have been compared to the eight-membered rings in the zeolite gismondine (Rinaldi *et al.* 1975). However, the eight-membered rings are nearly circular in gismondine (axial ratio = 1.1; Rinaldi *et al.* 1975), whereas in cavansite, the rings are elliptical in nature, with an axial ratio of 1.75 (this work).

Rinaldi *et al.* (1975) determined the crystal structure of dehydrated cavansite in order to evaluate the zeolitic properties of the layer of tetrahedra. They noted that the eight-membered rings in cavansite and the dehydrated phase possess the *UUUDDDDD* sequence of tetrahedra characteristic of gismondine. They noted that in gismondine, such a framework can undergo adjustments in order to accommodate different kinds and quantities of sorbates in the structure. Rinaldi *et al.* (1975) suggested that dehydrated cavansite, without the obscuring H_2O molecules in the hydrated structure, may possess catalytic activities suitable for uses in molecular sieve technology.

The vanadium–calcium layer

The vanadium–calcium layer consists of alternating V^{4+}O_5 square-based pyramids and irregular $\text{CaO}_4(\text{OH}_2)_4$ polyhedra that are linked together to form [100] ribbons in (010) (Fig. 2); the polyhedra alternate within the ribbon. Each VO_5 square-based pyramid links through two of its basal oxygen atoms to the neighboring Ca polyhedron on either side; thus the four basal oxygen atoms are shared with adjacent Ca polyhedra. The apical oxygen of the square-based pyramid does not bond to any other cation except hydrogen, but links adjacent chains through hydrogen bonding with atom H9a. The four oxygen atoms of the Ca polyhedra that are not linked with the V^{4+}O_5 square-based pyramids are part of H_2O molecules.

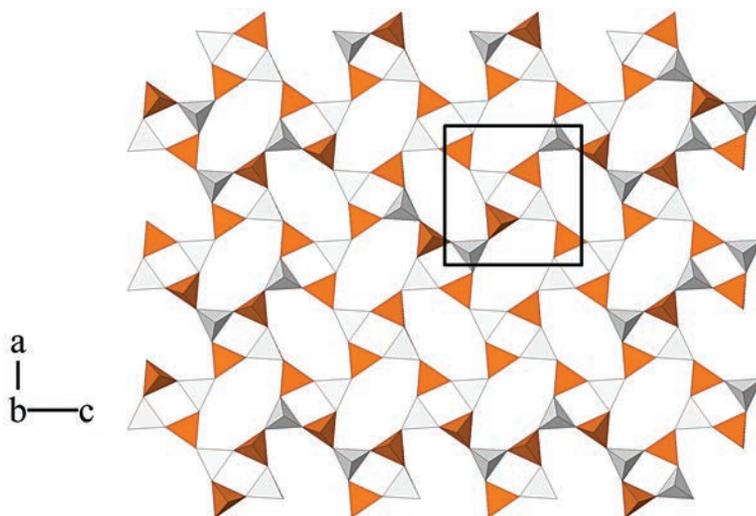


FIG. 1. The silicate layer of the atomic arrangement in cavansite. Gray polyhedra represent Si1 tetrahedra, which have apical oxygen atoms, O1, whereas the orange polyhedra represent Si2 tetrahedra with apical oxygen atoms, O2. The unit cell is shown.

