

In summary, this would appear to be an unusual occurrence of pyrrhotite unmixing from chalcopyrite with no cubanite present. It might be noted in passing that a very careful study of crystal boundaries and of the crystallographic relationships between the different minerals present may be necessary before the origin of the veinlike masses may be determined.

The writer wishes to express his thanks to Professor W. H. Newhouse of the Department of Geology, Massachusetts Institute of Technology, for proposing the investigation and for valuable suggestions offered during its progress, and to the Geological Survey of Canada for permission to use the material collected while with them.

### STABILITY RELATIONS OF A COLORADO PISANITE (CUPRIAN MELANTERITE)

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Several specimens of pisanite, the isomorphous mixture of cupric and ferrous sulphates with 7 H<sub>2</sub>O, were collected in the Rico mining district in southwestern Colorado during the 1931 field season. Following Schaller's suggestion<sup>2</sup> the mineral should be called cuprian melanterite, as it contains more iron than copper. The rapid dehydration of the specimens after collection suggested a laboratory study of the relation between water content and humidity in this mineral. The results, which are recorded in this paper, have proved of considerable importance in the preservation of specimens and in the analytical determination of water of crystallization. The writer wishes to acknowledge his indebtedness to his colleague Mr. T. S. Lovering, for many valuable suggestions regarding the laboratory investigation, and to Mr. P. G. Nutting, also of the Geological Survey, for notes on the dehydration method adopted.

The cuprian melanterite was found only in one stope of the Wellington mine at Rico. It occurs as crusts on timbers or on the walls of a large body of pyrite which has almost completely re-

<sup>1</sup> Published by permission of the Director, U. S. Geological Survey, The Colorado State Geological Survey Board, and the Colorado Metal Mining Fund.

<sup>2</sup> Schaller, W. T., Adjectival ending of chemical elements used as modifiers to mineral names: *Am. Mineral.*, 15, pp. 566-574, 1930.

placed a bed of limestone. The pyrite body contains considerable galena and sphalerite and a little chalcopyrite as the ore minerals. The principal post-mining oxidation products other than cuprian melanterite are gypsum, chalcantite, and a yellow sticky mud composed of one or more hydrous ferric sulphates. The waters in this part of the Wellington mine contain noteworthy amounts of ferric sulphate, copper sulphate and free sulphuric acid.

The cuprian melanterite, which ranges in color from pale delicate green, tinged with blue, to a darker bluish green, does not differ appreciably in its optical and other physical characteristics from those recorded in the literature for the mineral. The refractive indices as determined by Mr. Charles Milton of the U. S. Geological Survey are:  $\alpha = 1.473$ ,  $\beta = 1.478$ ,  $\gamma = 1.483$ ; with  $\gamma - \alpha = .010$ .

The results of an approximate analysis by Dr. R. C. Wells of the Survey are given in table 1. The material when analyzed by him had adsorbed deliquescent water and part of the iron had oxidized. Later when the laboratory study outlined below had furnished means for closely controlling the water content, Mr. F. G. Hills of the Colorado School of Mines Experimental Plant kindly made a partial analysis of material known to contain the seven molecules of water required by the formula of the mineral. Unfortunately it was then impossible to obtain samples which had not undergone slight oxidation since collection.

TABLE 1

Cuprian melanterite (pisanite), Rico, Colo. Analysts: 1, R. C. Wells; 2, F. G. Hills		
	1	2
CuO	7.2	
FeO	18.0	16.98
Fe <sub>2</sub> O <sub>3</sub>	..	1.18
ZnO	1.3	} $\approx 18.04$ FeO
MgO	tr.	
SO <sub>3</sub>	28.6*	
H <sub>2</sub> O	45.0**	44.3
	100.0	

\* Calculated.

\*\* Calculated, and eliminating 3.8% excess water in material as weighed.

This corresponds approximately to the formula:  $2 [\text{FeSO}_4 \cdot 7\text{H}_2\text{O}]$   
 $[(\text{Cu}, \text{Zn})\text{SO}_4 \cdot 7\text{H}_2\text{O}]$ .

STABILITY RELATIONS

A laboratory study of the stability relations of the mineral was made in order to determine the humidity conditions under which it will remain stable. The results of that study lead to conclusions that seem important in any study of the hydrous sulphate minerals.

