MARSHITE AND OTHER MINERALS FROM CHUQUICAMATA, CHILE

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A detailed account of the mineralogy and paragenesis of the copper deposit at Chuquicamata, in the arid Atacama Desert of north Chile, has recently been published by M. C. Bandy (1938). While Dr. Bandy was carrying out his investigation at Harvard University, the present writer was employed as a staff geologist at the mine. During that time and since the publication of Bandy's paper, several additional minerals have been found at Chuquicamata. Of these, salesite, a new mineral, has recently been described (Palache and Jarrell, 1939), and the present paper is intended to list the others, and thus make as complete as possible the description of the mineralogy of this remarkable deposit.

MARSHITE

CuI

Marshite, the natural cuprous iodide, was discovered by C. W. Marsh (1893) in the oxidized zone of the lead, zinc, and silver deposit at Broken Hill in the arid region of western New South Wales. Spencer and Prior (1901) published a complete description of the crystals from Broken Hill. Aminoff (1922) has investigated the crystal structure, and various other workers have prepared or studied synthetic material.

In 1937, some crystals intimately associated with atacamite were found at the south end of the oxidized ore body at Chuquicamata. Because of their color, isotropic nature, and high index of refraction, they were suspected of being marshite. Dr. Berman later confirmed this identification. Recently Mr. Lester Zeihen of the mine staff at Chuquicamata has sent additional specimens to Harvard University.

Crystallography. Marshite is isometric hextetrahedral. Professor Palache examined the crystals and found that the principal faces present are the cube (100) and tetrahedron (111), which, due to oscillation, give the crystals a striated appearance, as illustrated in Fig. 1. The zone between the cube and tetrahedron is rounded due to the effect of tristetrahedral faces. Several crystals were measured, one of which yielded definite signals from the two forms m(113) and $\beta(223)$, shown in Fig. 2. The striated zones gave weak reflections from other forms, none of which however is assured. Spencer (1901) has commented upon the similarity of the crystallography to that of sphalerite, and Aminoff (1922) has shown the crystal structure of the two minerals to be comparable.

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Physical properties. The crystals, which range up to several millimeters across, are transparent and have an adamantine luster. When first found, they are colorless or light honey-colored. Some of them were kept for about a year at Chuquicamata, and showed no sign of change. Recently, however, some of the crystals that had been kept in darkness at Cambridge, but not protected from the air, have become salmon to reddish colored, although otherwise remaining intact. At the same time other crystals, kept in glass-stoppered bottles, but exposed to light, have remained colorless; hence the change to a reddish color seems to be promoted by contact with humid air, rather than by exposure to light.*



FIG. 1. Marshite.

FIG. 2. Marshite.

The streak of the Chuquicamata material is only faint yellow as contrasted with the bright yellow streak that Spencer (1901) considered so striking.

Mr. Zeihen first reported that marshite was fluorescent. The color under the ultraviolet light is dark red.

The average of several determinations of the density on the microbalance gave a value of 5.68. The density calculated from Aminoff's dimensions for the unit cell is 5.60.

A small prism was cut and polished on one of the crystals, and the indices of refraction, shown in Fig. 3, for various wave lengths were determined on the one-circle goniometer by the minimum deviation method with a monochromatic illuminator. The indices are slightly lower than those obtained by Spencer on the Broken Hill material, but this small discrepancy is perhaps explained by the slight difference in chemical composition of the marshite from the two localities. The exceedingly high dispersion, exceeding that of diamond, is noteworthy.

* It has been suggested that the reddish discoloration may be due to a chemical reaction with the enclosing paper. This has not, as yet, been verified.



FIG. 3

Chemical composition. The analyses of the Broken Hill and Chuquicamata material, together with the ideal composition of CuI, are given below.

COMPOSITION OF MARSHITE

	1	2	3
Cu	33.01%	32.35	33.37
I	66.67	65.85	66.63
Ag	None	1.19	
C1	0.33	_	
	100.01	99.39	100.00

1. Marshite from Chuquicamata, Chile. F. A. Gonyer, analyst.

2. Marshite from Broken Hill, N.S.W. G. T. Prior, analyst (1902).

3. Ideal composition of CuI.

For the analysis of the marshite from Chuquicamata, it was necessary to eliminate numerous tiny crystals of atacamite. This was done with the electromagnet, and before the analysis was made the sample was estimated to contain less than 1% atacamite. The amount of chlorine present in the analysis would demand about 5% of atacamite. In addition, the presence of such a large quantity of atacamite would require more copper and less iodine than the analysis shows, while in its present form the Cu-I ratio of the analysis agrees well with the ideal composition of CuI. It therefore seems best to consider most of the chlorine of the Chuquicamata material to be present in the mineral itself, and not due to mechanically admixed atacamite.

Upon heating in the closed tube, purple fumes of iodine are given off, which condense higher up the tube as purple crystals of iodine.

Occurrence. All the specimens come from the south end of the open pit, within 12 to 24 meters of the original surface. The marshite, with atacamite, lines fractures in the sericitized and kaolinized granodiorite. In this section of the mine, antlerite, otherwise the principal oxidized copper mineral at Chuquicamata, is not stable.

