

# Vanadiocarpholite, $Mn^{2+}V^{3+}Al(Si_2O_6)(OH)_4$ , a new mineral from the Molinello mine, northern Apennines, Italy

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**Abstract:** Vanadiocarpholite,  $Mn^{2+}V^{3+}Al(Si_2O_6)(OH)_4$ , occurs at the Molinello mine (Liguria, Italy) in mm-thick veins and in open fissures in a silicified wood sample from Mn-ore bearing cherts. Vanadiocarpholite is found as millimetric aggregates of acicular crystals associated with coatings and crystals of dark-green volborthite and quartz; rarely strongly elongated [001] prismatic crystals up to 400  $\mu m$  are also found. The crystals vary in colour from honey yellow-brown and brown (prismatic crystals) to pale straw-yellow (acicular crystal aggregates); they are brittle (prismatic crystals) to flexible (acicular crystals), transparent and non-fluorescent, with vitreous to silky lustre (prismatic crystals and acicular crystal aggregates, respectively) and nearly white streak; they show a perfect {010} cleavage; parting and twinning were not observed. The empirical formula of vanadiocarpholite, derived from microprobe analyses and structural refinement, approaches the ideal formula,  $Mn^{2+}V^{3+}Al(Si_2O_6)(OH)_4$ ; however, a wide compositional range is detected, mainly due to a solid solution with carpholite ( $V^{3+}$  vs Al substitution). X-ray single crystal data give the refined cell parameters  $a = 13.830(2)$  Å,  $b = 20.681(3)$  Å,  $c = 5.188(1)$  Å and  $V = 1483.86$  Å<sup>3</sup> in the space group *Ccca*. Micrometric crystals of vanadiocarpholite were also investigated by transmission and analytical electron microscopy. TEM analyses show a good agreement with WDS and XRD data, but disordered layer stacking sequences are observed. The crystal structure refinement indicates vanadiocarpholite to be isotypic with carpholite, therefore it belongs to the carpholite group together with carpholite, magnesiocarpholite, ferrocapholite, balipholite and potassic-carpholite.

**Key-words:** vanadiocarpholite, new mineral, carpholite group, solid-solution series, physical and chemical data, X-ray powder pattern, crystal structure, TEM analysis.

## Introduction

A great variety of rare and new minerals have been found in the manganese ore deposits of the Val Graveglia, Northern Apennines, eastern Liguria, Italy. Some of them are vanadium minerals such as saneroite, medaite, palenzonaite, gamagarite, volborthite, tangeite, reppiaite, vanadomalayaite and cavoite. In this paper we report the occurrence of a new vanadium mineral species, vanadiocarpholite, found at the Molinello manganese mine. Both the mineral and the name, derived from the chemical composition and the relationships with the carpholite group minerals, have been approved by the I.M.A. Commission on New Minerals and Mineral Names (ref. 2003 - 055). 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

Manganese ores occur in Eastern Liguria as layered mineralizations, massive lenses and boudins near the stratigraphic base of the chert sequences ("Diaspri di Monte Alpe" Formation) overlying Jurassic ophiolites. A general overview of these Mn-ores is presented in Cabella *et al.* (1998). The most abundant ore mineral is braunite (from braunite + quartz assemblage), formed during the tectonometamorphic re-equilibration under prehnite-pumpellyite facies conditions ( $T = 275 \pm 25^\circ C$ ;  $P = 2.5 \pm 0.5$  kbar; Cortesogno *et al.*, 1979; Lucchetti *et al.*, 1990) which affected the ophiolites and their sedimentary cover. 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 assem-

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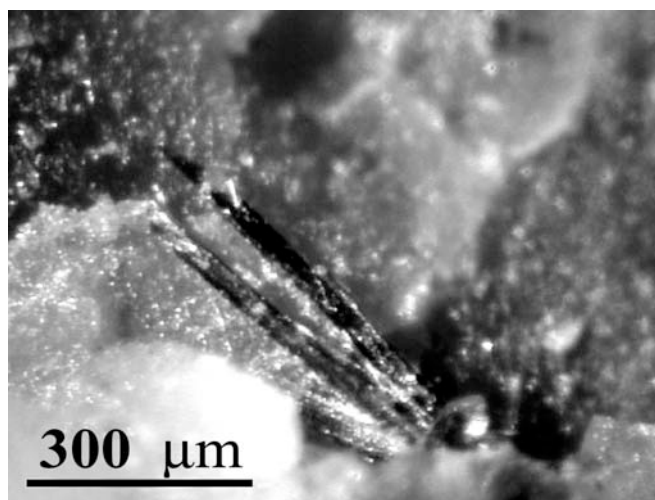


Fig. 1. Prismatic crystals of vanadiocarpholite together with quartz in an open fissure.

