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In situ dehydration behavior of zeolite-like cavansite: A single-crystal X-ray study

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Abstract

To track dehydration behavior of cavansite, $Ca(VO)(Si_4O_{10})\cdot 4H_2O$ [space group *Pnma*, a = 9.6329(2), b = 13.6606(2), c = 9.7949(2) Å, V = 1288.92(4) Å^3] single-crystal X-ray diffraction data on a crystal from Wagholi quarry, Poona district (India) were collected up to 400 °C in steps of 25 °C up to 250 °C and in steps of 50 °C between 250 and 400 °C. The structure of cavansite is characterized by layers of silicate tetrahedra connected by $V^{4+}O_5$ square pyramids. This way a porous framework structure is formed with Ca and H_2O as extraframework occupants. At room temperature, the hydrogen bond system was analyzed. Ca is eightfold coordinated by four bonds to O of the framework structure and four bonds to H_2O molecules. H_2O linked to Ca is hydrogen bonded to the framework and also to adjacent H_2O molecules. The dehydration in cavansite proceeds in four steps.

At 75 °C, H_2O at O9 was completely expelled leading to 3 H_2O pfu with only minor impact on framework distortion and contraction [V = 1282.73(3) Å^3]. The Ca coordination declined from originally eightfold to sevenfold and H_2O at O7 displayed positional disorder.

At 175 °C, the split O7 sites approached the former O9 position. In addition, the sum of the three split positions O7, O7a, and O7b decreased to 50% occupancy yielding 2 H_2O pfu accompanied by a strong decrease in volume [V = 1206.89(8) Å^3]. The Ca coordination was further reduced from sevenfold to sixfold.

At 350 °C, H_2O at O8 was released leading to a formula with 1 H_2O pfu causing additional structural contraction (V = 1156(11) Å^3). At this temperature, Ca adopted fivefold coordination and O7 rearranged to disordered positions closer to the original O9 H_2O site.

At 400 °C, cavansite lost crystallinity but the VO^{2+} characteristic blue color was preserved. Stepwise removal of water is discussed on the basis of literature data reporting differential thermal analyses, differential thermo-gravimetry experiments and temperature dependent IR spectra in the range of OH stretching vibrations.

Keywords: Cavansite, dehydration, crystal structure, hydrogen bonding

Introduction

Cavansite, $Ca(VO)(Si_4O_{10})\cdot 4H_2O$, is a porous layer silicate, dimorphous with pentagonite. The mineral's name is derived from the chemical elements of which it is composed: calcium (ca-), vanadium (-van-), and silicon (-si). Discovered in 1960 at Owyhee Dam, Malheur County (Oregon, U.S.A.), cavansite is a relatively rare mineral (Staples et al. 1973). It occurs in cavities and veinlets in basalt and vugs in tuff as radiating greenish-blue prismatic crystals associated with calcite, analcime, thomsonite, heulandite, stilbite, and apophyllite (Staples et al. 1973). However, the largest and best samples come from Poona district in India where cavansite occurs in tholeiitic basalts of the Deccan Volcanic Province (Phadke and Apte 1994), and in pores of altered basalt breccias and tuffaceous andesite in association with calcite, heulandite, stilbite, and rare apophyllite (Powar and Byrappa 2001). More recently, cavansite has also been reported from basalts in Rio Grande do Sul in southern Brazil (Frank et al. 2005) and from Aranga quarry, Kaipara district, North Island New Zealand (Thornton 2004).

The structure of cavansite was solved by Evans (1973) but crystal quality and experimental setup did not allow the determination of hydrogen positions. However, Solov'ev et al. (1993) reported the location of the hydrogen atoms attached to H_2O molecules. Corresponding identifications of hydrogen-bond systems have recently been repeated by Hughes et al. (2011).

The atomic arrangement in cavansite consists of undulating pyroxenoid-like $(SiO_3)_n$ chains joined laterally into sheets parallel to the **a-c** plane to form a network of four-and eight-membered rings in (010). Adjacent chains have the tetrahedral apices pointing alternately up and down along the **b** axes (Evans 1973). The sheets are cross-linked via the basal square of VO_5 pyramids, which are completed by one short apical V-O bond of ca. 1.6 Å (e.g., Evans 1973; Solov'ev et al. 1993; Hughes et al. 2011) named vanadyl group. This VO^{2+} ion is responsible for the brilliant sky blue color of the crystals (Rossman 2011). A porous three-dimensional framework is formed by the linkage of tetrahedral sheets with VO_5 square pyramids. Large cavities in the structure are occupied in zeolite-like fashion by Ca and coordinating H_2O molecules. Calcium has four bonds to oxygen atoms of silicate tetrahedra and four bonds to H_2O molecules completing an eightfold coordination.

The cavansite framework shows strong similarities to that of gismondine, $CaAl_2Si_2O_8\cdot 4H_2O$. However, in gismondine the exposed

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tetrahedral apices in adjacent layers are linked directly to each other to form a three-dimensional aluminosilicate network (Fischer 1963) and not via vanadyl-type VO_5 square pyramids as in cavansite.

The dimorphism of cavansite and pentagonite is based on the difference in linkages in the silicate layer. Undulating $(SiO_3)_n$ chains are discernible in both, but in cavansite these chains are joined laterally into sheets made up of fourfold and eightfold rings, while in pentagonite they are differently joined so that only sixfold rings are formed (Evans 1973).

Cavansite has not yet been synthesized in the laboratory but other open-framework silicates containing vanadium are reported. Wang et al. (2002) describe two open-framework vanadosilicates, VSH-1K and VSH-2Cs that contain a similar structural motif found in the natural minerals cavansite and pentagonite. Moreover, a series of novel vanadium silicates with open-framework and microporous structures has been synthesized under mild hydrothermal conditions with free channel diameters as large as 6.5 Å (Wang et al. 2002). Ten distinct framework types containing vanadyl groups have been identified and show a great potential to be used as molecular sieves or in catalysis due to their high thermal stability and ion-exchange properties (Wang et al. 2002).

Previous structural studies of the dehydration behavior of cavansite are limited to a room-temperature single-cystal X-ray diffraction experiment of a crystal previously partly dehydrated under vacuum at 220 °C (Rinaldi et al. 1975). In addition, differential thermal analysis (DTA) and differential thermo-gravimetry (DTG) (Phadke and Apte 1994; Powar and Byrappa 2001; Ishida et al. 2009), in situ FTIR and Raman spectroscopy (Prasad and Prasad 2007) were done.

The aim of this study is to further characterize the hydrogen-bond system and the in situ dehydration behavior of cavansite using single-cystal X-ray diffraction on crystals from Wagholi quarry, Poona district (India). This investigation was initiated by a supposed contradiction: Solov'ev et al. (1993) report H_2O III with the highest atomic displacement parameter and the longest bond to Ca, also confirmed by Hughes et al. (2011). At first glance, one should assume that, upon heating, H_2O III with the weakest bond is expelled first. However, the structural study of partly dehydrated cavansite by Rinaldi et al. (1975) indicates that H_2O (their W1) close to H_2O III (room temperature) is the most stable one before complete dehydration occurs accompanied with structural breakdown.

Experimental methods

A cavansite single crystal from Wagholi, Poona district, Maharashtra, India of approximate dimensions 0.1 × 0.1 × 0.5 mm was selected for our structure study and mounted in an open 0.1 mm diameter quartz-glass capillary.

Single-crystal X-ray diffraction data were collected with a Bruker APEX II diffractometer using Mo*K*α (λ = 0.71073 Å) X-ray radiation with 50 kV and 30 mA X-ray power. To study in situ dehydration, complete data sets were collected in steps of 25 °C up to 250 °C and in steps of 50 °C up to 400 °C using a self-constructed temperature controlled hot nitrogen blower. Before data collections the crystal was kept at least 30 min at the next measuring temperature.

