

Ronneburgite, $K_2MnV_4O_{12}$, a new mineral from Ronneburg, Thuringia, Germany: Description and crystal structure

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ABSTRACT

Ronneburgite is a new chain vanadate mineral from Ronneburg, Thuringia, Germany. It occurs as reddish-brown crystals of equant, flattened, or short prismatic habit, up to 0.5 mm in length. The crystals have an adamantine luster and are translucent. Ronneburgite is biaxial negative with refractive indices $n_\alpha = 1.925(5)$, $n_\beta = 1.960(10)$, $n_\gamma = 1.988(4)$, and $2V_x = 82^\circ$. Electron microprobe analysis ($K_2O = 16.93$, $MnO = 12.44$, $MgO = 0.62$, $V_2O_5 = 68.54$; total = 98.53 wt%) gives the empirical formula $K_{1.91}Mn_{0.93}Mg_{0.08}V_{4.00}O_{11.96}$, which simplifies to $K_2MnV_4O_{12}$. Ronneburgite is monoclinic, space group $P2_1/n$, with $a = 8.183(3)$, $b = 9.247(3)$, $c = 8.651(2)$ Å, and $\beta = 109.74(2)^\circ$. The measured density is 2.84 g/cm³; the calculated density for $Z = 2$ is 2.85 g/cm³. Single-crystal X-ray structure determination ($R_1 = 0.046$ for 1846 reflections) shows that ronneburgite contains infinite vierer-single metavanadate chains $[(VO_3)_n]^{n-}$ of corner-sharing VO_4 tetrahedra along [101]. Although the empirical formula and calculated bond valences indicate that V is 5+ and Mn is 2+, the crystal color, a “poor” structural compatibility index, and Mn-O distances between those expected for Mn^{2+} -O and Mn^{3+} -O indicate that some Mn^{3+} and V^{4+} ions are present. K^+ ions and octahedral Mn^{n+} ions bridge between the metavanadate chains by coordinating to their oxygen atoms.

INTRODUCTION

During a reinvestigation of minerals from the Ronneburg U deposit near Gera, Thuringia, Germany, a reddish-brown mineral (Fig. 1) was found by one of the authors (T.W.) and F. Rüter (Gera). Only a few samples were recovered. A semi-quantitative energy-dispersive X-ray analysis showed the composition to be different from that of any known mineral. Subsequent investigations confirmed that the mineral is a new species. The mineral has been named ronneburgite after the locality. Both mineral and name have been approved by the IMA Commission on New Minerals and Mineral Names prior to publication (vote 98-069). Type material is deposited in the Mineralogical Collection of the Bergakademie Freiberg, Germany, as No. 78908.

OCCURRENCE AND PARAGENESIS

The Ronneburg U deposit was mined from 1949 to 1990. This deposit was Europe’s most productive U-mining field: about 7% of the world’s U production came from the Ronneburg area. The U mineralization is mainly found in Ordovician, Silurian, and Devonian slates and limestones.

The complex mineralogy of the Ronneburg deposit was recently described by Witzke and Rüter (1998), where ronneburgite is mentioned as the unidentified sample “RB 210.” More than 230 mineral species are currently known from the Ronneburg deposit. Ronneburgite was found on the mine dump of the Lichtenberg open-cast pit, which is situated at the southwest margin of Ronneburg, and was active from 1958 to 1977.

Ronneburgite is associated with hummerite ($KMgV_3O_{14} \cdot 8H_2O$), gypsum, epsomite, picromerite, hematite, and an unidentified brownish K-Mg-Mn-vanadate. Epsomite and picromerite were formed later than ronneburgite. A few meters from the ronneburgite occurrence, the Ca-vanadate minerals sincosite, simplotite, and straczekite were observed at the mine dump. The Cu-vanadate volborthite was found in the oxidation zone of the Lichtenberg open-cast pit. Ronneburgite is an alteration product, likely to have formed at low temperatures under oxidizing conditions with pH neutral to basic (Evans and White 1987; Schindler et al. 2000). A primary V mineral from Ronneburg is not known to date.

