ANSERMETITE, MnV$_2$O$_6$•4H$_2$O, A NEW MINERAL SPECIES WITH V^{5+} IN FIVE-FOLD COORDINATION FROM VAL FERRERA, EASTERN SWISS ALPS

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ABSTRACT

Ansermetite, MnV$_2$O$_6$•4H$_2$O, is a new mineral species from the metamorphosed synsedimentary exhalative Mn deposit of Fianel, Val Ferrera, Eastern Swiss Alps. The crystals are carmine red, transparent, with an orange streak and adamantine luster. The Mohs hardness is ~3, D$_{calc}$ = 2.49 g/cm^3, D$_{meas}$ = 2.57(2) g/cm^3. Ansermetite has an excellent cleavage along {110}, the prism, and an uneven fracture. It is biaxial with n_{min} = 1.797 and n_{max} = 1.856 (Na$_D$, 22.5°C), strongly pleochroic between yellow orange (*X*) and ruby red (*Z*), and non-fluorescent. Chemically, ansermetite is near the end-member composition MnV$_2$O$_6$•4H$_2$O, containing only small amounts of arsenic (0.93 wt% As$_2$O$_5$) and strontium (0.20 wt% SrO). Ansermetite is monoclinic, *C*2/*c*, *a* 13.171(2), *b* 10.128(1), *c* 6.983(1) Å, β 111.572(2)°, *V* 866.3(2) Å^3, *Z* = 4. The crystal structure was solved with direct methods on the basis of 701 reflections with *I* > 2σ(*I*) and refined to R_1 = 7.01%. The structure is isotypic with that of synthetic CoV$_2$O$_6$•4H$_2$O and MnV$_2$O$_6$•4H$_2$O. It contains V^{5+} in distorted square pyramidal coordination with five atoms of oxygen, and Mn^{2+} in octahedral coordination with four atoms of oxygen and two H$_2$O groups. The VO$_5$ polyhedra share edges to form chains extending along [001], and linked by MnO$_4$(H$_2$O)$_2$ octahedra. This arrangement results in a three-dimensional framework defining tunnels that host the two H$_2$O groups per formula unit belonging to MnO$_4$(H$_2$O)$_2$ octahedra as well and two additional free H$_2$O groups. Ansermetite forms crystalline crusts up to ~500 μm in thickness and several square centimeters in surface filling thin open fractures cross-cutting V-rich Mn–Fe silicate–oxide ores. Ansermetite is associated to fianelite, Mn$_2$V(V,As)O$_7$•2H$_2$O, Fe oxyhydroxides and silica. Ansermetite and fianelite represent the latest stage of V mobility at the Fianel deposit. Ansermetite is stable at ambient conditions, but is unstable in air and aqueous solutions at temperatures above ~50 to 85°C. Ansermetite is likely to have crystallized from near neutral to mildly acidic groundwater during the Quaternary.

Keywords: ansermetite, new mineral species, crystal structure, metavanadate, Starlera mine, Val Ferrera, Eastern Swiss Alps.

SOMMAIRE

L'ansermetite, MnV$_2$O$_6$•4H$_2$O, nouvelle espèce minérale, a été découverte dans le gisement de manganèse synsédimentaire exhalatif et métamorphisé de Fianel, Val Ferrera, Alpes orientales, en Suisse. Les cristaux sont rouge carmin et transparents, avec un trait orange et un éclat adamantin. La dureté de Mohs est environ 3, D$_{calc}$ = 2.49, D$_{mes}$ = 2.57(2) g/cm^3. L'ansermetite possède un excellent clivage le long de {110}, le prisme, et une fracture inégale. C'est un minéral biaxe avec n_{min} = 1.797 et n_{max} = 1.856 (Na$_D$, 22.5°C), fortement pléochroïque allant du jaune orange (*X*) à rouge rubis (*Z*), et non-fluorescent. Sa composition s'approche

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de celle du pôle, $MnV_2O_6 \cdot 4H_2O$, et contient un peu d'arsenic (0.93% As_2O_5, poids) et de strontium (0.20% SrO). Elle est monoclinique, $C2/c$, a 13.171(2), b 10.128(1), c 6.983(1) Å, β 111.572(2)°, V 866.3(2) Å^3, Z = 4. Nous en avons résolu la structure cristalline par méthodes directes en utilisant 701 réflexions ayant $I > 2\sigma(I)$, et nous l'avons affiné jusqu'à un résidu R_1 de 7.01%. La structure est isotypique de celle des composés synthétiques $CoV_2O_6 \cdot 4H_2O$ et $MnV_2O_6 \cdot 4H_2O$. Elle contient V^{5+} avec un agencement de cinq atomes d'oxygène en pyramide carrée difforme, et le Mn^{2+} en coordinence octaédrique avec quatre atomes d'oxygène et deux groupes de H_2O. Les polyèdres VO_5 partagent des arêtes pour former des chaînes le long de [001], et elles sont interliées au moyen d'octaèdres $MnO_4(H_2O)_2$. Cet agencement mène à une trame tri-dimensionnelle avec des tunnels, où logent les deux groupes de H_2O par unité formulaire contribués par les octaèdres $MnO_4(H_2O)_2$ ainsi que deux groupes de H_2O additionnels. L'ansermetite se présente en croûtes cristallines atteignant une épaisseur de ~500 μm et plusieurs centimètres carrés tapissant de minces fentes ouvertes recoupant le minerai vanadifère à silicate et oxydes de Mn–Fe. Elle est associée à la fianelite, $Mn_2V(V,As)O_7 \cdot 2H_2O$, des oxyhydroxides de fer et de la silice. L'ansermetite et la fianelite représentent le stade ultime de mobilisation de vanadium dans ce gisement. L'ansermetite est stable aux conditions ambiantes, mais est instable dans l'air et dans des solutions aqueuses à une température supérieure à l'intervalle ~50 à 85°C. Elle a probablement cristallisé à partir de l'eau phréatique neutre ou légèrement acide au cours du Quaternaire.