CCD area-detector data were integrated and an empirical absorption correction was applied using the Apex2 v. 2011.4-1 software package. Data-collection parameters and refinement parameters are given in Table 1. Neutral atom scattering-factors were used for structure refinement with SHELXL-97 (Sheldrick 2008). Hydrogen positions were extracted from difference-Fourier maps applying the restraint H-O

Table 1. Parameters for X-ray data collection and crystal-structure refinement of cavansite

	Cavansite (RT)	Cavansite (75 °C)	Cavansite (175 °C)	Cavansite (350 °C)
Crystal data				
Unit-cell dimensions (Å)	*a* = 9.6329(2)	*a* = 9.60900(10)	*a* = 9.4746(4)	*a* = 9.39(5)
	b = 13.6606(2)	*b* = 13.6833(2)	*b* = 13.2620(5)	*b* = 13.11(8)
	c = 9.7949(2)	*c* = 9.7559(2)	*c* = 9.6050(4)	*c* = 9.39(5)
Volume (Å^3)	1288.92(4)	1282.73(3)	1206.89(8)	1156(11)
Space group	*Pnma* (No. 62)	*Pnma* (No. 62)	*Pnma* (No. 62)	*Pnma* (No. 62)
Z	4	4	4	4
Chemical formula	$Ca(VO)(Si_4O_{10})\cdot 4H_2O$	$Ca(VO)(Si_4O_{10})\cdot 3H_2O$	$Ca(VO)(Si_4O_{10})\cdot 2H_2O$	$Ca(VO)(Si_4O_{10})\cdot 1H_2O$
Intensity measurement				
Crystal shape	prismatic	prismatic	prismatic	prismatic
Crystal size (mm)	0.1 × 0.1 × 0.5	0.1 × 0.1 × 0.5	0.1 × 0.1 × 0.5	0.1 × 0.1 × 0.5
Diffractometer	APEX II SMART	APEX II SMART	APEX II SMART	APEX II SMART
X-ray radiation	Mo*K*α λ = 0.71073 Å	Mo*K*α λ = 0.71073 Å	Mo*K*α λ = 0.71073 Å	Mo*K*α λ = 0.71073 Å
X-ray power	50 kV, 30 mA	50 kV, 30 mA	50 kV, 30 mA	50 kV, 30 mA
Monochromator	graphite	graphite	graphite	graphite
Temperature	293 K	348 K	448 K	623 K
Time per frame	10 s	10 s	10 s	10 s
Max. θ	30.5	30.5	30.5	30.5
Index ranges	$-13 \le h \le 13$	$-13 \le h \le 13$	$-12 \le h \le 13$	$-10 \le h \le 10$
	$-19 \le k \le 19$	$-19 \le k \le 19$	$-18 \le k \le 18$	$-14 \le k \le 14$
	$-13 \le l \le 13$	$-13 \le l \le 13$	$-7 \le l \le 13$	$-10 \le l \le 10$
No. of measured reflections	10723	16172	7406	4845
No. of unique reflections	2039	2027	1900	916
No. of observed reflections [$I > 2\sigma(I)$]	1859	1864	1644	731
Refinement of the structure				
No. of parameters used in refinement	116 + 7 restraints	105	102	102
R_{int}	0.0258	0.0280	0.0328	0.0531
R_σ	0.0188	0.0154	0.0292	0.0382
$R1, I > 2\sigma(I)$	0.0232	0.0294	0.0295	0.0593
*R*1 , all data	0.0262	0.0323	0.0369	0.0783
w*R*2 (on F^2)	0.0682	0.0856	0.0901	0.1833
GooF	1.057	1.068	0.988	1.149
$\Delta\rho_{min}$ (–e/Å^3)	–0.58 close to V	–0.73 close to O7b	–0.56 close to V	–0.78 close to V
$\Delta\rho_{max}$ (e/Å^3)	0.49 close to O3	0.87 close to O8	0.74 close to O7	0.79 close to Ca

= 0.95(1) Å and refined with fixed isotropic displacement parameters. The experimentally derived hydrogen-bond system was confirmed by using bond-valence calculations (Brown and Altermatt 1985).

Initial atomic labels were those of Evans (1973) but the standard space-group setting *Pnma* was chosen in contrast to *Pcmn* preferred by Evans (1973) requiring interchange of **a** and **c**. The final refinement for the data collected at room temperature, based on 1859 observed reflections and 116 parameters with 7 restraints, converged at R1 = 0.0232. Refinements for the data collected at 75, 175, and 350 °C converged at R1 = 0.0294, R1 = 0.0295, and R1 = 0.0593, respectively. The smaller data sets reported at 175 °C and 350 °C (Table 1) are due to experimental problems. Between 150 and 175 °C, the crystal broke and only a limited number of reflections could be integrated. For 175 and 350 °C data, O positions of partly occupied H_2O sites were refined with common isotropic displacement parameters constrained to each other.

Results and discussion

Atomic coordinates and displacement parameters for the cavansite structure at room temperature, 75, 175, and 350 °C are given in Tables 2 and 3[1], respectively. Selected distances and angles of hydrogen bonds under ambient conditions are in Table 4. Table 5[1] compares the interatomic distances at room temperature, 75, 175, and 350 °C. Results of bond valence calculations for cavansite at room temperature are reported in Table 6[1]. (CIFs[1] are also available.)

Our structural study under ambient conditions confirmed the framework structure built by tetrahedral layers connected by vanadyl-type VO_5 square-based pyramids (Figs. 1–3) as reported by Evans (1973), Rinaldi et al. (1975), Solov'ev et al. (1993), and Hughes et al. (2011).

Moreover, we located the H atoms and defined the hydrogen-bond system (Figs. 1a–b and 3a). Our structure refinement with five located H positions indicates that there are three hydrogen bonds with H···O acceptor distances between 2.08 and 2.17 Å: O9-H9a···O6, O7-H7a···O9, and O7-H7b···O5. H8 is fixed by only weak hydrogen bonds and the corresponding H···O acceptor distance for the O8-H8···O3 hydrogen bond is 2.64 Å with d(O8···O3) = 3.56 Å. In general, the hydrogen bond system defined by us is similar to the findings by Solov'ev et al. (1993) and Hughes et al. (2011). The O6···H9a interaction links the $CaO_4(H_2O)_4$ polyhedron to the opposing apex of the V square-based pyramid (Fig. 1a), while the O5···H7b and O3···H8 interactions link the silicate layer to the extraframework occupants (Fig. 3a). The O9···H7a interaction, not reported in the study of Solov'ev et al. (1993) and Hughes et al. (2011), connects two H_2O molecules located inside the elliptical channels parallel to **b** formed by eight-membered rings of tetrahedra. Solov'ev et al. (1993) and Ishida et al. (2009) assumed other interactions (Table 7). In particular, the angle between donor-hydrogen-acceptor (DHA) is probably too narrow (less than 120°) for the assumed hydrogen bonds (H_2O)1-H2···O4, (H_2O)2-H3···O3 and (H_2O)3-H5···O6 (Solov'ev et al. 1993).

Table 2a. Atomic coordinates and U_{eq} (U_{iso}) (Å^2) values for cavansite at RT

Site	Occ.	x	y	z	U_{eq}
V	1	0.02594(4)	0.25	0.09618(4)	0.01042(9)
Ca	1	−0.38231(4)	0.75	−0.08263(5)	0.01275(10)
Si1	1	−0.18305(4)	0.53318(3)	−0.09496(4)	0.00808(9)
Si2	1	−0.10728(4)	0.45691(3)	0.18382(4)	0.00766(9)
O1	1	−0.17796(11)	0.65027(8)	−0.08597(11)	0.0128(2)
O2	1	−0.08731(12)	0.34231(8)	0.20600(11)	0.0137(2)
O3	1	−0.20339(11)	0.47968(9)	0.05164(11)	0.0144(2)
O4	1	−0.04191(11)	0.48914(8)	−0.16578(11)	0.0122(2)
O5	1	−0.31477(11)	0.49541(8)	−0.18514(11)	0.0112(2)
O6	1	−0.0430(2)	0.25	−0.05191(19)	0.0237(4)
O7	1	−0.46993(18)	0.88139(14)	0.05339(19)	0.0442(4)
H7a	1	−0.421(3)	0.869(3)	0.136(2)	0.080*
H7b	1	−0.5615(16)	0.891(3)	0.081(4)	0.080*
O8	1	−0.6383(2)	0.75	−0.1258(3)	0.0374(5)
H8	1	−0.685(3)	0.6944(17)	−0.093(3)	0.080*
O9	1	−0.2832(4)	0.75	0.1898(4)	0.0775(11)
H9a	1	−0.330(5)	0.75	0.276(3)	0.080*
H9b	1	−0.192(2)	0.75	0.230(5)	0.080*

* U_{iso} of hydrogen was fixed.