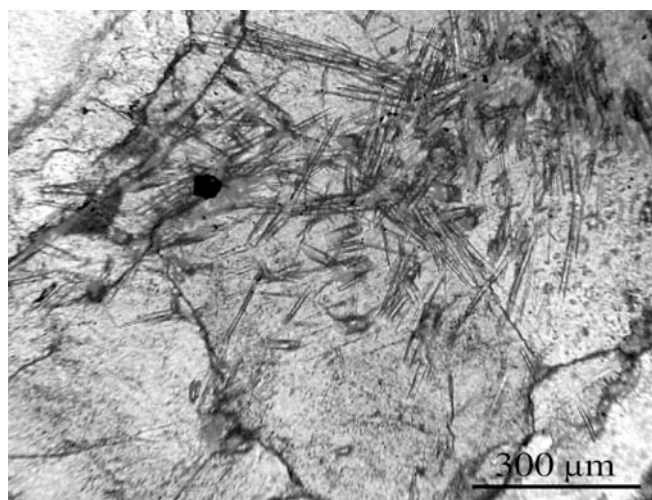


Fig. 2. Photomicrograph of vanadiocarpholite crystals in a quartz vein (parallel polarizers).

blages. Hydrothermal fluids circulating along fractures, at decreasing metamorphic conditions, led also to the concentration of dispersed elements such as As, Ba, Cu, Sr, V and the precipitation of a great variety of uncommon minerals. The presence of silicified wood, already described by Cortesogno & Galli (1974), strongly influenced the micro-chemical environment and locally created small reducing areas, probably by oxidation of organic matter. As a consequence, elements like copper and vanadium were selectively concentrated in these reduction spots and local mobilization and reconcentration processes led to the genesis of V-rich mineral assemblages in late-stage hydrothermal veins and cavities. Members belonging to a wide range of solid-solution between carpholite and vanadiocarpholite, related to the substitution reaction  $Al \rightleftharpoons V^{3+}$ , have been found in a silicified wood from the Molinello

mine. They occur together with quartz, volborthite,  $Cu_3(OH)_2V_2O_7 \cdot 2H_2O$ , lenoblite,  $V_2O_4 \cdot 2H_2O$ , roscoelite,  $K(V,Al,Mg)_2(SiAl)_4O_{10}(OH)_2$ , and chalcocite,  $Cu_2S$ .

Vanadiocarpholite occurs either in open fissures (Fig. 1) or in mm-thick veins (Fig. 2), commonly forming millimetric aggregates of acicular crystals associated with dark-green coats and crystals of volborthite and quartz; rarely, strongly elongated prismatic crystals up to 400  $\mu m$  are also found. Vanadiocarpholite ranges in colour from honey yellow-brown and brown (prismatic crystals) to pale straw-yellow (acicular crystal aggregates) with nearly white streak. Prismatic crystals are brittle with a vitreous lustre and a perfect  $\{010\}$  cleavage, whereas acicular crystals are flexible and are characterized by silky lustre. The lack of suitable material prevented the determination of Mohs's and micro-indentation hardness. A density value of 3.10  $g/cm^3$  was measured using a Westphal balance and Clerici's solution. Among the crystals of the solid solution, two were chosen for chemical and structural analyses with V contents close to the end-points of the detected vanadium range: a  $V^{3+}$ -rich carpholite (VrC) and a vanadiocarpholite (VC). The calculated density assumes the values 3.08  $g/cm^3$  and 3.15  $g/cm^3$  for the VrC and VC crystals, respectively. Optically vanadiocarpholite is biaxial (+) with negative elongation, pleochroic with  $\alpha$  = yellow-brown and  $\gamma$  = yellow-pinkish,  $\alpha = 1.684(2)$ ,  $\beta = 1.691$  (calc.),  $\gamma = 1.700(3)$  and  $2V = 85(2)^\circ$ , measured using monochromatic Na-light ( $\lambda = 589$  nm) at 25°C. The lack of suitable material prevented the complete determination of the indicatrix orientation within the crystal.

