

## Vyalsovite, a new sulfide-hydroxide of iron, calcium, and aluminum

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### ABSTRACT

The new mineral vyalsovite,  $\text{FeS} \cdot \text{Ca}(\text{OH})_2 \cdot \text{Al}(\text{OH})_3$ , has been found in forsterite skarns at the lower contact of the Talnakh gabbro-dolerite intrusion in Devonian dolomite. It occurs as 5- to 150- $\mu\text{m}$  grains and veinlets in association with valleriite, diaspore, djerfisherite, serpentine, and magnetite. This assemblage formed as a result of the replacement of minerals included in an earlier assemblage of chalcopyrite, forsterite, and spinel. Vyalsovite has an unusual composition and unique optical properties. It contains Fe 23.65, Ca 16.30, Al 10.94, S 13.17, Mn 0.23 wt%. In polished section, the mineral displays extreme reflection pleochroism from dark gray to crimson red. Reflectance in air at 540 nm is 8.15% for  $R_o$  and 11.4% for  $R_e$ . Reflectance spectra of vyalsovite  $R_o$  and  $R_e$  cross several times in the range from 250 to 800 nm. The optic sign of vyalsovite changes four times within this range. No other known ore mineral possesses such optical properties.

According to X-ray and electron diffraction data, vyalsovite is orthorhombic (possible space groups  $Cmmm$ ,  $C222$ ,  $Cmm2$ ,  $Cm2m$ ,  $Cmma$ ,  $C2ma$ ) with  $a = 14.20(1)$ ,  $b = 20.98(2)$ ,  $c = 5.496(4)$  Å. The calculated density is 1.96 g/cm<sup>3</sup> for the ideal composition and  $Z = 8$ .

### INTRODUCTION

While collecting samples from the lower zone of magnesian skarns underlying the Talnakh intrusion in the Noril'sk region, our attention was attracted to tiny clusters of a mineral resembling bornite in color. The samples came from prospecting holes in the eastern part of the Komsomol mine of the Talnakh deposit. Subsequent microscopic, chemical, and X-ray examination of the samples have shown that this material is a new mineral. The new mineral and name, vyalsovite, were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association in April, 1989. The name honors Leonid N. Vyalsov, a well-known specialist in reflected light optics, who studied this mineral's unique optical properties. A polished section of vyalsovite has been deposited at the Mineralogical Museum of the Academy of Sciences of the USSR and in the Mineralogical Laboratory of IGEM, Academy of Sciences of the USSR, both in Moscow.

### OCCURRENCE AND ASSOCIATIONS

Vyalsovite occurs in forsterite skarns in association with nonsulfide minerals and sulfides (Fig. 1). It forms clusters of tiny grains from 5–10 to 100–150  $\mu\text{m}$  in size. The earliest association includes forsterite and spinel. Forsterite is replaced by serpentine peripherally and along

cracks. Spinel with the composition  $\text{Mg}(\text{Al},\text{Fe})_2\text{O}_4$  (microprobe) forms irregular grains and clusters. Vyalsovite is usually closely associated with these spinel clusters (Fig. 1). A subsequent association is represented by chalcopyrite and pentlandite, which are interstitial to forsterite and spinel.

Serpentine, magnetite, valleriite, pyrite, djerfisherite, diaspore, and vyalsovite formed by replacement of the

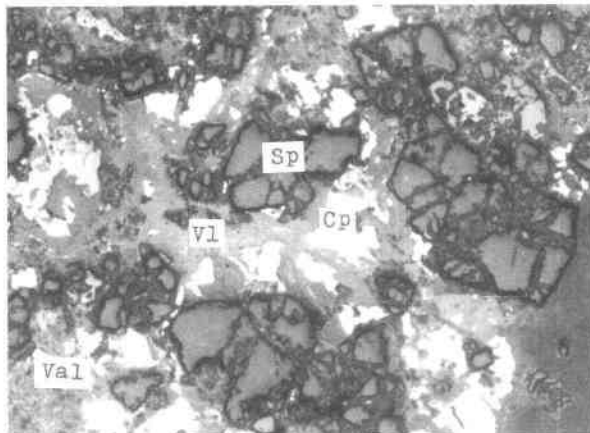


Fig. 1. Vyalsovite (VI, different shades of gray, reflection pleochroism) replaces chalcopyrite (Cp, white). Chalcopyrite is also replaced by valleriite (Val, fine-grained aggregates) and spinel (Sp, high-relief grains). Plane-polarized reflected light. Field width = 0.250 mm.

