

*On some crystallized sulphates from the province
of Huelva, Spain.*

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THE occurrence of melanterite, pisanite, and chalcantinite as secondary minerals resulting from the oxidation of pyrites masses containing copper is well known. It is not so well known that other metallic sulphates are from time to time found, and a brief description of the mode of occurrence of a few of these, in addition to some details of the composition of pisanite and chalcantinite, may be of interest.

Pisanite.—This mineral is of common occurrence at all the pyrites mines of Huelva and elsewhere, forming stalactites and stalagmites in those parts of the mines that are above drainage level though subject to more or less percolation of water. It is rarely found as well-formed crystals, save occasionally when a pool of strong sulphate water has been temporarily dammed back in some way, and then supersaturated through evaporation.

In copper content the mineral varies in all proportions from 2% or less up to a maximum of about 14%. Many natural crystals and stalactites of pisanite from the Rio Tinto mines have been analysed by the author and others in the Rio Tinto laboratories during the years 1882 to 1887, and the following show some of the results obtained, I-IV on crystals, and V on a stalagmitic mass:

	CuO.	FeO.	MnO.	NiO, CoO.	ZnO.	SO ₃ .	H ₂ O.	Total.
I.	4.82	19.67	0.31	0.10	1.13	28.98	44.76	99.77
II.	7.70	18.10	—	—	—	28.72	44.94	99.46
III.	10.58	15.40	—	—	—	28.82	44.52	99.32
IV.	11.51	15.08	—	—	0.35	28.66	44.70	100.30
V.	17.54	10.28	—	—	—	—	—	—

When the percentage of copper is below 5 to 7% (say 7 to 9% CuO) the crystals are light green in colour; above that percentage they become more blue, the depth of tint increasing roughly with the percentage of copper. The composition in all cases agrees with the formula $(\text{Cu,Fe})\text{SO}_4 \cdot 7\text{H}_2\text{O}$. The crystallization is in the monoclinic system, the crystals being simple combinations of the prism and the basal plane.

Any excess of copper in solution beyond the proportion of 14 % copper to 8 % iron forms chalcantite simultaneously with the highly cupreous pisanite. The old Sotiel mine near Calañas was set on fire many years ago, and water was turned on to put out the fire, as a result of which portions of the lower workings became waterlogged with a saturated solution of sulphates. Specimens taken from old timbers in this part of the mine, when subsequently drained, showed fine groups of crystals of both minerals, probably deposited simultaneously from the same solution. The chalcantite in these specimens doubtless contains less than 1 % Fe, as suggested by the experiments to be described later (p. 38).

Chalcantite.—Owing to the almost invariable presence of excess of iron in all the mine waters, this mineral is of less common occurrence than pisanite. Locally, however, for instance in the wall-rock, where pyrites is sometimes relatively scarce and copper impregnations abundant, chalcantite is sometimes found, as, for example, at the La Mimblera or San Diego mine near Zalamea, and also at the Monte Romero mine near Valdelamusa. The following is an analysis¹ of the chalcantite from the former locality, after eliminating extraneous insoluble matter. The deficiency of water to satisfy the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is no doubt due to the fact that the material had been kept for some days over sulphuric acid.

CuO.	FeO.	ZnO.	CaO.	MgO.	SO ₃ .	H ₂ O.	Total.
30.42	0.80	0.51	0.50	0.22	35.56	31.24	99.25

Coquimbite.—During the excavation of an opencast at the Concepcion mine, north-west of Zalamea, in the year 1911, an interesting group of sulphates was found in a filled-up cavity in the ore-body close to its cap, that probably represented an ancient caved-in working of the Roman period or earlier. The whole cavity had been filled with a mass of various mixed sulphates, deposited from solution around loose fragments of partially sulphatized pyrites that had fallen from the walls. Amongst the sulphates that were identified were coquimbite, copiapite, voltaite, and melanterite.

The coquimbite occurred interspersed in the mixture of sulphates as small, pinkish-violet crystalline masses. Occasionally, an isolated face

¹ This analysis, like all those that follow, was made by R. Serrano, a Spanish chemist, formerly in the employ of the Rio Tinto Co., the Huelva Copper and Sulphur Mines, and other English and French mining companies. The material was in most cases dried over sulphuric acid. Unfortunately, the effect of this treatment on the water of crystallization was not at the time appreciated. Apart from this, these hitherto unpublished analyses may be of some value.

can be discerned in these masses, but well-formed crystals are rare; in fact only three crystallized specimens were ever found, and of these two were poor, the crystals in one case being small, whilst in the other, although large, they are rough and ill formed. A fine specimen, now in the British Museum, shows to perfection the crystalline form of the mineral, namely, short, stout, hexagonal prisms ($2\frac{1}{2} \times 1\frac{1}{2}$ cm.) terminated by the basal plane, resembling the aragonite from Spanish localities both in size and in habit, even to the small prisms apparently embedded in the basal plane. Several hundredweights of the mass of mixed sulphates were broken up and examined for further crystals, but no other fine specimens could be found, and none showing even distinct crystal faces, except the two referred to.

The following analysis was made on pure selected material which had been kept over strong sulphuric acid for 48 hours. Here again the amount of water is rather lower than that required by the formula, viz. $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

Fe_2O_3 .	Al_2O_3 .	CaO.	MgO.	SO_3 .	H_2O .	Total.
25.84	2.25	0.15	0.16	44.19	27.25	99.84

Copiapite.—This was found with coquimbite in the Concepcion mine as masses of somewhat loosely aggregated, bright yellow, pearly scales, of which specimens are now in the British Museum and the Museum of Practical Geology, London. Sometimes the mineral appears to be quite pure, sometimes mixed with an undetermined, white, powdery material.