PHYSICAL AND OPTICAL PROPERTIES

Ronneburgite occurs as reddish-brown, equant, flattened or short prismatic crystals up to 0.5 mm in length (Fig. 2). The streak of the mineral is orange brownish. The crystals have an adamantine luster and are translucent. The mineral is brittle, its fracture is irregular, and it shows an indistinct cleavage in

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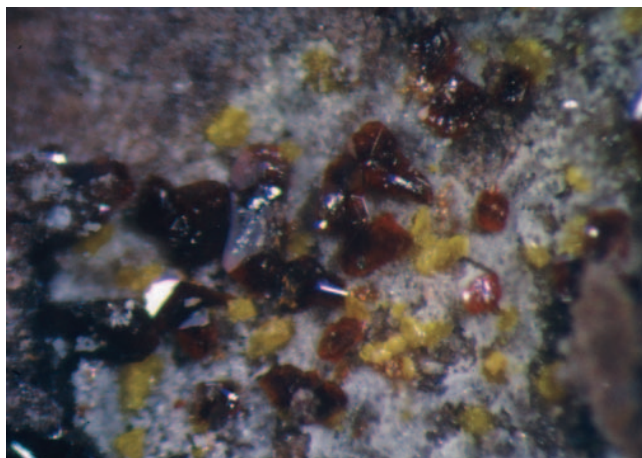


FIGURE 1. Reddish-brown ronneburgite crystals up to 0.3 mm in size, with yellow hummerite (photo F. Rürger).

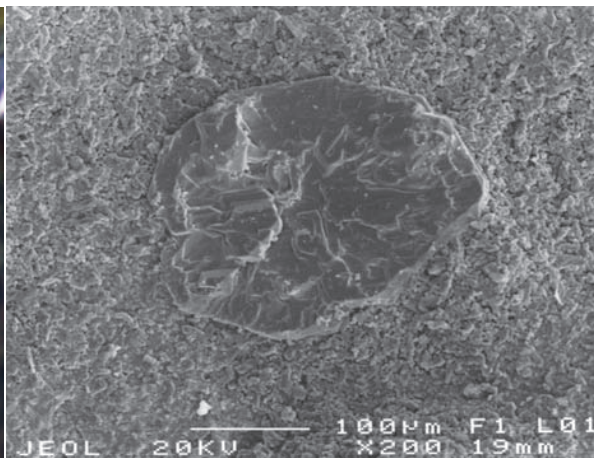


FIGURE 2. SEM micrograph of a ronneburgite crystal.

one direction. The Mohs hardness of ronneburgite is 3. The density, measured by the flotation method in a Na polytungstate solution, is 2.84(2) g/cm³ (mean of four determinations). The calculated density for $Z = 2$ is 2.85 g/cm³. Ronneburgite shows no fluorescence when irradiated with ultraviolet light, independent of the excitation frequency.

Optical properties were determined on grain mounts using Cargille immersion liquids. Refractive indices are $n_\alpha = 1.925(5)$, $n_\beta = 1.960(10)$, $n_\gamma = 1.988(4)$, $2V_x = 82^\circ$ (white light). Ronneburgite is, apparently, biaxial negative with a large optical angle, although an accurate value for the latter could not be measured. Thin grains show weak pleochroism: $X =$ brownish orange with distinct reddish tint, $Y =$ brownish orange, $Z =$ brownish orange; absorption $X \cong Y \approx Z$. Thicker crystals show weak pleochroism in dark red-orange. Interference colors are slightly anomalous. The determination of the optical properties was hampered by the strong absorption of the mineral, and by the fact that the grains were immediately attacked by those immersion liquids for which $n > 1.80$ in contact with air. The grains appeared to be relatively stable if the liquid was protected by a cover glass.