(Traduit par la Rédaction)

Mots-clés: ansermetite, nouvelle espèce minérale, structure cristalline, métavanadate, mine Starlera, Val Ferrera, Alpes orientales, Suisse.

INTRODUCTION

Metamorphosed Mn-rich deposits, such as at Långban in Sweden, the Kombat mine in Namibia, and at Franklin, New Jersey, U.S.A., are among the richest mineralogical "rain forests" on Earth (Pring 1995), and are still contributing a steady stream of new mineral species. Many of these minerals contain arsenic or vanadium as a major component. In this paper, we describe the occurrence and mineralogy of a new manganese vanadate, occurring in the small metamorphosed Mn–Fe deposit of Fianel, Canton Graubünden, Switzerland.

The mineral has been named ansermetite to acknowledge Stefan Ansermet's (b. 1964) contribution to the descriptive mineralogy and to the photography of the Alpine mineralogical wealth. As an autodidact mineralogist and assistant at the Musée Cantonal Géologique (Lausanne, Switzerland) and at the Musée Cantonal d'Histoire Naturelle (Sion, Switzerland), Stefan Ansermet has published a number of papers in amateur mineralogical journals, has coauthored several abstracts in international mineralogical conferences (Meisser & Ansermet 1996, Brugger & Ansermet 2000), and has recently published the first volume of a series of richly illustrated books about the mines and minerals of the Canton Valais (Ansermet 2001). The new mineral and its name have been approved by the International Mineralogical Association (proposal number 2002–017), and the type material is deposited at the Musée Géologique Cantonal, Lausanne, Switzerland (holotype specimen MGL #68936).

OCCURRENCE

Ansermetite occurs sparingly at the Fianel Fe–Mn mine near Ausserferrera, Ferrera Valley, Graubünden, Switzerland (Brugger & Gieré 1999, 2000). Fianel is a small Fe–Mn deposit of synsedimentary to diagenetic origin, embedded in the Triassic carbonates of the Suretta Nappe. It underwent a polyphase Tertiary metamorphism, climaxing at conditions of the blueschist to greenschist facies. The following three stages of vanadate crystallization have been recognized at Fianel: (1) medaite $(Mn,Ca)_6(V,As)Si_5O_{18}(OH)$ crystallizes along the main greenschist-facies Alpine schistosity (Brugger & Gieré 2000), (2) palenzonaite $NaCa_2Mn_2(VO_4)_3$, saneroite $Na_2Mn_{10}Vsi_{11}O_{34}(OH)_4$ and minor quantities of pyrobelonite $PbMnVO_4(OH)$ occur in veinlets filled with massive quartz, aegirine and rhodonite that cross-cut the main schistosity, and (3) fianelite (Brugger & Berlepsch 1996), ansermetite and Fe oxyhydroxides occur in thin fractures near or across the palenzonaite-bearing veinlets. Fianelite and ansermetite represent the latest stage in the remobilization of V that took place during a late phase of the Tertiary Alpine metamorphism or during recent supergene alteration.

APPEARANCE, PHYSICAL AND OPTICAL PROPERTIES

Ansermetite fills thin open fractures. The ansermetite crusts reach a thickness of up to ~500 μm and can cover several square centimeters. The excellent cleavage of ansermetite can be observed on the rim of the polycrystalline crusts. Rare individual crystals up to 100 μm across display a typical monoclinic habit. An attempt to obtain SEM images of ansermetite crystals was unsuccessful, as the crystals "exploded" under the electron beam and the vacuum. Even in the environmental scanning electron microscope (ESEM), we obtained only poor photographs of single crystals of ansermetite (Fig. 1b). The Electroscan E3 ESEM was operated at 28 kV with a water vapor pressure of 5.7 Torr. Polished sections reveal that the rim of many grains of ansermetite includes tiny (<10 μm) crystals of As-poor fianelite (Fig. 1a, Table 1).