Table 2b. Atomic coordinates and U_{eq} (U_{iso}) (Å^2) values for cavansite at 75 °C

Site	Occ.	x	y	z	U_{eq}
V	1	0.02600(5)	0.25	0.09027(4)	0.01219(11)
Ca	1	−0.38248(5)	0.75	−0.08753(5)	0.01422(12)
Si1	1	−0.18529(5)	0.53429(4)	−0.09246(5)	0.00969(11)
Si2	1	−0.10434(5)	0.45653(3)	0.18578(5)	0.00934(12)
O1	1	−0.17964(14)	0.65118(10)	−0.08307(14)	0.0150(3)
O2	1	−0.08347(15)	0.34199(10)	0.20472(14)	0.0169(3)
O3	1	−0.20289(14)	0.48168(11)	0.05573(14)	0.0174(3)
O4	1	−0.04573(13)	0.49007(10)	−0.16576(14)	0.0146(3)
O5	1	−0.31993(13)	0.49792(10)	−0.17994(13)	0.0138(3)
O6	1	−0.0455(3)	0.25	−0.0566(2)	0.0294(5)
O7	0.270(8)	−0.4471(11)	0.8517(9)	0.1035(13)	0.0448(11)*
O7a	0.245(7)	−0.3993(11)	0.8184(8)	0.1464(11)	0.0448(11)*
O7b	0.557(10)	−0.4643(5)	0.8806(4)	0.0570(6)	0.0448(11)*
O8	1	−0.6396(4)	0.75	−0.0987(5)	0.0756(14)
O9	0.105(8)	−0.295(3)	0.75	0.188(3)	0.0448(11)*

* U_{iso} of oxygen was constrained to a common isotropic displacement parameter.

[1] Deposit item AM-12-079, Tables 3, 5, and 6, and CIFs. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

Table 2c. Atomic coordinates and U_{eq} (U_{iso}) (Å^2) values for cavansite at 175 °C

Site	Occ.	x	y	z	U_{eq}
V	1	0.03479(5)	0.25	0.09988(5)	0.01642(12)
Ca	1	−0.38889(6)	0.75	−0.07578(6)	0.01849(14)
Si1	1	−0.19261(6)	0.52653(4)	−0.08317(6)	0.01415(13)
Si2	1	−0.09206(6)	0.46155(4)	0.19910(6)	0.01366(13)
O1	1	−0.18823(15)	0.64770(11)	−0.07596(16)	0.0199(3)
O2	1	−0.05978(17)	0.34527(11)	0.22691(16)	0.0218(3)
O3	1	−0.20100(16)	0.47554(13)	0.07010(16)	0.0226(3)
O4	1	−0.05458(16)	0.48034(11)	−0.16282(16)	0.0196(3)
O5	1	−0.33434(16)	0.48941(11)	−0.16389(15)	0.0189(3)
O6	1	−0.0552(3)	0.25	−0.0398(3)	0.0337(6)
O7	0.162(12)	−0.430(2)	0.7778(16)	0.1679(16)	0.044(3)*
O7a	0.203(10)	−0.3625(16)	0.7750(11)	0.1759 (12)	0.044(3)*
O7b	0.142(14)	−0.397(3)	0.810(2)	0.161(2)	0.044(3)*
O8	1	−0.6409(5)	0.75	−0.0485(8)	0.121(2)

* U_{iso} of oxygen was constrained to a common isotropic displacement parameter.

Table 2d. Atomic coordinates and U_{eq} (U_{iso}) (Å^2) values for cavansite at 350 °C

Site	Occ.	x	y	z	U_{eq}
V	1	0.0374(2)	0.25	0.0993(2)	0.0323(6)
Ca	1	−0.3884(3)	0.75	−0.0715(3)	0.0373(8)
Si1	1	−0.1968(2)	0.52399(16)	−0.0781(2)	0.0256(6)
Si2	1	−0.0833(2)	0.46265(16)	0.2073(2)	0.0243(6)
O1	1	−0.1921(6)	0.6461(4)	−0.0706(7)	0.0373(15)
O2	1	−0.0485(6)	0.3461(4)	0.2374(6)	0.0378(15)
O3	1	−0.1946(6)	0.4739(5)	0.0777(6)	0.0366(15)
O4	1	−0.0631(5)	0.4784(4)	−0.1666(6)	0.0309(14)
O5	1	−0.3434(6)	0.4873(4)	−0.1524(6)	0.0310(14)
O6	1	−0.0568(12)	0.25	−0.0373(12)	0.061(3)
O7	0.25(3)	−0.517(6)	0.780(4)	0.134(6)	0.129(18)*
O7b	0.22(3)	−0.415(7)	0.782(4)	0.181(6)	0.129(18) *
O8	0.24(4)	−0.590(9)	0.75	0.018(10)	0.129(18)*

* U_{iso} of oxygen was constrained to a common isotropic displacement parameter.

TABLE 4. Hydrogen bond distances (Å) and O-H···O angles (°)

Species	D-H	H···A	D···A	<(DHA)	Hydrogen bond
H_2O	0.957(10)	2.081(12)	3.033(4)	173(5)	O9-H9a···O6
H_2O	0.946(10)	2.17(3)	2.871(4)	130(3)	O7-H7a···O9
H_2O	0.939(10)	2.642(13)	3.564(2)	167(3)	O8-H8···O3
H_2O	0.934(10)	2.12(3)	2.897(2)	140(3)	O7-H7b···O5

Notes: Hydrogen positions were determined with the restraint O-H is 0.95(2) Å. D = donor; A = acceptor.

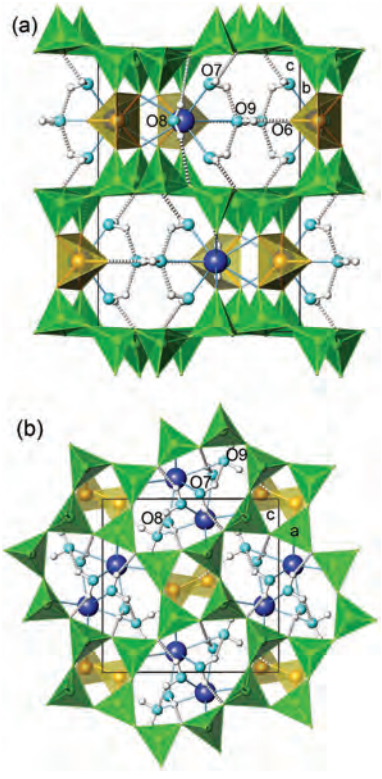


FIGURE 1. Framework of cavansite at room temperature. The green polyhedra represent Si tetrahedra, while the yellow polyhedra are the V square-based pyramids. Calcium is in blue and oxygen of H_2O are shown as light blue spheres with attached small white spheres representing H. Hydrogen-bond acceptor interactions are shown by gray dashed connectors. The water molecules O7, O8, and O9 are labeled. (**a**) Projection along the **a** axis showing the silica layers linked by vanadyl-type VO_5 square based pyramids. (**b**) View of the cavansite structure parallel to **b** showing the porous character of the structure high-lighting the four-and eight-member rings of tetrahedra. (Color online.)

