

to have lengthened because the ratio of $Mg^{2+}:Al^{3+}$ in the starting materials was greater than the ratio of 7:3. Brucite was present in Run V-9 and boehmite was present in Run V-10; from this it seems that the range of the solid solution of Mg^{2+} and Al^{3+} in the hydroxide layer is limited. Valleriite was not produced at the temperature of 700°C in any of the runs, and valleriite was also not produced at the temperature of 650°C in Run V-3. From this fact, the upper stable temperature of this mineral appears to be between 600°C and 650°C.

REFERENCES

- EVANS, H. T., MILTON, C., CHAO, E. C. T., ADLER, I., MEAD, C., INGRAM, B., AND BERNER, R. A. (1964) Valleriite and the new iron sulfide, mackinawite, *U. S. Geol. Surv. Prof. Pap.* 475-D, 64-69.
- , AND ALLMANN, R. (1968) The crystal structure and crystal chemistry of valleriite, *Z. Kristallogr.*, 127, 73-93.
- SPRINGER, G. (1968) Electronprobe analyses of mackinawite and valleriite, *Neues Jahrb. Mineral. Monatsh.* 8, 252-258.
- TUTTLE, O. F. (1949) Two pressure vessels for silicate-water systems, *Geol. Soc. Amer. Bull.* 60, 1727-1729.

THE AMERICAN MINERALOGIST, VOL. 55, NOVEMBER-DECEMBER, 1970

A "VALLERIITE-TYPE" MINERAL FROM
NORIL'SK, WESTERN SIBERIA¹

D. C. HARRIS, L. J. CABRI, J. M. STEWART,
Mineral Sciences Division, Mines Branch, Ottawa.

ABSTRACT

Electron microprobe analysis of a "valleriite-type" mineral from Noril'sk, western Siberia, yields a formula $(Cu_{0.98}Fe_{1.00}S_2) \cdot 1.472 [Fe(OH)_2]$, which is the most iron-rich variant of this mineral reported to date.

INTRODUCTION

The structure of valleriite from Loolekop, South Africa, determined very recently by Evans and Allmann (1968), has been interpreted as layers of copper-iron sulphide alternating with layers of Mg-Al hydroxide. The formula for the Loolekop material is



Springer (1968) re-examined valleriites from two localities: Kaveltorp, Sweden and Palabora, South Africa with the electron microprobe an-

¹Sulphide Research Contribution No. 20, Mineral Sciences Division.

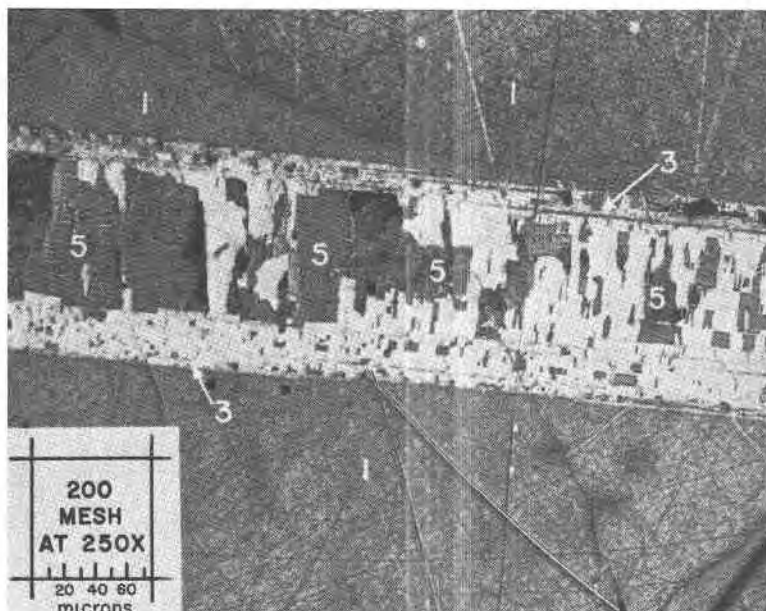


FIG. 1. Photomicrograph showing the oriented "valleriite" inclusions (5) in a cubanite lath (3), set in a matrix of talnakhite (1). The surface of the "valleriite" varies from smooth to rough.

