

A RE-EXAMINATION OF XANTHOPHYLLITE [CLINTONITE]¹ FROM THE TYPE LOCALITY

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ABSTRACT

Xanthophyllite, the yellow variety, from the type locality was examined mineralogically. It was found to be very little different from the green variety, valuevite. Thus the use of varietal names does not seem justified. An associated mineral, described by Rose (1842) as talc, was determined to be a chlorite, sheridanite. Chemical analyses of the type xanthophyllite and of the sheridanite are given.

INTRODUCTION

In 1951 one of the authors (S. A. F.) published a paper entitled "Xanthophyllite," in which a study on the green variety, valuevite, was reported. At that time it was stated, because of inability to obtain any of the type yellow material described by Rose (1842), that there was some doubt whether the yellow and green varieties were actually the same species.

Recently some of the yellow material from the original source became available for study. Accordingly, this paper is a report on the mineralogical properties of the type material with an evaluation of its relationship to valuevite.

Except for chemical analyses which were done by one of the authors (S. A.), all aspects of the investigation were carried out by the others.

MATERIAL

Xanthophyllite was first described by Rose (1842) as having occurred in a talc schist near Zlatoust in the Shishim Mountains of the Southern Urals in Russia. Two samples were obtained, one (BM 96546) consisting of a few flakes and the other (ROM M25402) consisting of a portion of what appeared to have been an ellipsoidal nodule. The latter had a round

¹In a paper now in the course of preparation, the authors will recommend that the species name "clintonite" encompass all trioctohedral brittle micas including xanthophyllite.

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cross-section about 3 cm in diameter. The outer surface was rust-stained with a crust consisting of numerous tiny crystals of magnetite and a number of pale brown crystals of perovskite. The body of the specimen consisted of coarse grained, flaky, pale yellow xanthophyllite with a central core, about one centimetre diameter, of a white, very fine-grained mineral. The latter had been described by Rose (1842) as consisting of the same material as the schist, namely talc.

In addition, several valuevite samples were re-examined. One (BM 62806), from Achmatovsk in the Urals, was first described by Koksharov (1875, 1884) and studied by Forman (1951); the other two, one pale green and the other dark green, were from the Chichibu Mine located about 100 km N.W. of Tokyo in Japan and have been studied by Harada *et al.* (1965).

METHODS

X-ray diffraction studies were carried out on all the xanthophyllite and valuevite samples using precession, Weissenberg, and powder techniques. Cell dimensions and space groups were derived by using a combination of all x -ray data. The white core of sample ROM M25402 was too fine grained to lend itself to anything other than powder techniques. This was done using both film and diffractometer.

Complete chemical analyses were carried out on xanthophyllite from ROM M25402 and on the white powder from its core. The latter bottomed at a depth of about 1.3 cm and only 80 mg of material could be obtained. Each was carefully cleaned by repeated centrifugations with suitable heavy liquids.

In order to provide maximum results with minimum sample consumption, an analytical scheme was devised incorporating features of both "classical" and "rapid" rock analysis, together with some innovations. Two National Bureau of Standards samples, of compositions similar to the samples, were analyzed concurrently, as a check on recoveries. Residues and filtrates were examined spectrographically, where necessary, to check completeness of separations. Five-milligram portions of each sample were also analyzed semi-quantitatively on the spectrograph.

To determine silica, 10-mg samples were fused with sodium hydroxide and the molybdenum blue reaction applied, using differential spectrophotometry.

Fifty-milligram samples were then dried to give H_2O- and ignited for H_2O+ . After $HF-H_2SO_4$ decomposition, the R_2O_3 group was separated conventionally, but weighed as the 8-hydroxyquinoline complexes. Iron was determined photometrically on the redissolved precipitate and alumina by difference (spectrographic analysis revealed no other elements

in the R_2O_3 precipitate). Calcium was separated as the oxalate (after adding a known amount to the white material to facilitate separation from magnesium) and magnesium was separated with 8-hydroxyquinoline.

A 10-mg sample of the white material and an 80-mg sample of the xanthophyllite were decomposed by HF-H₂SO₄ treatment, and potassium and sodium determined by flame photometry, using scaled-down versions of established techniques. Specific gravities were obtained by standard techniques using pycnometers.

All samples were examined under the petrographic microscope in appropriate immersion oils.

