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## HYDROUS SULPHATES FORMED UNDER FUMEROLIC CONDITIONS AT THE UNITED VERDE MINE<sup>1</sup>

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### INTRODUCTION

The minerals described in this paper are the result of a fire that has been burning in the mine of the United Verde Copper Company, at Jerome, for a number of years. According to Robert E. Tally<sup>3</sup> the first fire started in the fall of 1894, on the 300 ft. level, and was the result of a cave in the Hampton ore body. Much of the ore contains abundant pyrite, and the specific gravity of this mineral is high. The collapse of this stope, together with the consequent friction produced by the fragments of ore in settling, may have raised the temperature of the mass several degrees; but, undoubtedly, spontaneous combustion was a more important factor in starting the fire. In recent years stripping operations with steam shovels have exposed the still hot rocks impregnated with these minerals.

These sulphates, therefore, have formed so recently, some within a few months, that one might justly question the propriety of calling them minerals; but as they are the result of natural processes it is certainly just as reasonable to consider them as minerals as are those that are now forming around hot springs.

### ACKNOWLEDGMENTS

The writer is under obligations to Mr. Robert E. Tally, General Manager of the United Verde Copper Company for permission to publish the results of this investigation; and to Dr. F. N. Guild, Professor of Optical Mineralogy at the University of Arizona for considerable help with the crystal measurements and the determination of the optical properties. The analyses of the minerals were

<sup>1</sup> Published by permission of the Director of the Arizona Bureau of Mines.

<sup>2</sup> Field geologist, United Verde Copper Company.

<sup>3</sup> Tally, Robert E., Mine-fire methods employed by the United Verde Copper Co. *Trans. Am. Inst. Min. Eng.*, vol. 55, pp. 186-202, 1917.

made by Dr. T. F. Buehrer, Professor of Analytical Chemistry at the University of Arizona. Mr. E. D. Gardner, Supt. of the Southwestern Station of the U. S. Bureau of Mines kindly furnished the writer with the analyses of gases collected by himself and Mr. G. W. Jones.

#### GENERAL GEOLOGY

A brief description of the general geology and character of the ores in this mine, undoubtedly will be a help to the reader better to understand the nature of the burning material as well as the condition under which the minerals have been formed.

The ore at the United Verde Mine occurs along the edges and partly within a pyritic chimney which pitches to the northwest at a steep angle. An intrusion of diorite forms the northwest wall and appears to have localized the mineral-bearing solutions as the pyritic mass occupies an embayment in this diorite. To the south and east are schistose greenstones with more or less recrystallized sedimentary material, and these rocks have been invaded by an intrusion of rhyolite porphyry which is now also quite schistose. These rocks, as well as the ores, are pre-Cambrian in age.

Massive pyrite is the most abundant constituent of this chimney, and ore bodies in this mine often contain as much as 30 or 40 per cent of sulphur. This pyrite is fine-grained, and is intimately intergrown with quartz, together with small amounts of chalcopyrite, sphalerite, and arsenopyrite. Another type of ore is found in black schist consisting very largely of a dark green chlorite and in it the pyrite and chalcopyrite occur as irregular bands. Such ore rarely contains over 25 per cent sulphur. The copper in these ores is almost entirely in the mineral chalcopyrite although lesser amounts of tennantite and bornite are present. A little galena has also been found.

Certain portions of this pyritic chimney, especially near the diorite contact, contain irregular masses of fine-grained quartz which are locally known as jasper. Much of this quartz is white to light gray in color, but some is red or brown due to iron oxides. This quartz is thoroughly shattered and traversed by numerous cracks. Here, the sulphates developed from the burning area are most abundant, although some occur along cracks in the massive pyrite.

## METHODS USED TO EXTINGUISH FIRES

According to Tally<sup>4</sup> various methods were tried to extinguish the fires. The fire areas were first flooded with water, but this procedure was not a success. Carbon dioxide was used and then steam; all however, were unsuccessful. The Plenum system was then tried and found to be effective. This consists of forcing air under a pressure of from 2 to 5 lbs. into the fire district. This air not only forced back the hot gases but also cooled the adjacent rocks. Tally<sup>5</sup> states that when the bulkheads were first opened, the ground was red hot, and the air forced in such an area reduced the temperature from 1200°F. (650°C.) to 120°F. (65°C.) in six weeks.

Many of the hydrous sulphates were probably formed when water was first used to put out the fires. Conditions, however, must have varied from time to time, as the various sulphates are not mutually intergrown, but rather occur as crystals of one composition resting on those of another.

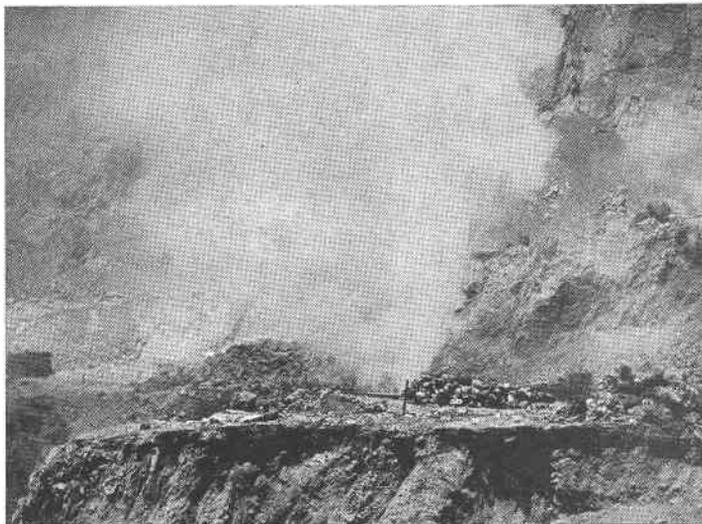


FIG. 1.

<sup>4</sup> *Op. cit.*, p. 187.

<sup>5</sup> *Op. cit.*, pp. 188-189.

## FIRE GASES

Considerable smoke was issuing from cracks and churn drill holes in the floor of the pit at the time these minerals were collected. Sulphur vapors rising from one of the drill holes is shown in the illustration as Fig. 1. During the latter part of 1924, five samples of these gases were collected by E. D. Gardner and G. W. Jones of the U. S. Bureau of Mines.