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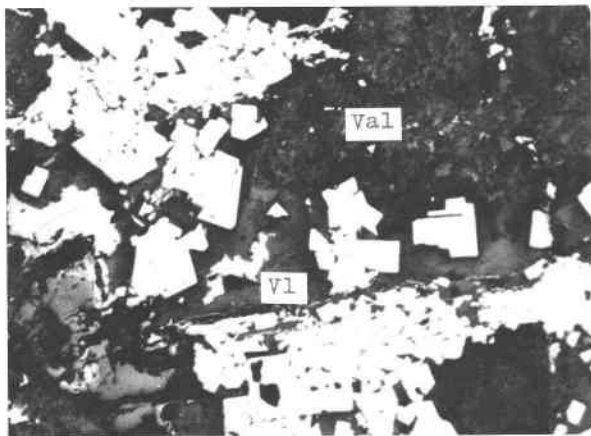


Fig. 2. Vyalsovite (VI) and valleriite (Val) fill the interstices among crystals and aggregates of pyrite. Plane-polarized reflected light. Field width = 0.250 mm.

minerals of earliest associations. Serpentine and magnetite replace forsterite and spinel, respectively. Valleriite replaces chalcopyrite (Fig. 1) and sometimes occurs in association with serpentine. Crystals, grain aggregates, and veinlets of pyrite intergrown with magnetite are associated with chalcopyrite. Tiny segregations of djferfisherite occur among chalcopyrite or vyalsovite masses. Interestingly, diaspore ( $\text{HAlO}_2$ ) occurs in this assemblage. Diaspore grains, hardly distinguishable from spinel, are located along the margins of sulfide aggregates and among the spinel clusters.

Vyalsovite replaces chalcopyrite completely, occurs as discontinuous rims, or cements pyrite grains (Fig. 2) occurring with chalcopyrite. Intergrowths of vyalsovite with djferfisherite, diaspore, and valleriite are common. Vyalsovite veinlets have been observed locally in the forsterite skarns.

### OPTICAL PROPERTIES

On a broken surface, the fine veinlets and aggregates of vyalsovite are crimson in color. In polished section, the optical properties of the mineral are unusual. More than 15 grains of vyalsovite were characterized optically. On the basis of all the data, the mineral may be considered pseudo-uniaxial. In isotropic ( $R_o$ ) and nearly isotropic sections, vyalsovite is dark gray;  $R_o$  corresponds to the minimum reflectance. In sections parallel to the optic axis, and thus showing  $R_o$  and  $R_e$ , the mineral has extreme bireflectance and reflection pleochroism (dark gray to crimson red). Between crossed polars, the colors are even more extreme (dark gray to bright orange-red). Accordingly, there is the impression that between crossed polars vyalsovite has a higher reflectance than it has without the analyzer. In oil, the colors observed with a single polar are somewhat deeper, but the anisotropism remains about the same as in the air.

$R_o$  values of vyalsovite (Table 1) decrease gradually from 250 to 800 nm (normal dispersion), and maxima of

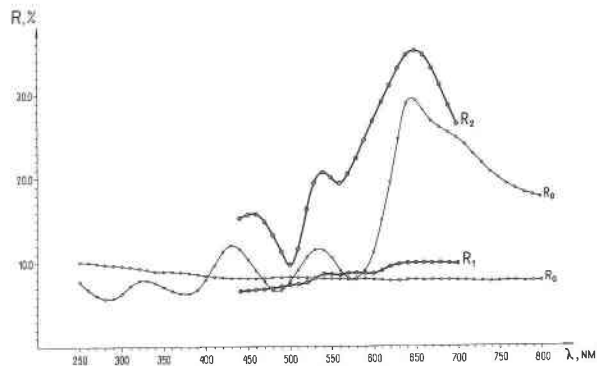


Fig. 3. Reflectance curves of vyalsovite ( $R_o$  and  $R_e$ ) and erdite ( $R_1$  and  $R_2$ ). Data for erdite from Czamanske et al. (1980).

the  $R_o$  curve are weakly expressed. The  $R_e$  curve is characterized by distinct maxima at 325, 427, 534, and 645 nm (strong) and 700 nm (weak). The  $R_o$  and  $R_e$  reflectance curves cross several times, resulting in optic sign changes four times in the range from 250 to 800 nm (Fig. 3). No other known ore mineral possesses such optical properties.