TABLE 7. Hydrogen-bond system in Solov'ev et al. (1993), Ishida et al. (2009), Hughes et al. (2011), and the present study

Solov'ev et al. (1993)	Ishida et al. (2009)	Hughes et al. (2011)	This study
$(H_2O)1$-H1···O5	O7-H1···O5	O7-H7b···O5	O7-H7b···O5
$(H_2O)1$-H2···O4			
			O7-H7a···O9
$(H_2O)2$-H3···O3			
$(H_2O)2$-H3···O3			O8-H8···O3
	O8-H2···O2		
	O8-H2···O1		
$(H_2O)3$-H4···O6	O9-H3···O6	O9-H9a···O6	O9-H9a···O6
$(H_2O)3$-H5···O6			
	O9-H4···O7		
	O9-H5···O7		

Moreover, Ishida et al. (2009) reported two hydrogen bonds (O9-H4···O7 and O9-H5···O7) with the distance between acceptor and hydrogen greater than 3.1 Å and two hydrogen bonds (O8-H2···O2 and O8-H2···O1) with the DHA angle less than 120°. We did not consider the above interactions because they are not consistent with the geometric criterion for hydrogen bonds.

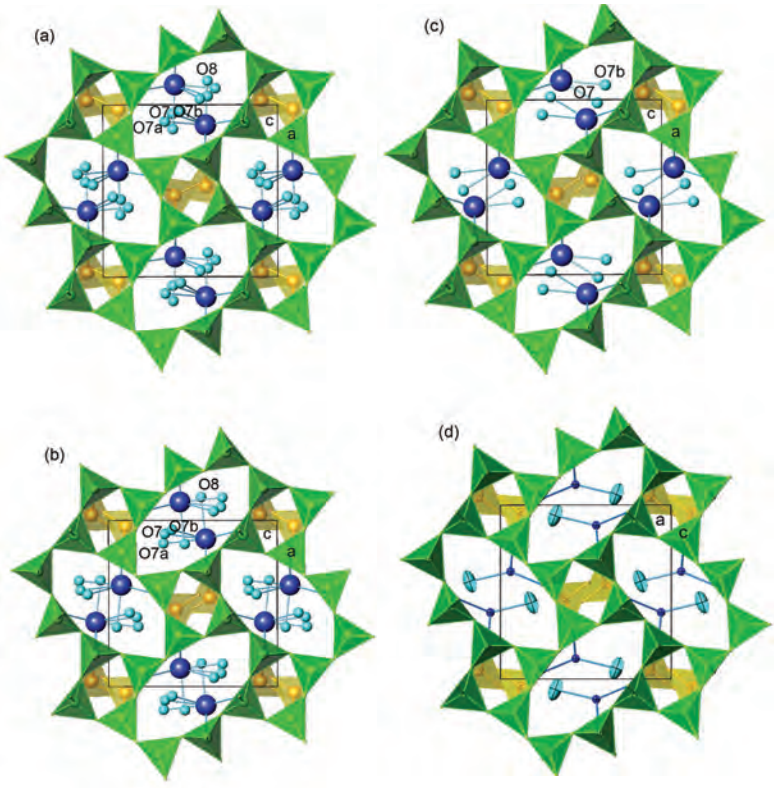
Without considering H in bond-valence calculations, the H_2O molecules are characterized by an oxygen bond-valence sum (bvs) < 0.5 valence units (v.u.). According to a model by Ferraris and Ivaldi (1988), which is here simplified, the bvs for a donor of a hydrogen bond may be increased by 0.8 v.u. and the bvs of acceptor oxygen may be increased by 0.2 v.u., indicating that O7, O8, and O9 represent H_2O molecules. This finding is in contrast to the interpretation of Ishida et al. (2009) suggesting, by applying the "valence-matching principle," the existence of H_3O^+ and OH^-.

Our in situ dehydration experiments at elevated temperature and dry N_2 atmosphere showed that cavansite starts losing H_2O already at 50 °C. At this temperature, H_2O at O9 displayed positional disorder and was split into O9 and the subsite O9a, ca. 1 Å apart. The sum of occupancies for O9 and O9a decreased to 0.84(4). Moreover, at 50 °C O7 was split into three positions (O7, O7a, and O7b) indicating substantial disorder. The distances between O7-O7a, O7-O7b, O7a-O7b, and O7b-O7b′ are 0.45, 1.22, 0.79, and 2.28 Å, respectively. The displacement onto three different positions probably models dynamic disorder.

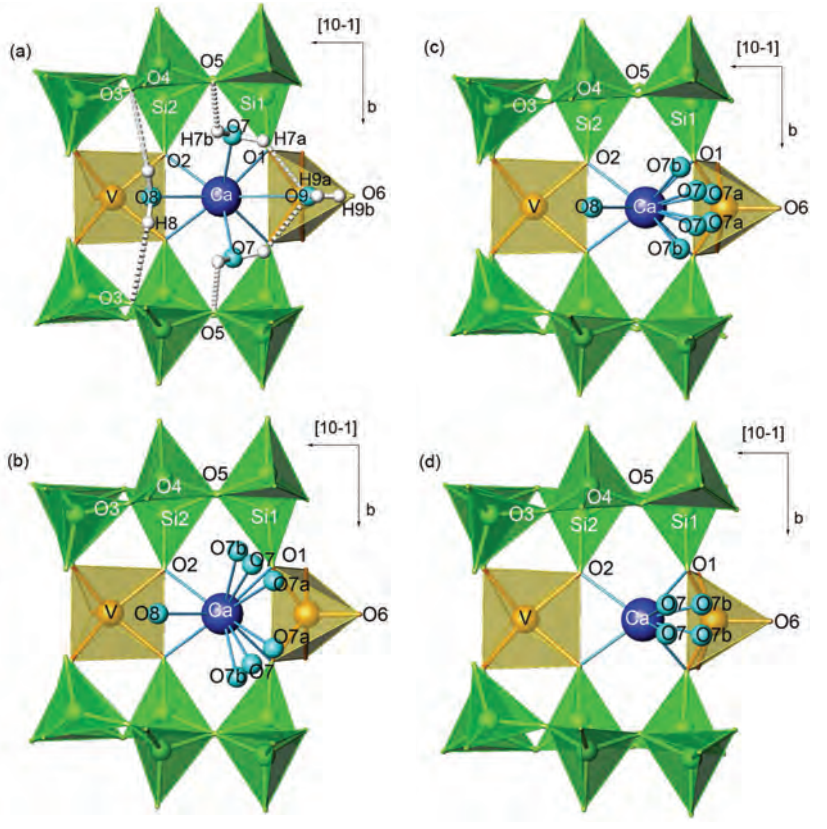
At 75 °C, the O9 site became almost vacant and the unit-cell volume decreased from 1288.92(4) $Å^3$ at room temperature to 1282.73(3) $Å^3$ leading to a formula with 3 H_2O pfu (Fig. 2a). The coordination of Ca decreased from eight to seven (Table 5[1]) accompanied by shortening the mean Ca-O distance from 2.473 to 2.469 Å.

At 175 °C, the displacement of O7 at three different positions was still observed but in a slightly modified arrangement (Fig. 2b). H_2O at the O7 subsites began to approach the former O9 position, on the mirror plane. In addition, the sum of the three displaced positions O7, O7a, and O7b decreased to 50% occupancy leading to a formula with 2 H_2O pfu. Decreased H_2O content reduced the volume to 1206.89(8) $Å^3$ and Ca became sixfold coordinated with subsequent shortening of the mean Ca-O distance from 2.469 to 2.359 Å. The release of H_2O molecules acts as a promoter of structural modification in the porous three-dimensional framework (Alberti and Martucci 2011). In particular, at 175 °C the angle between Si2-O5-Si1 decreased from 131.46(9)° to 128.24(10)° (Table 5[1]) leading a slight compression of the pore system due to the release of H_2O molecules.