MINERAL CHEMISTRY

Chemical analyses of ronneburgite were performed by both energy-dispersive (EDS) and wavelength-dispersive (WDS) X-ray spectrometry. An EDS spectrum revealed K, Mn, V, and O as the only elements present. The measured K:Mn:V ratio was about 2:1:4 (Witzke and Rürger 1998). Quantitative analyses were conducted with a Cameca SX 100 electron microprobe operated at an acceleration voltage of 15 kV and a beam current of 10 nA with orthoclase (K), rhodonite (Mn), MgO (Mg), and VSi₂ (V) as standards. The CAMECA program PAP was used for data reduction. The crystal was analyzed at 20 different points. The average analysis (wt% and standard deviation) is given in Table 1. The low total of 98.53 wt% may be caused by a small loss of K under vacuum conditions and the impact of the electron beam. No other elements with $Z \geq 5$ were detected. The empirical formula calculated for $V = 4$ is $K_{1.91}Mn_{0.93}Mg_{0.08}V_{4.00}O_{11.96}$, which corresponds well to the ideal

TABLE 1. Chemical analysis for ronneburgite, $K_2MnV_4O_{12}$

oxide	wt% (meas.)	standard deviation	wt% (calc.)
K ₂ O	16.93	0.16	17.50
MnO	12.44	0.48	13.46
MgO	0.62	0.23	
V ₂ O ₅	68.54	0.66	69.04
Total	98.53		100.00

formula $K_2Mn^{2+}V^{5+}_4O_{12}$. The valences of Mn and V were deduced from considerations of electroneutrality and are relatively consistent with the crystal structure (see Discussion Section).

X-RAY POWDER DIFFRACTION

The X-ray powder diffraction pattern (Table 2) was recorded using a Siemens D5000 diffractometer with $CuK\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) and a secondary graphite monochromator. The reflections were indexed by using the results of the single-crystal study. Refinement of the powder diffraction data gave a monoclinic cell with $a = 8.155(4)$, $b = 9.229(4)$, $c = 8.636(4) \text{ \AA}$, and $\beta = 109.84(3)^\circ$; $V = 611.4(3) \text{ \AA}^3$.

CRYSTAL STRUCTURE

A single crystal of dimensions $0.15 \times 0.11 \times 0.025 \text{ mm}$ was mounted on a Siemens four-circle computer-controlled P3 diffractometer equipped with graphite monochromator and a pulse-height analyzer. The unit-cell parameters and diffraction intensities were measured at 23 °C using molybdenum $K\alpha$ radiation ($K\alpha_1 = 0.70930$; $K\alpha_2 = 0.71359 \text{ \AA}$). The centric space group $P2_1/n$ was unambiguously indicated by the conditions for reflection ($h0l$, $h+l = 2n$; $0k0$, $k = 2n$); this unit cell was selected because its β angle was closest to 90° [best reduced (Niggli) cell]. Centricity was further indicated by the value of the centricity indicator, 0.906 (compare with 0.968 for centric and 0.736 for non-centric, both equal-atom values). Two formula units of $K_2MnV_4O_{12}$ (formula weight = 528.90 amu) are present per unit cell. The unit-cell parameters were determined at 22 °C by least-squares refinement of 34 reflections within the range $11^\circ < 2\theta < 27^\circ$; $a = 8.183(3)$, $b = 9.247(3)$, $c = 8.651(2) \text{ \AA}$, and $\beta = 109.74(2)^\circ$; $V = 616.1(2) \text{ \AA}^3$. All 2724 unique reflections with $2\theta < 70^\circ$ were recorded.

TABLE 2. Powder diffraction data for ronneburgite

<i>l</i>	<i>d</i> _{meas.}	<i>d</i> _{calc.}	<i>h k l</i>
25	6.864	6.859	-1 0 1
20	6.105	6.098	0 1 1
27	5.914	5.899	1 1 0
32	5.509	5.505	-1 1 1
9	4.269	4.272	1 1 1
25	3.957	3.954	1 2 0
18	3.841	3.836	2 0 0
55	3.701	3.699	-2 1 1
100	3.336	3.333	1 2 1
50	3.118	3.119	-1 2 2
17	3.048	3.049	0 2 2
36	3.000	3.000	1 1 2
64	2.878	2.878	-1 0 3
		2.877	0 3 1
68	2.752	2.753	-2 2 2
14	2.437	2.442	-1 2 3
14	2.413	2.410	2 0 2
8	2.339	2.335	0 2 3
9	2.308	2.307	0 4 0
17	2.210	2.209	1 4 0
		2.208	1 3 2
7	2.132	2.136	2 2 2
10	2.065	2.063	-2 1 4
10	2.017	2.019	-4 0 2
8	2.001	2.003	-2 4 1
28	1.968	1.966	3 3 0
19	1.884	1.885	2 1 3
28	1.860	1.859	-4 1 3
18	1.791	1.791	-3 2 4
7	1.777	1.777	2 2 3