In oil, the form of the  $R_e$  curve remains the same but the values of  $R_o$  decrease considerably. No crossing of  $R_o$  and  $R_e$  curves is observed; the mineral is optically positive over the range 250–800 nm. This differing behavior in air and in oil testifies to an exceedingly strong dispersion of absorption and refraction for the mineral. However, the optical constants  $n$  and  $k$  have not been calculated for vyalsovite because of the relatively small size of its grains. In this case, small errors in the measurements of  $R$  lead to rather large errors in the calculated values of  $n$  and  $k$ .

Color values derived from  $R_e$  and  $R_o$  are not informative because of the complex form of the  $R_e$  curve.

In strong bireflectance, reflection pleochroism, and bright color effects of anisotropism, vyalsovite resembles covellite, umangite, and yushkinite. But all these minerals have different  $R_o$  and  $R_e$  curves, and usually the curves cross at only one point. In oil, the reflectance curves of covellite, umangite, and yushkinite cross, whereas those of vyalsovite do not.

The optical properties of vyalsovite resemble those of erdite (Czamanske et al., 1980), but there are essential differences. First, there is a difference in the form of the reflectance curves  $R_o$  (vyalovite) and  $R_1$  (erdite) (Fig. 3). The curve  $R_o$  of vyalovite is almost flat; the  $R_o$  values remain nearly constant, decreasing only slightly on all the intervals of measurement. Erdite is characterized by slightly increasing values of  $R_1$ . Second, the  $R_e$  curve of vyalovite is considerably lower than  $R_2$  of erdite, although the maxima of these curves coincide. Third, the most essential distinction is the multiple crossing of the  $R_o$  and  $R_e$  curves of vyalovite;  $R_1$  and  $R_2$  of erdite do not cross. Czamanske et al. (1980) note that erdite tarnishes rapidly and its surface becomes black in several

**TABLE 1.** Reflectance ( $R_{\text{av}}$  in %) of vyalsovite measured at 10-nm intervals

$\lambda$ (nm)	$R_o$	$R_e$	$\lambda$ (nm)	$R_o$	$R_e$	$\lambda$ (nm)	$R_o$	$R_e$	$\lambda$ (nm)	$R_o$	$R_e$
250	10.1	7.7	390	8.6	6.9	530	8.2	11.6	670	7.8	26.6
260	10.1	6.8	400	8.5	8.0	540	8.2	11.4	680	7.8	25.8
270	9.9	6.0	410	8.4	9.8	550	8.1	10.5	690	7.8	25.3
280	9.8	5.8	420	8.2	11.5	560	8.0	9.2	700	7.8	24.7
290	9.7	5.9	430	8.2	12.0	570	8.0	8.3	710	7.8	23.7
300	9.6	6.5	440	8.1	11.6	580	8.0	8.2	720	7.8	22.7
310	9.5	7.4	450	8.1	10.2	590	8.0	9.1	730	7.8	21.7
320	9.4	8.0	460	8.1	8.9	600	7.9	11.2	740	7.8	20.7
330	9.2	8.0	470	8.1	7.7	610	7.9	15.1	750	7.8	19.9
340	9.0	7.6	480	8.2	6.8	620	7.9	20.0	760	7.8	19.2
350	9.0	7.2	490	8.3	6.9	630	7.9	25.0	770	7.8	18.7
360	9.0	6.8	500	8.3	7.8	640	7.9	29.0	780	7.8	18.2
370	8.8	6.5	510	8.3	9.3	650	7.9	29.1	790	7.8	17.9
380	8.8	6.5	520	8.2	10.8	660	7.8	27.9	800	7.8	17.5

Note: Reflectance of vyalsovite measured by L.N. Vyalsov with microspectrophotometers MSPH-P-2 and MSPHUL-312. Objective lens 20 $\times$ , N.A. = 0.40. Diameter of measured field 15  $\mu\text{m}$ . Zeiss-calibrated standards Si, SiC, and (W,Ti)C. Measured surface is perpendicular to the incident light beam.

days. The polished surface of vyalsovite remains unchanged as do the values of  $R_o$  and  $R_e$ .

