

X-ray, thermal and infrared studies of cavansite from Wagholi western Maharashtra, India

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Deep lagoon-blue crystals of cavansite occur in cavities in agglomerated breccia associated with Deccan basalts at Wagholi, western Maharashtra. X-ray, thermal and infrared studies, reported in this communication, suggest that cavansite is a 3-dimensional vanadosilicate network analogous to gismondine. Water molecules occur in the mineral both as loosely held and tightly bound crystal water.

Introduction

The rare hydrated calcium vanadium silicate $\text{Ca}(\text{VO})(\text{Si}_4\text{O}_{10}) \cdot 4\text{H}_2\text{O}$, cavansite, was first described by Staples et al. (1973) from cavities and veinlets in basalts and tuffs of Oregon, U.S.A. Its crystal structure was reported by Evans (1973) on the basis of detailed X-ray diffraction studies. According to him, the mineral has a silicate-layer structure in which the layers are held together by VO^{2+} groups and Ca^{2+} ions. He stated that H_2O molecules are probably zeolitic.

Some species of aluminosilicates form an important group of tectosilicate minerals. They can selectively adsorb or reject foreign molecules of appropriate molecular size to their structure. This property attracts a technological attentions for their use as molecular sieves. In recent years, the structural analogues of aluminosilicates, viz., aluminophosphates, berylosilicates, berylophosphates, zincosilicates and vanadosilicates are becoming more significant because of their large pore sizes with unusual structure and properties that are not seen in aluminosilicate zeolites. Aluminosilicate zeolites occur in large quantity in nature as zeolites with 54 representatives. Aluminophosphate zeolites are obtained only synthetically without natural counterparts, whereas vanadosilicate zeolites occur rarely in nature. Although cavansite was reported in 1973 by Staples et al., and its structure was refined in the same year by Evans et al., a systematic characteri-

zation had not yet given. Hence very little is known about the zeolitic behaviours particularly with reference to the existence of water molecules, their concentration, structural relation, removal and adsorption of water, the nature of cavities in the structure and so on.

Very few studies on cavansite are available because the mineral is rare. It has been reported from agglomerated breccia associated with Deccan basalts at Wagholi near Pune (Poona) in Maharashtra, India, by Wilke et al. (1989). Samples of the Wagholi cavansite have been subjected to X-ray diffraction, thermal and infrared spectroscopic studies and the results are presented in this communication.

Wagholi cavansite

The cavansite samples studied were obtained from a basalt quarry at Wagholi about 15° northeast of Pune on the Pune-Aurangabad highway. The mineral occurs in cavities in agglomerated breccia overlying hard and compact basalt and it is associated with calcite, heulandite, stilbite and rare apophyllite. It is usually developed on stilbite or heulandite and occurs in aggregates of prismatic crystals, often in sheaf-like form (Fig. 1). The cavansite crystals are of deep lagoon-blue colour and vary in length from a few mm to about 15 mm. In thin sections they are pleochroic from intense blue (X) to pale blue (Y=Z). The mineral is biaxial-positive with $2V=51^\circ$. The refractive indices are $n_a=1.540(1.534)$, $n_b=1.545(1.539)$ and $n_g=1.550(1.553)$ (Wilke et al., 1989). The values given in the bracket correspond to the present work.

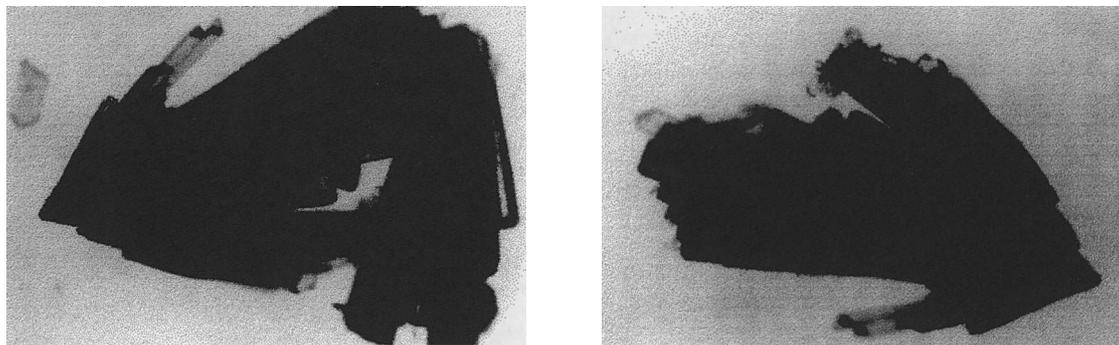


Figure 1. Characteristic photograph of Wagholi cavansite ($\times 10$).