From 200 to 350 °C the population of H_2O at O8 decreased from 1.0 to 0.24(4) while the displacement parameter at 350 °C became 3 times larger than at 200 °C due to assumed dynamic disorder. At 350 °C, O7 was split into two positions while the O7a site became empty. O7 and O7b together still preserved 50% occupation but moved closer to the original O9 H_2O site on the mirror plane. As a consequence of release of H_2O at O8 leading to a formula with 1 H_2O pfu (Fig. 2c), Ca adopted fivefold coordination associated with reduction of the unit-cell volume to 1156(11) $Å^3$. The release of H_2O at O8 led to a further decrease of the Si2-O5-Si1 angle to 126.2(4)° (Table 5[1]) causing additional deformation of the pore system. Breakdown of the



◀**FIGURE 2.** Framework of cavansite and channel occupants in space-group setting *Pnma*; (**a**) at 75 °C, (**b**) at 175 °C, and (**c**) at 350 °C. (**d**) Framework of cavansite by Rinaldi et al. (1975) showing only one H_2O molecule (W1) after dehydration at 220 °C under vacuum, refined at room temperature with anisotropic displacement parameters. The space group setting is *Pcmn*. (Color online.)



◀**FIGURE 3.** Portion of the cavansite structure focusing on Ca coordination. (**a**) Cavansite at room temperature showing the hydrogen-bond system. The O9-H9a···O6 hydrogen bond is not shown because it points toward the observer. (**b**) Cavansite at 75 °C. The H_2O molecule at O9 has been expelled and the H_2O molecule at O7 is split into three positions. The Ca coordination is reduced from eight to seven. (**c**) Cavansite at 175 °C. The sum of the three displaced positions O7, O7a, and O7b was equal to 50% occupancy. The Ca coordination was reduced from sevenfold to sixfold. (**d**) Cavansite at 350 °C. The population at O8 is 0.24(4) and it is omitted in the picture. On average Ca is fivefold coordinated. (Color online.)

structure, observed at approximately 400 °C, probably resulted from removal of the residual H_2O molecule split at the O7 and O7b sites.

The crystal structure of partly dehydrated cavansite from Oregon, U.S.A., was reported by Rinaldi et al. (1975). After heating in vacuum at 220 °C only one water molecule per Ca was found in the structure (Fig. 2d). The results of Rinaldi et al. (1975) represent a dehydration state, which we observed in situ at 350 °C with the major difference that in their room-temperature data W1 was refined with anisotropic displacement parameters, whereas we used split positions (O7 and O7a) to model dynamic disorder at elevated temperature. Thus, due to the interaction of vacuum and heating the dehydration found by Rinaldi et al. (1975) occurred at lower temperature. The supposed contradiction that the H_2O molecule with the longest bond to Ca at room temperature (H_2O III of Solov'ev et al. 1993) is the most stable one upon dehydration (W1 of Rinaldi et al. 1975) could be explained. As expected, softly bonded H_2O III (O9 in this study) is released first (75 °C). However, with increasing temperature (above 175 °C) H_2O I of Solov'ev et al. 1993 (corresponding to O7 in this study) adopts a position close to the mirror plane, which roughly resembles the original O9 site. It is important to underline that the O7 subsites (this study; corresponding to W1 of Rinaldi et al. 1973) have much shorter distances to Ca (Table 5[1]) than the original position of H_2O III (O9 in this study).

Our dehydration steps (Fig. 4) observed at different temperatures correlate with the thermo-gravimetric data reported by Phadke and Apte (1994), Powar and Byrappa (2001), Prasad and Prasad (2007), and Ishida et al. (2009) (Table 8). The four steps of weight loss in succession correspond to the expulsion of four water molecules, one at a time. The dehydration steps (from the DTA curves) at 95, 225, 350, and 450 °C (Ishida et al. 2009) are at higher temperatures than the transitions at 75, 175, 350, and 400 °C in our dehydration study. Moreover, above 500 °C (Prasad and Prasad 2007) and above 400 °C (this study) cavansite decomposes to an amorphous phase after losing the last H_2O molecule at O7. It should be considered that the temperature values reported for the DTA-DTG curves (Phadke and Apte 1994; Powar and Byrappa 2001; Prasad and Prasad 2007; Ishida et al. 2009) are referred to the peak and not to the onset of the steps of weight loss. This explains the different temperature values between the thermo-gravimetric data and our results.

The O-H stretching region in the wavelength range 4000 to 3000 cm^{-1} of the IR spectrum of cavansite is characterized by four peaks at 3648, 3592, 3548, and 3490 cm^{-1}, and a shoulder at 3250 cm^{-1} (Powar and Byrappa 2001). These results are in agreement with the spectra reported by Prasad and Prasad (2007) and Ishida et al. (2009). On the low-frequency tail of the OH-characteristic absorptions Ishida et al. (2009) reported an additional poorly resolved absorption at 3186 cm^{-1}. Only the observed intense O-H modes at high wave numbers correlate with the observed donor-acceptor distances (Table 4). According to the hydrogen bond-length vs. IR frequency correlation by Libowitzky (1999) absorptions between 3490 and 3592 cm^{-1} correspond to donor-acceptor (O···O) distances of ca. 2.9–3.5 Å, which agrees with the D-A distances in Table 4. The shoulders at 3250 and 3186 cm^{-1} correspond to donor-acceptor distances of 2.72 Å and below. Such strong hydrogen bonds were not observed in terms of D-A distances for cavansite.

Prasad and Prasad (2007) also report an IR spectrum of the OH-characteristic region at 177 °C showing absorptions at 3561 and 3608 cm^{-1} corresponding in intensity and shape to those at 3552 and 3606 cm^{-1} found at room temperature. A trace of the 3250 cm^{-1} absorption was still evident at 177 °C. Our structural study indicated that at 175 °C H_2O at O9 was expelled and O7 and subsites were half occupied. The room-temperature IR spectra (Powar and Byrappa 2001; Prasad and Prasad 2007; Ishida et al. 2009) may therefore be interpreted such that the band at 3648 cm^{-1} is due to the very weak hydrogen bond O9-H9b···O? (not specified in our study) or to O9-H9a···O6. The band at 3490 cm^{-1} is assigned to O7-H7···O9 in agreement (Table 4) with the hydrogen bond-length vs. IR frequency correlation by Libowitzky (1999).

Dehydration behavior as observed for cavansite is typical of zeolites and in particular of gismondine, $CaAl_2Si_2O_8 \cdot 4H_2O$, which has a similar crystal structure (Rinaldi and Vezzalini

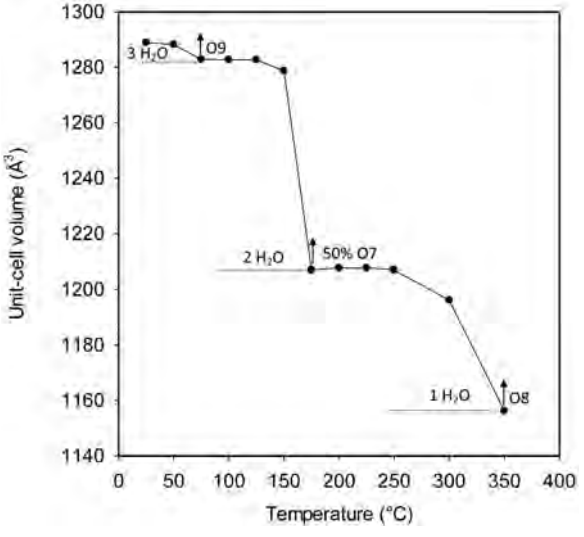


FIGURE 4. Development of unit-cell volume vs. temperature for in situ dehydration experiments of cavansite. With exception of the 350 °C data, the size of the symbols is larger than the associated e.s.d. values.

