

ART. XXXVII.—*Two Varieties of Calciovolborthite* (?) from Eastern Utah; by W. F. HILLEBRAND and H. E. MERWIN.

ABOUT nine or ten years ago Mr. J. M. Boutwell brought to the United States Geological Survey specimens of minerals from a mining prospect near Richardson, in the canyon of Grand River, Southeastern Utah. One of these, yellow-green in color, was found to be, on the basis of quantitative tests by one of us (H.) in the Survey laboratory, a hydrous vanadate of copper; the other, greenish yellow, a hydrous arseno-vanadate of copper and calcium. These minerals have been referred to in print\* by Mr. Boutwell, but the analyses were not published, since it was expected that more material would become available for study. This hope was not realized and most of the specimens were later destroyed by fire.

Soon after first sight of the minerals one of us (H.) saw, in the Utah exhibit at the World's Fair in St. Louis in 1904, splendid specimens of what seemed to be one or both of these minerals, but nothing definite could be learned as to their source, nor is it known what became of them.

A "green encrusting mineral" called volborthite is mentioned in the Quarterly of the Colorado School of Mines (vol. iii, No. 3, 1909) as having been found in a mining prospect, now abandoned, at or near Garos (Garos?) in Park County, Colorado, and it was said that fine specimens were exhibited at the World's Fair in St. Louis. From the imperfect description it would seem as if this might be related to or identical with one of the minerals from Utah.

Within the past two years we have received from the Foote Mineral Co. of Philadelphia, a mineral on sandstone from Paradox Valley, Montrose County, Colorado, which is beyond doubt identical with one of Mr. Boutwell's minerals, as revealed by recent comparison with the microscope.

It seems then timely to put on record our present knowledge of the minerals, although the analyses made long ago by one of us (H.) lead to no clearly-defined formulas. It is to be remembered that only Mr. Boutwell's material has been analyzed. In the case of the yellow green mineral the analyses had to be made on as little as 0.2, 0.16, and 0.13 grams, respectively, of the scrapings and pickings from the sandstone on which it occurred. For the greenish yellow mineral two half-gram portions were available, each yielding about 0.4 gram of soluble components. But for neither mineral was the soluble matter solely the mineral under study. Small amounts of carbonates and perhaps silicate of copper were included

\* U. S. Geol. Survey, Bulletin 260, pp. 205-206.

besides ferric and other oxides, foreign to the vanadates, but complicating the analysis and interfering with deductions.

Both minerals occur, sometimes on the same hand specimen, in rosettes and patches of minute reticulated scales on surfaces of sandstone, often intimately associated with thin coatings and stains of other copper minerals—carbonates and possibly chrysocolla—which made it impossible to secure material of great purity for analysis. Mr. Boutwell mentions occasional "carnotite and small yellow crystals, slightly darker than this carnotite," as being "intimately associated with the green crystals," but we have observed neither of these on the specimens now available. The rosette forms spoken of are often distributed singly, but more often grouped and intermingled, presenting then a very handsome appearance, especially in the case of the yellow green mineral.

1. *Yellow-Green Variety*.—Rosettes and patches of reticulated scales. The aggregates have a dark yellow-green color (YG), Shade 1, of the Bradley Color Scale.\* In powder and in scales under the microscope the color is brilliant green yellow (GY). But few data as to crystalline form could be obtained from the material from Paradox Valley, Colorado, but that from Richardson, Utah, furnished a few triangular, hexagonal and elongated scales, which, within the limits of error ( $3^\circ$ ), possessed hexagonal symmetry. However, the mineral is not hexagonal, but probably monoclinic, as the optical study showed. On account of the aggregated character of the material nothing definite can be said concerning the hardness and cleavage of the mineral, although the thinnest scales appear to be cleavage fragments. Lack of material of sufficient purity prevented the determination of the specific gravity.