Table 1. Chemical compositions of the two refined crystals: V-rich carpholite (VrC) and vanadiocarpholite (VC).

Oxide	VrC (wt%)	VC (wt%)	Range (wt%)
K <sub>2</sub> O	0.18	0.98	0.05 - 1.03
CaO	0.00	0.00	0.00 - 0.11
MnO	17.79	18.10	16.08 - 18.13
MgO	1.27	1.02	0.89 - 1.90
FeO	0.32	0.30	0.00 - 1.33
TiO <sub>2</sub>	0.00	0.00	0.00 - 0.05
V <sub>2</sub> O <sub>3</sub>	11.29	20.94	11.15 - 21.03
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00 - 0.01
Al <sub>2</sub> O <sub>3</sub>	23.04	14.53	14.14 - 23.04
SiO <sub>2</sub>	35.43	33.61	31.88 - 35.95
H <sub>2</sub> O by difference	10.68	10.52	
Total	100.00	100.00	

The chemical range from 54 microprobe analyses of several crystals, pertaining to the solid solution carpholite - vanadiocarpholite, is also reported.

### Chemical composition

Quantitative analyses (54) of several crystals were performed with an ARL-SEMQ electron microprobe in wavelength-dispersion mode (WDS) using an accelerating voltage of 15 kV (sample current of 20 nA) with a beam spot size of about 4  $\mu m$ , peak and background counting

times of 20 and 5 s, respectively. Interference effects due to peak overlaps (V on Cr and Ti on V) were corrected using the PROBE 5.2 software (Donovan & Rivers, 1990). Natural and synthetic standards were used for both standardization and interference correction for the elements in brackets: albite (Si, Al), chromite (Cr), ilmenite (Fe, Ti), forsterite (Mg), spessartine (Mn), diopside (Ca), microcline (K), and metallic V (V). The mean chemical analyses of the two crystals VrC and VC used for the structure refinements are reported in Table 1, along with the compositional variation range detected on different crystals from the holotype sample. Each analysed crystal showed homogeneous composition. Other analysed elements (in particular Na and F) are below their detection limits. A check by atomic absorption spectrometry excluded the presence of Li, detected in other referenced minerals of the carpholite group. H<sub>2</sub>O could not be determined directly because of the small amount of material. The empirical formulae, based on 10 anions, are  $K_{0.01}(Mn_{0.85}Mg_{0.11}Fe_{0.02})(V^{3+}_{0.51}Al_{1.52})(Si_{1.99}O_6)(O_4H_{4.00})$  for the VrC crystal and  $K_{0.07}(Mn_{0.90}Mg_{0.09}Fe_{0.01})(V^{3+}_{0.98}Al_{1.00})(Si_{1.97}O_6)(O_4H_{4.11})$  for the VC crystal. Four (OH) groups per formula unit are assumed, taking into account the formulae of the minerals belonging to the carpholite group and the structure refinement results.

The analysed crystals from veins and fractures show a wide range of composition depending on the V<sup>3+</sup> vs Al diadochic substitution (Fig. 3), thus suggesting a wide

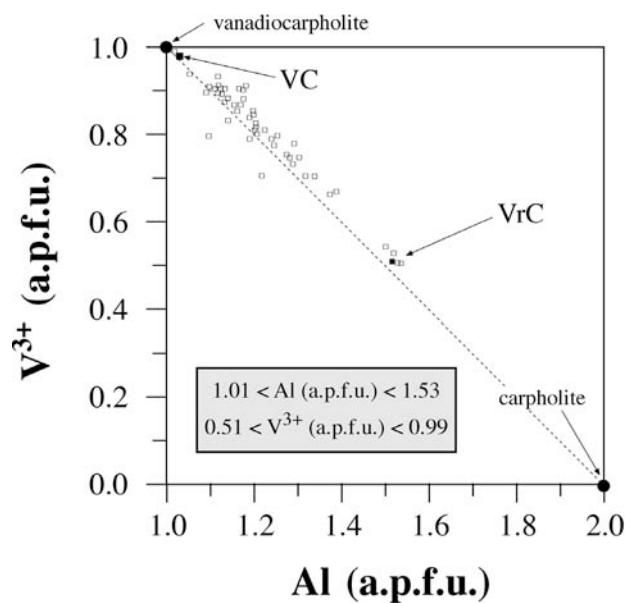


Fig. 3. Al vs V<sup>3+</sup> diagram (atoms per formula units) showing the observed chemical range from WDS analyses. The compositions of the two refined crystals (VrC and VC) are indicated by arrows.

