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Cavoite, CaV_3O_7, a new mineral from the Gambatesa mine, northern Apennines, Italy

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Abstract: Cavoite, CaV_3O_7, occurs at the Gambatesa mine (Liguria, Italy) filling microcavities in massive bands of caryopilite + calcian rhodochrosite ± quartz. Cavoite has been found as very rare radiated aggregates of strongly elongated prismatic to acicular crystals up to about 0.28 mm in length, closely associated with an unidentified silicate phase. The crystals vary in colour from colourless to olive green-brown; they are brittle, transparent and non-fluorescent, with vitreous lustre and near white streak; no cleavage, parting or twinning were observed. The mean empirical formula from microprobe analyses, based on seven oxygen atoms, is $(Ca_{0.95}Mn_{0.03}K_{0.02})(V_{2.79}Si_{0.22})O_7$. It well approaches the ideal one, CaV_3O_7, taking into account that the chemical determinations (presence of K, Mn and Si) are possibly affected by contamination due to the close association with the unidentified silicate. The powder-diffraction data give the refined cell parameters a = 10.42(2) A, b = 5.28(2) A, c = 10.34(2) A and V = 568.2 A^3 in the space group *Pnam*. Micrometric crystals of cavoite were also investigated by means of transmission and analytical electron microscopy. Cavoite is the natural analogue of the synthetic CaV_3O_7, whose structural study is reported in literature together with that of the isostructural phases SrV_3O_7 and CdV_3O_7.

Key-words: cavoite, new mineral, physical and chemical data, X-ray powder pattern, TEM analysis.

Introduction

In the manganiferous ores of the Val Graveglia, northern Apennines, Italy, a complex network of veins and fractures allowed the formation of a great variety of rare and new minerals; among these, vanadium minerals, as saneroite, medaite, palenzonaite, gamagarite, volborthite, tangeite, reppiaite, and vanadomalayaite (Basso *et al*., 1994 and references therein), are frequent. In this paper we report a new vanadium mineral species found at the Gambatesa mine, near the village of Reppia.

Because of the scarcity of material, specimens of the new mineral suitable to obtain experimental data about *e.g*. hardness, density, optical properties and crystal structure were not found.

Both the mineral and the name, derived from the chemical composition, have been approved by the I.M.A. Commission on New Minerals and Mineral Names (ref. 2001–024). Type material is deposited in the collection of the Dipartimento per lo Studio del Territorio e delle sue Risorse (Dip.Te.Ris), Università di Genova, Italy.

Occurrence and physical properties

In Eastern Liguria, manganese ores occur near the bottom of chert sequences ("Diaspri di Monte Alpe" Formation) overlaying Jurassic ophiolites and consist of braunite-bearing layers within hematite-rich cherts. A general overview of these Mn-ores is presented in Cabella *et al*. (1998).

Tectono-metamorphic re-equilibration under prehnite-pumpellyite facies conditions (T = 275 ± 25 °C; P = 2.5 ± 0.5 kbar; Cortesogno *et al*., 1979; Lucchetti *et al*., 1990) affected ophiolites and their sedimentary covers; sedimentary Mn-oxides and hydroxides equilibrated to braunite-dominated assemblages. A complex vein and fracture system developed, mainly localized at the fold hinges, inducing reaction processes responsible for the formation of Mn-silicate and/or Mn-carbonate assemblages at the expense of braunite + quartz assemblages.

Fluids circulating along later fractures, at decreasing metamorphic conditions, led to the concentration of elements such as V, As, Ba, Sr and the precipitation of a great variety of uncommon minerals.

Cavoite occurs filling microcavities in massive bands of caryopilite + calcian rhodochrosite ± quartz. The assemblages developed, replacing tephroite + rhodonite veins, within the braunite layers. The alteration of tephroite + rho-

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donite to caryopilite and carbonates assemblages is referred to the increased activity of CO_2-bearing and Ca-rich hydrous fluids in the veins, which also induced V mobilization.

