



# Elastic behavior and pressure-induced structural modifications of the microporous $\text{Ca}(\text{VO})\text{Si}_4\text{O}_{10}\cdot 4\text{H}_2\text{O}$ dimorphs cavansite and pentagonite



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## ABSTRACT

The behavior of natural microporous cavansite and pentagonite, orthorhombic dimorphs of  $\text{Ca}(\text{VO})(\text{Si}_4\text{O}_{10})\cdot 4\text{H}_2\text{O}$ , was studied at high pressure by means of *in situ* synchrotron X-ray powder diffraction with a diamond anvil cell using two different pressure-transmitting fluids: methanol:ethanol:water = 16:3:1 (m.e.w.) and silicone oil (s.o.). *In situ* diffraction-data on a cavansite sample were collected up to 8.17(5) GPa in m.e.w., and up to 7.28(5) GPa in s.o. The high-pressure structure evolution was studied on the basis of structural refinements at 1.08(5), 3.27(5) and 6.45(5) GPa. The compressional behavior is strongly anisotropic. When the sample is compressed in s.o. from  $P_{\text{amb}}$  to 7.28(5) GPa, the volume contraction is 12.2%, whereas **a**, **b** and **c** decrease by 1.6%, 10.3% and 0.3%, respectively. The main deformation mechanisms at high-pressure are basically driven by variation of the T–O–T angles.

Powder diffraction data on a pentagonite sample were collected up to 8.26(5) GPa in m.e.w. and 8.35(5) GPa in s.o. Additional single-crystal X-ray diffraction experiments were performed in m.e.w. up to 2.04(5) GPa. In both cases, pressure-induced over-hydration was observed in m.e.w. at high pressure. The penetration of a new  $\text{H}_2\text{O}$  molecule leads to a stiffening effect of the whole structure. Moreover, between 2.45(5) and 2.96(5) GPa in m.e.w., a phase transition from an orthorhombic to a triclinic phase was observed. In s.o. pentagonite also transformed to a triclinic phase above 1.71(5) GPa. The overall compressibility of pentagonite and cavansite in s.o. is comparable, with a volume contraction of 11.6% and 12.2%, respectively.

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## 1. Introduction

Microporous heteropolyhedral frameworks [1] have recently attracted technological attention leading to a shift of interest from zeolites *sensu stricto* (tetrahedral frameworks with cation-exchange capacity and reversible dehydration) to zeolite-like structures (open-framework materials with ion-exchange capacity). Natural microporous cavansite and pentagonite, dimorphs of  $\text{Ca}(\text{VO})(\text{Si}_4\text{O}_{10})\cdot 4\text{H}_2\text{O}$ , have sparked our interest due to the technological potential of their porous framework made up by vanadyl-type pyramids connecting silicate tetrahedral sheets. In the last years, many studies addressing hydrothermal preparation procedures of new

synthetic microporous vanadosilicates [2–4] aimed to optimize synthesis in order to obtain large quantities [5,6]. Such frameworks can fulfill many properties comparable to traditional zeolite structures such as microporosity, ion exchange and sorption applications. Moreover, the presence of transition metal ions in the framework makes these materials potentially usable for catalysis. Vanadium can adopt several oxidation states and vanadium silicates appear to be more stable than the corresponding phosphates [4]. In this light, the investigation of the thermo-elastic stability of vanadosilicates is crucial to evaluate their functionality for technical applications.

Non-ambient conditions can induce important structural changes in microporous materials, modifying physico-chemical properties and affecting their possible applications. Because of their applicative relevance, the thermal and baric stability of

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zeolites have been investigated extensively. Framework topology and extraframework content are crucial factors influencing structure deformation mechanisms not only upon thermal treatment but also under high-pressure conditions. Microporosity does not necessarily connote high compressibility, as several zeolites are less compressible than other rock-forming minerals (for example  $\alpha$ -quartz, [7]). Deformation mechanisms are governed by the topological configuration of the framework while the extraframework content influences the compressibility. The mechanism leading to topological changes in aluminosilicate frameworks can be described as tilting of rigid tetrahedra around O atoms [8,9]. Of particular interest, the high-pressure behavior of microporous materials can be affected by the nature of the pressure-transmitting medium used for the experiment. Using pore-penetrating pressure-transmitting media, it is possible to investigate pressure-induced over-hydration (PIH) effects. In contrast, non-penetrating media are used to study compressibility, *P*-induced phase transitions, and amorphization. The most commonly used fluids for microporous materials are: methanol:ethanol (4:1) and methanol:ethanol:water (16:3:1) mix, glycerol and silicone oil. These pressure-transmitting media have different freezing points and hydrostaticity as a function of pressure [10,11].

Our interest on the behavior of microporous materials with non-tetrahedral polyhedra at high pressure started after observing that the presence of octahedral Al in the framework of ALPO-34 leads to a stiffening of the framework upon compression if compared to SAPO-34 with tetrahedral Al [12]. Thus, the effect of the unusual presence of vanadyl-type square based pyramids on framework distortion and compressibility is of remarkable interest. In this light, our study represents the first investigation on high pressure behavior of heteropolyhedral vanadosilicate frameworks.

