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Thermal behaviour of cavansite from Wagholi, India

BIRCH (1977) described isolated sky-blue rosettes of the rare vanadium mineral cavansite $[\text{Ca}(\text{VO})\text{Si}_4\text{O}_{10}\cdot 4\text{H}_2\text{O}]$ from an uncertain location in Pune district, Maharashtra, India; since then, detailed work by Arvind Bhale (Wilke *et al.*, 1989) resulted in the successful location of this mineral in one of the stone quarries at Wagholi, about 14 km from Pune. Besides the other two known occurrences from Oregon, USA, from where Staples *et al.* (1973) described this mineral and named it from its major chemical constituents Ca, V and Si, Wagholi is the only other known locality. Evans (1973) gave a detailed solution to the structure of cavansite and its polymorph pentagonite.

At Wagholi, cavansite occurs in cavities in tholeiitic basalts of the Deccan Volcanic Province. It is always associated with zeolites and other cavity minerals like calcite, okenite, apophyllite, etc. This paragenesis is very similar to that from the localities in the USA, although at Wagholi pentagonite is not recorded. Optical properties and other physical characters of cavansite from Wagholi are almost identical with those given by Staples *et al.* (1973) and the material is generally highly superior to that from Oregon in quality. The samples from Wagholi, under the microscope, show parallel extinction, R.I. ranging from $\alpha = 1.544 (\pm 0.002)$ to $\gamma = 1.550 (\pm 0.002)$ and biaxial interference figure with $2V\gamma$ around 50° , a strong dispersion $r < v$, $c = \text{Bxa}$ and length slow character. These characters are almost identical with those given by Staples *et al.* (1973) except that the pleochroism of the Wagholi material is different. Parallel to the b -axis the colour is deep blue while that parallel to the a axis is also quite strong in shades of blue instead of being colourless, particularly when the needles are thicker. The cavansite needles are pellucid and

are free from any visible inclusions even at high magnification ($\times 800$).

Confirmation of the Indian material as cavansite was obtained from the X-ray powder diffraction patterns (Cu target and Ni filter). However, it is noteworthy that the Wagholi cavansite includes a CuCl phase, tentatively identified using XRD during the search match. Though the deep bluish green colour of the mineral is likely to be due to the absorption properties of V^{2+} , the possibility that the CuCl phase contributes to the colour of this mineral needs to be examined further as the contaminant is identified only by XRD. The possibility of this phase influencing the thermal characters of cavansite is ruled out on account of its insignificant amount.

Though detailed mineralogical information is available through the papers published by Staples *et al.* (1973), Evans (1973) and Wilke *et al.* (1989), there is no record of the thermal behaviour and the positions of the water molecules and their loss on heating. The availability of large crystals prompted the present authors to undertake investigations of the thermal behaviour of cavansite using Indian samples.

The DTA, DTG and TG curves (Fig. 1) have been recorded during continuous heating up to a maximum of 1000°C on the Hungarian manufactured 'Derivatograph' (OD Type 102, MOM), at the Department of Geology, University of Poona. The X-ray diffractograms (Figs. 2*a,b,c*) were obtained on a 'Rigaku' diffraction system DMax IVC (operating voltage of 50 kV and current of 25 mA) at the Department of Archaeology, Deccan College, Pune. Sample preparation and conditions of the heating experiments are summarized in Table 1.

TABLE 1. Sample preparation and conditions of heating experiments

Sample	Agate mortared, 400 mg
Packing density	loosely packed, no pressure
Sample holder	Pt crucible
Reference inert	Preheated alumina
Furnace atmosphere	Air
Thermocouples	Pt-Pt ₉₀ /Rh ₁₀
Rate of heating	10°C/min
DTA, DTG sensitivity	1/10 and 1/15
TG sensitivity	100 mg
Apparatus	'Derivatograph' OD Type 102

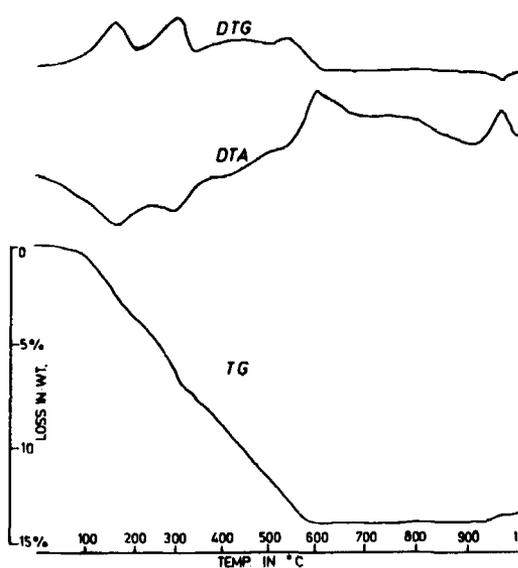


FIG. 1. DTA, DTG and TG curves of cavansite from Wagholi, India.