TABLE I  
ANALYSES OF GASES FROM THE STEAM SHOVEL PIT, UNITED VERDE MINE<sup>6</sup>

No.	Source of Sample	CO <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CH <sub>4</sub>	SO <sub>2</sub>	H <sub>2</sub> S	N <sub>2</sub>
1	From cracks in ground at bottom of pit	1.83	16.04	0.02	0.10	0.01	1.30	0.00	80.78
2	" " " "	4.67	11.78	0.07	0.14	0.06	1.75	—	81.53
3	" " " "	0.37	20.20	0.01	0.02	0.00	0.19	—	79.21
4	Horizontal pipe from churn drill hole	1.84	7.20	0.02	0.19	0.01	5.80	0.00	84.94
5	Vertical pipe in churn drill hole	0.94	12.49	0.01	0.10	0.00	5.90	—	80.56

The most interesting feature of these analyses is the high content of nitrogen and oxygen, and suggests a considerable admixture of air. As the ground is somewhat broken and cracked by mining operations it is difficult to collect a sample that is not contaminated with atmospheric gases. Thus, in sample number 3, the nitrogen and oxygen total over 99 per cent, and this sample is, therefore, almost entirely air. In only two samples, numbers 4 and 5, does the sulphur dioxide approach 6 per cent. Parts of the fire are in areas of stoped ground containing abundant mine timbers, and the gases of sample number 2 are probably from such an area as the carbon dioxide content is 4.67 per cent.

Large metal hoods were placed over some of the vents from which a large volume of gas was issuing, as a protection to the workmen in the pit. Later, when the interior of these hoods were examined, it was found that the sides of the hood as well as fragments of rock on the ground were coated with a thin film,

<sup>6</sup> Analyses by G. W. Jones, Pittsburgh Station, U. S. Bureau of Mines.

often as globules, of a shiny, dark substance. A chemical examination of this mineral shows it to be a mixture of arsenic and sulphur. A more complete description of this mineral will be found on another page.

As this dark mineral is now being deposited, it is hardly likely the hydrous sulphates described in this paper were formed from gases closely approximating in composition those given above. These sulphates were probably all formed when water was first used to extinguish the fire and the mine flooded. The gases then must have contained a large percentage of water vapor which reacted with the sulphides of iron and copper and carried these constituents to higher levels where the hydrous sulphates were deposited. It is impossible for these sulphates to have been deposited from solutions. These gases carried, in addition to water vapor and sulphur trioxide, small amounts of ferrous and ferric iron, aluminum, copper, sodium, and, at times, potassium. These metallic elements cannot have been deposited from solutions, but on the contrary were carried as gases; however, it is not definitely known whether they were transported as oxides or as molecules having the composition of the mineral as deposited.

TABLE II.  
ANALYSES OF HYDROUS SULPHATES

	1	2	3	4	5	6	7	8	9
H <sub>2</sub> O	45.28	31.03	22.83	31.33	22.15	31.72	18.82	20.64	16.13
SO <sub>3</sub>	37.84	38.45	38.63	39.34	39.68	44.05	46.30	47.90	47.83
Fe <sub>2</sub> O <sub>3</sub>	0.52	27.12	36.31	20.84	19.12	14.69	22.57	28.07	14.34
Al <sub>2</sub> O <sub>3</sub>	13.48	nil?	0.55	2.55	2.11	6.93	1.52	1.41	6.06
CuO	nil	2.26	nil	nil	15.78	nil	11.29	nil	—
FeO	nil	0.38	0.41	7.01	1.49	nil	nil	nil	8.82
MgO	nil	nil	nil	nil	nil	nil	nil	nil	1.55
CaO	0.19	nil	nil	nil	nil	nil	nil	nil	—
K <sub>2</sub> O	nil	0.24	nil	nil	nil	nil	nil	0.06	4.52
Na <sub>2</sub> O	2.06	1.74	2.73	0.88	1.23	2.13	nil	1.23	—
Total	99.37	101.22	101.46	101.95	101.56	99.52	100.50	99.30	99.25

- |              |                  |              |
|--------------|------------------|--------------|
| 1. Alunogen  | 4. Louderbackite | 7. Ransomite |
| 2. Copiapite | 5. Guildite      | 8. Rogersite |
| 3. Butlerite | 6. Coquimbite    | 9. Voltaite  |

Analyses 1 to 8 inclusive by Dr. T. F. Buehrer.

Analysis 9 by Mr. Chas. Anderson.<sup>7</sup>

<sup>7</sup> Anderson, Chas., Voltaite from Jerome, Ariz., *Am. Mineral.*, vol. 12, p. 288, 1927.

These analyses have been arranged according to the increasing per cent of sulphur trioxide. On the basis of this constituent they may be divided into two groups; the first five are over 37 per cent and under 40 per cent while the remaining four are between 44 per cent and 48 per cent of sulphur trioxide. If the water content is used as a basis for separation into groups three stand out clearly; the first group comprises analyses 3, 5, 7, 8, and 9 and in these the water varies between 16 and 23 per cent. In group two, which includes analyses 2, 4, and 6 the water is close to 31 per cent; while the third group contains only analysis 1 with the exceptionally high water content of over 45 per cent.

In most of these minerals the ferric iron, although variable in the different minerals, is the most important metallic element; however, alunogen, analysis 1, is a straight, hydrous sulphate of alumina with only a small amount of ferric oxide. Most of these minerals are, therefore, essentially hydrous, ferric sulphates.

Of the bivalent elements copper is present as a part of the molecular constitution in guildite, analysis 5, and ransomite, analysis 7; but in copiapite the amount is only a little over two per cent, and here it is, most likely, an impurity. Ferrous iron enters into the composition of louderbackite and voltaite, while magnesia was noted only in the latter mineral. The lime in the alunogen is certainly present as an impurity.

Univalent elements found are potassium and sodium. Potash is present in three of the minerals, but only in the voltaite is it important; in the other two analyses in which it is shown, it is very likely an impurity. The persistent, though small amount of soda in nearly all these analyses is quite puzzling. To consider it as entering into the molecular composition would make the formula for some of these minerals extremely complex. In just what form the soda is present is unknown. If as an impurity, most likely as the hydrous sulphate; for it does not enter into the composition of alunogen, copiapite, and coquimbite, although present in all three of these minerals.

Extreme care was used in selecting material for these analyses. Some of the sample of each of the minerals was crushed and examined microscopically to ascertain the presence or absence of visible impurities. In louderbackite, analysis 7, a little pyrite was noted, and this was found difficult to eliminate; but as the mineral

was simply dissolved in water no pyrite should go in solution. For this reason the ferrous iron in louderbackite is believed to be a part of the molecule.

All these sulphates are soluble in cold water; some more so than others, but in boiling water they dissolve quickly. Coquimbite is the least soluble of the group. Many of them hydrolize on dissolving and give rise to a brown precipitate of ferric hydroxide.

Some of these minerals are normal salts; others are basic or acid salts. Specimens of voltaite appear to liberate sulphuric acid readily, for the paper wrapping soon turns brown, becomes brittle, and is acid to the taste. The others, apparently, appear to be perfectly stable in the dry air of the southwest.