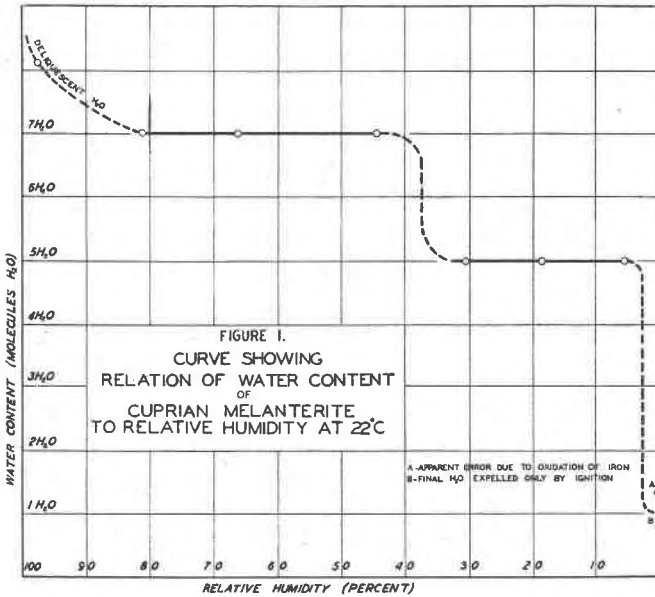
Briefly, the method of attack was to allow weighed samples to come to equilibrium in atmospheres of known humidity. The relative humidities over various concentrations of sulphuric acid were calculated from standard tables of chemical and physical constants and powdered samples of the mineral were placed in desiccators containing these solutions of acid. When the samples had come to equilibrium, as shown by the accordance of several daily weighings, they were then placed over acid corresponding to a slightly lower humidity. Abrupt changes in weight were found to

TABLE 2

H <sub>2</sub> SO <sub>4</sub> Solution	Sp. Gr. @ 22 deg. C.	Relative Humidity (%)*	Sample Weight grams	Loss in Weight	Remarks
1	1.040	97.8	See remarks		Increased in wt. and finally dissolved.
2	1.180	81.3	1.000	—	Blue green, corresponds to 7H <sub>2</sub> O.
3	1.260	66.6	0.998	—	No change.
4	1.357	44.6	0.998	—	No change.
5	1.425	30.7	0.865	0.135	Greenish white, loss of 2H <sub>2</sub> O to give pentahydrate.
6	1.490	18.7	0.865	—	No change.
7	1.598	5.3	0.865	—	No change.
8	1.835	near 0	0.646	0.354	Dark gray; loss of 4 more H <sub>2</sub> O to give monohydrate.

\* Relative humidity =  $\frac{\text{Partial pressure of water vapor in air over H}_2\text{SO}_4}{\text{Partial pressure of water vapor in air over H}_2\text{O}}$  @22°C.

occur at three points, the losses in weight corresponding closely to the removal of a definite number of molecules of water of crystallization. Six of the seven molecules of water were thus removed at a constant temperature of 22° C., but the seventh can be removed only at a much higher temperature. The experimental results are tabulated in Table 2 and shown graphically in Fig. 1.



As shown in Fig. 1 the broken curved lines do not represent a gradual loss of water over a considerable humidity range, and it seems probable that the changes shown occur at definite points corresponding to the vapor pressures of the several hydrates at 22° but at present the data are insufficient to allow the plotting of a sharper curve. The temperature varied within limits of about 5° C., but no weighings were made until the temperature had remained at approximately 22° for several hours.

The loss in weight over concentrated acid was slightly less than that which would correspond with the removal of six molecules of water. This apparent discrepancy is accounted for by the fact that part of the iron was oxidized during the process of desiccation, with consequent increase in weight. Mr. F. G. Hills found that approximately 25% of the iron in the dehydrated material was in the ferric

condition. Since reducing atmospheres are seldom found in nature it was not thought worthwhile to repeat the experiments under conditions which would prevent the oxidation of ferrous iron.