solid-solution field between carpholite and vanadiocarpholite. The simplified formula of the end-member vanadio-

Table 2. X-ray diffraction pattern for a powder of vanadiocarpholite crystals compared to the patterns calculated for the refined crystals VrC and VC.

h	k	l	observed		calculated (VrC)		calculated (VC)	
			d(Å)	I	d(Å)	I	d(Å)	I
2	2	0	5.746	100	5.731	100	5.748	100
0	4	0	5.150	18	5.113	28	5.170	18
1	1	1	4.720	14	4.692	37	4.729	34
1	3	1	3.952	3	3.936	5	3.971	4
2	2	1	3.844	7	3.828	17	3.851	16
4	0	0	3.460	15	3.460	16	3.458	15
0	6	0	3.430	7	3.409	9	3.447	13
4	2	0	3.279	7	3.278	6	3.279	7
1	5	1	3.134	3	3.119	8	3.149	7
3	3	1	3.075	22	3.067	35	3.082	42
2	6	0			3.058	14	3.085	10
4	4	0	2.872	8	2.866	10	2.974	9
4	2	1	2.770	7	2.764	23	2.772	19
3	5	1	2.641	26	2.630	55	2.648	61
2	6	1			2.628	26	2.652	23
0	8	0	2.574	4	2.557	6	2.585	7
4	4	1	2.516	4	2.503	3	2.514	3
1	3	2	2.380	3	2.371	12	2.391	10
2	4	2	2.189	4	2.180	13	2.198	11
2	8	1	2.182	3	2.173	8	2.194	7
4	0	2	2.065	6	2.064	10	2.075	9
6	2	1			2.062	9	2.064	7
5	7	1	1.878	6	1.872	21	1.882	22
6	0	2	1.717	6	1.717	6	1.723	7
6	8	0			1.713	8	1.720	8
7	5	1	1.684	2	1.682	10	1.686	8
4	10	1	1.673	6	1.666	4	1.679	3

Table 3. Crystal structure data for V-rich carpholite (VrC) and vanadiocarpholite (VC).

VrC	
Refinement formula	$K_{0.01}(Mn_{0.87}Mg_{0.13})(V_{0.49}Al_{0.51})Al(Si_2O_6)(OH)_4$
Space group	<i>Ccca</i>
Z	8
a,b,c,V	13.840(1)Å, 20.452(2)Å, 5.143(1)Å, 1455.76 Å <sup>3</sup>
Scan mode	$\omega - 2\theta$
Measured reflections	1586 ( $2 \leq \theta \leq 27.5^\circ$ , $-17 \leq h \leq 17$ , $0 \leq k \leq 26$ , $0 \leq l \leq 6$ )
Unique reflections	837
Observed reflections ( $I > 3\sigma_I$ )	480
$R_W$ (observed)	0.041
R (observed)	0.047
R (all)	0.096
VC	
Refinement formula	$K_{0.08}(Mn_{0.92}Mg_{0.08})(V_{0.84}Al_{0.16})(Al_{0.85}V_{0.15})(Si_2O_6)(OH)_4$
Space group	<i>Ccca</i>
Z	8
a,b,c,V	13.830(2)Å, 20.681(3)Å, 5.188(1)Å, 1483.86 Å <sup>3</sup>
Scan mode	$\omega - \theta$
Measured reflections	2436 ( $2 \leq \theta \leq 30^\circ$ , $-19 \leq h \leq 19$ , $0 \leq k \leq 28$ , $0 \leq l \leq 7$ )
Unique reflections	1085
Observed reflections ( $I > 3\sigma_I$ )	687
$R_W$ (observed)	0.031
R (observed)	0.036
R (all)	0.073

Table 4. Atomic coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>) for V-rich carpholite (VrC) and vanadiocarpholite (VC).