#### DESCRIPTION OF MINERALS

The study of this group of sulphates shows four of them to be species previously known and catalogued, while five of them are new to science. Some of them occur as beautiful crystals, nearly symmetrical in their development, though minute in size. As these are all water soluble sulphates etched faces are common and they give a poor signal, but this etching, in part at least, was probably due to hot vapors that also deposited minerals of a later stage. It was, therefore, necessary to measure a number of crystals of each mineral to determine accurately  $\phi$  and  $\rho$ , and also to find all possible forms existing.

The drawings of the various crystals have been somewhat idealized, chiefly to avoid increasing the number of text figures, and yet to bring out the symmetry and to show all the forms observed.

In the succeeding pages the sulphates will be described in alphabetical order followed by a description of a sulphur and arsenic compound.

#### ALUNOGEN

Alunogen occurs as a crust of variable thickness suggesting that it more or less filled the cracks in which it was deposited. One piece collected was more than an inch in thickness, and, apparently, did not entirely fill the fissure in which it was deposited as the terminal faces of the crystals project beyond this edge. In none of the specimens, however, were these crystals present as single individuals large enough to be mounted and measured. They are always

intergrown, and it was found impossible to orient them on a goniometer. Crystallization was transverse to the walls of the fissure.

On breaking a specimen the color of the mineral is white and rather chalky in texture, but on examination with a hand lens the thin crystal flakes on the edge of the specimen invariably appeared to be colorless. At first this chalky appearance was thought to be due to alteration, perhaps a slight dehydration due to the rather dry climate of Arizona, but a microscopic examination of crushed fragments of this apparently opaque material showed them to be perfectly clear and colorless. The luster is pearly, especially of the thin, crystal flakes on the edge of the specimens, and to a lesser extent throughout the crystalline mass, but on a fracture surface it is vitreous.

Dana<sup>8</sup> gives the crystallization as monoclinic. The habit of this mineral from the Jerome locality is apparently as thin tabular crystals parallel to the clinopinacoid and elongated in the direction of the *c* axis.

One direction of cleavage is highly perfect; and, as a microscopic examination of these cleavage fragments always shows an extinction angle, this cleavage appears to be parallel to the clinopinacoid (010). A second direction of cleavage, somewhat imperfect, and at right angles to the first, may be parallel to the orthopinacoid (100). The fracture is conchoidal.

The specific gravity of this mineral was determined with the Westphal balance using methylene iodide and benzene as liquids. This method gave 1.785 as the specific gravity. This mineral is just slightly softer than gypsum and the hardness is, therefore, between 1.5 and 2.0. It is rather brittle and breaks into long, slender, cleavage fragments.

Indices of refraction were determined by using immersion liquids which were checked on an Abbé refractometer. These indices are likely to be in error as much as five points in the third decimal place. The results gave  $\alpha = 1.472$ ,  $\beta = 1.479$ ,  $\gamma = 1.482$ . The birefringence is 0.01. Optically, the mineral is positive. The extinction angle  $Z$  to *c* is approximately 40°.

A chemical analysis shows the mineral to be essentially a hydrated sulphate of alumina, and is a normal salt.

<sup>8</sup> Dana, E. S., A system of mineralogy, p. 958.

## ANALYSIS OF ALUNOGEN

	Percentages	Ratios		
H <sub>2</sub> O	45.28	2.516	2.516	18.64
SO <sub>3</sub>	37.84	0.473	0.473	3.50
Fe <sub>2</sub> O <sub>3</sub>	0.52	0.003	} 0.135	1.00
Al <sub>2</sub> O <sub>3</sub>	13.48	0.132		
CaO	0.19	—		
Na <sub>2</sub> O	2.06	0.033		
Total	99.37			

The most striking feature of this analysis is the high water content. Together the water and sulphur trioxide total over 83 per cent. By comparison with the other sulphates described in this paper alunogen differs chiefly in the high percentage of alumina and the low ferric oxide content, while the reverse is true of the other sulphates. The small amount of lime shown in the analysis is undoubtedly present as an impurity. This is also essentially true of the soda; for, if the soda were an essential part of the molecular constitution, the formula would be quite complex. Calculating the molecular ratios and considering the combined alumina and ferric oxide as unity, the formula for the alunogen from Jerome corresponds fairly closely with that given by Dana, namely:  $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 18\text{H}_2\text{O}$ . The ratios would be even closer if a small amount of water and sulphur trioxide were deducted to satisfy the lime present in the analysis. This lime is probably present as the hydrous sulphate, gypsum.

## BUTLERITE (NEW MINERAL)

This new mineral was found coating fragments of rock used in stope filling; and, as a cement very effectively binds these fragments together. Often, especially where the coating is thin, orange-colored crystals abound. In one specimen butlerite was found associated with copiapite, and appeared to have been formed somewhat later.

The individual crystals are seldom as much as a millimeter in length, and much less in width. Examined with a hand lens they appeared to belong to the tetragonal system, bipyramidal class, but measurements on a goniometer show them to be orthorhombic in crystallization. The crystal terminates in a sharp edge where the two dome faces  $r(101)$  come together. Only three forms were observed on this mineral; the pyramid  $o(111)$ ; the two orthodomies,

$r(101)$  and  $s(302)$ . The first two forms were observed on all the crystals measured, but the face  $s$  is rare. No trace was seen of the pinacoids or prisms. Several minute faces were noted near the edges and measurements show  $\rho$  to vary on these faces from  $78^\circ 15'$  to  $85^\circ 10'$ . They are never in the proper position to correspond with a prism or pinacoid and are therefore ignored. In general, all the reflections obtained on these crystals were good.

TABLE III.  
CRYSTALLOGRAPHIC ELEMENTS OF BUTLERITE.

Letter	Symbols		$\phi$ angle	$\rho$ angle
	Miller	Gdt.		
$o$	(111)	1	$47^\circ 46'$	$63^\circ 43'$
$r$	(101)	10	$90^\circ 00'$	$56^\circ 42'$
$s$	(302)	$\frac{3}{2}0$	$90^\circ 00'$	$66^\circ 45'$

Axial ratios  $a:b:c=0.9005:1:1.3606$ .

Crystallization is orthorhombic, and a drawing of this crystal is shown as Fig. 2.

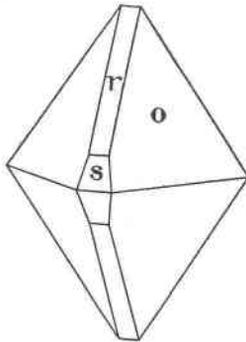


FIG. 2. Drawing of a crystal of Butlerite.

Butlerite is of a deep orange color and corresponds to OR-O, 9'-k in Ridgway's Color Standards and Nomenclature. Thin films are more nearly a pale yellow-orange. The streak is faint yellow.

One direction of cleavage is perfect and this is apparently parallel to the  $b$  pinacoid; the other is imperfect and also pinacoidal. The luster on a fracture surface is vitreous. Hardness about 2.5,

and the specific gravity as determined with the Westphal balance was found to be 2.548.