Cavoite has been found as very rare radiated aggregates of strongly elongated prismatic to acicular crystals up to about 0.28 mm in length. Only very few acicular crystals show a composition near to CaV_3O_7 and they are closely associated with an unidentified silicate phase. The crystals vary in colour from colourless to olive green-brown; they are brittle, transparent and non-fluorescent, with vitreous lustre and near white streak; no cleavage, parting or twinning were observed.

Due to the unusual scarcity of available material and to the reduced sizes of the needle-like crystals (up to 2 μm in width as measured by electron microscope) hardness and density could not be measured. The density, 3.51 g/cm^3, is calculated from empirical formula. Concerning the optical data a value of about 2 was roughly measured for a refractive index, but the accuracy of the evaluation is low due to the interference of the associated phase.

Chemical composition

Ten spot chemical analyses were carried out on two distinct crystals by means of an electron microprobe (PHILIPS SEM 515 electron microscope equipped with EDAX PV9100 spectrometer) in energy-dispersion mode, with an accelerating voltage of 15 kV and a beam current of about 2 nA. Clinopyroxene (Ca), fayalite (Mn, Si), amphibole (K), and metallic vanadium (V) were used as reference standards for the elements in brackets. Other elements, if present, were below their detection limits.

The mean chemical composition is reported in Table 1, along with an indication of variability and the most SiO_2-poor analyses. The mean empirical formula, based on seven oxygen atoms, is $(Ca_{0.95}Mn_{0.03}K_{0.02})(V_{2.79}Si_{0.22})O_7$. It well approaches the ideal one, CaV_3O_7, taking into account that the chemical determinations (presence of K, Mn and Si) are possibly affected by contamination due to the close association with the unidentified silicate. This contamination is probably responsible also for the colour variation from olive green-brown, peculiar to CaV_3O_7, to nearly colourless.

The unidentified silicate chemical composition varies in the ranges (wt%): MgO 3.78 – 6.33, K_2O 1.67 – 2.94, CaO 0.53 – 1.91, MnO 2.45 – 3.50, VO_2 21.93 – 24.17 and SiO_2 41.24 – 49.97 (total from 73 to 85), but a possible misunderstanding on these data may be expected related to an unknown degree of contamination of the analyzed silicate crystals by cavoite.

Table 1. Chemical composition of cavoite.

Oxide	Mean (wt%)	Range (wt%)	Most SiO_2-poor (wt%)		
CaO	17.76	15.90–18.35	15.90	17.02	18.35
MnO	0.70	0.30– 0.82	0.32	0.67	0.74
K_2O	0.35	0.20– 0.78	0.20	0.39	0.28
VO_2	76.80	75.62–82.02	82.02	79.77	77.98
SiO_2	4.31	0.92– 6.86	0.92	2.06	2.75
Total	99.92		99.36	99.91	100.10

X-ray powder-diffraction analysis

The X-ray powder-diffraction analysis was performed by a Gandolfi camera (diameter 57.3 mm) using a V filtered Cr*K*α radiation and with silicon as internal standard. Relative intensities were assigned visually and the reflections were indexed in the non-standard space group *Pnam* (n. 62) on the basis of the pattern reported for the synthetic CaV_3O_7 (Bouloux & Galy, 1973).

The measured powder data, reported together with those of the synthetic CaV_3O_7 in Table 2, give the refined cell parameters: a = 10.42(2) A, b = 5.28(2) A, c = 10.34(2) A and V = 568.2 A^3.