Methodology

An aggregate of cavansite crystals, occurring in association with stilbite, was crushed, and pure, deep-blue fragments of the mineral, free from adhering secondary minerals, were hand picked under a binocular microscope. These fragments were then ground to -200 mesh in an agate mortar. Grinding was carried out in short spells of less than a minute to avoid any loss of water due to friction/heating. This powder was used for experimental studies. An X-ray powder diffractogram in the 2θ range $5-75^\circ$ was obtained on a Philips Model TW 1710 diffractometer using $\text{CuK}\alpha$ radiation. The single crystal X-ray diffraction studies were carried out using ENRAF-NONIUS CAD-4 X-ray diffractometer equipped with a graphite monochromator. $\text{MoK}\alpha$ radiation was used. TG and DSC curves were obtained on a Rigaku Model TG-DSC 8110 thermoflex with an attachment of TAS-100 thermal analysis station.

Infrared spectra were obtained at room temperature for Wagholi cavansite not subjected to heat treatment. For this purpose, 3 mg of cavansite was mixed with 297 mg of KBr and compressed into discs, which were scanned by a Perkin-Elmer Model 783 double-beam IR spectrophotometer with NaCl optics. The scanning was done over the frequency range 200 to 4000 cm^{-1} . The instrument was calibrated with polystyrene 1601.4 reference standard. Repeated scans gave very consistent results.

X-ray diffraction

The powder patterns of cavansite were indexed and the unit cell dimensions, orthorhombic, with $a=9.6914$, $b=9.7325$, $c=13.6052\text{ \AA}$, $V=1283.25\text{ \AA}^3$ were obtained. These values correspond to those obtained by Staples et al. (1973).

A prismatic crystal of ($0.1\times 0.1\times 0.2\text{ mm}$) was

selected and mounted on an ENRAF-NONIUS CAD-4 Single Crystal Diffractometer. Unit cell parameters were determined from automatic centering of about 25 reflections in the range $2<O<32^\circ$ ($R=0.1$). Lorentz-polarization factors were applied, but no absorption corrections were made. The single crystal X-ray diffraction studies gave the following cell parameters for the cavansite from Wagholi region, India: orthorhombic, space group, Pcmn , $a=9.6914$, $b=9.7325$, $c=13.6052\text{ \AA}$, $Z=4$, $V=1283.25\text{ \AA}^3$. This data corresponds with the earlier published data (Evans, 1973; Rinaldi et al., 1975). As a complete refinement of crystal structure of this mineral is already done by previous authors, the metal-oxygen distances were not re-determined here. We then limited our work to the precise determination of the cell parameters R-factor calculated by using previous data for the present observations gave $R=0.1$. The structure of cavansite consists of a framework of 4-fold and 8-fold rings with SiO_4 tetrahedra, three of four apices are shared with other tetrahedra, and the fourth corner is coordinated to one V atom and one Ca atom, with loosely bound water molecules. The structure clearly suggests that the hydrated vanadosilicate is zeolitic in nature with an unusual structural topology. This structure is closely similar to that of gismondine. However, in gismondine the exposed tetrahedral apices in adjacent layers are linked, not through VO^{2+} groups, but directly to form a three-dimensional aluminosilicate network.

Thermal analysis

As indicated above, finely ground cavansite was subjected to thermal studies on a Rigaku thermoflex. The sample was dried at 50°C in near vacuum (1 mmHg) for one hour to remove adhering moisture. About 7 mg of powder was then heated at a constant heating rate of $6^\circ\text{C}/\text{min}$ through temperature range of $25-800^\circ\text{C}$ with a sensitivity of 50 mV full scale. DSC and TG curves

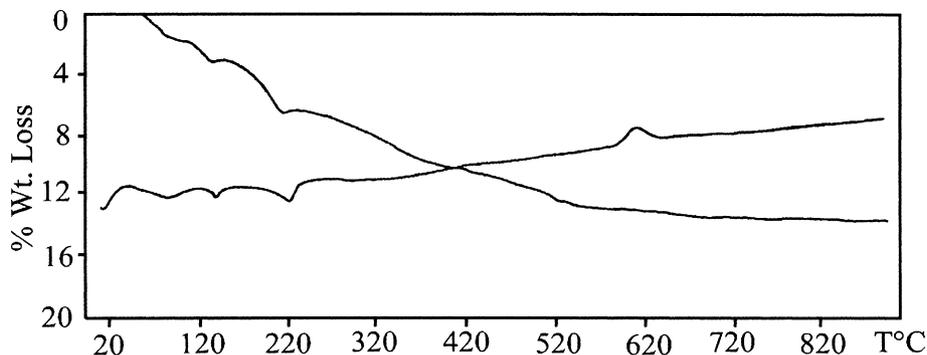


Figure 2. TG/DSC curves for Wagholi cavansite.