VrC					
Atom	site occupancy	x/a	y/b	z/c	Beq
K	0.012(3)	0	3/4	1/4	1
Mn/Mg	0.87(1)/0.13	0	0.8744(1)	3/4	0.59
V/Al <sub>1</sub>	0.49(1)/0.51	0.1867(1)	3/4	3/4	0.79
V/Al <sub>2</sub>	0/1	0	0.9616(1)	1/4	0.54
Si	1	0.1939(1)	0.8796(1)	0.4111(4)	0.48
O <sub>1</sub>	1	0.2046(3)	0.8002(2)	0.4255(10)	0.77
O <sub>2</sub>	1	0.0818(3)	0.8999(2)	0.4021(10)	0.56
O <sub>3</sub>	1	0.2473(4)	0.9106(2)	0.6671(8)	0.68
OH <sub>1</sub>	1	0.1010(3)	0.8082(2)	0.8856(10)	1.03
OH <sub>2</sub>	1	0.0681(3)	0.9667(2)	0.9303(10)	0.58
H <sub>1</sub>	1	0.907	0.806	0.438	
H <sub>2</sub>	1	0.135	0.969	0.937	
VC					
Atom	site occupancy	x/a	y/b	z/c	Beq
K	0.168(2)	0	3/4	1/4	1
Mn/Mg	0.92(1)/0.08	0	0.8770(1)	3/4	0.77
V/Al <sub>1</sub>	0.84(1)/0.16	0.1836(1)	3/4	3/4	0.86
V/Al <sub>2</sub>	0.15(1)/0.85	0	0.9619(1)	1/4	0.50
Si	1	0.1939(1)	0.8791(1)	0.4096(2)	0.58
O <sub>1</sub>	1	0.2031(2)	0.8007(1)	0.4209(6)	0.75
O <sub>2</sub>	1	0.0822(2)	0.8999(1)	0.4058(6)	0.78
O <sub>3</sub>	1	0.2493(2)	0.9096(1)	0.6625(5)	0.71
OH <sub>1</sub>	1	0.0982(2)	0.8084(1)	0.8838(6)	1.31
OH <sub>2</sub>	1	0.0689(2)	0.9664(1)	0.9262(6)	0.86
H <sub>1</sub>	1	0.898	0.799	0.427	
H <sub>2</sub>	1	0.132	0.962	0.924	

Coordinates of hydrogen atoms are from  $\Delta F$ .

Table 5. Selected interatomic distances (Å) and angles (°) for V-rich carpholite (VrC) and vanadiocarpholite (VC).

	VrC	VC		VrC	VC
2 Mn/Mg-O <sub>2</sub>	2.181(5)	2.169(3)	2 V/Al1-O <sub>1</sub>	1.975(5)	2.022(3)
2 -OH <sub>1</sub>	2.067(4)	2.082(3)	2 -O <sub>1</sub>	2.033(4)	2.084(3)
2 -OH <sub>2</sub>	2.306(4)	2.271(3)	2 -OH <sub>1</sub>	1.819(4)	1.827(3)
average	2.185	2.174		1.942	1.978
2 V/Al <sub>2</sub> -O <sub>2</sub>	1.867(4)	1.894(3)	Si-O <sub>1</sub>	1.633(4)	1.627(3)
2 -OH <sub>2</sub>	1.898(5)	1.934(3)	-O <sub>2</sub>	1.607(4)	1.605(3)
2 -OH <sub>2</sub>	1.973(4)	1.986(3)	-O <sub>3</sub>	1.638(5)	1.645(3)
			-O <sub>3</sub>	1.624(5)	1.630(3)
average	1.913	1.938		1.626	1.627
4 K-O <sub>1</sub>	3.144(4)	3.127(3)	Si-O <sub>3</sub> -Si	134.0(3)	134.7(2)
4 -O <sub>2</sub>	3.361(4)	3.400(3)			
4 OH <sub>1</sub>	2.623(5)	2.629(3)			
4 -OH <sub>1</sub>	3.749(5)	3.757(3)			
average	3.219	3.228			

carpholite is  $\text{Mn}^{2+}\text{V}^{3+}\text{Al}(\text{Si}_2\text{O}_6)(\text{OH})_4$ , which requires: MnO 20.09, Al<sub>2</sub>O<sub>3</sub> 14.44, V<sub>2</sub>O<sub>3</sub> 21.23, SiO<sub>2</sub> 34.03, H<sub>2</sub>O 10.21, Total 100.00 wt%.

### X-ray powder-diffraction analysis

The X-ray diffraction pattern for a powder of selected vanadiocarpholite crystals was obtained by a Philips PW-3710 diffractometer, using Ni-filtered CuK $\alpha$  radiation and NaF as internal standard. The calculated patterns for VrC and VC were obtained by means of the LAZY PULVERIX program (Yvon *et al.*, 1977) using the structural models resulting from the refinements as input data. A comparison among these patterns is reported in Table 2.