Optically, butlerite is negative. The indices of refraction as determined with immersion liquids checked on the Abbé refractometer are:  $\alpha=1.604$ ;  $\beta=1.674$ ;  $\gamma=1.731$ . These are probably slightly in error in the third decimal place. The mineral is slightly pleochroic;  $X$  = pale brownish yellow,  $Z$  = pale canary yellow. The birefringence is moderately high.

ANALYSIS OF BUTLERITE			
	PERCENTAGES	RATIOS	
H <sub>2</sub> O	22.83	1.270	5.47
SO <sub>3</sub>	38.63	0.483	2.08
Fe <sub>2</sub> O <sub>3</sub>	36.31	0.227	}0.232
Al <sub>2</sub> O <sub>3</sub>	0.55	0.005	
FeO	0.41	0.006	1.00
Na <sub>2</sub> O	2.73	0.044	
	101.46		

As shown by the analysis above, butlerite is essentially a hydrous sulphate of ferric iron. The soda, although present to nearly 3 per cent, is probably an impurity; and so is the ferrous iron. Combining the ferric iron and alumina, and taking this molecular ratio as unity, the formula for butlerite is, (Fe, Al)<sub>2</sub>O<sub>3</sub> · 2SO<sub>3</sub> · 5H<sub>2</sub>O.

The ratio would be even closer to this formula if a small amount of water and sulphur trioxide were deducted to satisfy the soda present in the analysis.

This mineral is named in honor of Dr. G. M. Butler, Dean of the College of Mines and Engineering, University of Arizona.

An artificial sulphate having the composition of butlerite was prepared by Posnjak and Merwin.<sup>9</sup> On analysis this salt was found to contain: Fe<sub>2</sub>O<sub>3</sub> 38.50 per cent; SO<sub>3</sub> 39.13 per cent; H<sub>2</sub>O 22.07 per cent (by difference); and corresponds closely with the analysis of butlerite given above. They found the indices of refraction to be:  $\alpha=1.588$ ;  $\beta=1.678$ ;  $\gamma=1.749$ ; and these are nearly the same as determined for butlerite by the writer. However, the salt prepared by Posnjak and Merwin is monoclinic in crystallization, and is stable in solutions only below 100°. It is possible that butlerite was formed at higher temperatures by vapors, and this may account for the difference in crystallization.

<sup>9</sup> Posnjak, E., and Merwin, H. E., The system Fe<sub>2</sub>O<sub>3</sub>—SO<sub>3</sub>—H<sub>2</sub>O: *Jour. Am. Chem. Soc.*, vol. 44, pp. 1978–1979, 1922.

As shown by the gnomonic projection, butlerite is clearly orthorhombic.

#### COPIAPITE

Copiapite associated with coquimbite was found as an alteration product of voltaite at Jerome by Chas. Anderson.<sup>10</sup> The copiapite collected by the writer does not appear to be an alteration product, but was deposited as such along fissures in the rock. One specimen obtained consists of a crust nearly a centimeter in thickness coating hematite and limonite; and here the mineral is massive. Copiapite was found also as an aggregate of minute, thin crystalline plates, hexagonal in outline, and occupying cavities in granular pyrite associated with louderbackite. Small, rounded grains occur embedded in rogersite; and thin, bladed crystals several millimeters in length occur with butlerite.

The habit commonly observed on copiapite from this locality is as thin, pseudo-hexagonal plates parallel to  $a(100)$ . Microscopic examination of these flakes shows the pinacoid  $a(100)$ , the base  $c(001)$  and a clinodome. The prismatic crystals are elongated parallel to  $c$  and flattened parallel to  $b(010)$ . Terminal faces are absent, and they were probably destroyed by the vapors that deposited the butlerite. These two habits are shown as Figs. 3a and 3b. The crystallization is monoclinic.

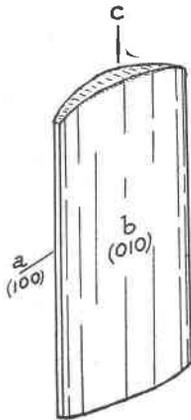


FIG. 3a

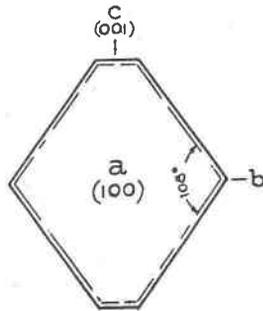


FIG. 3b

FIG. 3a. Copiapite elongated parallel to  $c$  axis

FIG. 3b. Copiapite as flat pseudo-hexagonal plates parallel to  $a(100)$

<sup>10</sup> *Op. cit.*

Color is variable; in the thicker, prismatic crystals it is a deep, honey yellow; and the massive variety and the small flakes are citron. Cleavage parallel to  $b(010)$  is perfect; to  $a(100)$  imperfect. The fracture is conchoidal, and the luster vitreous in the smaller flakes to oily in the thicker crystals. The mineral is translucent. Specific gravity 2.092.

The mineral is biaxial. Indices of refraction, all  $\pm 0.005$ , determined with oils are:  $\alpha = 1.525$ ;  $\beta = 1.540$ ;  $\gamma = 1.595$ . The mineral is pleochroic with  $X =$  canary yellow;  $Y =$  colorless;  $Z =$  greenish yellow.

ANALYSIS OF COPIAPITE

	PERCENTAGES	RATIOS	
H <sub>2</sub> O	31.03	1.724	10.20
SO <sub>3</sub>	38.45	0.481	2.84
Fe <sub>2</sub> O <sub>3</sub>	27.12	0.169	1.00
CuO	2.26	0.028	Probably Impurities
FeO	0.38	0.005	
K <sub>2</sub> O	0.24	0.002	
Na <sub>2</sub> O	1.74	0.028	
	<hr/> 101.22		

Copiapite is essentially a hydrous sulphate of ferric iron; and, therefore, the copper, ferrous iron, potash, and soda are probably present as impurities. These impurities must be present as soluble sulphates. The molecular ratios given above are nearly 1:3:10, but if some sulphate and water is deducted to satisfy the constituents present as impurities, the ratios more nearly approach those given for copiapite by Dana, namely,  $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 18\text{H}_2\text{O}$ .

The physical properties also correspond with those given for copiapite.

COQUIMBITE

This is a well known species of ferric sulphate, and its occurrence as an alteration product of voltaite from Jerome was first described by Anderson<sup>11</sup> in an article published in this Journal. The material collected by the writer, however, is not an alteration product, and appears to have been deposited as coquimbite.

Coquimbite occurs as a crystal-studded lining on cavities in the broken rock. A freshly broken surface sparkles beautifully in the sunlight due to the large number of perfectly smooth crystal faces.