alyzer. This work showed that the Palabora material is the ordinary Mg- and Al-containing valleriite, whereas the Kaveltorp samples contain more iron than can be accounted for by the sulphide sublattice. This suggests that there must be some iron in the hydroxide lattice replacing aluminum or magnesium. The formula derived for the Kaveltorp mineral is



In addition to the ordinary valleriite at Palabora, there is also another variety of this mineral, which occurs in the magnetite-apatite-olivine rock of that district. This valleriite contains more iron and less aluminum than the ordinary valleriite, and gives a formula



Valleriite from Noril'sk, western Siberia, has been reported independently by Genkin and Vyal'sov (1967), Cabri and Traill (1966), and Cabri (1967). Genkin and Vyal'sov reported on valleriite and mackinawite, and gave X-ray powder data and optical and heating properties for valleriite, including X-ray powder data for the Noril'sk "valleriite."

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR "VALLERIITE-TYPE"
MINERAL FROM NORIL'SK, WESTERN SIBERIA

<i>hkl</i>	This Study			Genkin and Vyal'sov (1967)			
	<i>a</i> = 3.778 ± .002 Å <i>c</i> = 34.147 ± .01			Noril'sk			
	<i>d</i> (calc)Å	<i>I</i> (est)	<i>d</i> (meas)Å	(2)		(3)	
			<i>I</i> (est)	<i>d</i> (meas)Å	<i>I</i> (est)	<i>d</i> (meas)Å	
00.3	11.382	9	11.38	3	11.44	4	11.56
		2	7.24 ^a				
00.6	5.691	10	5.69	10	5.65	10	5.71
00.9	3.794	8	3.788	5	3.77	5	3.81
10.1	3.257	9	3.259	6	3.28	9	3.27
10.2	3.214			4	3.24	1	3.21
		2	3.146 ^a				
10.4	3.055	6	3.049 ^b	4	3.03		
10.5	2.951	1	2.952				
00.12	2.846	2	2.845	1	2.85	1	2.79
		2	2.770 ^a	1	2.77		
10.7	2.717						
		2	2.674 ^a				
10.8	2.597	1	2.592				
		4	2.486 ^a	3	2.48	3	2.51
10.10	2.363	1	2.359	3	2.36		
00.15	2.277		2.269	3	2.27	3	2.28
10.11	2.252	6					
		5	2.142 ^a	5	2.14		
10.13	2.048	5	2.049				
10.14	1.956	1	1.958				
00.18	1.897		1.897	6	1.902	7	1.911
11.0	1.889	7					
11.3	1.864	7	1.869 ^b	9	1.864	2	1.877
11.6	1.793						
10.16	1.788	1	1.790				
10.17	1.712						
11.9	1.692					3	1.692
20.1	1.634						
20.2	1.629	4	1.630	2	1.635	2	1.633
00.21	1.626						
20.4	1.608						
20.5	1.592	5	1.600	4	1.598	3	1.599
10.19	1.575		1.577 ^b				
11.12	1.574	2					
20.7	1.551						
20.10	1.475	1	1.476				

114.6 mm dia. Debye-Scherrer Camera. Fe-Filtered Co Radiation

Space group $R\bar{3}m$ (Evans and Allmann, 1968).^a Extra reflections.^b Talmakhite reflections.

(2) Vein formation in "cubic chalcopyrite".

(3) Fine-grained lamellar crystals of valleriite from a cavity in "cubic chalcopyrite".

Cabri's identification was based on an X-ray powder pattern using a 57.3-mm-diameter Debye-Scherrer camera, and the similarity of its optical properties to those of other valleriites. He was not certain of the identity of similar finer grained material which occurs as replacements

within cubanite lamellae and reported this also as valleriite or mackinawite; hence, a restudy of this material was undertaken.

For a description of the copper-nickel ores of the Talnakh deposit, Noril'sk, the reader is referred to a recent paper by Genkin *et al.* (1969).

THE "VALLERIITE-TYPE" MINERAL

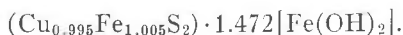
Electron microprobe analyses were made of the Noril'sk "valleriite" in a vuggy sample kindly supplied by the Leningrad Mining Museum and labelled as "cubic chalcopyrite." Analyses of inclusions in cubanite (Figure 1) and of larger areas of "valleriite" that had previously been X rayed, gave an average composition for several grains of Fe 43.8 ± 0.5 percent, Cu 20.0 ± 0.5 percent, S 20.3 ± 0.5 percent, total 84.1 ± 4 percent. No other elements down to, and including, sodium could be detected; magnesium and aluminum, in particular, were looked for, but not detected.