### Refinement of the crystal structure

The two selected prismatic crystals VrC, with dimensions 0.037 x 0.044 x 0.25 mm, and VC, with dimensions 0.08 x 0.038 x 0.34 mm, were used for the single-crystal X-ray diffraction studies. The data collections were performed by means of an ENRAF-NONIUS MACH-3 automatic diffractometer using graphite-monochromatized MoK $\alpha$  radiation. The cell parameters were determined and refined using 25 reflections, measured at high  $\theta$  values, for both the crystals.

A semi-empirical absorption correction was applied using the  $\psi$  scan method (North *et al.*, 1968).

The crystal structures, were refined in the space group *Ccca* (no forbidden reflections were detected) using as starting values the corresponding positional parameters of the structural model proposed by Fuchs *et al.* (2001). Refinements were carried out by a modified version of the ORFLS program (Busing *et al.*, 1962), using the scattering factors for neutral atoms from the International Tables for X-ray Crystallography, vol. IV (1974). Scale factor, occupancies of K/□, Mn/Mg, and V/Al, positional and thermal

parameters were simultaneously derived. Final refinements were carried out with anisotropic temperature factors for all atoms (except for K, whose temperature factor was always fixed as isotropic with a value of 1 Å<sup>2</sup>). Tables 3, 4 and 5 summarize the experimental details and the results of the crystal structure refinements, which confirm vanadiocarpholite (VC) as being isotypic with carpholite.

### TEM analysis

Selected area electron diffraction (SAED) patterns and high-resolution (HRTEM) images were collected using a JEOL JEM-2010 transmission electron microscope (TEM), operated at 200 kV and equipped with a energy-dispersive X-ray spectrometer (EDS) system (OXFORD PENTAFET). A double-tilt sample holder was used. Samples were prepared by an ultrasonic suspension of a ground powder in iso-propanol, which was then deposited onto a lacey carbon-covered copper grid. Both SAED and HRTEM images were collected close to ideal Scherzer defocus conditions on aligned crystallites.

The observation of the sample at low magnification indicates the presence of thin elongated crystals (Fig. 4). TEM-EDS analyses carried out on these crystals are qualitatively in good agreement with the results obtained by WDS.

SAED patterns collected under different zone axes may be successfully indexed according to the structural data obtained by X-ray single crystal diffraction analysis reported in this work. HRTEM observation shows that the disordered layer stacking sequences are a fairly common feature for vanadiocarpholite; in particular, relatively extended zones characterised by an ordered regular stacking sequence are found coexisting with highly defective small zones. Figure 5 shows an indexed SAED pattern collected along the [110] zone axis: streaking perpendicular to the *c*\* direction is evident, revealing disordered layer stacking sequences. Figure 6 shows an HRTEM

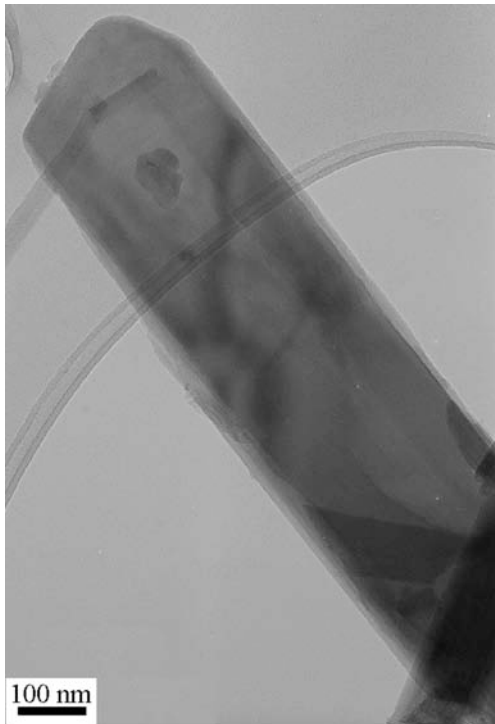


Fig. 4. Low magnification TEM image of a vanadiocarpholite crystal.

image obtained along the same direction providing evidence of the coexistence of 11.50 Å periodicities, corre-