Several conclusions of interest to those charged with the analysis or preservation of specimens of the type described here may be drawn from the experimental results. Although the vapor pressures of the various hydrates of pure cupric or ferrous sulphates have been determined by a number of workers, no data for the equilibrium conditions of the mixed sulphates have been available heretofore. It is obvious that in order to preserve specimens of the type described above they must be kept in an atmosphere of between 50% and 80% relative humidity. U. S. Weather Bureau records show a surprisingly large daily variation in relative humidities, so that even though the average monthly or yearly humidity in any locality falls well within the limits specified, it is unwise to place much reliance on natural conditions for preservation of rare or valuable specimens. It would seem far better to place them in desiccators over some medium that would insure an atmosphere of the correct humidity over long periods of time. Sulphuric acid is easy to use and to control, but there is some danger of spillage, and evaporation of water will produce marked changes in humidity. The International Critical Tables<sup>3</sup> list a number of solids, whose saturated solutions in contact with the solid phase give close control of the humidity of the surrounding atmosphere.

Chemical analyses and determination of the optical properties of the hydrous sulphates would be of much more value were they made on samples in equilibrium with atmospheres whose relative humidity was known. Certainly no chemist who has occasion to work with such compounds can fail to recognize the value of analyzing material known to contain the "correct" number of molecules of water of crystallization. It is probable, too, that the tendency for ferrous iron to oxidize is stronger when the mineral is not in equilibrium with the atmosphere. Whether small differences in the amount of water of crystallization affect the optical properties of the sulphate minerals has not been determined, but the possibility of such effects is evident.

The geological importance of the relationship between water of crystallization and humidity is not yet entirely clear, but it seems probable that humidity controls in part the formation of the vari-

<sup>3</sup> International Critical Tables, Vol. I, pp. 67-68, *New York*, 1926.

ous species, as well as their stability after they are formed. A detailed study of the stability relations of the isomorphous series of copper, iron and zinc sulphates is now in progress, and the writer hopes to present data for the equilibrium relations of several members of the series at a later date.

## NOTES AND NEWS

### OCCURRENCE OF RUBIDIUM, GALLIUM AND THALLIUM IN LEPIDOLITE FROM PALA, CALIFORNIA

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Lepidolite from the Stewart mine at Pala, Calif., has been reported to contain about 0.3%  $\text{Cs}_2\text{O}$ .<sup>1</sup> Various lepidolites from this locality have been analyzed by Schaller, who, however, makes no mention of rubidium, cesium, gallium or thallium.<sup>2</sup> It is interesting to note that the element rubidium was originally discovered in a lepidolite from Saxony, by Bunsen.<sup>3</sup> Traces of gallium have been reported in lepidolite from San Bernardino County, Calif.<sup>4,5</sup>

A sample of grayish white lepidolite obtained from the Sickler mine at Pala was examined spectrographically, using an electric arc as the source of excitation of the spectra, which were photographed by means of a large Gaertner quartz spectrograph. Examination of the plate revealed spectral lines due to rubidium, cesium, gallium and thallium, as well as other elements. (Fig. 1.)

Rubidium chloride and cesium chloride were subsequently prepared from the lepidolite. The method in brief consisted of decomposing sintered lepidolite with sulphuric acid, concentrating the rubidium and cesium first as alums and then as chlorostannates. The rubidium and cesium were freed from potassium by fractionally recrystallizing as rubidium cesium chlorostannate, and were

<sup>1</sup> R. M. Santmyers, *Information Circular No. 6215*, U. S. Bureau of Mines, 1930.

<sup>2</sup> W. T. Schaller, *U. S. Geol. Surv., Bull.* **419**, p. 287.

<sup>3</sup> R. Bunsen, *Ber. Akad. Berlin*, 273, **1861**, *Chem. News*, **3**, 357, 1861; *Phil. Mag.*, [4], **22**, 55, 1861.

<sup>4</sup> J. Papish and D. A. Holt, *J. Phys. Chem.*, **32**, 142, 1928.

<sup>5</sup> Since submitting this article for publication, there has come to the author's attention an article by W. J. Schiefflen and T. W. Capon (*J. Soc. Chem. Ind.*, **27**, 549, 1908), in which it is stated that during the preparation of lithia from Pala lepidolite, rubidium and cesium alums were obtained in one stage of the process. Schiefflen and Capon do not state, however, that rubidium and cesium occurred in the lepidolite.