TEM analysis

Material from the holotype sample was analyzed with a JEOL JEM-2010 transmission electron microscope (TEM) operated at 200 kV. The analytical electron microscope (AEM) investigations were performed using an energy-dispersive X-ray spectrometer (EDS) system (OXFORD PENTAFET). Selected area electron diffraction (SAED) patterns and AEM data were used for the mineral characterization. The specimens for TEM examination were prepared starting from selected grains, crushed by means of a micro-tool (tweezer) and deposited onto a Cu support grid coated with a holey carbon film. The EDS analyses revealed for some crystals a composition very near to Ca = 25 %at and V = 75 %at, in agreement with the cationic ratio of CaV_3O_7. Traces of Si are present and probably due to impurities. Other ele-

Table 2. Comparison between powder-diffraction data of cavoite (present study) and synthetic CaV_3O_7 (Bouloux & Galy, 1973) (d in A).

	cavoite		synthetic		cavoite		synthetic
h k l	*d*	*I*	*d*	*h k l*	*d*	*I*	*d*
2 0 0	5.16	M	5.25	0 1 5	1.93	VW	1.930
2 0 2	3.60	VVW	3.69	2 0 5			
2 1 1	3.45	W	3.50	0 2 4	1.85	M	1.854
1 1 2				1 2 4	1.82	VW	1.824
2 1 2	3.00	S	3.023	4 1 4	1.73	VW	1.740
0 1 3	2.88	W	2.902	0 0 6			
2 0 3			2.886	6 0 2	1.65	VW	1.651
0 2 0	2.63	VW	2.651	4 0 5	1.62	VW	1.625
4 0 0			2.614	6 1 2	1.56	W	1.575
0 0 4	2.59	VVW	2.593	0 3 3			
4 0 3	2.07	VW	2.085	2 1 6			

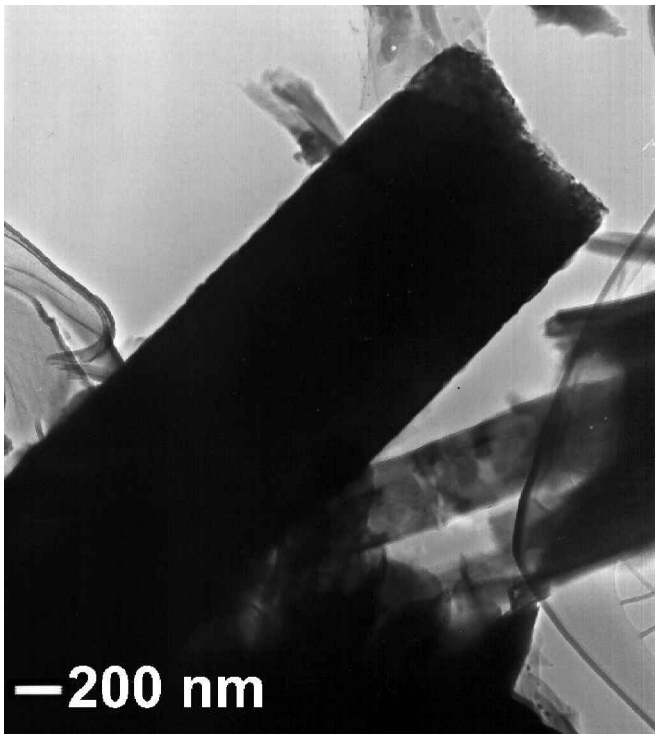

Fig. 1. TEM image of a cavoite crystal (large and black) together with some crystals of the associated unidentified silicate phase (light and dark grey).

ments, if present, are below their detection limits. SAED patterns for these crystals, indexed in the space group *Pnam*, lead to values of cell edges within the ranges a = 10.40 – 10.43 A, b = 5.25 – 5.28 A and c = 10.33 – 10.37 A, in agreement with the ones refined from powder data. A TEM image of a micrometric crystal of cavoite (large and dark), whose EDS analysis gives a composition very near to the ideal one, is shown in Fig. 1 together with some crystals of the associated unidentified silicate phase.

The crystals of cavoite provide electron diffraction patterns consistent with the structure of synthetic CaV_3O_7: Fig. 2 shows two SAED patterns viewed down $[2\bar{1}3]$ and $[1\bar{1}0]$ zone axes, respectively. It should be pointed out that the $[1\bar{1}0]$ pattern shows some kinematically forbidden reflections. For example, the 001 reflection should be absent because in the space group *Pnam* the reflection condition for the (00*l*) planes is $l = 2n$. Anyway dynamical scattering events may occur and, for example, the allowed 110 diffracted beam may be rediffracted by the $(\bar{1}\bar{1}1)$ planes giving the reflection 001.