TABLE 8. Comparison between the results of thermo-gravimetric analysis of cavansite reported by Phadke and Apte (1994), Powar and Byrappa (2001), Prasad and Prasad (2007), and Ishida et al. (2009), all values in °C

Phadke and Apte (1994)	Powar and Byrappa (2001)	Prasad and Prasad (2007)	Ishida et al. (2009)
150	120	87	125
	200	197	
290		277	250
440			400
530		500	510

Note: Temperatures correspond to the maxima of DTG curves and not to the onset of dehydration.

1985; Vezzalini et al. 1993; Milazzo et al. 1998). As reported by Van Reeuwijk (1971), five metastable phases were created while heating gismondine, at ca. 70, 87, 108, 196, and 280 °C before final collapse. At 350 °C, a structural transformation takes place and the formation of high-temperature Ca-feldspar starts. Compared to cavansite, structural modifications in gismondine upon dehydration are much more severe. Between ambient conditions (H_2O/Ca = 4) and 160 °C (H_2O/Ca = 2) the normalized unit-cell volume of gismondine reduced by 17%, whereas in cavansite the volume change between room temperature (H_2O/Ca = 4) and 350 °C (H_2O/Ca = 1) amounts to only 10%. This difference is also corroborated by changes in T-O-T angles. In the temperature range cited above, average T-O-T angles in gismondine decrease from 146 to 132° (Rinaldi and Vezzalini 1985; Vezzalini et al. 1993) whereas average T-O-T angles in cavansite decrease from 132 to 130° (Table 5[1]). Furthermore, in the course of dehydration gismondine undergoes several phase transitions (Milazzo et al. 1998), whereas in cavansite dehydration proceeds rather smoothly within the same space group. The limiting Ca coordination seems to be responsible for phase transitions or structural collapse in gismondine and cavansite before complete dehydration. The lowest Ca coordination number in cavansite appears to be five and removal of the last H_2O molecule caused structural destruction. The high-temperature structure of gismondine before structural breakdown has not been solved (Milazzo et al. 1998). Thus the limiting Ca coordination in gismondine remains unknown. The critical limit in Ca coordination has been reported for several Ca-containing zeolites but this limit alone cannot be taken as reference to determine the framework breakdown (Cruciani 2006).

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Tables 3a–3d for deposit.

TABLE 3a. Anisotropic displacement parameters (Å^2) for cavansite at RT

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V	0.00849(16)	0.00949(16)	0.01330(17)	0	0.00076(11)	0
Ca	0.01036(19)	0.01118(19)	0.0167(2)	0	0.00069(14)	0
Si1	0.00635(17)	0.00920(18)	0.00869(18)	0.00054(13)	–0.00063(12)	0.00008(13)
Si2	0.00691(17)	0.00834(17)	0.00772(17)	0.00053(12)	0.00091(12)	0.00042(13)
O1	0.0093(5)	0.0098(5)	0.0193(5)	–0.0007(4)	0.0002(4)	–0.0007(4)
O2	0.0154(5)	0.0091(5)	0.0168(5)	0.0015(4)	0.0052(4)	0.0021(4)
O3	0.0122(5)	0.0212(6)	0.0099(5)	0.0039(4)	–0.0014(4)	–0.0003(4)
O4	0.0082(4)	0.0113(5)	0.0172(5)	–0.0015(4)	0.0026(4)	–0.0001(4)
O5	0.0103(5)	0.0122(5)	0.0111(5)	0.0019(4)	–0.0039(4)	–0.0013(4)
O6	0.0231(9)	0.0287(10)	0.0192(8)	0	–0.0052(7)	0
O7	0.0340(9)	0.0489(11)	0.0498(10)	–0.0273(9)	0.0089(7)	0.0048(7)
O8	0.0146(9)	0.0319(11)	0.0658(16)	0	–0.0048(10)	0
O9	0.066(2)	0.109(3)	0.058(2)	0	0.0091(17)	0

Table 3b. Anisotropic displacement parameters (Å^2) for cavansite at 75 °C

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V	0.0098(2)	0.0118(2)	0.0150(2)	0	0.00105(14)	0
Ca	0.0119(2)	0.0135(2)	0.0173(2)	0	0.00026(17)	0
Si1	0.0071(2)	0.0116(2)	0.0104(2)	0.00078(15)	–0.00049(15)	–0.00016(15)
Si2	0.0082(2)	0.0101(2)	0.0097(2)	0.00080(15)	0.00136(15)	0.00053(15)
O1	0.0107(6)	0.0122(6)	0.0220(7)	–0.0010(5)	0.0014(5)	–0.0002(4)
O2	0.0189(6)	0.0110(6)	0.0207(6)	0.0016(5)	0.0079(5)	0.0029(5)
O3	0.0132(6)	0.0262(7)	0.0127(6)	0.0049(5)	–0.0020(5)	–0.0008(5)
O4	0.0098(5)	0.0142(6)	0.0199(6)	–0.0018(5)	0.0039(5)	–0.0005(5)
O5	0.0121(6)	0.0154(6)	0.0138(6)	0.0030(5)	–0.0049(4)	–0.0021(4)
O6	0.0289(12)	0.0370(13)	0.0222(10)	0	–0.0080(9)	0
O8	0.0215(15)	0.099(3)	0.106(4)	0	–0.0007(18)	0

Table 3c. Anisotropic displacement parameters (Å^2) for cavansite at 175 °C

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V	0.0140(2)	0.0168(2)	0.0185(2)	0	0.00103(17)	0
Ca	0.0163(3)	0.0197(3)	0.0194(3)	0	–0.0001(2)	0

Si1	0.0108(2)	0.0170(3)	0.0146(3)	0.00178(17)	–0.00055(18)	0.00016(17)
Si2	0.0124(2)	0.0155(2)	0.0131(2)	0.00137(17)	0.00162(17)	0.00114(18)
O1	0.0153(6)	0.0172(7)	0.0272(8)	–0.0011(6)	0.0017(5)	–0.0002(5)
O2	0.0248(7)	0.0168(7)	0.0237(7)	0.0027(5)	0.0087(6)	0.0043(6)
O3	0.0180(7)	0.0328(9)	0.0169(7)	0.0063(6)	–0.0025(5)	–0.0008(6)
O4	0.0144(7)	0.0194(7)	0.0250(7)	0.0001(5)	0.0050(6)	–0.0003(5)
O5	0.0158(7)	0.0220(7)	0.0190(7)	0.0037(5)	–0.0051(5)	–0.0018(5)
O6	0.0326(13)	0.0404(14)	0.0282(13)	0	–0.0086(11)	0
O8	0.035(2)	0.172(6)	0.157(6)	0	0.029(3)	0

Table 3d. Anisotropic displacement parameters ($Å^2$) for cavansite at 350 °C

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V	0.0308(12)	0.0317(11)	0.0343(13)	0	0.0063(10)	0
Ca	0.0358(14)	0.0357(14)	0.0405(17)	0	–0.0030(12)	0
Si1	0.0211(12)	0.0300(12)	0.0255(14)	0.0024(9)	–0.0021(9)	0.0000(8)
Si2	0.0241(11)	0.0293(11)	0.0195(13)	0.0015(9)	0.0041(9)	0.0008(9)
O1	0.030(3)	0.033(3)	0.049(4)	0.001(3)	0.002(3)	0.000(2)
O2	0.048(4)	0.032(3)	0.033(4)	0.004(3)	0.016(3)	0.006(3)
O3	0.034(3)	0.054(4)	0.022(3)	0.007(3)	–0.003(3)	–0.002(3)
O4	0.023(3)	0.035(3)	0.035(3)	0.003(2)	0.003(3)	0.000(2)
O5	0.031(3)	0.038(3)	0.024(3)	0.008(2)	–0.004(3)	–0.001(2)
O6	0.067(7)	0.068(7)	0.048(7)	0	–0.010(6)	0

TABLE 5 for deposit

TABLE 5. Interatomic distances (Å) and T-O-T angles (°) of cavansite under ambient conditions and after partial dehydration at 75, 175, and 350 °C

Ca coordination	RT	75 °C	175 °C	350 °C
Ca-O1 (2×)	2.3941(11)	2.3726(14)	2.3356(15)	2.292(11)
Ca-O2 (2×)	2.4418(12)	2.4081(14)	2.3291(16)	2.271(11)
Ca-O7 (2×)	2.3894(16)	2.407(9)	2.402(15)	2.31(5)
Ca-O7a (2×)		2.47(1)	2.453(11)	
Ca-O7b (2×)		2.409(4)	2.41(2)	2.42(6)
Ca-O8	2.501(2)	2.473(4)	2.402(5)	2.07(8)
Ca-O9	2.834(4)	2.82(3)		
Mean	2.473	2.469*	2.359*	2.260*

*The mean value of the split positions is given.

