

XANTHOPHYLLITE*

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ABSTRACT

New observations are made on two of the three known occurrences of xanthophyllite *var.* valuevite and compared with the published data on the third. These led to the following descriptions of the two. Valuevite from Achmatovsk, Russia is monoclinic with space group $C2/m$; the unit cell with $a=5.24$, $b=8.98$, $c=9.79$ kX, $\beta=100^{\circ}10'$, $a:b:c=0.584:1:1.090$ contains $\text{Ca}_2(\text{Mg}_4\text{Al}_2)(\text{Al}_{5.6}\text{Si}_{2.4})\text{O}_{20}(\text{OH})_4=2[\text{Ca}(\text{Mg}_2\text{Al})(\text{Al}_{2.8}\text{Si}_{1.2})\text{O}_{10}(\text{OH})_2]$; measured specific gravity=3.076. Optically negative, $\beta=1.662$, $\gamma=1.663$, $2V=19^{\circ}30'$ (all Na light).

Valuevite from Crestmore, California is chemically and crystallographically identical to Achmatovsk valuevite, the unit cell with $a=5.204$, $b=8.995$, $c=9.833$ kX, $\beta=100^{\circ}04'$, $a:b:c=0.5785:1:1.0987$, measured specific gravity 3.076. Optically negative, $\beta=1.659$, $\gamma=1.660$, $2V=21^{\circ}15'$ (all Na light). An indexed powder pattern is given for Crestmore valuevite.

Some doubt is raised as to whether the original yellow-coloured xanthophyllite is the same species as the green variety.

The brittle mica xanthophyllite was first described by Rose in 1840 as a wax-yellow mineral occurring near Zlatoust in the southern Urals of Russia. In view of its poor crystallinity, a crystallographic study was not made, but its general physical properties as well as several chemical analyses were published. Three further occurrences are recorded in the literature. Koksharov (1875) described a green variety, occurring near Achmatovsk (15 kilometres north of Zlatoust), to which he gave the varietal name waluevite [valuevite], because of the differences in colour and optics. Eakle (1916) and Sanero (1940) described occurrences of the green variety from Crestmore, California and Adamello, Italy, respectively. The latter two were identical with valuevite in all comparable properties.

Although a thorough study of the Adamello valuevite was made by Sanero, x -ray diffraction work has not been performed on any of the previous occurrences. The present paper gives the results of a mineralogical study of valuevite from both Achmatovsk and Crestmore. Unfortunately a sample of the original xanthophyllite could not be obtained, and there is some doubt as to whether the yellow and green varieties are actually of the same species.

Material and acknowledgements. The samples consisted of several flakes of the poorly crystallised Crestmore material (ROMM 16622) and one crystal of the Achmatovsk material (ROMM 6362) which was sufficiently well crystallised to permit rough measurement of four forms on the optical goniometer.

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Physical properties. Specific gravity determinations were made on both samples, using the Berman balance. The results are given in Table 1, together with those of other observers.

TABLE 1. XANTHOPHYLLITE: SPECIFIC GRAVITY

	Crestmore	Achmatovsk	Adamello	Zlatoust
S.A.F.	3.076	3.076	—	—
Sanero	—	—	3.075	—
Eakle	3.081	—	—	—
Koksharov	—	3.093	—	3.035-3.062
Rose	—	—	—	3.044

It can be readily seen that the specific gravity of the yellow variety from Zlatoust is of the same order as for the three green varieties and it cannot be distinguished from them on that basis.

X-ray crystallography. Laue diffraction patterns indicated a monoclinic symmetry and permitted selection of the proper axes for single crystal work. Rotation and Weissenberg photographs were taken about the *a* and *b* axes and precession photographs about the *b*-axis. The systematically missing spectra, namely

(*hkl*) present only with $h+k=2n$

(*h0l*) present only with $h=2n$

(*0k0*) present only with $k=2n$

lead to three possible space-groups C_2^3-Cm , C_2^3-C2 , and C_{2h}^3-C2/m with C_{2h}^3-C2/m being the most probable.

As shown in Table 2, the cell dimensions obtained agree fairly well with those obtained by Sanero on the Adamello material.