The ansermetite crusts are bordeaux-colored, whereas single crystals are carmine red. Ansermetite is transparent, with an orange streak and an adamantine luster, and displays no fluorescence under ultraviolet light. Optically, ansermetite is biaxial, with $n_{min} = 1.797$ and $n_{max} = 1.856$ (Na$_D$, 22.5°C), and displays a strong pleochroism between yellow orange (X) and ruby red (Z). The Mohs hardness is about 3. The good cleavage of ansermetite occurs along the monoclinic prism {110}; the mineral is brittle with an uneven fracture. An average density of 2.57(2) g/cm^3 has been measured on three grains by immersion in a mixture of diiodomethane and 1-chloronaphtalene. This value is slightly higher than the density of 2.49 g/cm^3 derived from the crystal-structure refinement. The discrepancy may reflect the presence of fianelite inclusions, but may also be due to ion exchange with the free H$_2$O molecules located within tunnels of the structure (see below).

Chemical Composition

Chemical analyses were carried out with a Cameca SX51 electron microprobe (Table 1), using the following probe standards: V: pure metal, As: synthetic GaAs, Mn: rhodonite, and Sr: strontianite. No additional element with atomic number ≥ 9 was detected (<0.1 wt%). The electron microprobe was operated at 15 kV, 20 nA,

counting times of 10 s on the peaks and 5 s on each side of the peak for background. A tightly focused beam was scanned over a ~25 µm^2 surface in order to minimize sample damage. This surface had to be reduced to about 3×3 µm^2 to analyze the small inclusions of fianelite. The quality of the analytical procedure was verified by analyzing simultaneously large (up to 5 mm) crystals of reppiaite from Val Graveglia, Italy. The resulting empirical formula of reppiaite (average of four analytical results, normalized to a total of seven cations) is $(Mn_{4.980}Sr_{0.004})(OH)_4(V_{1.843}As_{0.161}Si_{0.003})O_8$, sum = 99.65%, in excellent agreement with the simplified formula $Mn_5(OH)_4(VO_4)_2$ (Basso *et al.* 1992). The empirical chemical formula obtained for ansermetite is $(Mn_{0.99}Sr_{0.004})(V_{1.99}As_{0.013})O_6 \cdot 2H_2O$ (Table 1).

TABLE 1. COMPOSITION OF ANSERMETITE AND THE ASSOCIATED FIANELITE

	Ansermetite (dehydrated)				Fnl[§]
	Average (8 pts.)	Range		Recalculated[†]	
V$_2$O$_5$ wt%	62.25	60.62	64.08	53.80	46.29
As$_2$O$_5$	0.51	0.07	0.93	0.44	2.50
MnO	24.12	23.11	25.19	20.85	38.50
SrO	0.16	0.11	0.20	0.14	0.16
CaO					0.56
H$_2$O$_{calc}$	12.40	12.03	12.75	24.77	9.69
Sum	99.44	96.33*	102.47*	100.00	97.70
V^{5+} *apfu*	1.989	1.973	1.999		1.894
As^{5+}	0.013	0.002	0.024		0.081
Σtet. sites	2.002	1.997	2.009		1.975
Mn^{2+}	0.988	0.974	1.003		2.019
Sr	0.004	0.003	0.006		0.006
Ca					0.037
Σoct. sites	0.992	0.979	1.009		2.062
H	4.00	4.00	4.00		4.00
O	8.00	8.00	8.00		9.00

The electron-microprobe data for ansermetite were normalized to 8 O atoms per formula unit (*apfu*), and a fixed content of 4 H *apfu*, reflecting the fact that 2 (H$_2$O) groups per formula unit were lost in the vacuum during the analysis. †Ansermetite composition recalculated to 100%, assuming 4 (H$_2$O) groups per formula unit. Fianelite: normalization on 9 O and 4 H atoms per formula unit. * Range in analytical totals; the large spread reflects the poor polish resulting from sample dehydration in the vacuum. § Fnl: Fianelite, average of four points.
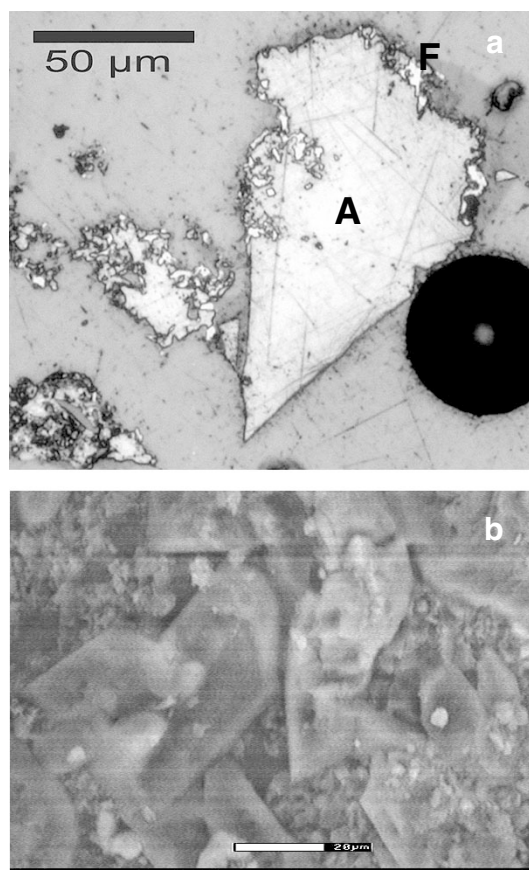

Fig. 1. Paragenesis and morphology of ansermetite. (a) Reflected light microphotograph of a large crystal of ansermetite (A) with small crystals of fianelite (F; higher reflectivity). The crystal is embedded in epoxy resin; a large air bubble can be seen on the lower right. (b) Environmental scanning electron microscope image of the ansermetite.