An optic axis and the bisectrix  $\gamma$  emerge at angles of about  $50^\circ$  in air on opposite sides of the normal to the plane of the scales. The optic axis is strongly dispersed, with the red fringe of the hyperbola on the convex side. Measurements of the optical axial angle,  $2V$ , gave the following average results from values that varied  $5^\circ$  for different sections: in Li-light  $68^\circ$ , Na-light  $83^\circ$ , TI-light  $89^\circ$ . The mineral is, therefore, optically positive for red and negative for violet. The measurements indicate that the bisectrices are dispersed. Determination of the extinction position of plates for light of different colors established the essential coincidence of the optic planes for all colors, although most sections do not extinguish completely in white light. The dispersion is, then, inclined, and the mineral is probably monoclinic. The indices of refraction,  $\alpha$  and  $\beta$ , for Na-light, measured by immersion in highly refracting liquids, are 2.01 and 2.05.  $\gamma$  calculated = 2.10.

\* This scale can be found in Mulliken's Identification of Pure Organic Compounds; Wiley & Sons, New York.

The extremely strong inclined dispersion is noteworthy. Between the optic axes for Li-light and Tl-light there are angles of 28° and 7°. The axis emerging in the field of the microscope is dispersed 7°. The bisectrices are dispersed 18°. The plane of the optic axes bisects the angle of the triangular plates. This relation and inclined dispersion are strong evidence of monoclinic symmetry. The absorption of light by the crystals was studied in a general way by observing them in light of different wave lengths. No sharp absorption bands were disclosed and there is little absorption in the bright part of the spectrum, but beyond 530 $\mu\mu$  and 630 $\mu\mu$  absorption in all three of the principal directions increases steadily and sensibly equally, except that beyond 470 $\mu\mu$  differences are noticeable.

2. *Greenish Yellow Variety.*—The arsenical variety of the mineral has the same reticulate appearance as that just described. The color is dull green (G, shades 1 and 2), and is in some cases only a thin film covering crystals of the yellow-green mineral. This fact was not known when the analyses were made, hence it is possible that the composition found represents a mixture. Under the microscope the green crusts are seen to be very minute, doubly refracting crystals of refractive index about 1.92. They absorb at the ends of the spectrum, noticeably beyond 500 $\mu\mu$  and 660 $\mu\mu$ . This mineral is pseudo-morphic after the yellow-green variety.

	Yellow-Green		Green-Yellow	
	Percentages	Mol. Ratio	Percentages	Mol. Ratio
V <sub>2</sub> O <sub>5</sub> .....	30.6*	} 175	16.0*	} 168
As <sub>2</sub> O <sub>5</sub> .....	1.1		17.2*	
P <sub>2</sub> O <sub>5</sub> .....	.3		.8	
CuO .....	48.4*	} 713	37.1*	} 769
CaO .....	3.9*		15.3	
BaO .....	2.7		2.3	
MgO .....	.3	} 7	.5	} 2
K <sub>2</sub> O .....	.7		.2	
Na <sub>2</sub> O .....				
H <sub>2</sub> O, 105° — .....	1.8	100	1.0	55
H <sub>2</sub> O, 105° + .....	6.4	355	4.3	239
CO <sub>2</sub> .....	2.4	} 60	.9	} 32
SiO <sub>2</sub> .....	.6		.7	
Fe <sub>2</sub> O <sub>3</sub> .....	.8		.5	
Mn <sub>3</sub> O <sub>4</sub> } .....			3.2	
Co <sub>3</sub> O <sub>4</sub> } † .....				
Al <sub>2</sub> O <sub>3</sub> } .....				
	100.0		100.0	

\* Mean of two closely agreeing results.

† As weighed after precipitation together. Original condition unknown.

*Analyses and Discussion.*—In calculating the analytical results shown on the preceding page there was deducted 30.6 per cent of matter insoluble in very dilute nitric acid in the case of the yellow-green mineral, and 13.5 per cent in the other, and calculating to 100. The original analytical summations were 99.5 and 101 respectively.