### CHEMICAL COMPOSITION

The chemical composition of vyalsovite was determined with a Cameca Camebax microprobe using an accelerating voltage of 10 kV, a beam current of 58 nA for O (15 kV and 21 nA for all other elements), and a variety of standards (Table 2). During the calculations of O content, the data of Ruste (1979) served as the source of mass absorption coefficients. ZAF corrections were determined using several standards. The choice of standards for O was based on the similarity of absorbed current ( $i$ ) between the standard and the analyzed sample; thus,  $i_{\text{TiO}_2}/i_{\text{std}} = 1.00$ ,  $i_{\text{cp}}/i_{\text{std}} = 0.99$ ,  $i_{\text{pyrope}}/i_{\text{std}} = 1.05$ . During the quantitative determination of O, the superposition of  $\text{AlK}\beta$  (III order) and  $\text{OK}\alpha$  emission lines was also considered.

The reproducibility of results using various standards was 1.5% for S, 1.6% for Fe, and 5.0% for O. The  $\text{SK}\alpha$  line profiles for sulfide (FeS) and sulfate ( $\text{FeSO}_4$ ) show that the  $\text{S}^{6+}$  peak is shifted 0.005  $\text{\AA}$  relative to the  $\text{S}^{2-}$  peak. The shift corresponds to a loss of X-ray intensity of approximately 17%. The profiles of the  $\text{SK}\alpha$  line of the analyzed sample and of the FeS standard completely coincide, suggesting the presence of "sulfide" S in the mineral.

The presence of C could not be detected in any of the six samples by microprobe analysis (accelerating voltage 10 kV, current 85 nA, and counting time 40 s). The C detection limit was 0.5 wt% (99% confidence level).

The analytical results (Table 2) yield the formula  $\text{FeS}\cdot(\text{Ca},\text{Mn})(\text{Al},\text{Fe})(\text{OH})_3$ , where  $\text{Ca} > \text{Mn}$  and  $\text{Al} > \text{Fe}$ . The presence of OH group is based on the following considerations:

1. If Ca, Al, Mn, and part of the Fe are present in vyalsovite as oxides, the O content should be approximately 17 wt%. According to the analytical data, the O concentration is close to 32–33 wt%.

2. If the OH group is present, the value of  $\text{O}_{\text{meas}}$  should

approximate  $\text{O}_{\text{calc}}$ . Taking into account a significant error in O determination ( $\sim 3\%$  relative), the presence of  $\text{H}_2\text{O}$  in vyalsovite could not be excluded. However, the min-

**TABLE 2.** Electron microprobe analyses of vyalsovite

Elements	Grain no. (wt%)						Detection limit	
	1	2	3	4	5	6		
Ca	C	16.25	16.31	16.37	16.23	16.30	16.48	
	D, %	0.23	0.29	0.44	0.79	0.34	0.21	0.02
	$S\sqrt{I_{\text{ave}}}$	1.10	1.48	1.50	1.80	1.70	1.08	
Al	C	10.93	10.93	11.04	10.86	10.94	10.92	
	D, %	0.26	0.29	0.26	0.35	0.26	0.25	0.03
	$S\sqrt{I_{\text{ave}}}$	0.99	1.08	0.95	1.29	0.98	0.95	
Fe	$C_{\text{sum}}$	23.50	23.90	23.65	23.65	23.65	23.76	
	$C_{\text{sulf}}$	22.82	22.99	22.90	23.08	22.93	23.16	
	$C_{\text{oxid}}$	0.68	0.91	1.00	0.57	0.72	0.60	
	D, %	0.56	0.66	1.10	1.07	0.50	0.72	0.03
	$S\sqrt{I_{\text{ave}}}$	0.76	0.92	1.60	1.47	0.70	1.00	
	S	C	13.10	13.20	13.15	13.25	13.17	13.30
D, %		0.40	0.35	0.43	0.36	0.26	0.22	0.02
$S\sqrt{I_{\text{ave}}}$		1.20	0.95	1.16	0.95	0.70	0.61	
Mn	C	0.70	0.16	0.10	0.43	0.23	0.13	
	D, %	0.22	0.10	0.04	0.07	0.09	0.05	0.05
	$S\sqrt{I_{\text{ave}}}$	1.30	1.50	1.14	0.96	1.48	1.04	
O	C	33	33	33	32	33	32	
	D, %	0.96	0.90	2.10	1.80	2.10	2.13	0.08
	$S\sqrt{I_{\text{ave}}}$	0.80	0.50	1.16	1.00	1.14	1.19	
$\Sigma$	97.48	97.50	97.56	96.42	97.29	96.59		
$\text{O}_{\text{calc}}$	33.40	33.33	33.63	33.02	33.23	33.19		
$\text{H}_{\text{calc}}$	2.08	2.08	2.10	2.07	2.08	2.07		
$\Sigma_{\text{calc}}$	99.96	99.91	100.29	99.52	99.60	99.85		
$Z_{\text{ave}}$	15.7	15.7	15.6	15.6	15.7	15.6		