From the AEM and SAED analysis it may be inferred that the examined crystals are characterized by the same compositional and structural features reported for synthetic CaV_3O_7.

Unfortunately TEM analysis does not improve the very poor data relative to the unidentified silicate phase. This mineral appears as parallel aggregates of acicular polycrystalline individuals, less than 0.4 μm in diameter. It shows diffraction effects of very poor quality and the EDS analyses, probably affected by contamination due to the associated cavoite, give compositions running in the ranges of oxide percents above reported.

Relationships to other minerals

Cavoite is the natural analogue of the synthetic CaV_3O_7, whose structural study is reported in Bouloux & Galy (1973) together with those of the isostructural phases SrV_3O_7 and CdV_3O_7. The CaV_3O_7 structure may be described as built up by corrugated layers of edge-sharing $[V^{4+}O_5]$ square pyramids linked by Ca atoms. Other minerals involving V^{4+} with square pyramidal coordination polyhedron are known and their structures are characterized by lower degrees of condensation of the $[VO_5]$ pyramids than cavoite. The condensation takes place in all the cases by sharing edges and with the apical oxygens of adjacent pyramids pointing to opposite sides. In haradaite, $Sr_2V_2O_2(Si_4O_{12})$ (Takéuchi & Joswig, 1967), and in its Ba analogue suzukiite (Matsubara *et al.*, 1982) as well as in the two dimorphs cavansite and pentagonite, $Ca(VO)(Si_4O_{10})\cdot 4H_2O$ (Evans, 1973), the $[VO_5]$ pyramids are isolated. Double pyramids $[V_2O_8]$ share corners with $[V^{5+}O_4]$ tetrahedra in the bronze melanovanadite, $CaV_4O_{10}\cdot 5H_2O$ (Konnert &

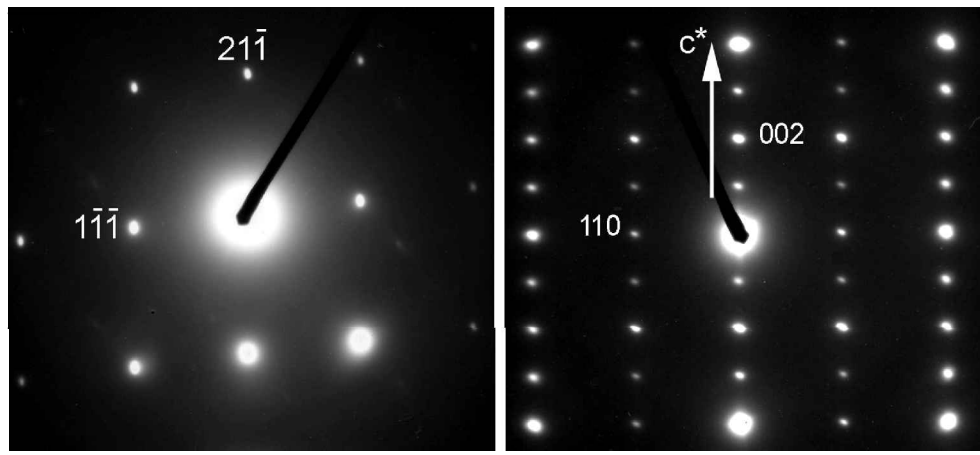

Fig. 2. SAED patterns collected on cavoite crystals viewed down $[2\bar{1}3]$ (left) and $[1\bar{1}0]$ (right).

Evans, 1987). Finally, the condensation increases to chains in the Sb_2VO_5 polytypes stibivanite-2*M* (Kaiman *et al*., 1980) and -2*O* (Merlino *et al*., 1989).

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