V coordination	RT	75 °C	175 °C	350 °C
V-O1 (2×)	2.0026(11)	2.0032(14)	2.0017(15)	2.01(1)
V-O2 (2×)	1.9843(11)	1.9843(14)	1.9718(15)	1.980(9)
V-O6	1.5956(18)	1.590(2)	1.590(3)	1.559(13)
Mean	1.914	1.913	1.907	1.908

Si1 coordination	RT	75 °C	175 °C	350 °C
Si1-O1	1.6027(12)	1.6030(15)	1.6090(16)	1.60(1)
Si1-O3	1.6231(12)	1.6239(15)	1.6220(16)	1.60(1)
Si1-O4	1.6406(11)	1.6357(14)	1.6343(15)	1.620(8)
Si1-O5	1.6298(11)	1.6279(13)	1.6269(15)	1.617(9)
Mean	1.624	1.623	1.623	1.609

Si2 coordination	RT	75 °C	175 °C	350 °C
Si2-O2	1.5922(12)	1.5908(14)	1.5947(16)	1.59(1)
Si2-O3	1.6231(12)	1.6202(14)	1.6233(16)	1.612(9)
Si2-O4	1.6248(11)	1.6283(14)	1.6265(16)	1.625(9)
Si2-O5	1.6234(11)	1.6230(13)	1.6251(15)	1.625(9)
Mean	1.616	1.616	1.617	1.613

T-O-T angles	RT	75 °C	175 °C	350 °C
Si2 O3 Si1	136.36(8)	136.92(9)	135.18(10)	137.3(4)
Si2 O4 Si1	127.78(7)	127.77(9)	127.32(10)	127.0(5)
Si2 O5 Si1	131.42(7)	131.46(9)	128.24(10)	126.2(4)
Mean T-O-T	131.85	132.05	130.25	130.17

TABLE 6 for deposit

TABLE 6. Results of bond valence calculations for cavansite RT, parameters from Brown and Altermatt (1985)

Site	O1	O2	O3	O4	O5	O6	O7	O8	O9	Bvs[#]
V	0.56	0.59				1.67				3.97
	2 × →	2 × →								
Ca	0.28	0.26					0.29	0.23	0.11	2.00
	2 × →	2 × →					2 × →			
Si1	1.06		0.97	0.93	0.95					3.91
Si2		1.04	0.97	0.96	0.97					3.93
H7a							0.8		0.2	1
									2 × ↓	
H7b					0.2		0.8			1
H8			0.2					0.8		1
								2 × ↓		
H9a						0.2			0.8	1
H9b									1*	1
Bvs[#] without H					1.92	1.67	0.29	0.23	0.11	
Bvs[#] with H	1.90	1.89	2.14	1.89	2.12	1.87	1.89	1.83	2.31	

[#] bond valence sum.

*No acceptor was found for H9b.

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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Ca Ca -0.38248(5) 0.7500 -0.08753(5) 0.01422(12) Uani 1 2 d S . .
Si1 Si -0.18529(5) 0.53429(4) -0.09246(5) 0.00969(11) Uani 1 1 d . . .
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O5 O -0.31993(13) 0.49792(10) -0.17994(13) 0.0138(3) Uani 1 1 d . . .
O6 O -0.0455(3) 0.2500 -0.0566(2) 0.0294(5) Uani 1 2 d S . .
O7 O -0.4471(11) 0.8517(9) 0.1035(13) 0.0448(11) Uiso 0.270(8) 1 d P . .
O7A O -0.3993(11) 0.8184(8) 0.1464(11) 0.0448(11) Uiso 0.245(7) 1 d P . .
O7B O -0.4643(5) 0.8806(4) 0.0570(6) 0.0448(11) Uiso 0.557(10) 1 d P . .
O8 O -0.6396(4) 0.7500 -0.0987(5) 0.0756(14) Uani 1 2 d S . .
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O3 0.0132(6) 0.0262(7) 0.0127(6) 0.0049(5) -0.0020(5) -0.0008(5)
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O6 0.0289(12) 0.0370(13) 0.0222(10) 0.000 -0.0080(9) 0.000
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 All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell s.u.'s are taken
 into account individually in the estimation of s.u.'s in distances, angles
 and torsion angles; correlations between s.u.'s in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
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V O1 2.0032(14) 5_565 ?
V O1 2.0032(14) 3_545 ?
V Ca 3.4255(7) 5_565 ?
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V Ca 3.4325(7) 6_556 ?
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Ca O1 2.3726(14) . ?
Ca O7 2.408(9) . ?
Ca O7 2.408(9) 7_575 ?
Ca O2 2.4081(14) 4_464 ?
Ca O2 2.4081(14) 6_565 ?
Ca O7B 2.409(4) . ?
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Ca O7A 2.472(10) . ?
Ca O7A 2.472(10) 7_575 ?
Ca O8 2.473(4) . ?
Ca O9 2.82(3) . ?
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Si1 O3 1.6239(15) . ?
Si1 O5 1.6279(13) . ?
Si1 O4 1.6357(14) . ?
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Si2 O4 1.6283(14) 5_565 ?
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O1 Ca O7B 80.47(11) . 7_575 ?
O7 Ca O7B 83.8(4) . 7_575 ?
O7 Ca O7B 14.9(3) 7_575 7_575 ?
O2 Ca O7B 93.47(16) 4_464 7_575 ?
O2 Ca O7B 146.75(14) 6_565 7_575 ?
O7B Ca O7B 95.8(3) . 7_575 ?
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O7 Ca O7A 59.2(5) . 7_575 ?
O7 Ca O7A 18.1(3) 7_575 7_575 ?
O2 Ca O7A 124.8(3) 4_464 7_575 ?
O2 Ca O7A 165.0(2) 6_565 7_575 ?
O7B Ca O7A 73.7(3) . 7_575 ?
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 'Ca'  'Ca'   0.2262   0.3064
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_details
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Ca Ca -0.38889(6) 0.7500 -0.07578(6) 0.01849(14) Uani 1 2 d S . .
Si1 Si -0.19261(6) 0.52653(4) -0.08317(6) 0.01415(13) Uani 1 1 d . . .
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Si2 Si -0.09206(6) 0.46155(4) 0.19910(5) 0.01366(13) Uani 1 1 d . . .
O1 O -0.18823(15) 0.64770(11) -0.07596(16) 0.0199(3) Uani 1 1 d . . .
O2 O -0.05978(17) 0.34527(11) 0.22691(16) 0.0218(3) Uani 1 1 d . . .
O3 O -0.20100(16) 0.47554(13) 0.07010(16) 0.0226(3) Uani 1 1 d . . .
O4 O -0.05458(16) 0.48034(11) -0.16282(16) 0.0196(3) Uani 1 1 d . . .
O5 O -0.33434(16) 0.48941(11) -0.16389(15) 0.0189(3) Uani 1 1 d . . .
O6 O -0.0552(3) 0.2500 -0.0398(3) 0.0337(6) Uani 1 2 d S . .
O7 O -0.430(2) 0.7778(16) 0.1679(16) 0.044(3) Uiso 0.162(12) 1 d P . .
O7A O -0.3625(16) 0.7750(11) 0.1759(12) 0.044(3) Uiso 0.203(10) 1 d P . .
O7B O -0.397(3) 0.810(2) 0.161(2) 0.044(3) Uiso 0.142(14) 1 d P . .
O8 O -0.6409(5) 0.7500 -0.0485(8) 0.121(2) Uani 1 2 d S . .