<sup>11</sup> *Op. cit.*

Generally, these crystals are attached to the wall rock by a prism face, but sometimes they are set on the base and then a complete array of small, first and second order pyramidal faces may be observed surrounding the base. The mineral was also found surrounding fragments of charred wood, and then it was beautifully banded in different shades of light gray.

This mineral was found associated with guildite in some specimens and with voltaite in others. It appears to have been formed earlier than guildite and after the voltaite was deposited.

The crystallization is trigonal, and the habit is in thin plates parallel to the base. The larger crystals are thicker and often quite symmetrical. In all, five different forms were noted, and these were found on all the crystals measured. Many of the crystals, especially where they are intergrown, show only the pyramid  $d(11\bar{2}2)$  with the first and second order prisms and base. On one crystal only the base and one prism were observed. Fig. 4 shows all the forms observed on a single crystal, and the drawing is only slightly idealized.

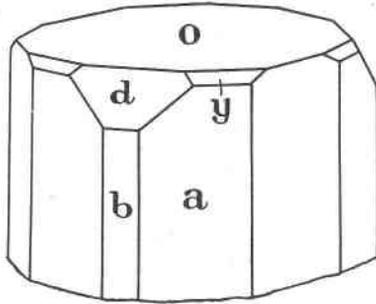


FIG. 4. Drawing of a crystal of Coquimbite from Jerome.

TABLE IV.  
CRYSTALLOGRAPHIC ELEMENTS OF COQUIMBITE

Letter	Symbols		$\phi$ angle	$\rho$ angle
	Bravais	Gdt.		
<i>o</i>	(0001)	0		0° 00'
<i>d</i>	(11 $\bar{2}$ 2)	$\frac{1}{2}$	30° 00'	58° 28'
<i>y</i>	(10 $\bar{1}$ 2)	$\frac{1}{2}$ 0	0° 00'	44° 17'
<i>b</i>	(01 $\bar{2}$ 0)	$\infty$	30° 00'	90° 00'
<i>a</i>	(10 $\bar{1}$ 0)	$\infty$ 0	0° 00'	90° 00'

These results would give an axial ratio considerably higher than that published by Dana or Goldschmidt, but the values for the various forms are sufficiently close to establish the species beyond any doubt. This is especially true when compared with the results of a chemical analysis.

The base and prism faces gave good, clear signals, but unfortunately, this was only occasionally true of the pyramidal faces.

Coquimbite from Jerome is colorless and beautifully transparent. In the larger crystals the mineral has a faint lavender tint. This is the least soluble of all the sulphates found at this locality, but readily dissolves in boiling water. The mineral has perfect prismatic cleavage, and on a fracture surface the luster is vitreous. Hardness 2.5 to 3. Specific gravity 2.066.

It is uniaxial and optically positive. Indices of refraction determined with oils are  $\epsilon = 1.572$ ;  $\omega = 1.536$  and are probably slightly in error in the third decimal place. The birefringence is moderate.

ANALYSIS OF COQUIMBITE			
	PERCENTAGES	RATIOS	
H <sub>2</sub> O	31.72	1.762	22.02
SO <sub>3</sub>	44.05	0.551	6.89
Fe <sub>2</sub> O <sub>3</sub>	14.69	0.092	} 0.160 2.00
Al <sub>2</sub> O <sub>3</sub>	6.93	0.068	
Na <sub>2</sub> O	2.13	0.034	
	<hr/> 99.52		

Soda is here clearly an impurity. An interesting feature of the analysis is the alumina, which, in this case, is nearly half the ferric iron. Combining the molecular ratios for alumina and ferric iron and considering this value equal to two, the formula for this mineral becomes,  $2(\text{Fe, Al})_2\text{O}_3 \cdot 7\text{SO}_3 \cdot 22\text{H}_2\text{O}$ .

This corresponds with the composition of coquimbite given by Dana.

#### GUILDITE (NEW MINERAL)

This new mineral is relatively rare and occurs as individual crystals varying in size up to one-half centimeter in width. It is closely associated with both coquimbite and ransomite.

At first glance these crystals appear to be cubes, and the crystallization isometric, but a careful examination shows the base

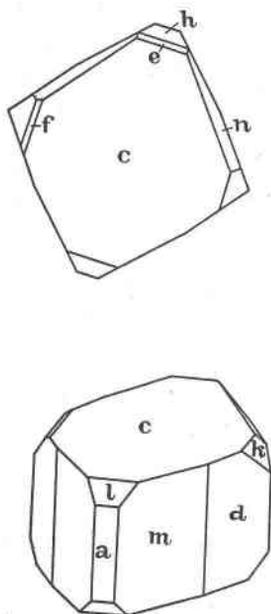


FIG. 5. Idealized drawing of Guildite.

to be inclined to the prism face. The monoclinic crystallization and symmetry was definitely established by measuring the crystals. A total of 10 different forms were found. These are the base  $c(001)$ ; front pinacoid  $a(100)$ ; the unit prism  $m(110)$ ; a second prism  $d(540)$ ; clinodome  $k(011)$ ; a plus and a minus orthodome; a pyramid; and two small curved forms. Although a number of crystals were measured, on none was a trace found of the side pinacoid  $b(010)$ . The plus orthodome  $l(101)$  does not fall in the correct position on the gnomonic projection, and  $\rho$  for this face is probably between  $2^\circ$  and  $3^\circ$  below the theoretical value. An interesting feature of this mineral are the prisms. They never occur together; either the crystal has developed the unit prism faces  $m(110)$  or else the prism  $d(540)$ ; and the pyramid  $n(346)$  occurs along with the latter.

In the table below no values are given for  $\phi$  and  $\rho$  for the two domes  $e$  and  $f$ . These are small curved faces, and the reflections obtained suggest the symbol for  $e$  to be  $(\bar{1}02)$  and for  $f$   $(012)$ .

TABLE V.  
CRYSTALLOGRAPHIC ELEMENTS OF GUILDITE

Letter	Symbol		$\phi$ angle	$\rho$ angle	Remarks
	Miller	Gdt.			
<i>c</i>	(001)	0	90° 00'	15° 17'	
<i>a</i>	(100)	$\infty 0$	90° 00'	90° 00'	
<i>m</i>	(110)	$\infty$	44° 55'	90° 00'	
<i>d</i>	(540)	$\infty \frac{4}{5}$	38° 35'	90° 00'	
<i>k</i>	(011)	01	11° 15'	55° 07'	
<i>l</i>	(101)	+10	90° 00'	56° 29'	error 2-3°
<i>h</i>	(101)	-10	90° 00'	48° 33'	
<i>n</i>	(346)	$-\frac{1}{2}, \frac{2}{3}$	25° 20'	46° 44'	
<i>e</i>	(102)	$-\frac{1}{2} 0$	variable	variable	curved face
<i>f</i>	(012)	$0 \frac{1}{2}$	"	"	" "

Axial ratio  $a:b:c = 1.037:1:1.407$ ,  $\mu = 74^\circ 43' = 180 - \beta$ .