TABLE 2. XANTHOPHYLLITE: LATTICE DIMENSIONS¹

	Crestmore	Achmatovsk	Adamello
<i>a</i>	5.204 kX	5.24 kX	5.20 kX (5.21Å) ²
<i>b</i>	8.995	8.98	9.00 (9.02)
<i>c</i>	9.833	9.79	9.95 (9.97)
β	100°04'	100°10'	100°03'

¹ Using $CuK\alpha_1=1.5374$ kX

² Values given by Sanero, possibly they are in kX units.

Geometrical crystallography. Measurements were made on the one crystal from Achmatovsk on the optical goniometer. The reflections were very poor and since the only good reflecting face was the base $c(001)$, the crystal was set up in a polar position and the angles between the base and three other observable forms were measured. The indices were determined from a stereographic projection. No effort was made to determine an axial ratio from the goniometric measurements. Table 3 shows the forms listed by Hintze (1897) who adopted Koksharov's setting, Dana (1892) who adopted Tschermak's setting, and the forms observed by the author. The indices of all the forms in the new setting are listed in column 1.

TABLE 3. XANTHOPHYLLITE: FORMS

New Setting	Hintze	Dana	S.A.F.
$c(001)$	$c(001)$	$c(001)$	(001)
$x(301)$	$x(101)$	$x(\bar{1}02)$	(301)
$z(905)$	$Z(304)$	$z(\bar{3}08)$	
$t(011)$	$t(023)$	$t(013)$	
$v(023)$	$v(049)$	$v(029)$	
$r(034)$	$r(012)$	$r(014)$	
$Y(038)$	$Y(014)$	$Y(018)$	
$h(0.9.16)$	$h(038)$	$h(0.3.16)$	
$\sigma(335)$	$s(113)$	$\sigma(\bar{1}16)$	
$o(337)$	$o(114)$	$o(\bar{1}18)$	
$\omega(338)$	$\omega(229)$	$\omega(\bar{1}19)$	(338)
$k(\bar{1}13)$	$o'(\bar{1}14)$	$k(118)$	
$N(\bar{3}31)$	$N(110)$	—	
$s(\bar{3}37)$	$s'(\bar{1}13)$	$s(116)$	
$w(\bar{3}.3.10)$	—	$w(119)$	
$L(\bar{3}91)$	$L(130)$	$L(130)$	
$d(\bar{3}95)$	$d(\bar{1}32)$	$d(134)$	($\bar{3}95$)
$n(\bar{3}.9.25)$	$n(\bar{1}.3.12)$	$n(1.3.24)$	

The axial ratio adopted by Hintze was

$$a:b:c=0.57736:1:1.62214; \quad \beta=90^{\circ}0'$$

The transformation to the new setting is as follows:

$$\text{Hintze to S.A.F.} = 100/010/\sqrt[3]{0\frac{2}{3}}$$

The axial ratio adopted by Dana was

$$a:b:c=0.57735:1:3.24427; \quad \beta=90^{\circ}0'$$

The transformation to the new setting is as follows:

$$\text{Dana to S.A.F.} = \bar{1}00/0\bar{1}0/\sqrt[3]{0\frac{1}{3}}$$

The transformation takes this form since Dana adopted Tschermak's setting which was front to back. The axial ratios derived using the *x*-ray cell dimensions are:

Achmatovsk material— $a:b:c=0.584:1:1.090$; $\beta=100^{\circ}10'$

Crestmore material— $a:b:c=0.5785:1:1.0987$; $\beta=100^{\circ}04'$

Dana's setting is comparable to a single-layer mica, as described by Hendricks (1939), which has been forced into a 3-layer setting. Koksharov's is similar, with the 3-layer *c*-axis cut in two, producing effectively a $1\frac{1}{2}$ -layer mica.

TABLE 4. ACTUAL MEASUREMENTS ON ACHMATOVSK XANTHOPHYLLITE

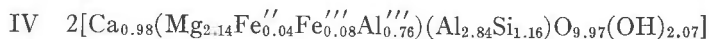
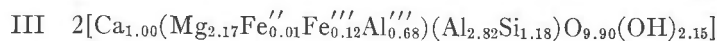
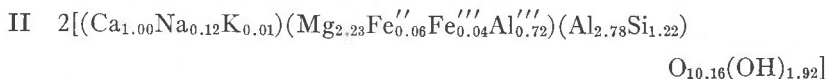
	S.A.F.	Hintze	Dana
$c\omega(001):(338)$	$35^{\circ}41' (2)$	$35^{\circ}47\frac{1}{3}'$	$35^{\circ}47'$
$cx(001):(301)$	$70\ 32 (1)$	$70\ 24\frac{1}{2}$	$70\ 24\frac{1}{2}$
$cd(001):(395)$	$70\ 30 (2)$	$70\ 24\frac{1}{2}$	$70\ 24\frac{1}{2}$

The figures in parentheses following the author's measurements denote the number of measurements made.