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Ca 0.0163(3) 0.0197(3) 0.0194(3) 0.000 -0.0001(2) 0.000
Si1 0.0108(2) 0.0170(3) 0.0146(3) 0.00178(17) -0.00055(18) 0.00016(17)
Si2 0.0124(2) 0.0155(2) 0.0131(2) 0.00137(17) 0.00162(17) 0.00114(18)
O1 0.0153(6) 0.0172(7) 0.0272(8) -0.0011(6) 0.0017(5) -0.0002(5)
O2 0.0248(7) 0.0168(7) 0.0237(7) 0.0027(5) 0.0087(6) 0.0043(6)
O3 0.0180(7) 0.0328(9) 0.0169(7) 0.0063(6) -0.0025(5) -0.0008(6)
O4 0.0144(7) 0.0194(7) 0.0250(7) 0.0001(5) 0.0050(6) -0.0003(5)
O5 0.0158(7) 0.0220(7) 0.0190(7) 0.0037(5) -0.0051(5) -0.0018(5)
O6 0.0326(13) 0.0404(14) 0.0282(13) 0.000 -0.0086(11) 0.000
O8 0.035(2) 0.172(6) 0.157(6) 0.000 0.029(3) 0.000

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;
 All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell s.u.'s are taken
 into account individually in the estimation of s.u.'s in distances, angles
 and torsion angles; correlations between s.u.'s in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
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V O2 1.9718(15) 7_565 ?
V O2 1.9718(15) . ?
V O1 2.0017(15) 5_565 ?
V O1 2.0017(15) 3_545 ?
V Ca 3.3629(8) 5_565 ?
V Ca 3.4082(8) 6_556 ?
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Ca O7B 2.415(19) 7_575 ?
Ca O2 2.3291(16) 4_464 ?
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Ca O1 2.3356(15) 7_575 ?
Ca O1 2.3356(15) . ?
Ca O7 2.402(15) . ?
Ca O7 2.402(15) 7_575 ?
Ca O8 2.402(5) . ?
Ca O7A 2.453(11) . ?
Ca O7A 2.453(11) 7_575 ?
Ca V 3.3629(8) 5_565 ?
Si1 O1 1.6090(16) . ?
Si1 O3 1.6220(16) . ?
Si1 O5 1.6269(15) . ?
Si1 O4 1.6343(15) . ?
Si2 O2 1.5947(16) . ?
Si2 O3 1.6233(16) . ?
Si2 O5 1.6251(15) 4_465 ?
Si2 O4 1.6265(16) 5_565 ?
Si2 Ca 3.5468(6) 6_556 ?
O1 V 2.0017(15) 5_565 ?
O2 Ca 2.3291(16) 6_556 ?
O4 Si2 1.6265(15) 5_565 ?
O5 Si2 1.6251(15) 4_464 ?
O7 O7A 0.65(2) . ?
O7 O7B 0.53(2) . ?
O7 O7 0.74(4) 7_575 ?
O7 O7A 0.954(17) 7_575 ?
O7 O7B 1.21(4) 7_575 ?
O7A O7A 0.66(3) 7_575 ?
O7A O7 0.954(17) 7_575 ?
O7A O7B 0.58(2) . ?
O7A O7B 1.18(4) 7_575 ?
O7B O7 1.21(4) 7_575 ?
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O6 V O2 106.17(9) . . ?
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O2 V O1 146.65(7) 7_565 5_565 ?
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Ca V Ca 117.876(18) 5_565 6_556 ?
O7B Ca O7B 38.4(15) . 7_575 ?
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O7B Ca O2 125.6(7) 7_575 4_464 ?
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O7B Ca O1 80.6(7) . 7_575 ?
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O7B Ca O7 12.7(5) . . ?
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O7B Ca O7 12.7(5) 7_575 7_575 ?
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O1 Ca O7 92.6(6) . 7_575 ?
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O7B Ca O7A 28.1(9) . 7_575 ?
O7B Ca O7A 13.8(5) 7_575 7_575 ?
O2 Ca O7A 138.6(4) 4_464 7_575 ?
O2 Ca O7A 153.7(3) 6_565 7_575 ?
O1 Ca O7A 89.8(4) 7_575 7_575 ?
O1 Ca O7A 80.8(3) . 7_575 ?
O7 Ca O7A 22.6(4) . 7_575 ?
O7 Ca O7A 15.3(5) 7_575 7_575 ?
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O7B Ca V 95.6(6) . 5_565 ?
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Si2 O2 V 127.10(9) . . ?
Si2 O2 Ca 128.38(8) . 6_556 ?
V O2 Ca 104.52(6) . 6_556 ?
Si1 O3 Si2 135.18(10) . . ?
Si2 O4 Si1 127.32(10) 5_565 . ?
Si2 O5 Si1 128.24(10) 4_464 . ?
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O7 O7 O7B 15.5(15) 7_575 7_575 ?
O7A O7 O7B 28.4(14) 7_575 7_575 ?
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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_atom_sites_solution_hydrogens    geom
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Si1 Si -0.1968(2) 0.52399(16) -0.0781(2) 0.0256(6) Uani 1 1 d . . .
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Si2 Si -0.0833(2) 0.46265(16) 0.2073(2) 0.0243(6) Uani 1 1 d . . .
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O2 O -0.0485(6) 0.3461(4) 0.2374(6) 0.0378(15) Uani 1 1 d . . .
O3 O -0.1946(6) 0.4739(5) 0.0777(6) 0.0366(15) Uani 1 1 d . . .
O4 O -0.0631(5) 0.4784(4) -0.1666(6) 0.0309(14) Uani 1 1 d . . .
O5 O -0.3434(6) 0.4873(4) -0.1524(6) 0.0310(14) Uani 1 1 d . . .
O6 O -0.0568(12) 0.2500 -0.0373(12) 0.061(3) Uani 1 2 d S . .
O7 O -0.517(6) 0.780(4) 0.134(6) 0.129(18) Uiso 0.25(3) 1 d P . .
O7B O -0.415(7) 0.782(4) 0.181(6) 0.129(18) Uiso 0.22(3) 1 d P . .
O8 O -0.590(9) 0.7500 0.018(10) 0.129(18) Uiso 0.24(4) 2 d SP . .

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Si1 0.0211(12) 0.0300(12) 0.0255(14) 0.0024(9) -0.0021(9) 0.0000(8)
Si2 0.0241(11) 0.0293(11) 0.0195(13) 0.0015(9) 0.0041(9) 0.0008(9)
O1 0.030(3) 0.033(3) 0.049(4) 0.001(3) 0.002(3) 0.000(2)
O2 0.048(4) 0.032(3) 0.033(4) 0.004(3) 0.016(3) 0.006(3)
O3 0.034(3) 0.054(4) 0.022(3) 0.007(3) -0.003(3) -0.002(3)
O4 0.023(3) 0.035(3) 0.035(3) 0.003(2) 0.003(3) 0.000(2)
O5 0.031(3) 0.038(3) 0.024(3) 0.008(2) -0.004(3) -0.001(2)
O6 0.067(7) 0.068(7) 0.048(7) 0.000 -0.010(6) 0.000

_geom_special_details
;
 All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell s.u.'s are taken
 into account individually in the estimation of s.u.'s in distances, angles
 and torsion angles; correlations between s.u.'s in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
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V Ca 3.394(17) 6_556 ?
Ca O8 2.07(8) . ?
Ca O2 2.271(11) 4_464 ?
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Ca O1 2.292(11) . ?
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Ca O7B 2.42(6) . ?
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Si2 O5 1.625(9) 4_465 ?
Si2 Ca 3.486(15) 6_556 ?
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O5 Si2 1.625(9) 4_464 ?
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