If  $\text{CO}_2$  and  $\text{SiO}_2$  are allowed for as normal carbonates and metasilicates, an assumption not entirely in accord with the facts, but the best that can be made, the molecular ratios become:

	$\text{V}_2\text{O}_5$	RO	$\text{H}_2\text{O}$ total	$\text{H}_2\text{O}$ , below 105°
Yellow-green .....	1	3.73	2.6	2.03
Green-yellow .....	1	4.37	1.75	1.42

In view of the character of the material analyzed and the doubt expressed a little above as to the homogeneity of one of the samples, the above ratios do not permit us to decide that the two minerals should receive different formulas. The difference is most marked in the water, but under the circumstances this should not force a decision, especially since we know nothing, in the first place, as to the function of the water—whether truly water of crystallization or in its amount a function of atmospheric humidity and temperature—nor, in the second place, how much of it is to be assigned to contaminating minerals. Until better material and better analyses are available we prefer to regard the minerals as related to each other and of the same type formula, the green derived from the yellow by partial replacement of  $\text{V}_2\text{O}_5$  by  $\text{As}_2\text{O}_5$  and of  $\text{CuO}$  by  $\text{CaO}$ .

When it comes to establishing the relationship of these minerals to others already known, difficulty arises also. Unquestionably the nearest known relative is calciovolborthite, for which, on the basis of widely divergent analyses, Dana gives the formula  $4(\text{Cu,Ca})\text{O} \cdot \text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ .

Optical data concerning calciovolborthite are entirely lacking. We do not feel justified in making new species out of the minerals herein described, but choose to refer them both for the present to calciovolborthite, assigning that name to the yellow-green variety and arsenical calciovolborthite to the greenish-yellow derivative.

The original belief of one of us (H.) as published by Mr. Boutwell, that the arsenical variety is a new species, distinct from the other, we do not care to press, although it may prove to be so.

As to the name calciovolborthite, it is difficult to see how it ever came to be applied originally by Rammelsberg,\* since the

\* The name Kalk-volborthit was not used by Credner, the first describer of the mineral, as a statement in Dana's Mineralogy leads one to infer.

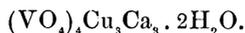
mineral called by it differs fundamentally from volborthotite, although the latter is also a copper vanadate. It is very unfortunate that a name so inappropriate and misleading should have been given.

In 1908 J. Antipoff\* gave in Russian a very unsatisfactory description of a new occurrence of uranium and vanadium minerals at Tuya Muyun, a hill in the Alai Mountains, in the province of Ferghana, Russian Turkestan.

One of the minerals mentioned is regarded as allied to volborthite, and is called Turkestan volborthite, although it approaches calciovolborthite far more closely in composition, as the figures below show :

V <sub>2</sub> O <sub>5</sub> .....	41.03
MoO <sub>3</sub> .....	.23
CuO .....	29.45
CaO .....	20.40
Fe <sub>2</sub> O <sub>3</sub> } .....	2.80
Al <sub>2</sub> O <sub>3</sub> }	
SiO <sub>2</sub> .....	1.10
H <sub>2</sub> O .....	4.55
	99.56

The formula assigned by the author is



Later, in 1909, K. Nenadkevitch† described, as the predominating vanadium mineral at the same locality, another vanadate under the name turanite, and assigned to it the formula 5CuO.V<sub>2</sub>O<sub>5</sub>.2H<sub>2</sub>O. It is said to occur as compact or radiating, olive-green, spherical concretions and kidney-like crusts in cavities of malachite and ore-bearing limestone.

Bureau of Standards and Geophysical Laboratory  
of the Carnegie Institution,  
Washington, D. C., Feb.

\* Gornii Journal, iv, 255-267, 1908. Through Neues Jahrb. für Min., etc., ii, p. 37, ref., 1909.

† Bull. Acad. Sci., St. Petersburg, 1909, 185-186.