Formula for  $N_{\text{cations}} = 3$

- $1 = \text{Fe}_{1.0}\text{S}_{0.99}(\text{Ca}_{0.98}\text{Mn}_{0.03})_{1.01}(\text{Al}_{0.98}\text{Fe}_{0.02})_{1.00}(\text{OH})_{5.00}$
- $2 = \text{Fe}_{1.0}\text{S}_{1.00}(\text{Ca}_{0.98}\text{Mn}_{0.01})_{0.99}(\text{Al}_{0.98}\text{Fe}_{0.03})_{1.01}(\text{OH})_{5.00}$
- $3 = \text{Fe}_{1.0}\text{S}_{0.99}\text{Ca}_{0.98}(\text{Al}_{0.98}\text{Fe}_{0.02})_{1.01}(\text{OH})_{5.00}$
- $4 = \text{Fe}_{1.0}\text{S}_{1.00}(\text{Ca}_{0.98}\text{Mn}_{0.02})_{1.00}(\text{Al}_{0.97}\text{Fe}_{0.03})_{1.00}(\text{OH})_{5.00}$
- $5 = \text{Fe}_{1.0}\text{S}_{1.00}(\text{Ca}_{0.99}\text{Mn}_{0.01})_{1.00}(\text{Al}_{0.98}\text{Fe}_{0.03})_{1.01}(\text{OH})_{5.00}$
- $6 = \text{Fe}_{1.0}\text{S}_{1.00}(\text{Ca}_{0.99}\text{Mn}_{0.01})_{1.00}(\text{Al}_{0.98}\text{Fe}_{0.02})_{1.00}(\text{OH})_{5.00}$

Note: Monochromators—LiF (Mn,Fe), PET (Ca,S), TAP (Al), ODRV (O); averaging of intensities was carried out using ten measurements; count time = 20 s; standards used—diopside (Ca), pyrope (Al,O), chemically pure Mn, trolite (S),  $\text{CuFeS}_2$  (Fe), and  $\text{TiO}_2$  (O); relative intensities were transformed to wt% with the program SAMARA for IBM EC-1033 (Sandomirskaya and Mirkin, 1979).  $\text{O}_{\text{calc}}$ ,  $\text{H}_{\text{calc}}$  = calculated for  $\text{FeS}\cdot\text{Ca}(\text{OH})_2\cdot\text{Al}(\text{OH})_3$ . C = element content, wt%; D, % = relative confidence interval (for  $a = 0.99$ ,  $n = 10$ ); S = least-squares mean deviation in intensity;  $I_{\text{ave}}$  = average intensity;  $S\sqrt{I_{\text{ave}}}$  = G. Goldstein's homogeneity criterion (Berner et al., 1982).