The X-ray powder diffraction data (Table 1) of the Noril'sk material, which contained a minor amount of talnakhite (name used for the new copper-iron sulfide described by Cabri, 1967), can be indexed as valleriite, using the structure of Evans and Allmann (1968), except for a few reflections. Some of these extraneous reflections were also reported by Genkin and Vyal'sov for the Noril'sk "valleriite." Since impurities other than talnakhite were not detected with the microprobe, the extra reflections must be attributed to the structure of the mineral.

Although the optical properties of the Noril'sk mineral are somewhat similar to other valleriites, the differences are distinct enough to be a guide to its identification. Chamberlain and Delabio (1965), reported the optical properties of valleriite as dull bronze, similar to graphite in color, with extreme bireflectance from creamy bronze to purple at high magnification. Anisotropism was extreme, with colors varying from white to bronze. The Noril'sk material, however, is bluish gray, with a distinct bluish color in contrast to magnetite. Bireflectance is moderate, varying from a light grey to a dark bluish gray, in comparison to the bronze color of valleriite. Anisotropism is distinct, but less intense than that of valleriite, with colors varying from light yellow to reddish purple.

DISCUSSION

The electron microprobe analysis of the so called "valleriite" in the Noril'sk sample yields a formula



From the formula, the calculated OH-concentration is 15.8 percent

which, combined with the microprobe analysis, gives a total of 99.9 percent. The X-ray powder pattern, indexed on Evans and Allmann's hexagonal cell yields cell dimensions a 3.778 and c 34.147 Å which are in close agreement with that of normal valleriite of a 3.792 and c 34.10 Å. The Noril'sk mineral appears to represent the end member of a series of "valleriite-type" minerals with the Mg-Al positions in the hydroxide layer occupied by Fe.

ACKNOWLEDGEMENT

We wish to thank Dr. J. Rucklidge, University of Toronto, who suggested the "valleriite-type" formula from our microprobe analysis.

REFERENCES

- CABRI, L. J. (1967) A new copper-iron sulfide. *Econ. Geol.* **62**, 910-925.
 ———, AND R. J. TRAILL (1966) New palladium minerals from Noril'sk, Western Siberia. *Can. Mineral.* **8**, 541-550.
 CHAMBERLAIN, J. A., AND R. N. DELABIO (1965) Mackinawite and valleriite in the Muskox intrusion. *Amer. Mineral.* **50**, 682-695.
 EVANS, H. T., JR., AND R. ALLMANN (1968) The crystal structure and crystal chemistry of valleriite. *Z. Kristallogr.*, **127**, 73-93.
 GENKIN, A. D., TRONEVA, N. V. AND ZHURAVLEF, N. N. (1969) Pervaya nakhodka v rudakh sul'fida kaliya, zheleza i medi—djerfisherite. *Geol. Rud. Mestorozhd.* **11**, (5), 57-64.
 ———, AND L. N. VYAL'SOV (1967) On valleriite i machinovite i usloviyakh ikh nakhozhdeniya v rudakh. *Geol. Rud. Mestorozhd.* **9**, (2) 94-106.
 SPRINGER, G. (1968) Electronprobe analysis of mackinawite and valleriite. *Neues Jahrb. Mineral. Monatsh.* **8**, 252-258.

THE AMERICAN MINERALOGIST, VOL. 55, NOVEMBER-DECEMBER, 1970

TUNGSTENIAN WULFENITES, MINA SAN SAMUEL,
CACHIYUYO DE LLAMPOS, CHILE

ALAN H. CLARK, *Department of Geological Sciences,
Queen's University, Kingston, Ontario, Canada*

AND

RICHARD H. SILLITOE, *Instituto de Investigaciones
Geológicas, Casilla 10465, Santiago de Chile.*

ABSTRACT

Chemical analyses and cell dimensions are presented for a wulfenite and for two $\text{Pb}(\text{Mo,W})\text{O}_4$ solid solutions from northern Chile. The latter are more molybdenum-rich than previously described "chillagites", and indicate that a complete series from wulfenite to stolzite may be represented in nature.