The H_2O content, equivalent to two H_2O groups per formula unit, was determined from the difference from 100% of the electron-microprobe-derived analytical totals. The value obtained is in conflict with that determined from the crystal-structure refinement, which shows unambiguously that ansermetite contains 4 H_2O groups per formula unit. This discrepancy is due to the partial dehydration of ansermetite in the vacuum of the electron microprobe (see below).

SINGLE-CRYSTAL X-RAY-DIFFRACTION STUDY

A platy reddish brown crystal fragment of ansermetite, about $0.01 \times 0.05 \times 0.20$ mm^3 in size and with perfect cleavage, was measured on a Bruker AXS three-circle diffractometer (equipped with a CCD 1000K area detector and a flat graphite monochromator) using Mo$K\alpha$ radiation from a fine-focus sealed tube (Table 2). The SMART system of programs (Bruker AXS 1998) was used for crystal-structure determination; the program SAINT+ (Bruker AXS 1999) was used for the data reduction, including intensity integration, background and Lorentz-polarization corrections. The program XPREP (Bruker AXS 1997) was used for an empirical absorption-correction based on pseudo Ψ-scans. From the space groups Cc and $C2/c$, raised as possibilities by the program XPREP, the centrosymmetric $C2/c$ was chosen in accordance with the results published by Liao *et al.* (1996), but our choice is not fully in agreement with the intensity statistics ($| E^2 - 1 | = 0.822$). The unit-cell content and dimensions for ansermetite and syn-thetic MnV$_2$O$_6$•4H$_2$O are given in Table 3, and calculated and measured X-ray powder-diffraction patterns are compared in Table 4.

The structure was solved by direct methods (program SHELXS, Sheldrick 1997a), which revealed all cation and O positions. In subsequent cycles of the refinement (program SHELXL, Sheldrick 1997b), four H positions were deduced from the difference-Fourier syntheses by selecting from among the strongest maxima at appropriate distances. H–O distances were constrained to be 0.90(5) Å. The final refinement was performed with anisotropic displacement parameters for all but the H positions (Tables 5, 6) and an empirical extinction-coefficient. The occupancy of the V site was refined and gave about 97% (full occupancy within six estimated standard deviations, Table 5). The refinement was stopped when the mean shift/esd for varied parameters dropped below 1%. A table of structure factors is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

The crystal structure of ansermetite is shown in Figure 2. It is isotypic with the structures of synthetic MnV$_2$O$_6$•4H$_2$O (Liao *et al.* 1996) and CoV$_2$O$_6$•4H$_2$O (Avtamonova *et al.* 1990). The structure contains V^{5+} in distorted square pyramidal coordination with five oxygen atoms, and Mn^{2+} in octahedral coordination with four oxygen atoms and two H_2O groups (Fig. 2a). The [VO$_5$] polyhedra form infinite zigzag single chains along [001] by sharing two of the four edges of the near-planar square basis with two neighboring [VO$_5$] poly-
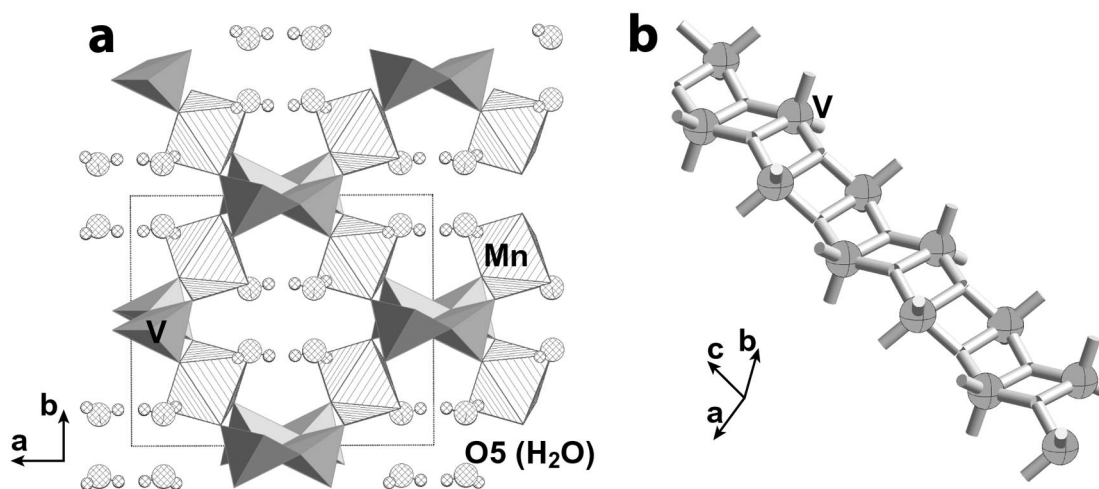