RESULTS AND DISCUSSION

The x-ray diffraction work showed all the samples of the green variety to be identical in cell dimensions but slightly different from the two samples of the yellow variety which were in themselves identical (Table 1). The statement by Rose (1842) that the latter was poorly crystalline, presumably morphologically, was verified under the petrographic microscope by the manner in which the mica plates were interleaved. None of the plates showed any form development whatsoever. Additional support came in the fact that repeated attempts to obtain untwinned flakes were unsuccessful.

TABLE 1. CELL DIMENSIONS OF XANTHOPHYLLITE AND
VALUEVITE
(Angstrom Units)

Variety	<i>a</i>	<i>b</i>	<i>c</i>	β
Yellow	5.20 ₄	9.02 ₆	9.81 ₂	100° 20'
Green	5.21 ₆	9.01 ₂	9.85 ₄	100° 05'

Single-crystal studies showed both varieties to consist of polysynthetic spiral twins, although it was less evident in the material from Achmatovsk. Sadanaga & Takéuchi (1961) have discussed twinning in micas in terms of spiral twins consisting of rotations about a c' axis (equivalent to c^* axis) with the angle of rotation designated as ω , and the composition plane (001). In the present case ω was established to be $\pm 120^\circ$, equivalent to the conventional mica twin about [310] or $[\bar{3}\bar{1}0]$. All were assigned to the space group considered to be most probable (Forman 1951, Takéuchi & Sadanaga 1959), $C2/m$, on the basis of extinction conditions determined from the precession and Weissenberg photographs.

The powder pattern (Table 2) of the yellow material was indexed on

the basis of this space group, with all reflections confirmed with the aid of single-crystal data.

The structural formula, based on the chemical analysis and specific gravity determination (Table 3), was calculated using $M = \frac{VG}{A}$ giving $(\text{Ca}_{0.98}\text{Na}_{0.02}\text{K}_{0.01})(\text{Mg}_{2.13}\text{Fe}_{0.11}\text{Al}_{0.76})(\text{Al}_{2.89}\text{Si}_{1.11})\text{O}_{9.92}(\text{OH})_{2.14}$. This represents the largest tetrahedral Al-Si ratio heretofore reported excepting that of Takéuchi & Sadanaga (1959) which was given as 2.95:1.05 but without relevant chemical data. Nevertheless the above formula is consistent with those reported for the green variety. They differ only slightly both in Al:Si ratio and in cell dimensions.

Optical examinations were restricted to the determination of optic sign, which was negative in every case, and to the index of refraction within the mica plates. It was found that spiral polysynthetic twinning occurred on such a fine scale that no flake could be reduced in size

TABLE 2. XANTHOPHYLLITE FROM ZLATOUST, SOUTHERN URALS, RUSSIA
(BM 96546, ROM M25402) X-RAY POWDER PATTERN

Monoclinic, $C2/m$; $a = 5.20_4$; $b = 9.02_6$; $c = 9.81_2 \text{ \AA}$; $\beta = 100^\circ 20'$;
 $Z = 2$; $S.G. = 3.10$

<i>I</i>	<i>d</i> (meas.)	(<i>hkl</i>)	<i>d</i> (calc.)	<i>I</i>	<i>d</i> (meas.)	(<i>hkl</i>)	<i>d</i> (calc.)
5	9.68	(001)	9.67	*	1.622	($\bar{1}$ 35)	1.621
3	4.50	(020)	4.52	$\frac{1}{2}$	1.609	(006)	1.609
$\frac{1}{2}$	3.82	(111)	3.82	*	1.578	{(152)}	1.577
$\frac{1}{2}$	3.55	($\bar{1}$ 12)	3.56			{(243)}	1.577
$\frac{1}{2}$	3.30	(022)	3.30	*	1.539	(242)	1.541
$\frac{1}{2}$	3.21	(003)	3.22			{(060)}	1.506
1	3.05	(112)	3.04	6	1.505	{(314)}	1.506
2	2.83	($\bar{1}$ 13)	2.83			{(330)}	1.484
$\frac{1}{2}$	2.59	{(201)}	2.59	5	1.485	{(135)}	1.486
		{(130)}	2.59			{(332)}	1.485
10	2.56	{(200)}	2.56			{(063)}	1.364
		{(131)}	2.57	3	1.363	{(334)}	1.362
		{(202)}	2.45	3	1.316		
5	2.45	{(131)}	2.45	3	1.296		
		{(201)}	2.37	$\frac{1}{2}$	1.261		
4	2.37	{(132)}	2.38	$\frac{1}{2}$	1.244		
		{(203)}	2.20	*	1.225		
4	2.20	{(041)}	2.20	*	1.208		
		{(132)}	2.20	3	1.186		
		{(202)}	2.11	*	1.124		
7	2.11	{(133)}	2.12	3	1.101		
		{(221)}	2.10	3	1.056		
4	1.931	(005)	1.931	$\frac{1}{2}$	1.025		
2	1.851	(043)	1.849	*	1.015		
		{(150)}	1.704	*	0.990		
2	1.705	{(311)}	1.702	3	0.981		
		{(151)}	1.661				
*	1.661	{(242)}	1.661				