TABLE 2. COORDINATES AND EQUIVALENT ISOTROPIC ATOMIC DISPLACEMENT PARAMETERS (\AA^2) OF ATOMS IN CAVANSITE AT 100 K (FIRST ROW) AND 296 K (SECOND ROW)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
V	0.403461(6)	1/4	0.527127(6)	0.00441(10)
	0.40796(2)	1/4	0.52610(2)	0.00958(4)
Ca	0.081188(8)	1/4	0.384158(7)	0.00538(10)
	0.08632(3)	1/4	0.38270(3)	0.01177(4)
Si1	0.092905(8)	0.033726(6)	0.184986(8)	0.00382(10)
	0.09326(3)	0.03399(2)	0.18476(3)	0.00784(4)
Si2	0.314548(8)	0.043079(6)	0.394816(8)	0.00367(10)
	0.31501(3)	0.04327(19)	0.39474(3)	0.00758(4)
O1	0.08484(2)	0.150457(15)	0.17923(2)	0.00609(2)
	0.08426(8)	0.15083(5)	0.17913(7)	0.01217(10)
O2	0.29352(2)	0.157711(15)	0.41364(2)	0.00677(3)
	0.29503(9)	0.15790(5)	0.41533(8)	0.01367(11)
O3	0.44562(2)	0.019683(18)	0.29592(2)	0.00688(3)
	0.44570(8)	0.01877(7)	0.29636(8)	0.01436(11)
O4	0.16568(2)	0.989344(16)	0.04467(2)	0.00605(2)
	0.16543(8)	0.98960(5)	0.04456(7)	0.01233(10)
O5	0.18145(2)	0.995496(15)	0.31844(2)	0.00555(2)
	0.18173(8)	0.99676(6)	0.31835(7)	0.01163(10)
O6	0.55289(4)	1/4	0.45740(4)	0.01021(4)
	0.55529(16)	1/4	0.45570(17)	0.0235(2)
OW7	0.94626(4)	0.11855(3)	0.47063(3)	0.01585(5)
	0.9388(3)	0.12314(18)	0.4635(2)	0.0654(7)
H7a	-0.1211(12)	0.1117(9)	0.4266(12)	0.034(3)
	-0.1294	0.1168	0.4201	0.078
H7b	-0.0728(12)	0.0887(8)	0.5460(12)	0.031(3)
	-0.0801	0.0936	0.5387	0.078
OW8	0.13254(5)	1/4	0.63927(4)	0.01471(6)
	0.1128(4)	1/4	0.6393(2)	0.0541(8)
H8a	0.1283(14)	0.2993(9)	0.6935(13)	0.047(4)
	0.1083	0.2993	0.6932	0.065
OW9	0.81138(7)	1/4	0.28676(7)	0.02668(11)
	0.8098(13)	1/4	0.295(2)	0.396(13)
H9a	-0.2705(18)	1/4	0.3162(17)	0.033(4)
	-0.2717	1/4	0.3235	0.475
H9b	-0.202(2)	1/4	0.197(2)	0.057(6)
	-0.2046	1/4	0.2052	0.475

TABLE 4. SELECTED BOND-DISTANCES (\AA) AND BOND-VALENCE VALUES (νu) IN CAVANSITE AT 100 AND 296 K

100 K				296 K				
		<i>d</i>	BV			<i>d</i>	BV	
V-	O6	1.6035(4)	1.63	O6	1.5893(14)	1.69		
	O2	1.9826(2)	0.58	O2 (x2)	1.9828(8)	0.58		
	O1 (x2)	1.9998(2)	0.56	O1 (x2)	2.0008(7)	0.56		
	<V-O>	1.9137	Σ 3.91	<V-O>	1.9113	Σ 3.97		
Ca-	OW7(x2)	2.3782(3)	0.33	O1 (x2)	2.3791(8)	0.33		
	O1 (x2)	2.3926(2)	0.32	OW7(x2)	2.3836(17)	0.32		
	O2(x2)	2.4419(2)	0.28	O2 (x2)	2.4153(8)	0.30		
	OW8	2.4989(4)	0.24	OW8	2.479(2)	0.25		
<Ca-O>	OW9	2.7922(7)	0.11	OW9	2.829(17)	0.10		
	<Ca-O>	2.4646	Σ 2.21	<Ca-O>	2.4579	Σ 2.25		
	Si1-	O1	1.6004(2)	1.07	O1	1.6002(8)	1.07	
		O3	1.6220(2)	1.01	O3	1.6210(8)	1.01	
O5		1.6308(2)	0.98	O5	1.6281(7)	0.99		
O4		1.6388(2)	0.96	O4	1.6364(7)	0.97		
<Si1-O>	1.623	Σ 4.02	<Si1-O>	1.6214	Σ 4.04			
Si2-	O2	1.5924(2)	1.09	O2	1.5910(8)	1.09		
	O3	1.6239(2)	1.00	O3	1.6225(8)	1.00		
	O5	1.6266(2)	0.99	O5	1.6233(7)	1.00		
	O4	1.6267(2)	0.99	O4	1.6264(7)	0.99		
<Si2-O>	1.6174	Σ 4.07	<Si2-O>	1.6158	Σ 4.08			
Bond-valence sums for oxygen atoms not forming H ₂ O molecules (hydrogen bonds not included)								
O1	1.95	O4	1.95	O1	1.96	O4	1.96	
O2	1.95	O5	1.97	O2	1.97	O5	1.99	
O3	2.01	O6	1.63	O3	2.01	O6	1.69	

The bond-valence parameters from Brese & O'Keeffe (1991).

The vanadyl (VO_6)²⁺ group of the square-based pyramid has the typical short vanadyl bond, 1.6035(4) \AA at 100 K and 1.5893(14) \AA at 296 K. The small difference in the vanadyl bond-distance and thus vanadyl bond-valence at the two temperatures cannot be explained by increased hydrogen bonding received from H9a at lower temperature, as the hydrogen bond distance to O6 at 100 K is 2.19 \AA , whereas at 296 K the distance is 2.09 \AA .