FIG. 2. Crystal structure of ansermetite. (a) Projection of the structure on (001). Gray pyramids are [VO$_5$] groups, and hatched octahedra are [MnO$_4$(OH$_2$)$_2$]. The O5-centered H_2O groups are shown; the O3-centered H_2O groups belong to the [MnO$_4$(OH$_2$)$_2$] octahedron and project on the O5 position on this projection. (b) View of the vanadate chains in ansermetite. The spheres represent V^{5+} ions, and the "rods" represent bonds to O^{2-} ions.

hedra (Figs. 2a, b). The two remaining oxygen atoms of the [VO$_5$] polyhedra are shared with two different [MnO$_4$(OH$_2$)$_2$] octahedra. As a result, the metavanadate single chains are connected by [MnO$_4$(OH$_2$)$_2$] octahedra, which share four equatorial vertices with four [VO$_5$] polyhedra belonging to two different chains (Fig. 2a). The remaining opposite vertices of the [MnO$_4$(OH$_2$)$_2$] octahedra are occupied by H$_2$O molecules (O3). This framework defines tunnels extending along [001], in which an additional H$_2$O group is located (O5; Figs. 2a, 3). A number of oxygen–oxygen distances lie in the range of strong to medium-strength hydrogen bonds (Table 7). Interestingly, the arrangement of the protons

in the synthetic analogue is disordered (Liao *et al.* 1996). Atom O3 linked to Mn is associated with four partly occupied proton positions, whereas three proton sites were resolved for O5. Although the structure refinement of natural ansermetite is of considerably lower quality (owing to crystal size and crystal quality) than the one of the synthetic analogue (Liao *et al.* 1996), we were able to extract an ordered arrangement of protons. The protons labeled H3A and H5A form strong hydrogen bonds (Fig. 3) parallel to (001), enhancing the structural channels. Atom H3A forms a hydrogen bond (2.13 Å) to O5, and H5A forms a hydrogen bond (2.17 Å) to O5 located across the cavity. H3B enhances the framework
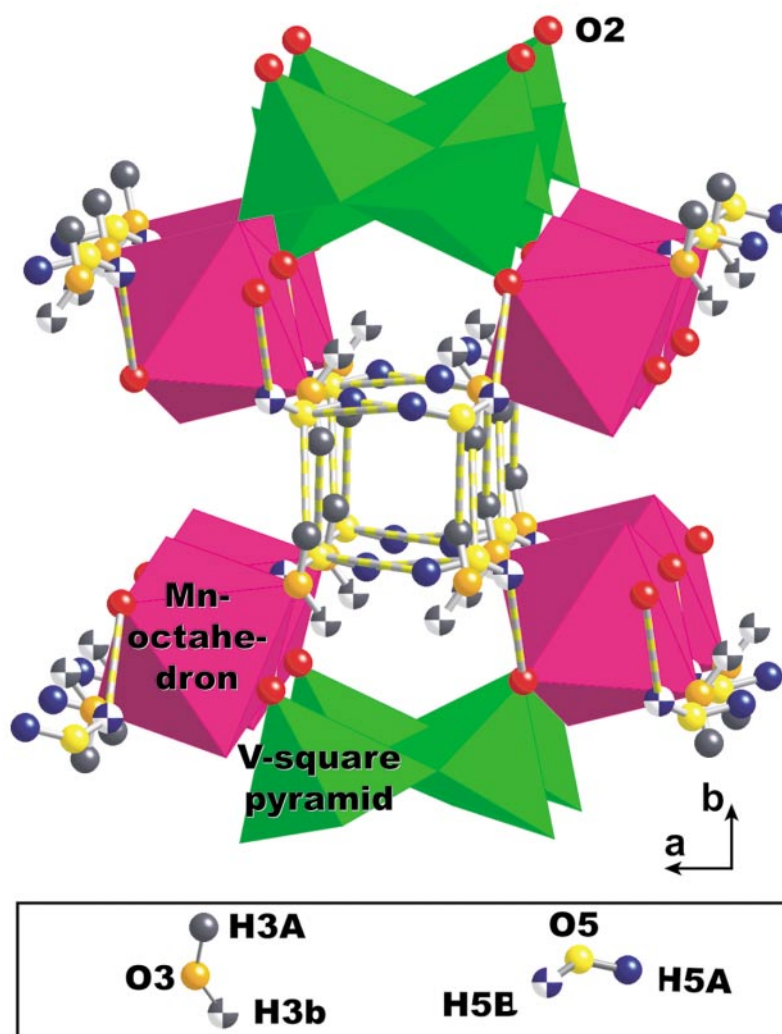

FIG. 3. System of hydrogen bonds viewed approximately parallel to *c*. O3 is part of the red Mn octahedron. O–H bonds are plain, and O…H hydrogen bonds are hatched. Only hydrogen bonds <2.2 Å are shown.