The crystal structure was determined by direct methods (program SHELXS; Sheldrick, 1997) and was refined by full-matrix least-squares procedures based on F^2 (program SHELXL 97-2; Sheldrick, 1997). SHELXS used the 122 reflections for which $E > 1.20$ to generate and sign-refine 256 solutions, 119 of which converged to the same solution with the lowest CFOM (combined figure of merit), 0.038; it showed the positions of all of the atoms in the structure with reasonable bond lengths and angles. Least-squares refinement, ultimately with anisotropic temperature factors (89 parameters altogether), converged quickly. The final discrepancy indexes are $R_1 = \Sigma |F_o - |F_c|| / \Sigma F_o = 0.046$ for the 1846 reflections with $F_o > 4\sigma(F_o)$ and 0.079 for all 2724 reflections; $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)]^2 / \Sigma (wF_c^2)^2\}^{1/2} = 0.107$ for all 2724 reflections. The final weight w was assigned using the formula $w = q/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = fF_o^2 + (1-f)F_c^2$, to give $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$, with a and b as refined parameters. The goodness-of-fit is 0.93. On the final difference Fourier map, the highest peak (1.2 $e\text{\AA}^{-3}$) and the deepest hole (-1.0 $e\text{\AA}^{-3}$) were both 0.73 Å from the Mn position; the next four highest peaks ranged from 0.86

to 0.74 $e\text{\AA}^{-3}$ and were between 0.74 and 0.97 Å from O5, K, O4, and O6, respectively. Atomic coordinates and anisotropic thermal parameters are listed in Table 3, and selected bond lengths are given in Table 4.

The crystal structure (Figs. 3–5) consists of infinite parallel chains of metavanadate ions, $[(VO_3)_n]^{n-}$ extending along [101], the $a+c$ glide direction of $P2_1/n$. Had $P2_1/c$ been chosen, the direction would have been parallel to the c glide. Each V^{5+} ion coordinates to two bridging O atoms ($V-O = 1.78\text{--}1.83$ Å) and, with shorter distances, to two non-bridging O atoms ($V-O = 1.61\text{--}1.66$ Å). There are two non-equivalent V atoms and four V atoms per metavanadate chain per unit cell to cause the chains to be vierer-single (Figs. 4 and 5). Mn^{2+} ions at inversion centers bridge between the metavanadate chains (Fig. 2) by coordinating octahedrally ($Mn-O = 2.12\text{--}2.17$ Å) to 75% of the non-bridging oxygen atoms. The K^+ ions also bridge between the metavanadate chains (Fig. 2); each K^+ has eight nearest-neighbor O atoms ($K-O = 2.79\text{--}3.03$ Å) and is 3.20 and 3.37 Å from two other O atoms. The K^+ ions approach most closely ($K-O = 2.79$ Å) those non-bridging O atoms (the remaining 25%) that do not coordinate to Mn^{2+} ions.

VIBRATIONAL SPECTROSCOPY

The infrared spectrum of ronneburgite was obtained from a small plate-like chip about $80 \times 65 \times 15$ μm in size. The analysis was performed in the transmission mode (ZnSe sample holder) using a BioRad FTS 40A infrared spectrometer equipped with an UMA 500 microscope; 500 scans (spectral range 500 to 4000 cm^{-1}) were made. The spectral resolution was 2 cm^{-1} . The IR absorption (Fig. 6) is dominated by a strong band at 1029 cm^{-1} , which is interpreted as being due to the symmetric stretching vibrations of the VO_4 tetrahedra. Low-intensity bands due to slight hydrocarbon contamination were observed around 2900 cm^{-1} , and no bands belonging to the sample itself were observed in the 1500–400 cm^{-1} range, confirming that ronneburgite is a water-free mineral.