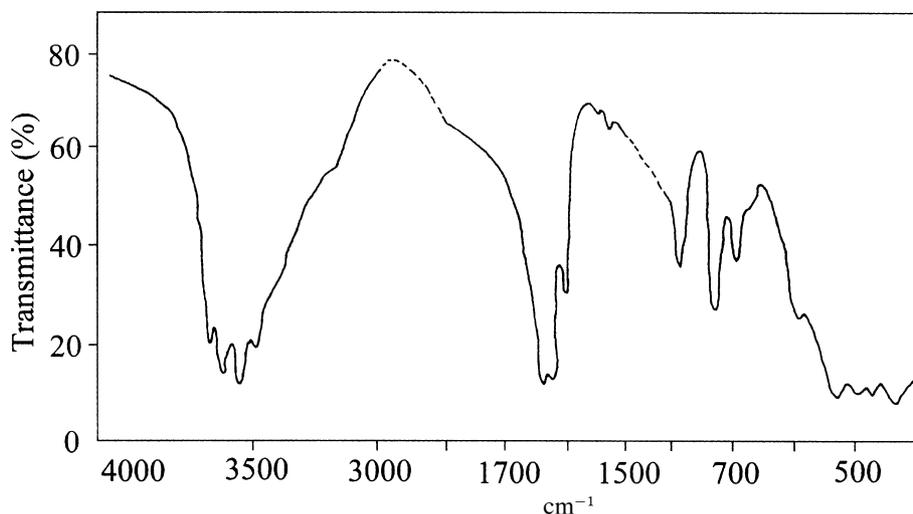


Figure 3. IR-spectrum of Wagholi cavansite.

with 100% full scale and 20% full scale were obtained. Peak temperatures were estimated from values of e.m.f. of thermocouple referred to standard tables furnished by the manufacturers. The runs at 100% and 20% full scale gave almost identical results. The curves obtained at 20% full scale are illustrated in Figure 2. It is noted that the DSC curve shows two endothermic peaks at 119°C (e.m.f.=4 mV) and 197°C (7 mV) and a small exothermic peak at 585°C (24 mV). The TG curve shows more or less continuous dehydration with accelerated loss at 2 stages broadly corresponding to the two endothermic peaks at 120°C and 200°C. The weight losses at these temperatures are respectively 2.8% and 6.4%. There is no accelerated/rapid weight loss corresponding to the exothermic peak at 585°C. At this stage, a weight loss of 13% was achieved. Further heating up to 800°C did not result in any significant weight loss, the total weight loss being 13.1%.

Infrared spectroscopy

The IR spectrum of cavansite is shown in Figure 3. As is evident from the figure, IR spectrum of cavansite exhibits, in the wavelength range 4000 to 3000 cm^{-1} , well-defined peaks at 3648, 3592, 3548 and 3490 cm^{-1} and a shoulder at 3250 cm^{-1} . Within the range of 1700–1600 cm^{-1} strong peaks are obtained at 1645 and 1635 cm^{-1} , and a sharp peak at 1610 cm^{-1} . There is a broad, strong band, without sharp peaks in the 1100 to 900 cm^{-1} range. In the region of 800 to 400 cm^{-1} , sharp peaks are recorded at 790, 730 and 698 cm^{-1} and less defined peaks at 600, 540, 500, 480 and 445 cm^{-1} .

Discussion

Vanadium is an important transitional element with valency states 2, 3, 4 and 5. Its abundance in the earth's crust is 0.017 wt.%. Though vanadium is highly reaction susceptible, it rarely forms perfect isomorphism in

the trivalent state with other transitional metals like Al, Cr, Fe, Mn. On the contrary V^{5+} and As^{5+} form perfect isomorphism. In cavansite, vanadium exists in the typical 4- and 5-valent states as indicated by its square-pyramidal coordination with oxygen. Whereas Ca^{2+} is in 7-fold coordination. This kind of variation in valency can be seen in several other elements. Here in case of cavansite, the vanadium exists both in tetra- and pentavalent states. But their proportions are not uniform. The hydroxyl groups present in cavansite adjust any charge imbalance. This kind of coordination of vanadium in cavansite gives unique structural properties, wherein no isomorphism with other transitional elements could be established. For example in most of silicates, Al, Cr, Mn, all form octahedral coordination, Fe form square pyramidal coordination with oxygen, and Al also forms a tetrahedral coordination. All of these elements are so similar to one another in their atomic radii that they show the possibility of isomorphous substitution. The structure of cavansite cannot accept these metals because of their octahedral coordination and also the closer affinity of V^{4+} or V^{5+} to Ca^{2+} than these elements. The structure of cavansite indicates secondary origin for this mineral and the crystallization must have taken place at lower *PT* conditions in the calcic and sodic environment.