Thermal effects. Figure 1 reveals loss of weight in four steps corresponding to a total weight loss of 13.25%. Two major losses took place with maxima at 150°C and 290°C respectively, seen from the DTA and the DTG curves. Nearly half of the total weight loss took place up to 320°C. Above this temperature the weight loss is roughly at a constant rate up to 610°C. There is no weight loss thereafter, and instead, a small but significant gain of 0.25% is noted over the last stage, with a maximum at 960°C. The DTG trace is almost a mirror image of the DTA and in respect of the change in weight of the sample, it is more informative than the TG trace. The last two steps of weight loss, in the temperature range of 320°C to 610°C are recognizable from the DTG as a broad, low hump with a crest at 440°C, and a narrow upwelling at 530°C. After reaching 610°C, marking the completion of the dehydration reaction, the DTG follows the baseline up to 900°C. The results of the thermo-analysis are summarized in Table 2.

X-ray diffraction. The X-ray powder diffraction patterns were obtained at room temperature for an unheated sample, for a sample heated to 610°C and for a sample heated to 1000°C. A reference to the JCPDS Card No. 250182 reveals and confirms the identity of the sample as cavansite. However, it

TABLE 2. Results of Thermo-analysis of cavansite from Wagholi, India

Peak temperatures in °C			
DTA		DTG	
Endothermic (-)	Exothermic (+)	(-)	(+)
150	595	150	960
290	960	290	
440		440	
530		530	
925			