The marshite crystals penetrate the atacamite and perch upon it. Probably the deposition of the minerals was essentially contemporaneous, although some of the atacamite formed after the marshite. The atacamite does not contain any appreciable amount of iodine, for its indices of refraction are normal, and no iodine is given off during heating in a closed tube.

It is interesting to note that on several occasions after blasting operations, small clouds of purplish smoke, which was shown to contain iodine, have been observed at Chuquicamata. Examination of the rock from which this gas came revealed no visible marshite or salesite. Dieseldorf (1899) has shown that several copper deposits in the arid portion of New South Wales similarly contain small quantities of iodine, although it is not present in sufficient quantities for its mineralogical nature to be recognized.

Olivenite

$Cu_3As_2O_8 \cdot Cu(OH)_2$

At rare intervals specimens of olivenite have been found at Chuquicamata. Excellent crystals were measured by Professor Palache and yielded the forms m(110), v(101) and e(011), shown in Fig. 4. The following optical properties were measured on specimens sent by Mr. Zeihen:

$\alpha = 1.780$	Biaxial positive
$\beta = 1.820$	2V near 90°
$\gamma = 1.865$	r < v, strong

Olivenite, when found here, has always been as small crystals embedded in porous aggregates of a green arsenate, which approximates chenevixite in composition. Occasionally small amounts of an unidentified blue arsenate (?) are also present. In previous descriptions of Chuquicamata, arsenates are stated to be relatively rare in the oxidized ore. Actually chenevixite is a common mineral in the center of the pit, and is occasionally found elsewhere. Specimens of it and the other arsenates that still contain remnants of enargite show that, where primary enargite is exposed to oxidation, copper arsenates will form in situ.



FIG. 4. Olivenite.

 $\begin{array}{c} \text{Libethenite} \\ \text{Cu}_3\text{P}_2\text{O}_8\cdot\text{Cu(OH)}_2 \end{array}$

A few specimens of dark olive-green crystals of libethenite perched on white, extremely kaolinized granodiorite were found on the west side of Bench E-4. This immediate area of kaolinized granodiorite contains sufficient copper to be classified as ore, although most of the rock in the vicinity is iron stained and barren of copper. Professor Palache first recognized the identity of the crystals by crystallographic measurements. The crystals show a combination of unit prism m(110) and unit pyramid s(111) about in the proportions of Fig. 5. The measurements are very close to those of crystals from the older known localities:

	No. of	Mean meas	ured angles	Calcu	ulated
	faces	φ	ρ	Φ	ρ
{110}	3	46°13′	90°00′	46°10′	90°00′
{111}	4	46 16	45 24	46 10	45 23

These crystals are apparently the first to be described on which there is no trace of the dome e(011), usually more prominent than the pyramid.

The optical properties of the crystals, which agree well with previously described material are:



FIG. 5. Libethenite.

With the exception of turquoise, libethenite is the only phosphate so far found in the oxidized ore. Its rare occurrence can only be regarded as exceptional, and it cannot be fitted into any general paragenetic sequence for the deposit.

Darapskite NaNO₃· Na₂SO₄· H₂O

Wetzel (1928) briefly noted that darapskite occurred at Chuquicamata. Actually it is a common mineral in certain zones within a few meters of the surface.

The following distinctive optical properties make it easily recognizable in aggregates with other minerals:

$\alpha = 1.390$	Biaxial negative
$\beta = 1.481$	$2V = \pm 25^{\circ}$
$\gamma = 1.488$	r > v, strong

The material available proved to be too intimately admixed with other minerals to permit of separating a pure sample for analysis.

MARSHITE FROM CHILE

Darapskite is found chiefly in veins up to six inches wide, intimately mixed with kroehnkite and bloedite. Good crystals have not been found. In some cases mirabilite or epsomite are also present in these veins. Both of the latter minerals are crystalline, colorless, and glassy when first broken out from the rock, but even in that dry air they break down to a white powder within a few minutes. Shellac or varnish are of little use in halting this process.

The presence, on the hillside approximately 2000 feet above the floor of the Calama Basin, of nitrate and iodine, both characteristic of the nitrate deposits in the basins of the Atacama desert, is of interest in connection with the origin of these deposits. After the sulphate radical, nitrate is the most abundant acid constituent of the groundwater at Chuquicamata.

WULFENITE

$PbMoO_4$

Mr. Zeihen recently recognized wulfenite in specimens from the north end of Bench E-4. It is found in dark gray masses, distinctive because of their adamantine luster, and associated with fine-grained antlerite. The optical properties are:

uniaxial negative $\epsilon = 2.30 \pm 0.02$ $\omega = 2.38 \pm 0.02$

Wet tests for molybdenum were also obtained.

These specimens came from what has been recognized as an area of primary molybdenite mineralization, in which most of the molybdenum was retained as lindgrenite during oxidation. Minor amounts of galena have also been recognized in polished sections of the ore.

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