A very interesting feature of this vanadosilicate mineral structure is the presence of cavities forming channels running along the *c*-axis just like in gismondine. In terms of purely layer-type structures, the linkage of layers in appears to be unique. In the recent years, the vanadophosphates are becoming materials of great interest owing to their microporous frameworks like the vanadosilicate.

The synthesis of vanadophosphate zeolites offers the possibilities of existence of their natural analogues or new minerals. The present studies of X-ray diffraction combined with thermal and infrared analyses on cavansite are showing a prospective nature of the vanadosilicate frameworks for molecular sieves, selective adsorption of gases, catalysis and so on. These studies clearly indicate also the zeolitic behaviour of cavansite.

It is found from the thermal analysis data that the weight losses at approximately 120°C and 200°C may respectively be ascribed to the removal of what have been termed as 'loosely held' and 'tightly bound' water molecules (Breger et al., 1970). Weight losses at these temperatures were reported, in heulandite, over sixty years ago by Milligan and Weiser (1937). The weight losses at approximately 120°C and 200°C which are 2.8% and 6.4% respectively can be attributed to 0.86 ($\gg 1$) and 1.97 ($\gg 2$) water molecules, while the maximum loss of

13% is due to the loss of 4 water molecules. The first two water molecules are being removed in two distinct stages and the other two are gradually get removed over a comparatively wide range of temperature (200 to 500°C). The small exothermic peak at 585°C without weight loss signifies a structural (phase) transition.

The removable 4 water molecules are thus zeolitic and probably distributed into the cavities of channels with stabilization due to weak ion-dipole and Van der Waal type of forces. Two more water molecules, which are proposed in the molecular formula, are probably bonded to calcium ions and are not removed even up to 800°C. These water molecules can be termed as tightly bound (crystal) water molecules. The form of the TG curve is similar to that obtained by Varadarajan and Mitra (1984) for heulandite. The thermal studies thus support the view that cavansite has a zeolitic structure and suggest that the water molecules occur in different crystallochemical environment. They are expelled in different stages of dehydration. The 13% weight loss is consistent with the chemical formula for cavansite with four water molecules, as proposed by Staples et al. (1973).

In case of minerals with zeolitic structure, the infrared measurements can yield information regarding their structure and structure-adsorbent interactions (Ward, 1979). Absorption bands occurring in the region 3750–3000 cm^{-1} are commonly attributed to hydroxyl group or water molecules and their values may indicate attachment. In the present case, the bands at about 3650 cm^{-1} (3648 cm^{-1}), 3585 cm^{-1} (3592 cm^{-1}) and 3550 cm^{-1} (3548 cm^{-1}) suggest that the water-molecules are attached to calcium, (Ward, 1979), and the absorptions are due to stretching (symmetric and antisymmetric) vibrations of -OH and cation-water bonding (Falk and Knop, 1973). The band at 3250 cm^{-1} probably represents bonding vibration of tightly bonded crystal water molecules (Van der Marcel and Beutelspacher, 1976). This tightly-bonded water molecule is also represented by the O-H stretching vibration at 3490 cm^{-1} and weak O-H bending vibration at 1645 and 1635 cm^{-1} (c.f. Van der Marcel and Beutelspacher, op.cit.).

The absorption bands recorded for cavansite are very similar to those reported in gismondine (Gadsden, 1975). The common bands are (cavansite/gismondine): 3548/3550 cm^{-1} , 3250/3250 cm^{-1} , 1645/1655 cm^{-1} , 790/785 cm^{-1} , 730/735 cm^{-1} , 698/685 cm^{-1} , 600/597 cm^{-1} , 445/440 cm^{-1} . The correspondence in absorption bands in the two minerals suggests a structural similarity between these two mineral recorded by Evans (1973).