Linkage of the two layers

The silicate layer bonds laterally with the vanadium-calcium layer to complete the atomic arrangement. An oxygen atom, either O1 or O2, at each of the four corners of the base of the VO_5 square-based pyramid is shared by the calcium polyhedron and a silicate tetrahe-

dron (Fig. 3). In the calcium polyhedra, these oxygen atoms are the only ones not forming H₂O molecules. Atoms O1 and O2 are the apical oxygen atoms of Si1 and Si2, respectively, and this is where the two different layers bond together. One Si1 and one Si2 tetrahedron link to two corners on one side on the base of the VO_5 square-based pyramid, and a Si1 and a Si2 tetrahedron from another silicate layer link to the remaining two corners of the base of the pyramid on the other side, with O2 and O1 atoms diagonally across the base of the pyramid from each other.

Evans (1973) conjectured on hydrogen bonding in the cavansite structure, although he was unable to locate the H atoms. He suggested that hydrogen bonding caused the close approach of O-H...O in any H₂O...O interaction, with an O-O distance less than 3.00 \AA . In this study, we located the H atoms and can define

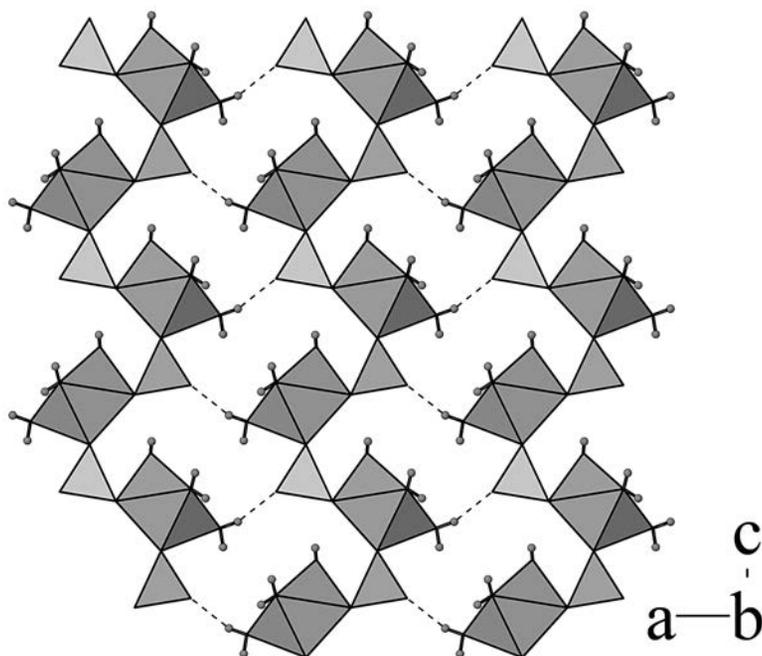


FIG. 2. The vanadium–calcium layer containing alternating $V^{4+}O_5$ square-based pyramids and irregular $CaO_4(OH_2)_4$ polyhedra. The dashed lines indicate hydrogen bonding between O6 and H9a. Note that only one side of the VO_5 square-based pyramid is seen.

a hydrogen bond as an approach of $O-H\dots O$ wherein the donor–acceptor H–O distance is less than 2.20 Å (Hughes *et al.* 2001). With this definition that recognizes the role of the H atom, there are two hydrogen bonds in cavansite. The O6–H9a interaction links adjacent ribbons in the calcium–vanadium layer (Fig. 2), and the O5–H7b interaction further links the layer of tetrahedra and the calcium–vanadium layer.

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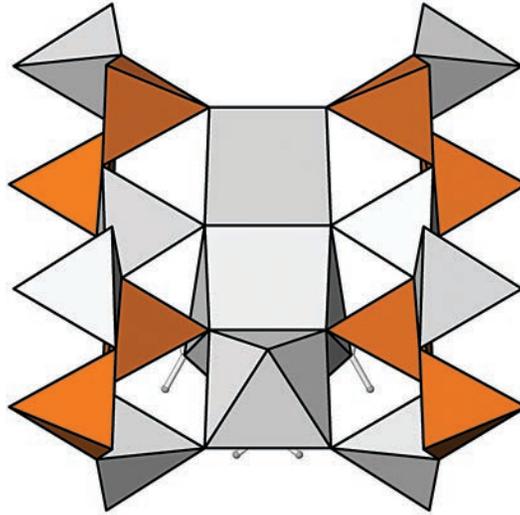


FIG. 3. The Si and V–Ca layers join laterally to complete the crystal structure of cavansite. The colors of the tetrahedra are as in Figure 1.

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