

ART. III.—*Chalcophyllite from Chile*; by EARL V. SHANNON.

The chalcophyllite described in the following article is from the Teniente mine of the Braden Copper Company, east of Rancagua, O'Higgins Province, Chile, where the mineral occurred in some abundance in a shear zone 150 meters from the surface. It was associated with tennantite from which it has presumably been derived by oxidation. The specimens were loaned for investigation by Prof. William E. Ford, to whom the writer is indebted for the privilege of describing the mineral. Credit is due Mr. James E. Harding, an engineer for the Braden Copper Company, who collected the material. The alteration of the mineral by dehydration on exposure to the air was noted by Mr. Harding, who packed the material in moist sawdust and sealed it in a tin box, in which it arrived in its original condition in New Haven, where the specimens have for several years since been kept under a bell jar in a moist atmosphere. These are perhaps the only specimens of fresh and unaltered chalcophyllite to be described, or preserved in their unaltered state in any collection.

The mineral occurs as emerald-green crusts of closely intergrown tabular crystals averaging about one millimeter in diameter and one-tenth millimeter in thickness. The crusts completely surround irregular fragments of the gangue, which is mainly iron-stained quartz, as though each specimen had formed separately in a clayey matrix. The luster is vitreous-adamantine and the color deep emerald green, there being none of the verdigris-green color and pearly luster on the basal pinacoid characteristically reported for chalcophyllite. When specimens are exposed to dry air, however, they quickly lose some water, with the development of a more bluish or verdigris-green color, and become less transparent, with a pearly luster resembling the specimens of chalcophyllite and tyrolite found in collections. The altered mineral also tends to disintegrate somewhat. In this behavior on exposure, the chalcophyllite is altogether similar to laumontite.

¹ Published by permission of the Secretary of the Smithsonian Institution.

The fresh chalcophyllite has about the hardness of gypsum (2) and possesses a perfect basal cleavage. When heated it decrepitates sharply with exfoliation and becomes almost black, and at a full red heat it fuses to a dark brown mass with loss of white fumes (arsenical?), and the fused mass is very difficultly soluble in acids. In the closed tube it gives abundant water and a thin, white sublimate, probably of arsenic acid. The powder is readily soluble in dilute nitric and hydrochloric acids, and is also soluble in ammonia, giving a deep blue solution.

Although appearing well crystallized, the material proved to be very poorly suited for goniometric examination. The seven crystals which were selected for measurement on the two-circle goniometer yielded very unsatisfactory results. They are hexagonal-rhombohedral in form and are tabular on the basal pinacoid, the thickness being about one-tenth the diameter. The basal pinacoid, though lustrous, is irregular and marked by concentric triangular patterns parallel to one set of rhombohedral planes. The base usually gives several signals somewhat widely spaced, and the rhombohedral planes are rounded and striated. The crystals, even the smallest, appear compound and made up of piles of individuals not in exactly parallel position, and there is oscillation between adjacent faces in the same vertical zone. The 32 rhombohedral angles measured on uniformly poor signals, both in the plus and minus sectors, gave an almost continuous series of values for rho, from $23^{\circ} 47'$ to $78^{\circ} 30'$, with no noticeable grouping. It is improbable that additional measurements on these crystals would be better than those already made. Most of the crystals are trigonal rhombohedral, although an occasional one suggests hemimorphic symmetry. This may be due to splitting on the perfect basal cleavage.

Optically the mineral is uniaxial and negative, the basal plates giving excellent interference figures. It is moderately pleochroic in pale green to almost colorless across the cleavage (along the *c* axis), and darker blue-green parallel to the cleavage. The normal unaltered mineral, with its full complement of water such as was used for analysis, has the following indices of refraction:

$$\omega = 1.618 \qquad \epsilon = 1.552 \qquad \omega - \epsilon = .066$$

Material which had been exposed to the air of a room for several days during a period of extreme humidity had altered slightly and had the indices:

$$\omega = 1.620 \qquad \epsilon = 1.560 \qquad \omega - \epsilon = .060$$

The same sample, powdered to pass 100 mesh, after standing over night in a desiccator over calcium chloride had become much more pearly and opaque in appearance, with the following greatly increased indices:

$$\omega = 1.680 \qquad \epsilon = 1.620 \qquad \omega - \epsilon = .060$$

A sample which had been dried to constant weight at 110° C. had similarly high indices, namely:

$$\omega = 1.680 \qquad \epsilon = 1.618 \qquad \omega - \epsilon = .062$$

In the several preceding cases the refractive indices of a portion which had been similarly treated were identical in all grains of the sample; when the sample which had been dried at 110° C. was allowed to stand over night in very humid air of a room, however, the resulting material was inhomogeneous in index, the smaller and very thin cleavage flakes retaining the high indices while thicker crystals gave varying lower indices, apparently proportional to the thickness, the very thickest plates being apparently nearly as low as the original undried sample. Throughout these several treatments of the samples the optical properties other than refractive index—the color and transparency under the microscope, the pleochroism, uniaxial negative character, and birefringence—remained essentially the same.