*Line is barely visible.

sufficiently to eliminate its effects. There were poor, and in some cases, unresolved interference figures so that it was futile to attempt to distinguish β and γ indices. Thus the refractive indices given must be considered as averages of the two indices. That for ROM M25402 and BM 96546, the yellow varieties, was 1.658. The two green samples from Japan gave 1.659. The others are given in Forman (1951) and vary from 1.659 to 1.663.

No simple explanation seems to be forthcoming to explain the difference in colour between the type yellow variety and the more common green variety. It would be convenient if the colour variations could be attributed to differences in the relative amounts of octahedrally-coordinated divalent and trivalent Fe. However, in those analyses of the green variety in which an attempt was made to distinguish the two valence states (Forman, 1951) Fe^{+3} exceeds Fe^{+2} in three of the four cases. In the fourth Fe^{+2} exceeds Fe^{+3} by a slight amount. In every case iron was a minor constituent, as it is in the yellow variety (Table 3). In the latter, no

TABLE 3. CHEMICAL ANALYSES OF
XANTHOPHYLLITE AND CHLORITE
FROM ROM M25402

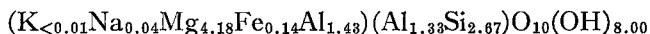
	Xanthophyllite	Chlorite
SiO_2	15.84	28.25
Al_2O_3	44.0	24.8
Fe_2O_3^*	2.04	1.99
CaO	13.01	0.02
MgO	20.33	30.42
Na_2O	0.26	0.23
K_2O	0.19	<0.01
H_2O^+	4.56	13.63
H_2O^-	0.00	0.19
Total	100.2 ₃	99.5 ₃
S.G.	3.10	2.62

*Total Fe calculated as Fe_2O_3 .

attempt was made to distinguish the two valence states. Conceivably, as outlined in Cotton & Wilkinson (1962), Fe^{+3} would produce a yellow colour if coordinated by oxygen, as it is in the yellow variety, and if charge transfer occurs. On the other hand, the green colour in valuevite could be explained by octahedrally-coordinated Fe^{+3} involving $d - d$ transitions. Unfortunately it is difficult to explain why Fe would occur in different states of excitation in the two varieties of xanthophyllite. In any event, absorption spectra of the two varieties were taken in the ultraviolet, visible, and infrared with no apparent differences between the two. Thus it is concluded that there is so little to choose between the properties of

xanthophyllite and valuevite that the latter name, for the green variety hardly seems justified.

The fine white material in the core of the specimen from Zlatoust, Russia (ROM M25402) was described by Rose (1842) as talc, similar to the surrounding schist rock. In actual fact this material gave an extremely sharp chlorite x -ray pattern. The structural formula, based on the chemical analysis (Table 3) and calculated on the basis of 28 negative charges for 10 oxygens and 8 hydroxyls, is



which classes it as a sheridanite, as defined by Foster (1962).

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REFERENCES

- COTTON, F. ALBERT & WILKINSON, G. (1962): *Advanced inorganic chemistry*. Interscience Publishers, New York.
- FORMAN, S. A. (1951): Xanthophyllite, *Am. Min.*, **36**, 450-7.
- FOSTER, MARGARET D. (1962): Interpretation of the composition and a classification of the chlorites, *U.S. Geological Survey Professional Paper*, **414-A**.
- HARADA, K., KODAMA, H. & SUDO, T. (1965): New mineralogical data for xanthophyllite from Japan, *Can. Mineral*, **8**, 255-62.
- [KOKSHAROV] KOKSHAROV, N. V. (1875, 1884): *Materialien zur Mineralogie Russlands*, **7, 9**, St. Petersburg.
- ROSE, G. (1842): *Reise nach dem Ural*, **2**, Berlin.
- SADANAGA, R. & TAKÉUCHI, Y. (1961): Polysynthetic twinning of micas, *Zeit. Krist.*, **116**, 406-29.
- TAKÉUCHI, Y. & SADANAGA, R. (1959): The crystal structure of xanthophyllite, *Acta Cryst.*, **12**, 945-6.

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