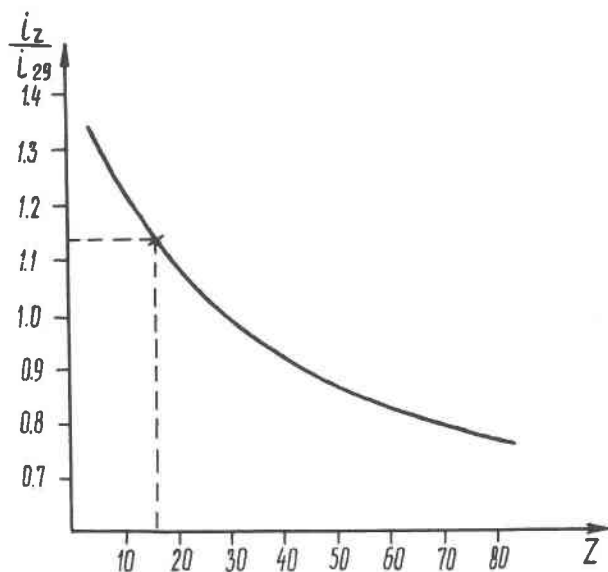


Fig. 4. Dependence of absorbed electron current on average atomic number.

eral is very stable under the electron beam, even at high accelerating voltage and beam current.

3. The variation of the absorbed current ( $i$ ) with the atomic number of a sample ( $Z$ ) is plotted in Figure 4. The average atomic number calculated from the analytical data coincides with the average atomic number derived from Figure 4.

Direct determination of the presence of  $H_2O$  or  $OH$  in vyalsovite could not be carried out by DTA or IR methods because of the lack of sufficient material. However, Raman spectroscopy (Dr. J. M. Beny, CRSCM, Orleans, France) indicates that  $Ca-OH$  and  $FeS$  bonds are present.

#### SYMMETRY AND UNIT-CELL DIMENSIONS

X-ray study of vyalsovite was hindered by the small size of its fine-grained aggregates. The mineral is intergrown with valleriite, and powder diffraction patterns of vyalsovite often show X-ray reflections of valleriite. The intensities of these reflections vary as a result of the differing proportions of valleriite and vyalsovite.

The X-ray powder diffraction pattern of vyalsovite (Table 3) differs from those of the chemically similar hybrid minerals valleriite, tochilinite (Organova et al., 1975), and yushkinite (Makeev et al., 1984). Therefore, the pattern cannot be indexed on the assumption that the vyalsovite structure contains interlayered sulfide and hydroxide units.

The unit-cell symmetry and dimensions of vyalsovite were determined using a transmission electron microscope (JEM-100C) equipped with a Kevex 5100 detector. The electron diffraction patterns are consistent with one of six possible space groups:  $Cmmm$ ,  $C222$ ,  $Cmm2$ ,  $Cm2m$ ,  $Cmma$ ,  $C2ma$  (Fig. 5). The values of the unit-cell dimensions calculated by means of a least-squares refinement of X-ray powder diffraction pattern data are

TABLE 3. X-ray powder diffraction data for vyalsovite

$hkl$	$d_{obs}$ (Å)	$hkl$	$d_{calc}$ (Å)	$hkl$	$d_{obs}$ (Å)	$hkl$	$d_{calc}$ (Å)
10	6.09	130	6.27	30	1.846	661	1.846
100	5.40	001	5.50			462	1.846
40	4.76	021	4.87	20	1.776	203	1.774
		310	4.62			800	1.775
10	3.59	400	3.55	20	1.728	043	1.730
10	3.26	151	3.25	40	1.676	681	1.674
20	2.88	421	2.87			482	1.673
10	2.70	112	2.68			770	1.680
20	2.58	171	2.59	10	1.648	572	1.649
20	2.48	460	2.49	10b	1.598	732	1.589
		280	2.46			662	1.596
20b	2.29	620	2.31	20b	1.520	752	1.521
		242	2.30			511.1	1.521
		371	2.30			861	1.520
20	2.24	332	2.25	10	1.487	311.2	1.487
		281	2.25			373	1.484
50	2.16	551	2.16	10b	1.405	513.0	1.403
		062	2.16	10b	1.345	932	1.343
10	2.07	570	2.062			711.1	1.347
		262	2.067	20b	1.319	314	1.317
		352	2.068			111.3	1.316
10	2.03	210.0	2.012			810.1	1.316
		710	2.019			106.0	1.316
		641	2.008	10	1.311	016.0	1.311
		442	2.007				
		172	2.005				
30	1.973	481	1.969				
30b	1.894	111.0	1.890				
		210.1	1.889				
		532	1.900				

Note: Analyzed with 57.3-mm Gandolfi camera,  $FeK\alpha$  radiation, visually estimated intensities, b = broad line. All data were used for least-squares refinement of cell parameters.