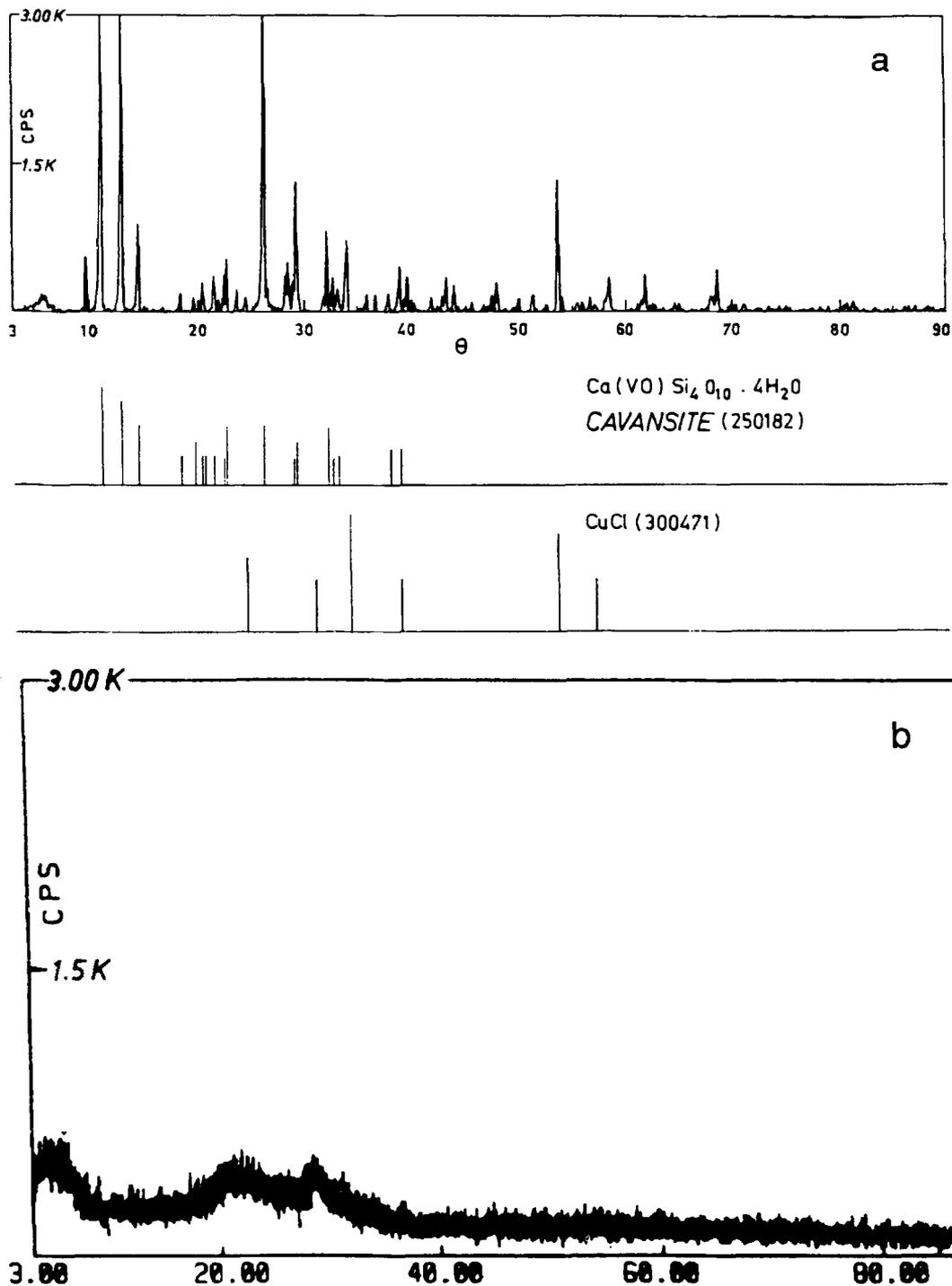


FIG. 2. X-ray diffractograms of cavansite from Wagholi, India. (a) before heating; (b) after heating up to 610°C; and (c) (next page) after heating up to 1000°C. Figures in brackets indicate JCPDS card number.

may be seen from Fig 2a, that it also contains a distinct CuCl phase, though as a negligible fraction. The sample on heating to 610°C changed its colour to mauve and at this stage, with complete dehydration, it turned amorphous (Fig. 2b). The diffraction pattern (Fig. 2c) of the sample heated to 1000°C indicates structural re-organization of three crystalline phases viz., low-cristobalite, low-quartz and an unnamed phase CaV₃O₇ (JCPDS Card No. 140111). The sample had turned pale yellow at this stage.

Discussion. The four steps of weight loss observed from the TG and the DTG curves relate to the expulsion of water molecules held in the structure of cavansite. Evans (1973) predicted four water molecules associated with the Ca²⁺ ions and stated that the thermal motion of H₂O molecules is greater the further the distance between them and the Ca²⁺ ion. The first two steps of weight loss in succession, observed in the present study, correspond to the expulsion of the two water molecules situated much further away, around 2.84 Å. They amount to nearly half of the

total weight loss and also cause rigidity in the cavansite cell whereby migration of the two remaining molecules, which are nearer to Ca²⁺ (2.392 Å and 2.516 Å respectively, calculated by Evans, 1973), becomes sluggish. Such behaviour is typical of zeolites and especially of gismondine which has an analogous crystal structure (Fischer, 1963; Fischer and Schramm, 1971) with four H₂O molecules p.f.u., similar to cavansite. Gismondine also undergoes lattice contraction when heated to 300°C and structural transformation takes place above this temperature. The thermal behaviour of gismondine is, however, quite complex with five main and a small number of minor stages of water loss (Gottardi and Galli, 1985) which is in agreement with six different water sites shown by Fischer and Schramm (1971), as against four stages of water expulsion in cavansite. There is thus ample justification in assigning a zeolitic nature to the water held by cavansite.

Though it is difficult to state precisely the temperature at which the two phases quartz and cristobalite were formed during the heating of