As a rule, the signals from these crystals were poor and it was found difficult to center the blurred image. Five crystals were measured to obtain a fair average value for *m*, and two crystals to determine *d*(540). Almost invariably, the base gave a group of closely spaced images. This, together with the poor reflections from the prism caused considerable trouble in properly aligning the crystal on the goniometer. The domes and the pyramid, when present, gave clear, sharp images. An idealized drawing of a crystal of guildite is shown as Fig. 5.

Guildite, in the larger crystals, is a deep, chestnut brown color, somewhat lighter in the smaller ones, and corresponds to 13'' m in Ridgway's color standards. Thin cleavage flakes are honey yellow, and the streak is pale, canary yellow. Crystals are translucent and cleavage fragments transparent.

Two directions of cleavage, both perfect, are present in this mineral; one is parallel to the base (001) and the other parallel to the front pinacoid (100). The fracture is conchoidal, and the luster vitreous. This mineral is quite brittle. Hardness about 2.5; and the specific gravity, as determined with the Westphal balance, was found to be 2.725.

Optically, guildite is positive. Indices of refraction determined with immersion liquids are:  $\alpha = 1.623$ ;  $\beta = 1.630$ ;  $\gamma = 1.684$ ; all

$\pm 0.005$ . The birefringence is 0.061. The mineral is quite pleochroic; X = pale yellow, Y = pale yellow, Z = greenish yellow.

ANALYSIS OF GUILDITE			
	PERCENTAGES	RATIOS	
H <sub>2</sub> O	22.15	1.231	17.46
SO <sub>3</sub>	39.68	0.496	7.03
Fe <sub>2</sub> O <sub>3</sub>	19.12	0.120	} 0.141
Al <sub>2</sub> O <sub>3</sub>	2.11	0.021	
CuO	15.78	0.198	} 0.219
FeO	1.49	0.021	
Na <sub>2</sub> O	1.23	0.020	3.11
	101.56		

Chemically, guildite is a hydrous sulphate of copper and ferric iron. Ferrous iron is isomorphous with copper oxide and alumina with ferric iron. Soda is probably an impurity. Combining the molecular ratios for alumina and ferric oxide and considering this unit equal to two, the formula for guildite becomes,  $3(\text{Cu, Fe})\text{O} \cdot 2(\text{Fe, Al})_2\text{O}_3 \cdot 7\text{SO}_3 \cdot 17\text{H}_2\text{O}$ .

This is a complex, hydrous sulphate containing both the RO and the R<sub>2</sub>O<sub>3</sub> radicals.

The mineral is named after Dr. F. N. Guild, Professor of Optical Mineralogy, and head of the Department of Geology at the University of Arizona.

#### LOUDERBACKITE (NEW MINERAL)

This mineral occurs as a thin crust, a few millimeters in thickness, coating massive, granular pyrite. It is relatively rare. Associated with it is copiapite as small, yellow flakes. Louderbackite, however, was formed later than copiapite. The mineral is crystalline, but no individual crystals were found that could be measured.

The color is pale chestnut brown in the thicker crusts, and corresponds to 11''-m in Ridgway's tables; colorless in thin slivers. The streak is white. Luster oily to vitreous; translucent to transparent. Hardness 2.5-3; specific gravity 2.185 determined with Westphal balance. Two directions of cleavage were noted, both good, and apparently pinacoidal.

Louderbackite is biaxial, and optically positive. It is not pleochroic. Indices of refraction, all  $\pm 0.005$ , determined with immersion liquids are:  $\alpha = 1.544$ ;  $\beta = 1.558$ ;  $\gamma = 1.581$ . Crushed fragments always give parallel extinction and the mineral is orthorhombic in crystallization.

ANALYSIS OF LOUDERBACKITE

	PERCENTAGES	RATIOS	
H <sub>2</sub> O	31.33	1.741	35.52
SO <sub>3</sub>	39.34	0.492	10.04
Fe <sub>2</sub> O <sub>3</sub>	20.84	0.131	} 0.156 3.18
Al <sub>2</sub> O <sub>3</sub>	2.55	0.025	
FeO	7.01	0.098	2.00
Na <sub>2</sub> O	0.88	0.014	
	101.95		

Chemically, louderbackite is a hydrous sulphate of both ferrous and ferric iron with a small amount of soda, probably present as an impurity. The presence of 7 per cent of ferrous iron is interesting. Although the mineral sometimes incloses small grains of pyrite the ferrous iron could hardly have been derived from pyrite as this sulphate is soluble in cold water. Dr. Buehrer took particular pains in separating the pyrite, both quickly and thoroughly, and the ferrous iron must, therefore, be considered a part of the molecular constitution. Considering the ferrous iron as unity and doubling the ratios, the formula for this mineral becomes:  $2\text{FeO} \cdot 3(\text{Fe}, \text{Al})_2\text{O}_3 \cdot 10\text{SO}_3 \cdot 35\text{H}_2\text{O}$ .

This sulphate is named after Dr. Geo. D. Louderback, Professor of Geology, University of California.

RANSOMITE (NEW MINERAL)

Ransomite occurs as crusts lining cavities in the crushed rocks and also as small tufts of radiating crystals. It is often associated with guildite and was formed somewhat later. Crystallization was transverse to the walls, and the unfilled space is often lined with well-developed, slender crystals showing abundant terminal faces. These minute, needle-like crystals are rarely more than a few millimeters in length.

The crystallization is orthorhombic, and the habit is as slender prisms elongated parallel to the *c* axis. Ransomite is rich in forms,

and ten in all were found by measuring five crystals. In no case were all the forms noted on a single crystal, and the drawing of a crystal of ransomite, Fig. 6, is highly idealized. This was done chiefly to avoid extra text figures. Very often the crystals terminated in a broad, inclined face, the dome  $d(301)$ ; and between this form and the prisms were found the small pyramidal faces. These crystals then appeared to have monoclinic symmetry. In another type the vicinal face  $r$  terminated the crystal.