The actual measurements made on the crystal are shown in Table 4 and are compared to those values listed by Hintze and Dana. Table 5 is an angle table calculated using the axial ratio derived by *x*-ray measurements on the Achmatovsk material.

Composition and cell content. Analyses for each occurrence of valuevite are shown in Table 6. Analysis I by Eakle was made on Crestmore material, and this, combined with the cell dimensions and specific gravity determined by the author, served to determine the structural formula. Number III by Clarke and Schneider (1892) and IV by Nikolajev (selected from Hintze) on Achmatovsk material were treated in the same manner. Number II on Adamello material was calculated using Sanero's cell dimensions and specific gravity.

The structural formulae are as follows:



It seems obvious that the chemical composition is constant from one oc-

TABLE 5. XANTHOPHYLLITE— $\text{Ca}_2\text{Mg}_4\text{Al}_2(\text{Al}_{5.6}\text{Si}_{2.4})\text{O}_{20}(\text{OH})_4$
 Monoclinic— $C2/m$; $a:b:c=0.584:1:1.090$; $\beta=100^\circ 10'$
 $p_0:q_0:r_0=1.868:1.073:1$; $\mu=79^\circ 50'$
 $p_0'=1.898$, $q_0'=1.090$, $x_0'=0.179$

Form	ϕ	ρ	ϕ_2	$\rho_2=B$	C	A
$c(001)$	$90^\circ 00'$	$10^\circ 10'$	$79^\circ 50'$	$90^\circ 00'$	$0^\circ 00'$	$79^\circ 50'$
$x(301)$	90 00	$80\ 20\frac{1}{2}$	9 40	90 00	70 10	9 40
$z(905)$	90 00	$74\ 27\frac{1}{2}$	$15\ 32\frac{1}{2}$	90 00	$64\ 17\frac{1}{2}$	$15\ 32\frac{1}{2}$
$l(011)$	9 $20\frac{1}{2}$	47 51	79 50	42 59	47 01	$83\ 05\frac{1}{2}$
$v(023)$	$13\ 51\frac{1}{2}$	36 49	79 50	$54\ 25\frac{1}{2}$	$35\ 34\frac{1}{2}$	81 45
$r(034)$	12 22	39 56	79 50	$51\ 10\frac{1}{2}$	$38\ 49\frac{1}{2}$	82 06
$Y(038)$	23 41	$24\ 03\frac{1}{2}$	79 50	68 05	21 55	$80\ 34\frac{1}{2}$
$h(0.9.16)$	16 18	$32\ 34\frac{1}{2}$	79 50	58 53	31 07	$81\ 18\frac{1}{2}$
$\sigma(335)$	$63\ 36\frac{1}{2}$	55 48	37 11	68 26	$46\ 50\frac{1}{2}$	$42\ 11\frac{1}{2}$
$o(337)$	64 48	$47\ 39\frac{1}{2}$	$45\ 12\frac{1}{2}$	$71\ 39\frac{1}{2}$	$38\ 38\frac{1}{2}$	48 02
$\omega(338)$	$65\ 21\frac{1}{2}$	44 26	$48\ 17\frac{1}{2}$	$73\ 01\frac{1}{2}$	$35\ 16\frac{1}{2}$	50 29
$k(\bar{1}13)$	$-51\ 17\frac{1}{2}$	$30\ 09\frac{1}{2}$	$114\ 23\frac{1}{2}$	71 41	38 33	113 05
$N(\bar{3}31)$	$-59\ 20$	81 00	$169\ 43\frac{1}{2}$	59 44	$89\ 54\frac{1}{2}$	$140\ 11\frac{1}{2}$
$s(\bar{3}37)$	$-53\ 37\frac{1}{2}$	$38\ 13\frac{1}{2}$	122 23	68 28	$46\ 44\frac{1}{2}$	119 53
$w(\bar{3}.3.10)$	$-50\ 01$	26 59	$111\ 18\frac{1}{2}$	73 03	35 20	$110\ 20\frac{1}{2}$
$L(\bar{3}91)$	$-29\ 20\frac{1}{2}$	$84\ 55\frac{1}{2}$	$169\ 43\frac{1}{2}$	$29\ 44\frac{1}{2}$	$89\ 56\frac{1}{2}$	119 13
$d(\bar{3}95)$	$-26\ 03\frac{1}{2}$	65 24	133 49	35 14	$70\ 10\frac{1}{2}$	$113\ 32\frac{1}{2}$
$n(\bar{3}.9.25)$	$-7\ 02\frac{1}{2}$	$21\ 34\frac{1}{2}$	$92\ 46\frac{1}{2}$	$68\ 35\frac{1}{2}$	$24\ 51\frac{1}{2}$	92 35