$a = 14.20(1)$ ,  $b = 20.98(2)$ , and  $c = 5.496(4)$  Å. The calculated density of vyalsovite is  $1.96 \text{ g/cm}^3$  for the composition  $FeS \cdot Ca(OH)_2 \cdot Al(OH)_3$ , with  $Z = 8$ .

#### DISCUSSION

A vyalsovite grain suitable for single-crystal structural study could not be found, and therefore knowledge of its structure is limited. Vyalsovite might be regarded as a mineral analogous to certain hybrid sulfide-hydroxide minerals. However, the optical properties of the mineral, its composition, and the peculiarities of its X-ray pattern suggest significant differences between vyalsovite and those hybrid minerals.

Based on optical properties, erdite ( $NaFeS_2 \cdot 2H_2O$ , Konnert and Evans, 1980) may to some extent be considered an analogue of vyalsovite. [The formula of erdite according to chemical analytical data is  $NaFeS_2 \cdot H_2O$ . In determining the structure, the best  $R$  factor was obtained with two molecules of  $H_2O$  (Czarnanske et al., 1980).] The similarity of the  $c$  dimensions ( $\sim 5.5$  Å) of the unit cells of erdite and vyalsovite suggests the presence of similar structural elements in these minerals. In erdite, edge-sharing  $[FeS_4]$  tetrahedra form chains parallel to  $c$  (Konnert and Evans, 1980) with a repeat distance (two links) of  $\sim 5.5$  Å. Two such chains intersect the  $a$  axis ( $a = 10.69$  Å) of erdite, at 0 and  $1/2$ . It is highly probable that analogous chains of edge-sharing  $[FeS_4]$  tetrahedra are present in the structure of vyalsovite and that they are

connected with the help of  $\text{Ca}(\text{OH})_6$  polyhedra (?) and  $\text{Al}(\text{OH})_6$  polyhedra (?) into a three-dimensional framework.

Hybrid minerals contain chemically heterogeneous layers (for example, sulfide-hydroxide). To insure an integral structure, it is necessary to provide for stable bonding between these heterogeneous layers. This is achieved by the opposite charges of these layers: (+) for the hydroxide layer as a result of the presence of trivalent cations in the positions of bivalent cations (for example,  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  instead of  $\text{Mg}^{2+}$  in valleriite); (-) for the sulfide layer as a result of partial filling of cation vacancies in a sulfur closest-packed array (for example,  $\text{Fe}_{1-x}\text{S}$  in tochilinite or  $\text{V}_{1-x}\text{S}$  in yushkinite). No deviation from the ratio  $\text{Fe}:\text{S} = 1:1$  and  $\text{Fe}:\text{Ca}:\text{Al} = 1:1:1$  has been established for vyalsovite. Its formula corresponds precisely to  $\text{FeS}\cdot\text{Ca}(\text{OH})_2\cdot\text{Al}(\text{OH})_3$ .

The authors initially considered vyalsovite to be a structural analogue of valleriite. However, the electron diffraction patterns of vyalsovite are unlike those of valleriite, tochilinite, and yushkinite. The patterns of vyalsovite have no pronounced hexagonal and tetragonal nets. X-ray powder patterns of the hybrid minerals show strong basal reflections: valleriite—(003), (006), (009), (00.18), (00.21); tochilinite—(001), (002), (006) (Organova et al., 1975). Repeated basal reflections are lacking in the X-ray powder pattern of vyalsovite. These diffraction data confirm a difference of structure types.

Valleriite and other sulfide-hydroxide hybrid minerals have layered structures with the formula  $(\text{Cu},\text{Fe})_{1-x}\text{S}\cdot[(\text{Mg},\text{Al},\text{Fe})(\text{OH})_2]$ . In vyalsovite,  $[\text{FeS}_4]^-$ ,  $[\text{Ca}(\text{OH})_6]^-$ , and  $[\text{Al}(\text{OH})_6]$ -polyhedra form a complex three-dimensional framework having the formula  $\text{FeS}\cdot\text{Ca}(\text{OH})_2\cdot\text{Al}(\text{OH})_3$ . (There may also be a variant of the structure when the tops of one cation polyhedron are occupied by S and OH simultaneously.) Raman spectroscopy suggests that the structure of vyalsovite is characterized by linkages of iron sulfide polyhedra and calcium (and aluminum) hydroxide polyhedra. A Raman spectrum of valleriite could not be obtained because it was destroyed completely by even the very low energy of a laser beam. This fact also suggests structural differences between vyalsovite and valleriite.