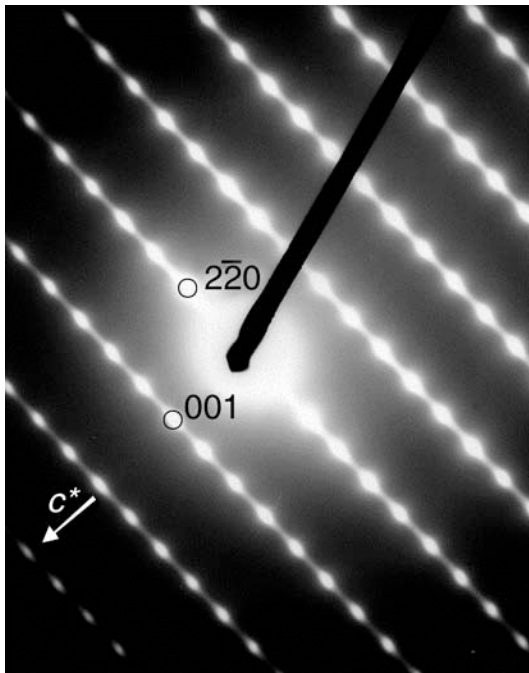


Fig. 5. Indexed SAED pattern collected on a vanadiocarpholite crystal along the [110] zone axis: streaking is evident perpendicular to  $c^*$ .

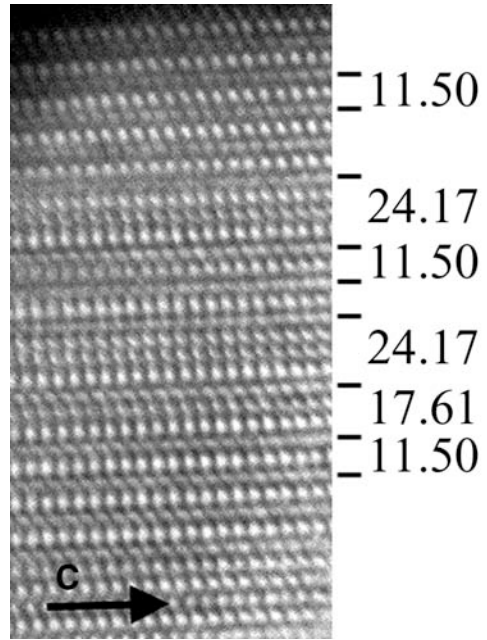


Fig. 6. Chain periodicity faults (HRTEM image) in a sample crystal: slabs of vanadiocarpholite (11.50 Å periodicity, corresponding to  $(1\bar{1}0)$  interplanar spacing) are intergrown with two other kinds of slab characterized by 24.17 Å and 17.61 Å periodicities, respectively.

sponding to the  $(1\bar{1}0)$  interplanar spacing of vanadiocarpholite, together with 24.17 Å and 17.61 Å periodicities.

## Conclusions and relationships to other minerals

We find evidence for a wide solid-solution field between carpholite and vanadiocarpholite from the analyses of several crystals of the holotype sample. The compositions vary, depending on the substitution reaction  $\text{Al} \rightleftharpoons \text{V}^{3+}$ , according to the formula  $(\text{K}, \square)(\text{Mn}, \text{Mg}, \text{Fe})(\text{V}^{3+}_x \text{Al}_{2-x})\text{Si}_2\text{O}_6(\text{OH})_4$ , with  $0.5 < x < 1.0$ . The structure refinements for two selected crystals, characterized by V-contents close to the end-points of the above interval, show that the carpholite crystal structure is preserved (isotypic phases) and that  $\text{V}^{3+}$  mostly substitutes for Al in the Al1 octahedral site. Therefore, disregarding minor substitutions in the Mn and Al2 sites as well as the negligible occupancy of the K site, the name vanadiocarpholite applies to each member of the solid-solution series with formula  $\text{Mn}(\text{V}^{3+}, \text{Al})\text{AlSi}_2\text{O}_6(\text{OH})_4$ , where the  $\text{V}^{3+}$  content is higher than 0.5 a.p.f.u. according to the “50 % rule” (Nickel, 1992), and the ideal end-member formula can be written as  $\text{MnV}^{3+}\text{AlSi}_2\text{O}_6(\text{OH})_4$ . Vanadiocarpholite therefore belongs to the carpholite group together with carpholite, magnesiocarpholite, ferrocapholite, balipholite and potassic-carpholite (Tait *et al.*, 2004).

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