It is very difficult to sort out the stretching frequencies of the free water molecules (because of the

Table 1. Infrared vibrations of H₂O in cavansite

Frequency (cm ⁻¹)		Type of motion & description	Symbol	Irreducible representation	Inference
3648		stretching	ν_1 or ν_s	A1	hydrogen bonded
3592	sharp	i) symmetric	ν_3 or ν_{as}	B2	or cation coordinated
3582		ii) antisymmetric			molecules.
3490					Ca coordinated water
					molecule.
3250	(shoulder)	bending	ν_2	A1	Ca coordinated water
					molecule.
1645	weak				
1635	weak	bending	ν_2	A1	ordinary water of
1610	sharp				hydration.
700		rotational		B2	water molecules in
730	sharp	vibration in crystal	ν_R	B1	cavities.
698				A2	
600	less	rotation	ν_R	-	rotational transitions.
540	defined				
500	less	translation		B1	cation-water
480	defined	(hindered in crystals)	ν_T	B2	stretching
445				A1	translation

hydrogen bonding amongst themselves) from the cation-bonded water molecules. The sharp peaks observed at 1610 (bending) and 790, 730 and 698 cm⁻¹ (rotational vibration frequencies) may be attributed to the presence of loosely bonded (or monomeric) water molecules in the cavities of the zeolitic structure. Such water molecules probably represent the ordinary water of hydration (not appreciably polarized). The less defined peaks at 500, 540 and 600 cm⁻¹ are difficult to interpret but their occurrence may be due to some rotational transitions involving interactions amongst the water molecules. Earlier workers for zeolites have reported the occurrence of such less defined peaks in this range. Table 1 gives the normal vibrations of H₂O molecules in cavansite.

Conclusions

X-ray diffraction, thermal and infrared studies of cavansite from Wagholi, near Pune in western Maharashtra suggest that in this mineral a three dimensional vanadosilicate network analogous to gismondine is involved in crystal structure with an unusual structural topology. The structural chemistry, thermal and infrared analyses indicate that the mineral cavansite has crystallized under lower temperature conditions (T= 110–120°C) in the calcic and sodic environment. The mineral is zeolitic and contains water molecules as loosely held in cavities or channels running along the c-

axis, as well as tightly bonded crystal water with calcium ions. The present work clearly indicates the zeolitic behaviour of cavansite with a scope for further studies in the direction of pore size, pore volume, ion exchanging properties and so on.

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References

- Breger, I.A., Chandler, J.C. and Zubovic, P. (1970) An infrared study of water in heulandite and clinoptilolite. *American Mineralogist*, 33, 835–840.
- Cotton, F. and Wilkinson, G. (1969) *Advanced Inorganic Chemistry*. Wiley Eastern, pp. 815, New Delhi.

- Evans, H.T. Jr. (1973) The crystal structures of cavansite and pentagonite. *American Mineralogist*, 58, 412-424.
- Falk, M. and Knop, O. (1973) Water-A Comprehensive Treatise, Vol. 2, (Franks, F. Ed.). Plenum Press, New York, Chapter 2.
- Gadsden, J.A. (1975) *Infrared Spectra of Minerals and Related Inorganic Compounds*. pp. 277, Butterworth Group, London.
- Milligan, W.V. and Weiser, H.B. (1937) The mechanism of dehydration of heulandite. *Journal of Physical Chemistry*, 41, 1029-1041.
- Rinaldi, R., Pluth, J.J. and Smith, J.V. (1975) Crystal structure of cavansite dehydrated at 220°C. *Acta Crystallographica*, B 31, 1598-1602.
- Riou, D. and Ferey, G. (1994) Oxyfluorinated microporous compounds. *Journal of Solid State Chemistry*, 111, 422-426.
- Staples, L.W., Evans, H.T.Jr. and Lindsey, J.R. (1973) Cavansite and pentagonite, new dimorphous calcium vanadium silicate minerals from Oregon, USA. *American Mineralogist*, 58, 405-411.
- Van der Marcel, H.W. and Bevelspacher, H. (1976) *Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures*. pp. 396, Elsevier, Amsterdam.
- Varadarajan, S. and Mitra, D. (1985) Dehydration and phase transformation studies of selected zeolites from Deccan trap. *Indian Mineralogist*, Sukheswala Volume, 244-256.
- Ward, J.W. (1979) Infrared studies of zeolite surfaces and surface reactions, In: *Zeolite Chemistry and Catalysis* (Rabo, J.A. Ed.). American Chemical Society Monograph, 171 (Second corrected printing), 118-284.
- Wilkes, H-J., Schnorrer-Kohler, G. and Bhalr, A. (1989) Cavansit aus Indien. *Lapis*, 14, 39-42.

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