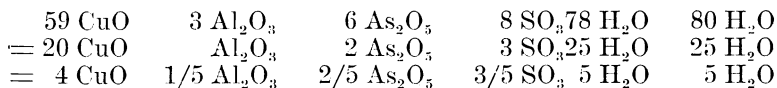
The marked variation in refractive index seems unquestionably to be directly connected with the variation in water content, this being the most definite and marked example of such a relation which has been described. The values for refractive indices of this mineral given in standard tables based upon museum specimens were determined without regard to the humidity and obviously do not represent constant values. It seems desirable, where optical methods are used to identify this mineral, when the state of hydration is not known, that

the material be desiccated over some drying agent before the refractive indices are measured.

The mineral was analyzed upon entirely fresh and unaltered material carefully selected by hand picking under a high power binocular microscope. The sample was examined optically and found homogeneous and pure except for the minor amount of quartz indicated by the analysis. Previous efforts to purify the material by the use of heavy solutions were unsuccessful, the mineral being quickly altered by contact with either methylene iodide or bromoform apparently by the formation of coatings of copper iodide and bromide respectively. The analysis gave the following results and ratios:

Constituent.	Per cent.	Ratios.		
Insol. (SiO ₂)	1.33			
CuO	46.54	.585	.146 × 4	1.01 × 4
Al ₂ O ₃	3.49	.034	.170 × 1/5	1.17 × 1/5
As ₂ O ₅	13.23	.057	.145 × 1	1.00 × 1
P ₂ O ₅67	.005		
SO ₃	6.67	.083		
H ₂ O + 110° C.	14.04	.779	.156 × 5	1.09 × 5
H ₂ O — 110° C.	14.40	.799	.159 × 5	1.10 × 5
	100.37			

The ratios yield no simple formula, but they may be simplified by the following reductions:



The result is complex but it seems the best that can be reached from the results of the analysis. Of the previously published analyses of chalcophyllite only one records the presence of the sulphate radical. This indicates either that the early analyses are exceedingly poor, that they were made upon materials of doubtful identity or that the sulphate is present in variable replacement of the arsenic acid. The analysis of Church, made on Cornish material, in 1870, is not widely different from these results so far as it goes, but water was determined by difference and sulphuric acid overlooked. The analysis

by Hartley,² which is the only thoroughly dependable modern analysis of chalcophyllite, was made on material from Cornwall and shows a remarkable agreement with the present writer's analysis on the material from Chile. Hartley suggested no formula, the ratios from his analysis being too complicated to yield any formula of probable relations. In the following table an interesting comparison is made between the analyses and the calculated composition:

	1	2	3	4
SiO ₂	1.33	3.00
CuO	46.54	48.15	45.93	48.24
Al ₂ O ₃	3.49	1.55	4.74	3.24
Fe ₂ O ₃	1.57
CaO10
MgO07
P ₂ O ₅67	.91
As ₂ O ₅	13.23	13.85	14.46	13.94
SO ₃	6.67	8.19	7.04	7.27
H ₂ O	28.44	undet.	28.26	27.31
	100.37	77.49	100.43	100.00

1. Analysis by the writer on material from Chile.
2. Analysis on a specimen from the same locality made by a chemist for Braden Copper Co. and furnished by Mr. James E. Harding.
3. Analysis by Hartley of chalcophyllite from Cornwall.
4. Composition to suit formula 4 CuO. 1/5 Al₂O₃, 2/5 As₂O₅, 3/5 SO₃, 10 H₂O.

Several slight changes may be made in the formula without, however, yielding any simpler result. The alumina is apparently essential, having been reported in all analyses, the apparent variation in its small amount doubtless being in part due to errors in determination such as incomplete precipitation or contamination with phosphoric acid. The water is apparently present in two states of combination, approximately one half being lost at 110° C. or in a desiccator over calcium chloride. The analyzed sample of the Chilean material reached constant weight at 110° C. with a loss of weight of 14.40 per cent, 14.26 per cent being lost the first hour. The material had

² Mineralogical Magazine, vol. 12, p. 120, 1898.

assumed an opaque bluish green color and pearly luster. Upon being allowed to stand for 64 hours over water the sample regained 13.40 per cent of water but still had the altered appearance. The balance (14.04 per cent) of the water is released somewhat below a red heat and apparently all in a single narrow temperature range. The amount of low temperature water apparently fluctuates directly with the water vapor pressure of the surrounding atmosphere. Drying out affects the physical properties, particularly the luster and transparency, and the change in appearance is permanent even when with increased humidity the water content approaches the maximum. At a full red heat the mineral is decomposed, probably with loss of arsenic acid.

The correspondence in composition between the Cornish and Chilean material is surprisingly close. It is desirable that further occurrences of this mineral be examined carefully, both optically and chemically, to throw additional light on the variation and chemical constitution of such an interesting and complex mineral.