TABLE 6. XANTHOPHYLLITE: CHEMICAL ANALYSES

	I	II	III	IV
SiO_2	16.74	17.11	16.85	16.39
TiO_2	—	tr.	tr.	—
Al_2O_3	42.70	41.71	42.33	43.40
Fe_2O_3	2.85	0.80	2.35	1.57
FeO	0.41	0.94	0.20	0.60
MnO	—	0.03	—	—
MgO	20.03	21.03	20.77	20.38
CaO	13.09	13.17	13.30	13.04
BaO	—	tr.	—	—
Na_2O	—	0.89	—	—
K_2O	—	0.12	—	—
H_2O	4.49	4.03	4.60	4.40
	100.31	99.83	100.40	99.78
S.G.	3.076(S.A.F.)	3.075(San)	3.076(S.A.F.)	3.076(S.A.F.)

currence to another. The ideal formula is hence



An extremely interesting feature is the Al:Si ratio which averages out to approximately Al:Si = 2.80:1.20. This is a much greater substitution of aluminium for silicon than is normally observed in the platy silicate minerals. It is approaching a 3:1 ratio which may indeed be the ideal ratio for the brittle micas. The extra charge on the silicon-oxygen sheet probably accounts for the slightly shorter *c*-axis than that observed in the dark-coloured micas, and explains to some extent the brittle nature of this mica.

The published analyses for the yellow xanthophyllite are extremely similar to those tabulated above. No attempt was made to work out its cell content using the cell dimensions of the green variety since this would imply crystallographic identity which has definitely not been established.

Optical properties. Optical studies were carried out on the materials from both Achmatovsk and Crestmore using Na light. Table 7 shows the values obtained as well as those of Eakle and Sanero:

TABLE 7. XANTHOPHYLLITE: OPTICAL DATA, $V=b$, OPTICALLY NEGATIVE

	α	β	γ	$2V$
Material Crestmore, S.A.F.	—	1.659	1.660	21°15'
Material Achmatovsk, S.A.F.	—	1.662	1.663	19°30'
Material Crestmore, Eakle	—	1.660	1.660	12°–18°
Material Adamello, Sanero	—	—	—	29°50' (2E)

Rose describes xanthophyllite (yellow variety) as being effectively uniaxial.

X-ray powder pattern. Sufficient material was available to make an *x*-ray powder pattern of the Crestmore material only. Table 8 lists the observed lines (Cu radiation) with their measured and calculated spacings. The intensities are based on 10 for the strongest line. The pattern was indexed, in part, using the cell dimensions derived by the single crystal *x*-ray work.

Conclusions. A complete mineralogical description of the yellow variety of xanthophyllite including its morphology and *x*-ray crystallography was not made, since none of it is available for study. However, the chemical analyses of the yellow and green varieties are almost identical, but the optical properties as described by Rose (yellow and almost uniaxial) differ from those shown for valuevite. Nevertheless, there is insufficient

TABLE 8. XANTHOPHYLLITE: $\text{Ca}(\text{Mg}_2\text{Al})(\text{Al}_{2.8}\text{Si}_{1.2})\text{O}_{10}(\text{OH})_2$:
 X-RAY POWDER PATTERN