TABLE 2. ANSERMETITE: DATA COLLECTION AND DETAILS
OF REFINEMENT PARAMETERS

Diffractometer	Siemens CCD system	X-ray power	50 kV, 40 mA
X-ray radiation	fine-focus sealed tube, MoKα	Temperature	293 K
Detector-to-sample		Maximum 2θ	55.50°
distance	5.439 cm	Resolution	0.7 Å
Rotation width	0.3°	Total number	
		of frames	1271
Frame size	512 * 512 pixels	Measuring time	
		per frame	300 seconds
Meas. reflections	2426	Obs. reflections	2352
Index range	−13 ≤ h ≤ 17	Unique reflections	947
	−13 ≤ k ≤ 11	Reflections > 2σ(I)	701
	−8 ≤ l ≤ 9		
R_{INT}	6.84%	R_σ	8.90%
Number of l.s.		GooF	1.278
parameters	75	$R_1, F_o > 4\sigma (F_o)$	7.01%
R_1, all data	11.05%	wR_2 (on F_o^2)	10.74%

$R_{INT} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma F_o^2$
$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$
$\text{Goof} = \sqrt{(\Sigma w[F_o^2 - F_c^2] / [n - p])}$
$P = (\max(F_o^2, 0) + 2 F_c^2) / 3$

$R_s = \Sigma \sigma(F_o^2) / \Sigma F_o^2$
$wR_2 = \sqrt{(\Sigma w[F_o^2 - F_c^2]^2 / \Sigma w[F_o^2]^2)}$
$w = 1 / (\sigma^2[F_o^2] + [0.0281 \text{ P}]^2 + 2.23 \text{ P})$

TABLE 3. UNIT-CELL DATA FOR NATURAL AND SYNTHETIC
$MnV_2O_6 \cdot 4H_2O$

	Natural (ansermetite)	Synthetic
Formula	$MnV_2O_6 \cdot 4H_2O$	$MnV_2O_6 \cdot 4H_2O$
System	monoclinic	monoclinic
Space group	C2/c	C2/c
a (Å)	13.171(2)	13.1656(6)
b (Å)	10.1280(10)	10.110(1)
c (Å)	6.9830(10)	6.9816(5)
β (°)	111.572(2)	111.559(5)
V (Å³)	866.3(2)	864.2(1)
Z	4	4
Reference	This study	Liao et al. (1996)

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR ANSERMETITE

h k l	d_{calc}	I_{calc}	d_{obs}	I_{obs}	h k l	d_{calc}	I_{calc}	d_{obs}	I_{obs}
1 1 0	7.805	100	7.82	100	3 1 1	2.873	9	2.877	5
2 0 0	6.124	5			2 2 2	2.845	9	2.842	5
1̄ 1 1	5.690	13	5.69	20	4̄ 0 2	2.800	10	2.799	5
0 2 0	5.064	10	5.06	20	0 2 2	2.733	12	2.737	10
1 1 1	4.500	28	4.51	30	4 2 0	2.620	12	2.626	10
0 2 1	3.993	6	3.98	10	4 2 1	2.201	3	2.200	5
2 2 0	3.903	24	3.91	30	2̄ 2 3	2.115	1	2.117	5
3̄ 1 1	3.901	10			6̄ 0 2	2.113	2		
1 3 0	3.255	26			6 0 0	2.041	5		
0 0 2	3.247	5			5̄ 1 3	1.995	5	1.992	5
4 0 0	3.062	8	3.065	10	5 3 0	1.983	8		
2 2 1	3.045	6			1̄ 3 3	1.890	6		
1̄ 3 1	3.031	11	3.029	70	1 5 1	1.879	5	1.879	10
3̄ 1 2	3.027	26			4̄ 4 2	1.878	5		

The X-ray-diffraction pattern of ansermetite (powder method) was measured with a
Gandolfi camera, 114.6 mm, FeKα, Mn-filtered radiation, 40 kV, 20 mA, 99 h
exposure time. Intensities were visually estimated. The calculated intensities are for the
crystal-structure model. Two lines at 3.862/5 and 3.509/60 cannot be indexed and are
attributed to unknown inclusions.

TABLE 5. ATOM-POSITION PARAMETERS AND EQUIVALENT
ISOTROPIC-DISPLACEMENT PARAMETERS (Å²) FOR ANSERMETITE

	x	y	z	U_{eq}
Mn	0.25	0.25	0	0.0188(5)
V†	0.10541(9)	0.47440(11)	0.19330(17)	0.0142(4)
O1	0.2047(4)	0.5795(5)	0.3004(7)	0.0254(12)
O2	0.1601(4)	0.3304(4)	0.1782(7)	0.0241(12)
O3	0.3885(5)	0.3589(6)	0.2165(8)	0.0348(14)
O4	0.9401(4)	0.4612(5)	0.0788(7)	0.0240(12)
O5	0.3934(5)	0.6246(6)	0.1073(9)	0.0393(15)
H3A	0.392(7)	0.445(5)	0.228(13)	0.05
H3B	0.426(6)	0.296(6)	0.234(14)	0.05
H5A	0.456(4)	0.644(8)	0.127(12)	0.05
H5B	0.348(6)	0.647(8)	0.167(12)	0.05

† occupancy of 0.975(6). All other positions are fully occupied.