TABLE VI  
CRYSTALLOGRAPHIC ELEMENTS OF RANSOMITE

Letter	Symbols		$\phi$ angle	$\rho$ angle	Remarks
	Miller	Gdt.			
$o$	(111)	1	30° 01'	30° 48'	
$s$	(211)	21	49° 40'	38° 17'	
$t$	(311)	31	59° 53'	45° 43'	
$d$	(301)	30	90° 00'	41° 15'	
$e$	(053)	$0\frac{5}{3}$	0° 00'	41° 13'	
$a$	(100)	$\infty 0$	90° 00'	90° 00'	
$b$	(010)	$0 \infty$	0° 00'	90° 00'	
$m$	(110)	$\infty$	30° 01'	90° 00'	$\phi$ from unit pyramid
$n$	(210)	$2 \infty$	49° 40'	90° 00'	$\phi$ from pyramid (211).
$r$	—	—	variable	2° 55'	vicinal face

Axial ratios  $a:b:c=1.7407:1:0.5168$

As will be noted in the above table three pyramids occur on ransomite; two domes; two pinacoids; two prisms; and a vicinal face  $r$ . The base (001) is not present. No symbols are given for the face  $r$  as  $\phi$  varies from 7° 30' to 18° 33' while  $\rho$  is constant at 2° 55'. This is probably a vicinal face. The signals were good from all faces except in the prism zone. In this zone a continuous band of light was noticed, generally faint, but with bright spots here and there. These bright spots correspond to the broader prism faces. The fainter portions may be due partly to internal reflections from the back side of the crystal, but are also due to a series of very narrow faces between prominent prisms or pinacoids, which, because of their extreme narrowness behave as a diffraction grating and diffuse the light.

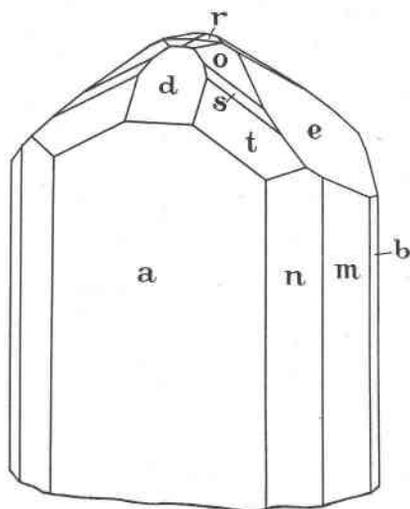


FIG. 6

FIG. 6. Idealized drawing of Ransomite.

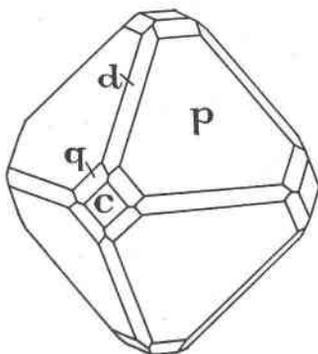


FIG. 8

FIG. 8. Idealized drawing of Voltaite from Jerome.

On plotting the position of the more prominent prism faces it was found they did not fall in the same zone of the base and corresponding pyramid. The average value for  $\phi$  is always larger than it should be. These relations are shown in the gnomonic projection as Fig. 7. In this figure the solid lines indicate the theoretical position and the dotted lines the position of the faces actually measured. Where a dotted line is of double length it indicates that two faces from two different crystals have the same value for  $\phi$ . Fig. 7 is a composite of the projections of five different crystals.

The reason for this discrepancy is not readily apparent, and if due to distortion, such distortion could have been caused only by internal stresses on cooling, as the mineral was formed near the surface in free space.

The color of ransomite is a bright sky blue and corresponds closely to 41'-f in Ridgway's color standards. The mineral is transparent in the smaller crystals and the luster is pearly on a cleavage face to vitreous on a cross fracture. The cleavage is perfect and is either pinacoidal or prismatic. Specific gravity 2.632; hardness 2.5.

Ransomite is optically positive and biaxial. The indices of refraction, all  $\pm 0.005$  are:  $\alpha = 1.631$ ;  $\beta = 1.643$ ;  $\gamma = 1.695$ .

## ANALYSIS OF RANSOMITE

	Percentages	Ratios	
H <sub>2</sub> O	18.82	1.046	7.36
SO <sub>3</sub>	46.30	0.578	4.07
Fe <sub>2</sub> O <sub>3</sub>	22.57	0.141	0.167
Al <sub>2</sub> O <sub>3</sub>	1.52	0.015	
CuO	11.29	0.142	1.00
	100.50		

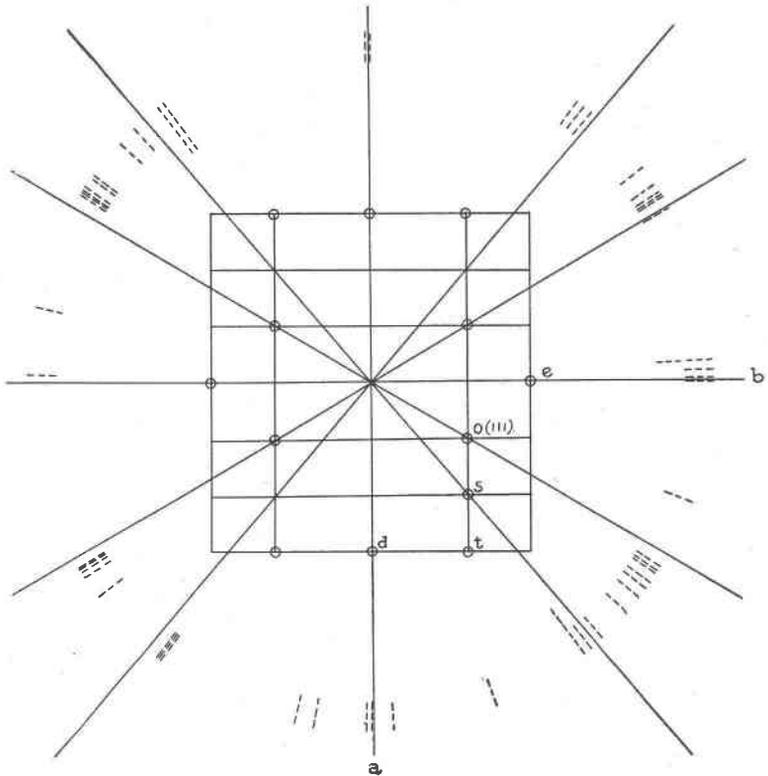


FIG. 7

FIG. 7. Gnomonic projection of Ransomite. Composite of five projections. Prism faces shown by dashed lines. See text for discussion.

Chemically, the mineral is a hydrous sulphate of ferric iron and copper, and a small amount of alumina is isomorphous with

ferric iron. With the molecular ratio of copper oxide as unity, the formula for ransomite becomes:  $\text{CuO} \cdot (\text{Fe}, \text{Al})_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 7\text{H}_2\text{O}$ .

This mineral is named in honor of Dr. F. L. Ransome, Professor of Economic Geology at the California Institute of Technology, and formerly of the University of Arizona and the United States Geological Survey.

ROGERSITE (NEW MINERAL)

Large lumps of a white color and consisting of an aggregate of minute, silky fibers were found associated with other sulphates at this locality. Embedded in these lumps are small, rounded grains of copiapite. Qualitative tests showed this white material to be a soluble sulphate of ferric iron and it is a new mineral.

The individual fibers or crystals when examined microscopically were found to be colorless and transparent. They are never as much as one half millimeter in length and are too small to be measured on a goniometer. It is not certain that terminal faces would have been found even if this were possible.