Raman spectra of ronneburgite were obtained by using a Jobin Yvon T64.000 laser-Raman spectrometer with an Olympus microscope. Spectra were excited by the 6760 Å line of a Kr^+ ion laser. The beam intensity, measured after the 50× objective, was 1.5 mW. The spectral resolution was 1 cm^{-1} . Ten accumulations (signal/dark) per 15 seconds were done in the subtractive mode. The Raman spectrum of ronneburgite shows a sharp and intense band at 952 cm^{-1} . This band, as well as the less intense bands in the region 700–1000 cm^{-1} , are as-

TABLE 3. Atomic coordinates and displacement parameters ($\times 10^4$) for ronneburgite

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Mn	0	0	0	111(3)	112(3)	90(3)	8(3)	19(2)	7(2)
V1	0.16696(7)	0.21242(6)	0.37929(6)	98(2)	133(2)	82(2)	-14(2)	14(2)	-10(2)
V2	-0.19886(8)	0.44235(7)	0.26056(7)	121(2)	147(3)	101(2)	8(2)	14(2)	8(2)
K	-0.1420(1)	0.19750(9)	0.5925(1)	245(3)	227(4)	204(4)	15(3)	107(3)	-1(3)
O1	0.1829(4)	0.0915(3)	0.5440(3)	251(14)	222(13)	111(10)	-28(11)	26(10)	33(9)
O2	-0.0247(4)	0.3158(4)	0.3435(4)	231(15)	373(18)	217(14)	153(13)	43(12)	63(12)
O3	0.1518(4)	0.1169(3)	0.2130(3)	236(13)	246(13)	135(11)	-53(11)	51(10)	-97(10)
O4	0.3389(4)	0.3168(3)	0.4142(3)	225(13)	176(12)	205(12)	-90(10)	69(11)	-49(10)
O5	-0.3351(4)	0.4264(3)	0.3650(3)	201(13)	241(14)	197(13)	47(11)	95(10)	-8(10)
O6	-0.1272(4)	0.6059(3)	0.2727(4)	361(18)	222(14)	330(16)	-122(13)	56(14)	-31(13)

Notes: This anisotropic temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

TABLE 4. Selected interatomic distances (Å) and angles (°) for ronneburgite

Mn-O3	2.136(3)	O3-Mn-O4	90.52(11), 89.48(11)
Mn-O4	2.121(3)	O3-Mn-O5	91.12(10), 88.88(10)
Mn-O5	2.171(3)	O4-Mn-O5	90.75(11), 89.25(11)
mean	2.143	mean dev. from 90°	0.80
VI-O1	1.781(3)	O1-VI-O2	107.44(14)
VI-O2	1.773(3)	O1-VI-O3	108.90(14)
VI-O3	1.656(3)	O1-VI-O4	113.18(14)
VI-O4	1.648(3)	O2-VI-O3	109.48(15)
mean	1.714	O2-VI-O4	111.52(16)
		O3-VI-O4	106.28(14)
		mean dev. from 109.46°	1.93
V2-O1	1.822(3)	O1-V2-O2	111.91(14)
V2-O2	1.795(3)	O1-V2-O5	108.85(14)
V2-O5	1.662(3)	O1-V2-O6	106.45(15)
V2-O6	1.612(3)	O2-V2-O5	108.21(14)
mean	1.723	O2-V2-O6	111.30(17)
		O5-V2-O6	110.11(17)
		mean dev. from 109.46°	1.64
K-O1	2.895(3), 2.993(3)		
K-O2	2.856(3)		
K-O3	2.840(3), 3.374(3)		
K-O4	2.842(3)		
K-O5	2.958(3), 3.029(3)		
K-O6	2.790(3), 3.199(4)		
mean, eight shortest	2.900		

signed to the internal stretching vibrations of the VO_4 tetrahedra. Bands in the lower frequency region, 150–500 cm^{-1} , may include vanadate bending as well as Mn-VO_4 vibrations, whereas vibrations involving K^+ ions are expected to have frequencies near or less than 100 cm^{-1} . The large number of bands in the VO_4 stretching region (here above 700 cm^{-1} : ν_1 , symmetric stretch; ν_3 , antisymmetric stretch), is consistent with the presence of two nonequivalent VO_4 groups in ronneburgite. The asymmetric appearance of the 952 cm^{-1} band, which has a shoulder at 942 cm^{-1} , may be due to the presence of a third kind of VO_4 tetrahedron due to cation substitution (such as V^{4+} for V^{5+} ; see Discussion Section).