TABLE 6. ANISOTROPIC-DISPLACEMENT PARAMETERS (Å²)
FOR THE CATIONS IN THE STRUCTURE OF ANSERMETITE

	$*U_{11}$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	0.0188(9)	0.020(9)	0.0188(8)	0.0021(7)	0.0083(6)	-0.0010(7)
V	0.0147(7)	0.0166(6)	0.0125(6)	0.0014(6)	0.0067(4)	-0.0012(5)
O1	0.028(3)	0.028(3)	0.022(3)	-0.009(2)	0.011(2)	-0.004(2)
O2	0.029(3)	0.024(3)	0.024(3)	0.005(2)	0.014(2)	0.002(2)
O3	0.025(3)	0.035(3)	0.042(3)	-0.004(3)	0.010(2)	-0.007(3)
O4	0.017(2)	0.040(3)	0.020(2)	0.002(2)	0.012(2)	0.003(2)
O5	0.045(4)	0.035(4)	0.042(4)	-0.004(3)	0.022(3)	-0.008(3)

* Anisotropic displacement parameters are given in the form exp $(-2\pi^2[h^2(a^*)^2 U_{11} + k^2(b^*)^2 U_{22} + ... + 2hka^*b^*U_{12}])$

of hydrogen bonds by connecting to the opposite O3
(2.41 Å). H5B connects to O2 (2.12 Å). The low bond-
valence at O2 (Table 8) is in line with acceptance of a
strong hydrogen bond from H5B.

RELATION TO OTHER SPECIES

Ansermetite is the third known vanadate of manga-
nese, after fianelite, $Mn_2V(V,As)O_7 \cdot 2H_2O$ (Brugger &
Berlepsch 1996) and reppiaite, $Mn_5(VO_4)_2(OH)_4$ (Basso
et al. 1992). Fianelite and ansermetite occur in close
association at the Fianel mine, whereas reppiaite is a
rare mineral occurring in the metamorphosed exhalative
deposits of manganese at Gambatesa, Val Graveglia,
Italy. Reppiaite forms under retrograde greenschist- to
zeolite-facies conditions.
Ansermetite is the first natural vanadate of manga-
nese in which V^{5+} occurs in five-fold square pyramidal
coordination. Evans & Hughes (1990) pointed out that
vanadium bronzes can be considered as various lateral
linkages of only two types of polyvanadate chains: a
divanadate chain $(V_2O_6)_n$, of the type found in
ansermetite, and a tetravanadate chain $(V_4O_{12})_n$ consist-
ing of four chains of octahedra. Minerals containing

isolated divanadate chains similar to those found in ansermetite include munirite, $NaVO_3 \cdot 1.9H_2O$ (Björnberg & Hedman 1977), metamunirite, $NaVO_3$ (Kato & Takayama 1984), rossite, $Ca(VO_3)_2 \cdot 4H_2O$ (Ahmed & Barnes 1963) and metarossite, $Ca(VO_3)_2(H_2O)_2$ (Kelsey & Barnes 1960).

Schindler *et al.* (2000a) used a bond-valence approach to rationalize the structural properties of vanadium minerals and the conditions of their formation from aqueous solution (*i.e.*, pH of the mother solution). They predicted that in a mineral formed in aqueous solution, a divalent cation in [6]-coordination occurring together with the $[V_2O_6]$ structural unit should bond to at least three transformer H_2O groups. This prediction was based on a comparison with rossite, metarossite, murinite and metamurinite. In ansermetite, $^{[VI]}Mn^{2+}$ bonds to two transformer H_2O groups only, showing that the predictions for vanadate minerals do not exactly match but are still in a reasonable range.

DEHYDRATION OF ANSERMETITE

Owing to recent interest in transition-metal oxide electrodes for lithium batteries, studies of the system V–Mn–O–H are available in the solid-state physics literature (*e.g.,* Kim *et al.* 2001, Le Gal La Salle *et al.* 2000). Ansermetite is easily synthesized at room temperature by precipitation from a stoichiometric $MnSO_4 \cdot H_2O$ and $NaVO_3$ solution at pH in the range 4.5–6.5 (Liao *et al.* 1996). The precipitation of ansermetite reflects the presence of metavanadate complexes such as $V_3O_9^{3-}$, $V_4O_{12}^{4-}$ or $HV_{10}O_{28}^{5-}$ in neutral to mildly acidic aqueous solutions at room temperature (*e.g.,* Greenwood & Earnshaw 1984, p. 1148). Evans & Garrels (1958) first pointed out the importance of pH in determining the speciation and polymerization of V^{5+} in solution; this in turn determines the nature of precipitating minerals.