 Monoclinic, $C2/m$; $a=5.204$, $b=8.995$, $c=9.833$ kX; $\beta=100^\circ 04'$; $Z=2$

I	$d(\text{meas.})$	(hkl)	$d(\text{calc.})$	I	$d(\text{meas.})$	(hkl)	$d(\text{calc.})$
2	4.52 kX	(020)	4.50 kX	$\frac{1}{2}$	1.690	$\left\{ \begin{array}{l} (240) \\ (\bar{1}51) \end{array} \right\}$	1.690
3	3.57	($\bar{1}$ 12)	3.56				1.689
8	3.23	(003)	3.23	$\frac{1}{2}$	1.656	$\left\{ \begin{array}{l} (\bar{2}42) \\ (151) \end{array} \right\}$	1.656
1	2.84	($\bar{1}$ 13)	2.83				1.656
10	2.56	$\left\{ \begin{array}{l} (200) \\ (032) \\ (\bar{1}31) \end{array} \right\}$	2.56	3	1.614	(006)	1.614
			2.55	7	1.499	(060)	1.499
			2.56	7	1.484	(330)	1.484
1	2.44	$\left\{ \begin{array}{l} (\bar{2}02) \\ (113) \\ (131) \end{array} \right\}$	2.45	1	1.362	$\left\{ \begin{array}{l} (225) \\ (332) \\ (\bar{3}34) \end{array} \right\}$	1.362
			2.44				1.362
			2.45				1.361
1	2.36	$\left\{ \begin{array}{l} (201) \\ (014) \\ (\bar{1}32) \end{array} \right\}$	2.38	1	1.313		
			2.34	$\frac{1}{2}$	1.292		
			2.37	$\frac{1}{2}$	1.274		
1	2.20	$\left\{ \begin{array}{l} (\bar{2}03) \\ (132) \end{array} \right\}$	2.20	$\frac{1}{2}$	1.242		
			2.20	$\frac{1}{2}$	1.185		
5	2.11	$\left\{ \begin{array}{l} (202) \\ (221) \\ (\bar{1}33) \end{array} \right\}$	2.12	$\frac{1}{2}$	1.099		
			2.10	$\frac{1}{2}$	1.055		
			2.11	$\frac{1}{2}$	1.019		
3	1.936	$\left\{ \begin{array}{l} (005) \\ (\bar{2}04) \\ (133) \end{array} \right\}$	1.936	$\frac{1}{2}$	0.981		
			1.937	$\frac{1}{2}$	0.961		
			1.937	$\frac{1}{2}$	0.932		
$\frac{1}{2}$	1.850	($\bar{1}$ 34)	1.851	$\frac{1}{2}$	0.886		
$\frac{1}{2}$	1.780	$\left\{ \begin{array}{l} (025) \\ (\bar{2}24) \end{array} \right\}$	1.779	$\frac{1}{2}$	0.862		
			1.779	$\frac{1}{2}$	0.809		
				$\frac{1}{2}$	0.787		

evidence to suggest that xanthophyllite and valuevite are not varieties of the same species of brittle mica.

REFERENCES

- CLARKE, F. W. & SCHNEIDER, E. A. (1892): Experiments upon the constitution of certain micas and chlorites, *Am. Jour. Sci.*, Ser. 3, 43, 378-386.
 DANA, E. S. (1892): *System of Mineralogy*, New York.

- EAKLE, A. S. (1916): Xanthophyllite in crystalline limestone, *Jour. Wash. Acad. Sci.*, **6**, 332-335.
- HENDRICKS, S. B. (1939): Polymorphism of the micas. With optical measurements by M. E. Jefferson, *Am. Mineral.*, **24**, 729-771.
- HINTZE, C. (1897): *Handbuch der Mineralogie*, **2**, Leipzig.
- [KOKSHAROV] KOKSHARÖW, N. V. (1875, 1884); *Materialien zur Mineralogie Russlands*, **7, 9**, St. Petersburg.
- ROSE, G. (1842): *Reise nach dem Ural*, **2**, Berlin.
- SANERO, E. (1940): La struttura della xantofillite, *Min. Roma*, **11**, 53-77.
- TSCHERMAK, G. & SIPÖCZ, L. (1879): Die Clintonitgruppe, *Zeit. Kryst.*, **3**, 496-515.