RELATED PHASES

Ronneburgite is only the second mineral to be found with unbranched metavanadate chains of vertex-linked tetrahedra. Alvanite, $(\text{Zn,Ni})\text{Al}_4(\text{VO}_3)_2(\text{OH})_{12} \cdot 2\text{H}_2\text{O}$, was the first (Pertlik and Dunn 1990). Ronneburgite has vierer-single chains; alvanite has zweier-single chains. Ronneburgite has only metavanadate chains with bridging cations; alvanite has metavanadate chains that are weakly linked by hydrogen bonding to brucite-like layers of $\text{Al}(\text{OH})_6$ and $(\text{Zn,Ni})(\text{OH})_6$ octahedra. The mean V-O

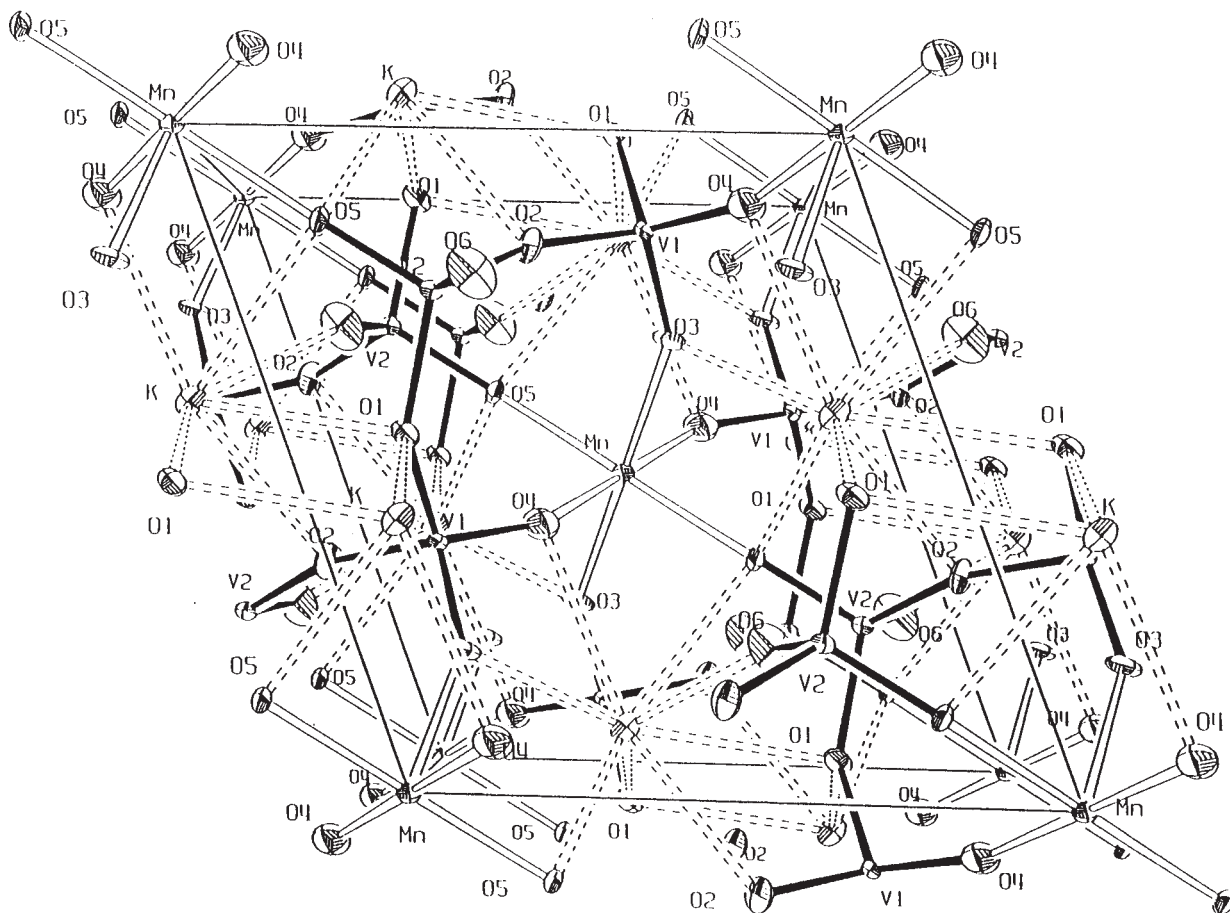


FIGURE 3. The crystal structure of ronneburgite; one complete unit cell is shown. V-O bonds are black, Mn-O bonds are white, and broken lines are used for the K-O bonds. The octahedral coordination of Mn^{2+} at an inversion center is clearly seen in the