Valleriite and tochilinite are widespread in copper-nickel ores of the Noril'sk region (Genkin et al., 1981). There are specific valleriite-bearing ore types in which valleriite (with tochilinite) forms nearly 20% of the ores. Unlike valleriite and tochilinite, vyalsovite occurs in very small amounts in only one section of the ore body in the zone where forsterite skarns are developed. The unusual composition of vyalsovite reflects the specific conditions of its formation. The assemblage vyalsovite + diasporite + djerfisherite + valleriite formed after chalcopyrite. The formation of vyalsovite involved volatile components, which ensured the availability of Ca from the dolomite underlying the intrusion and resulted in the replacement of chalcopyrite. A requisite amount of Al was released during the transformation of magnesium aluminum spinel. The process of diasporite crystallization proceeded si-

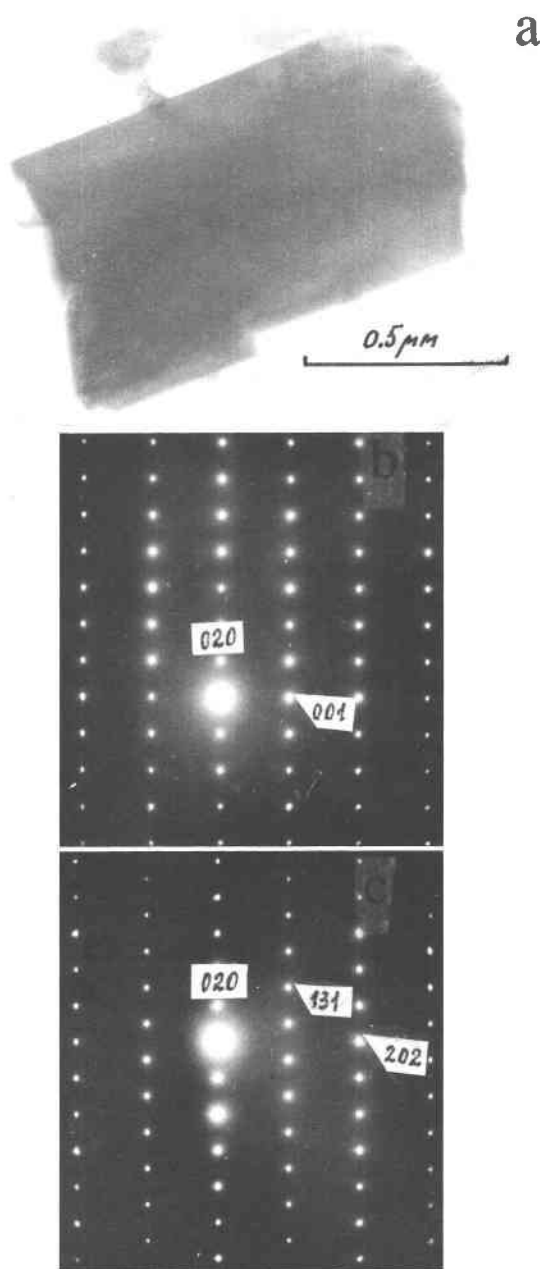
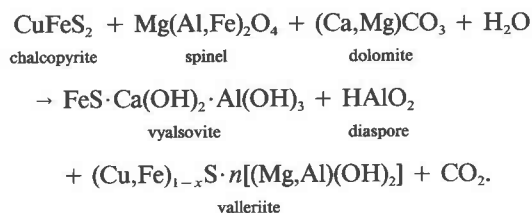


Fig. 5. Vyalsovite: electron photomicrograph (a) and microdiffraction patterns (b), (c) illustrating the face-centered lattice (C).

multaneously with the formation of vyalsovite. This process may be represented schematically by means of the following reaction:



This reaction led to the formation of the vyalsovite-bearing assemblages during the hydrothermal metamorphism of forsterite skarns.

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