Because of their small size it is possible to determine but a few of the physical properties. No cleavage was noted although one or more directions of cleavage may be present. The luster of the aggregate is silky; and, if the individual crystals could be examined, this property might be vitreous. Efforts to determine the specific gravity gave unsatisfactory results; the minute fibers remaining suspended for hours in liquids having different specific gravities. The hardness is unknown.

Optical tests show the mineral to be monoclinic in crystallization and elongated parallel to the *c* axis. The indices of refraction as determined with immersion liquids are:  $\alpha = 1.598$ ;  $\beta = 1.628$ ;  $\gamma = 1.654$ , all  $\pm 0.005$ .

The maximum extinction angle  $\alpha$  to *c* is  $27^\circ$ .

ANALYSIS OF ROGERSITE

	Percentages	Ratios	
H <sub>2</sub> O	20.64	1.147	6.03
SO <sub>3</sub>	47.90	0.599	3.15
Fe <sub>2</sub> O <sub>3</sub>	28.07	0.176	} 0.190 = 1.00
Al <sub>2</sub> O <sub>3</sub>	1.40	0.014	
K <sub>2</sub> O	0.06		
Na <sub>2</sub> O	1.23	0.020	
	<hr/>		
	99.30		

As may be readily seen from the above analysis, rogersite is a hydrous sulphate of ferric iron. Both soda and potash in this analysis are believed to be present as impurities. The mineral differs from the other sulphates described in this paper both in physical properties and chemical constitution. It is a new mineral species, and is named after Dr. Austin F. Rogers, Professor of Mineralogy at Stanford University, and past president of the Mineralogical Society of America.

An artificial ferric salt prepared by Posnjak and Merwin<sup>12</sup> corresponds closely in both composition and optical properties with rogersite. This salt formed slender, colorless laths, monoclinic in crystallization with an extinction angle  $\alpha$  to  $c$  between  $22^\circ$ – $26^\circ$ . The indices of refraction given by these writers is:  $\alpha=1.605$ ;  $\beta=1.635$ ;  $\gamma=1.657$ . They state the salt crystallizes readily and is stable in contact with its saturated solution from somewhat above  $50^\circ$  to  $150^\circ\text{C}$ .

#### VOLTAITE

Voltaite from this locality has been described by Mr. Chas. A. Anderson<sup>13</sup> in an article published in this Journal. Only a brief description, therefore, will be given here.

Most commonly, the mineral occurs at this locality as an aggregate of small crystal grains. Some good crystals, however, were found and measured. They are octahedrons with the dodecahedron on the edges and the cube on the ends. The trapezohedron  $q(112)$  was noted on one crystal. Fig. 8 is an idealized drawing of voltaite from this locality.

The color is black in crystals and thin fragments under the microscope have a greenish tint. The luster is vitreous to oily. The specific gravity was determined with the Westphal balance and found to be 2.611. Index of refraction  $n=1.594$ . The crushed powder when examined under crossed nicols exhibits very weak double refraction.

The alteration of voltaite to copiapite and coquimbite as noted by Anderson does not occur in the material collected by the writer. This is probably due to the drier climatic conditions existing at Tucson where the specimens have been kept for some time.

<sup>12</sup> *Op. cit.*

<sup>13</sup> *Op. cit.*

## MINERALS ASSOCIATED WITH THE HYDROUS SULPHATES

## SULPHUR

Sulphur appears to be in process of formation at the present time. Table I, on a preceding page, gives analyses of the gases issuing from churn drill holes and cracks in the rock. Very likely, some sulphur is being deposited below the surface from these gases.

This mineral was not observed in the steam shovel pit by the writer, but specimens were obtained by geologists of the United Verde Copper Company several years ago. The sulphur occurred as an aggregate of loose crystals filling a crack in the jaspery quartz.

An examination of these crystals with a hand lens showed the terminal faces to be replaced by a blunt, rounded end, suggesting that perhaps the mineral had been partly fused after it formed. The prismatic faces are well developed, but none of the crystals were measured.

## JEROMITE (NEW MINERAL)

A black, globular substance occurs as a coating on fragments of rock beneath iron hoods placed over vents from which sulphur dioxide gases are issuing. Qualitative tests show this substance to be a sulphide of arsenic containing some selenium.

The mineral is opaque, but the thin edges of slivers are translucent and of a cherry red color. The fracture is conchoidal, and the luster on this fracture-surface is adamantine, suggesting a high index of refraction. Crushed fragments examined microscopically were found to be isotropic, and the mineral is apparently not crystalline. The surface of these thin crusts appears as a fused mass of globules.

Associated with the globular masses are minute crystals consisting of octahedrons, translucent to transparent, and of a yellowish to orange color. They, too, are isotropic, and when measured were found to be isometric in crystallization. Not enough of the crystalline material was available for an analysis, but qualitative chemical tests show them to be a compound of arsenic and sulphur.

It is, therefore, possible that the rock fragments were originally coated with these orange-colored crystals and later fusion of these

crystals formed the dark substance which is amorphous in appearance. During fusion selenium may have been liberated from combination with either arsenic or sulphur, and the dark reddish color of jeromite may be due to this element.

ANALYSIS OF JEROMITE<sup>14</sup>

	Percentages
Sulphur	40.8
Selenium	7.5
Tellurium	Trace
Arsenic	46.8
Antimony	Trace
Insoluble	4.9 (by difference).
	<hr/> 100.0

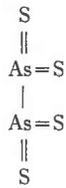
The mineral is soluble in boiling nitric acid, and the insoluble residue is probably finely divided particles of silica. If the analysis is recalculated free of this insoluble matter the percentages of sulphur, selenium, and arsenic are as follows:

	Percentages	Ratios	
Sulphur	42.9	1.34	} 2.18
Selenium	7.9	0.10	
Arsenic	49.2	0.66	1.00
	<hr/> 100.0		

Combining the selenium with sulphur, with which it is most closely related chemically, the ratio of arsenic to sulphur becomes nearly one to two. The formula for this mineral would then become  $\text{As}(\text{S}, \text{Se})_2$ . If the sulphur is divalent and carries two negative charges the arsenic would then be tetravalent. In most of its compounds where arsenic is the positive element the valence is generally three or five.<sup>15</sup> But the above formula is an empirical one, and if the ratios are doubled so as to read  $\text{As}_2(\text{S}, \text{Se})_4$ , then the arsenic would be pentavalent as indicated in the following structural formula:

<sup>14</sup> Analysis by Dr. T. F. Buehrer.

<sup>15</sup> Smith, Alex., General chemistry for colleges: p. 582, 1921.



Here one of the bonds of arsenic is assumed to be connected with another atom of arsenic. This, however, is purely hypothetical. More work will be required before this fact can be established.

The mineral is named after the city of Jerome near which it occurs; and, as here used, is applied only to the dark substance which appears to be amorphous.