middle. The origin is at the lower left back corner; a extends to the right and c extends upward, with b pointing nearly up out of the page.

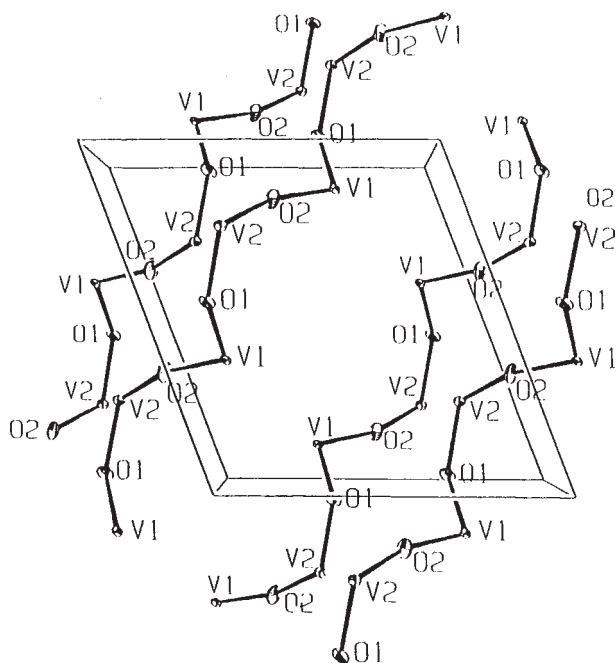


FIGURE 4. The metavanadate chains in ronneburgite; same orientation as in Figure 2.

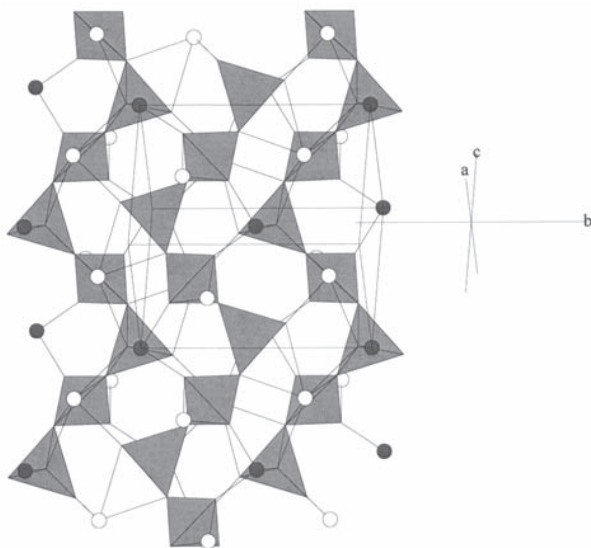


FIGURE 5. A tetrahedral representation of the crystal structure of ronneburgite. VO_4 tetrahedra, Mn (black circles), and K (white circles) are shown.

bridging distances are 1.793 Å in ronneburgite and 1.813 Å in alvanite; the mean non-bridging V-O distances are 1.644 and 1.634 Å. The smaller distortion of the VO_4 tetrahedra in ronneburgite is related to the stronger interactions that the metavanadate chains have with the neighboring cations. The bond valences for V in ronneburgite, 5.28 and 5.03 v.u., compare well with that in alvanite, 5.12 v.u. The other calculated