$MnV_2O_6 \cdot 4H_2O$ appears to be stable only at low temperature at atmospheric pressure. Liao *et al.* (1996) observed a relatively complex mechanism of dehydration as a function of H_2O activity and chemistry of the medium (Fig. 4). In contact with the solution from which it precipitated, $MnV_2O_6 \cdot 4H_2O$ (ansermetite) transforms rapidly at about ~100°C to a mixture of $MnV_2O_6 \cdot 2H_2O$

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å)
IN THE STRUCTURE OF ANSERMETITE

Mn-O1²	2.161(5)	V-O1	1.638(5)
Mn-O1³	2.161(5)	V-O2$_{apex}$	1.647(5)
Mn-O2⁵	2.167(4)	V-O4¹	1.886(5)
Mn-O2	2.167(4)	V-O4²	1.900(4)
Mn-O3	2.191(5)	V-O4⁶	2.029(5)
Mn-O3	2.191(5)	<V-O>	1.820
<Mn-O>	2.173		
O3-H3A	0.87(4)	O3-O5⁴	2.711(8)
O3-H3B	0.78(4)	O3-O3²	2.798(5)
O5-H5A	0.81(4)	O5-O5²	2.783(7)
O5-H5B	0.88(4)	O5-O2⁸	2.804(7)
		O3-O5⁷	2.805(8)

¹ -x + 1, -y + 1, -z   ² -x + 1, y, -z + ½   ³ -x + ½, y - ½, -z + ½
⁴ x, -y + 1, z - ½   ⁵ -x + ½, -y + ½, -z   ⁶ x - 1, y, z
⁷ x, y, z   ⁸ -x + ½, y + ½, -z + ½

TABLE 8. BOND-VALENCE SUMMATIONS FOR THE STRUCTURE
OF ANSERMETITE

	O1	O2	O3 (H_2O)	O4	O5 (H_2O)	Sum
Mn	0.37 ⁺²⁻	0.36 ⁺²⁻	0.34 ⁺²⁻			2.14
V	1.56	1.52		0.79		5.19
				0.77		
				0.55		
Sum	1.93	1.88	0.34	2.11	0	

Calculations made with the parameters from Brown & Altermatt (1985).
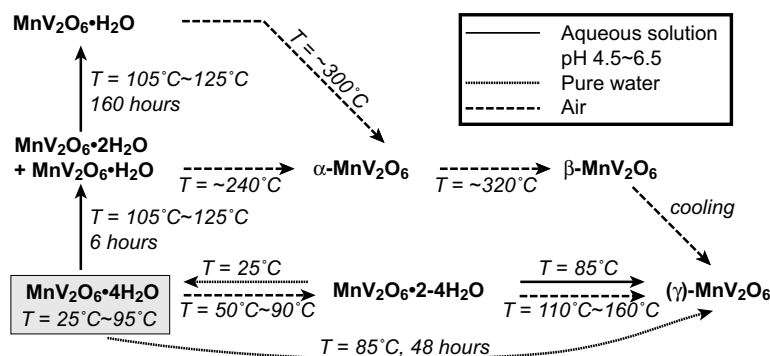

FIG. 4. Thermal stability of $MnV_2O_6 \cdot 4H_2O$ at atmospheric pressure, in aqueous solution and in air. Data from Liao *et al.* (1996).

and $MnV_2O_6 \cdot H_2O$. In the latter two compounds, vanadium has tetrahedral coordination (Liao *et al.* 1996). On the other hand, $MnV_2O_6 \cdot 4H_2O$ transforms to the anhydrous γ–MnV_2O_6, with a brannerite-type crystal structure within 2–3 days at 85°C in water. This reaction appears to be irreversible. When heated in air, $MnV_2O_6 \cdot 4H_2O$ transforms at ~50°C into $MnV_2O_6 \cdot 2$–$4H_2O$.

We also observed that the two weakly bound H_2O groups per formula unit (O5) are easily released in vacuum. This was first observed on polished sections: ansermetite showed a good initial polish, but came out of the EMP with a poor polish and prominently visible cleavage. Similarly, an attempt to obtain SEM pictures was unsuccessful, as the crystals exploded under the electron beam in the vacuum. Even under wet ESEM (5.7 Torr H_2O pressure), ansermetite is unstable and hard to photograph. A Guinier powder X-ray photograph obtained under vacuum (~10^{-5} bar) confirmed that within 40 minutes, a significant proportion of ansermetite is transformed into $MnV_2O_6 \cdot 2$–$4H_2O$. It therefore appears that ansermetite is highly reactive, owing to the collapse of the structure as the weakly bound H_2O groups escape.

The available information about the stability of $MnV_2O_6 \cdot 4H_2O$ suggests that ansermetite formed under near-surface conditions (T < 50°C) from a neutral to mildly acidic groundwater. Ansermetite would probably not survive under a hot dry climate, where surface temperatures in excess of 40°C can be attained. The occurrence of ansermetite can be compared to that of rossite, $Ca(VO_3)_2 \cdot 4H_2O$, which also precipitates from neutral aqueous solutions at room temperature (Ahmed & Barnes 1963). However, whereas ansermetite is stable under room-temperature conditions, rossite slowly dehydrates to metarossite (Ahmed & Barnes 1963), and murinite, to metamurinite (Kato & Takayama 1984). Using the coordination-number descriptors [1 + 4] and [2 + 3] introduced by Schindler *et al.* (2000b), Schindler *et al.* (2000a) showed that at the transition rossite–metarossite, the type of coordination of V^{5+} changes from [1 + 4] to [2 + 3], whereas in munirite and ansermetite, V^{5+} is already in [2 + 3] coordination.

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