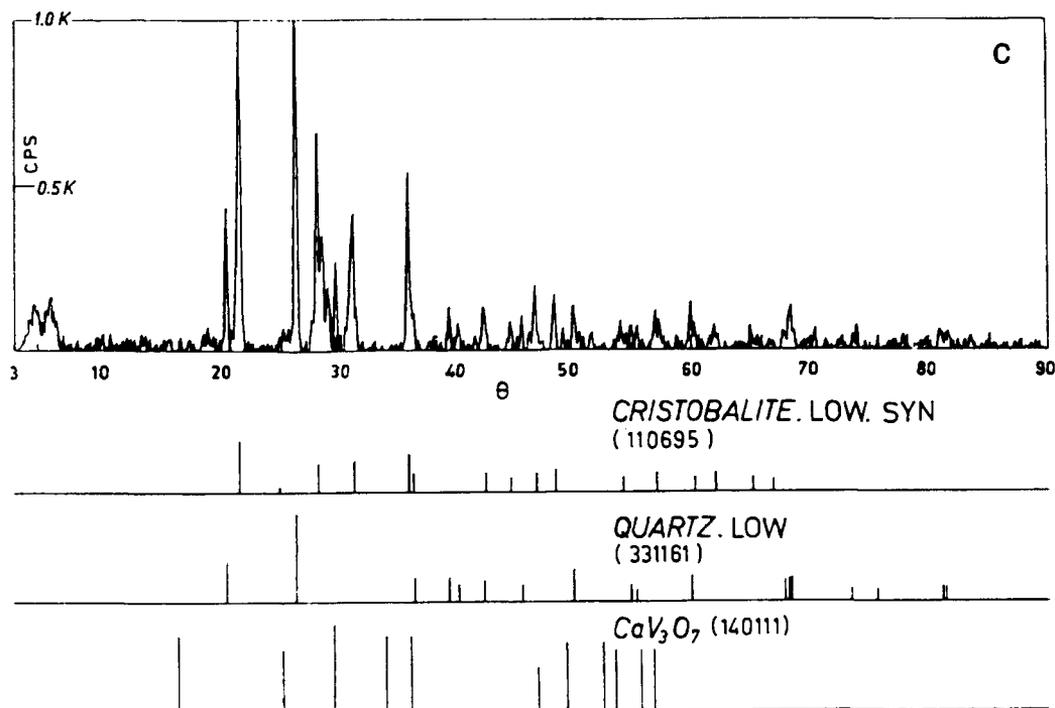


FIG. 2 (contd.). X-ray diffractograms of cavansite from Wagholi, India. (c) after heating up to 1000°C. Figures in brackets indicate JCPDS card number.

cavansite, it certainly took place above 610°C, when complete dehydration took place. The last endotherm at 925°C, in all probability, may be attributed to the formation of cristobalite, and the formation of CaV_3O_7 corresponds with the exotherm at 960°C, reflected in the DTG by gain in weight caused by oxidation. Thus the thermal behaviour of cavansite is highly characteristic and the DTA, TG and DTG may serve as excellent diagnostic patterns, in addition to colour, habit, optical properties and chemistry, for this mineral.

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KEYWORDS: thermal behaviour, cavansite, India, vanadium mineral, DTA, DTG, TG.

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References

- Birch, B. (1977) *Mineral. Rec.*, **8**, 61–2.
 Evans, H. T., Jr. (1973) *Amer. Mineral.*, **58**, 412–24.
 Fischer, K. F. (1963) *Amer. Mineral.*, **48**, 664–72.
 Fischer, K. F. and Schramm, V. (1971) *Adv. Chem. Ser.*, **101**, 250–58.
 Gottardi, G. and Galli, E. (1985) *Natural Zeolites*, Springer-Verlag, 409 pp.
 Staples, L. W., Evans, H. T., Jr. and Lindsay, J. R. (1973) *Amer. Mineral.*, **58**, 405–11.
 Wilke, H. J., Köhler, G. S. and Bhale, A. (1989) *Lapis*, **14**, 39–41.

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Choloalite: synthesis and revised chemical formula

CHOLOALITE, a rare secondary double tellurite of Cu(II) and Pb(II), was described by Williams (1981). Type material from the Mina La Oriental, Moctezuma, Mexico, corresponded with other specimens from Tombstone, Arizona, and Arabia. Wet chemical analyses of very small amounts of choloalite led to an assigned formula of $\text{CuPb}(\text{TeO}_3)_2 \cdot \text{H}_2\text{O}$ with the water content determined by the Penfield method on but 156 μg .

As part of a study of the supergene mineralogy and geochemistry of tellurium, we have had occasion to synthesise the majority of the known secondary tellurium minerals for further chemical experiments concerning their stabilities. Choloalite

is one of the minerals that has been synthesised and as a result we have been able to more accurately establish its composition as well as to measure infrared absorption and accurate X-ray powder diffraction data for the pure, synthetic phase.

Synthesis

Choloalite was synthesised by fusion of stoichiometric amounts of CuO, PbO and TeO_2 in a silica crucible. The product was annealed at 500°C for several hours. A deep green, crystalline, but somewhat porous product was obtained, and which proved to be choloalite.