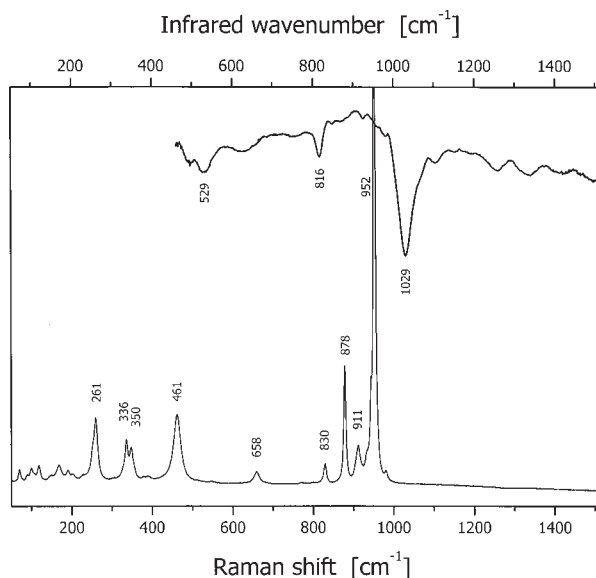


FIGURE 6. Infrared (upper) and Raman (lower) spectra of ronneburgite.

bond valences are 2.28 v.u. for Mn, 1.14 v.u. for K and 1.82–2.27 v.u. for O in ronneburgite, 3.13 and 3.16 v.u. for Al and 1.98 v.u. for $\text{Zn}_{0.5}\text{Ni}_{0.5}$ in alvanite.

The mineral fianelite, $\text{Mn}_2\text{V}(\text{V,As})\text{O}_7 \cdot 2\text{H}_2\text{O}$, is chemically related to ronneburgite. It contains ditetrahedral $\text{V}(\text{V,As})\text{O}_7$ groups (Brugger and Berlepsch 1996). As in ronneburgite, Mn is divalent and has octahedral coordination, whereas V is pentavalent and has tetrahedral coordination. Mn-O distances (2.11–2.30 Å), V-O distances (1.657–1.83 Å), Mn bond valences (2.07–2.10 v.u.), and V bond valences (4.99–5.07 v.u.) are similar to the values in ronneburgite.

Chain vanadates like munirite, $\text{NaVO}_3 \cdot 1.9\text{H}_2\text{O}$ and metamunirite, NaVO_3 , contain infinite chains of edge-sharing VO_5 groups (Evans 1991).

DISCUSSION

The reddish-brown color of ronneburgite indicates that a small amount of Mn^{3+} might be present. Because the measured Mn-O distances (2.12–2.18 Å, see Table 4) are intermediate between those for Mn^{2+} (2.205 Å for $[\text{VI}]\text{Mn}^{2+}$; Baur 1981), and those for Mn^{3+} (2.00 to 2.12 Å for $[\text{VI}]\text{Mn}^{3+}$; Foley et al. 1997), Mn could be in part in the trivalent state.

Additionally, Raman spectra suggest that some V^{4+} is present in ronneburgite. This may be due in part to a slight replacement of Mn^{2+} by Mn^{3+} , coupled with V^{4+} for V^{5+} . The calculated bond-valence values give no clear evidence for this replacement. The compatibility index (Mandarino 1981) for ronneburgite falls in the “poor” category, but a slight replacement would not have a great influence on the value of the compatibility index. A more probable reason for the “poor” compatibility index is a different k value (Mandarino 1981) for V_2O_5 (or MnO , K_2O) in chain vanadates. It should be noted that several components (Al_2O_3 , Ti_2O_3 , V_2O_3 , Cr_2O_3 , Mn_2O_3 , MgO) have special Gladstone-Dale constants for neso- and inosilicates, sulfates, and selenates.

An error caused by additional water in the structure is unlikely. No suitable maxima are observed in the Fourier difference map calculated from the final refinement. There is no evidence for additional oxygen (or water) in the ronneburgite structure, which is consistent with the finding that no O-H stretching and H-O-H bending vibrations are observed in the infrared absorption and Raman spectra.

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