Cavansite, and its dimorph pentagonite,  $\text{Ca}(\text{VO})(\text{Si}_4\text{O}_{10})\cdot 4\text{H}_2\text{O}$ , are the only known natural examples of microporous vanadosilicates. These minerals have been selected as representative of vanadosilicate frameworks for high-pressure study because of their large crystal size (mm range) and high crystal quality. The porous three-dimensional framework is built by tetrahedral sheets connected through  $\text{VO}_5$  square based pyramids. The  $\text{VO}_5$  pyramids are characterized by a short apical V–O bond of ca. 1.6 Å and four basal bonds of ca. 2.0 Å [13]. Pentagonite and cavansite are orthorhombic and characterized by undulating pyroxenoid-like  $(\text{SiO}_3)_n$  chains. These chains are laterally joined into sheets parallel to the **a**–**c** plane but they are made up to arrange a different network of rings in the two structures. In cavansite, the tetrahedral sheets consist of fourfold and eightfold rings, whereas in pentagonite there are only six-membered rings [13]. Moreover, in both dimorphic structures, adjacent chains have the tetrahedral apices pointing up and down along the **b** axis. Large cavities in the structure are decorated by Ca and  $\text{H}_2\text{O}$  molecules as extraframework components. The cavansite framework can be compared to that of gismondine,  $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]\cdot 4\text{H}_2\text{O}$  and amicitte,  $\text{NaK}[\text{Al}_2\text{Si}_2\text{O}_8]\cdot 2.5\text{H}_2\text{O}$ . In gismondine and amicitte (**GIS** frameworks), the same network of four- and eightfold rings as in cavansite is present. In gismondine, adjacent tetrahedral layers are linked directly to each other to form a three-dimensional aluminosilicate network [14] and not via vanadyl-type  $\text{VO}_5$  square pyramids as in cavansite. In cavansite, direct connection of the (010) tetrahedral layers without the  $\text{VO}_5$  group would produce a tetrahedral network topologically identical to that of gismondine.

The behavior of cavansite and pentagonite upon heating appears to be zeolitic in character. [15–19]. More recently, *in situ* single-crystal X-ray dehydration experiments on cavansite and pentagonite were conducted to highlight the relationship between stepwise dehydration and framework distortion [20,21]. The presence of  $\text{H}_2\text{O}$  molecules in the porous framework is usually the promoter of structural modifications in response to the applied

temperature. Moreover, the Ca coordination number coupled with the different flexibility of the frameworks seems to be responsible for either phase transitions or structural collapse in pentagonite and cavansite, respectively. The dehydration dynamics of cavansite were probed also by *in situ* synchrotron powder diffraction [22]. The knowledge of the pressure-induced structural modifications in cavansite is limited to a Raman spectroscopic study by Ravindran et al. [23]. Structural studies aiming to understand high-pressure behavior of pentagonite are missing.

## 2. Experimental methods

### 2.1. X-ray powder diffraction at ambient pressure

Cavansite and pentagonite crystals from Wagholi, Poona district, Maharashtra, India were selected and each sample was finely ground in a mortar to obtain a powder. The powders were placed into 0.3 mm glass capillaries and mounted on a goniometric spinning head. The X-ray powder diffraction (XRPD) experiments were performed at the SNBL (BM01A) beamline at ESRF (European Synchrotron Facility, Grenoble, France) with fixed wavelength of 0.682534 Å. All data were collected in the Debye–Scherrer geometry with a Dectris Pilatus2M detector. The sample-to-detector distance and the detector parameters were calibrated using a  $\text{LaB}_6$  NIST reference powder sample. One-dimensional diffraction pattern was extracted by integrating the two-dimensional image using the program FIT2D [24]. Rietveld profile fitting in the  $2\theta$  range was executed using the GSAS package [25] with the EXPGUI interface [26]. Initial structural models for cavansite and pentagonite were those of Evans [13] but, for cavansite, the standard space-group setting *Pnma* was preferred to *Pcmn* reported by Evans [13], requiring interchange of **a** and **c**. The background was fitted by a Chebyshev polynomial with 15 coefficients. The pseudo-Voigt profile function [27] was used with refined Gaussian (*GW*) and Lorentzian (*LX*) terms and a cut-off was applied for the peak intensity. The scale factor and  $2\theta$ -zero shift were refined. Soft-restrains were applied to the T–O distances [ $\text{Si–O} = 1.58(3)\text{–}1.66(4)$ ] and the weight was gradually decreased during the refinement up to a final value of  $F = 10$ . Other soft-restrains were applied for the V–O [one short bond  $\text{V–O} = 1.59(1)$  and four  $\text{V–O} = 1.98(1)\text{–}2.00(1)$ ]. The isotropic displacement parameters were constrained to a common value for the two tetrahedral sites. A second value was assumed for all framework oxygen-atoms, whereas the oxygen atoms at  $\text{H}_2\text{O}$  sites were constrained to a third value. The unit-cell parameters were refined in all cycles.

### 2.2. X-ray powder diffraction at high pressure

The *in situ* high pressure X-ray powder-diffraction data were collected using an ETHZ modified Merrill-Basset diamond anvil cell (DAC) [28] with flat culets of diameter 600  $\mu\text{m}$ . The samples were loaded into a hole of 250  $\mu\text{m}$  in diameter drilled in stainless steel gaskets pre-indented to 60–80  $\mu\text{m}$  thickness. In order to compare the compressibility behavior of cavansite and pentagonite, different experiments were performed using two different pressure-transmitting media: methanol:ethanol:water 16:3:1 (m.e.w.) as nominally penetrating *P*-transmitting medium, and silicone oil (s.o.), as non-penetrating *P*-transmitting fluid. Pressure was measured before and after the data collection at each pressure using the ruby fluorescence method [29] on the non-linear hydrostatic pressure scale [30].

#### 2.2.1. Cavansite

The pressure range investigated for the cavansite experiment in m.e.w. was from  $P_{\text{amb}}$  to 8.17(5) GPa, whereas in s.o. from  $P_{\text{amb}}$  to

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