Analysis of the pure yellow scales, which had been kept for some time over strong sulphuric acid, gave:

Fe_2O_3 , ¹	FeO.	CaO.	MgO.	SO_3 .	H_2O .	Insol.	Total.
30.65	0.72	0.50	0.50	47.97	18.72	0.10	99.16

Voltaite.—Amongst the other sulphates from the Concepcion mine, and particularly with coquimbite and accompanying melanterite in the fragments of sulphatized pyrites, several brilliant, black or greenish-black octahedra were noted. Some of these were picked out and analysed, with the following result:

Fe_2O_3 .	Al_2O_3 .	FeO.	CuO.	CaO.	MgO.	Alkalis.	SO_3 .	H_2O	Total.
11.38	2.14	14.47	0.22	0.90	3.00	3.65	47.02	16.44	99.22

This analysis corresponds to $\text{RO} : \text{R}_2\text{O}_3 : \text{SO}_3 : \text{H}_2\text{O}$ approximately as 3.5 : 1 : 6.5 : 10, or roughly $3\frac{1}{2}(\text{RO} \cdot \text{SO}_3) + (\text{R}_2\text{O}_3 \cdot 3\text{SO}_3) + 10\text{H}_2\text{O}$; in which the alumina replaces Fe_2O_3 , and the RO includes Fe'' , (Ca, Mg), and (K, Na) in the proportions of 4 : 2 : 1.

¹ Including a little Al_2O_3 not separately determined.

Other Sulphates from the Concepcion mine.—Intermingled with the sulphates described were masses of others less well characterized. In particular, pink tufts were observed, which looked as if they might be halotrichite. Unfortunately, however, they were not hermetically sealed, but put away wrapped in cotton, and through the lapse of time and the processes of efflorescence and oxidation the masses have fallen to pieces, and their characters are no longer distinguishable.

Some of this mineral was picked out as clean as possible at the time and subjected to analysis, with the following results:

Fe ₂ O ₃ .	FeO.	CaO.	MgO.	SO ₃ .	H ₂ O.	Insol.	Total.
27.08	0.98	0.91	0.20	48.48	20.19	0.71	98.55

This corresponds to the ratio of RO:R₂O₃:SO₃:H₂O as 3.5:17:61:112 or approximately 1:5:18:33, but no formula is suggested, chiefly because it seems likely that the material analysed was not after all homogeneous, but a mixture.

Roemerite (?).—Besides the fine specimens of pisanite and chalcantinite already referred to, the old workings in the Sotiel mine, near Calañas, yielded fine specimens of voltaite associated with melanterite in rapidly sulphatizing pyrites, and also a mineral which is perhaps roemerite.

The last was found as whitish or yellowish tufts of acicular crystals with silky lustre, arranged in partly radiated groups upon stalactites of pisanite. Analysis gave:

Fe ₂ O ₃ .	FeO.	CuO.	ZnO.	CaO.	MgO.	SO ₃ .	H ₂ O.	Total.
13.10	8.60	2.12	0.65	1.30	3.80	41.49	28.80	99.86

This analysis gives a ratio of RO:R₂O₃:SO₃:H₂O approximately as 3:1:6:19, corresponding with a formula 3(RO.SO₃)+R₂O₃.3SO₃+19H₂O.

Bloedite (?).—From old timber in a long-abandoned working in the Monte Romero mine, some white or very slightly greenish, transparent, crystallized crusts were removed and analysed, with the following results:

FeO.	CuO.	MgO.	Na ₂ O.	SO ₃ .	H ₂ O.	Insol.	Total.
2.90	1.63	14.83	7.41	44.63	25.62	1.80	98.82

This analysis suggests bloedite with impurities.

Goslarite.—Old levels in dry parts of these mines, particularly cross-cuts outside the ore-bodies themselves, but in rock more or less mineralized, frequently show efflorescences of melanterite upon the walls. Less frequently these efflorescences take the form of long, fine, silky fibres, from 3 to 12 inches in length, descending from the roof in huge

bunches; these consist sometimes of goslarite, sometimes of epsomite.¹ An analysis of fibrous goslarite in this form, taken from a cross-cut of the Almagrera mine at Tharsis, is as follows (after deducting 3.63 % insoluble):

ZnO.	Fe ₂ O ₃ .	FeO.	CuO.	NiO.	CaO.	MgO.	SO ₃ .	H ₂ O.	Total.
24.78	2.78	trace	0.96	0.66	0.30	0.55	28.12	41.32	99.47

The long silky fibres readily effloresce on exposure to the air, and break down to white powder; it is therefore not possible to preserve them except in hermetically-sealed vessels.

Artificial Crystallization of Copper-Iron Sulphates.

Artificial Pisanite.—Whilst at Rio Tinto, in the year 1888, after analysing several specimens of natural pisanite, the author's attention was attracted to the question of the maximum percentage of copper sulphate that can be induced to crystallize isomorphously with ferrous sulphate in the form of pisanite, and in particular to the ratio of copper to iron in the solutions and the crystals respectively. To this end a large quantity of solution of ferrous sulphate saturated at ordinary summer temperatures was prepared, and in various measured quantities of this solution different weighed amounts of copper sulphate were dissolved with the aid of gentle heat. This operation, in the case of the larger amounts of copper, resulted in throwing out of solution some of the iron. After cooling, the resulting mixed solutions were analysed, and then concentrated by natural evaporation in wide-mouthed jars (a process which in a dry, warm climate was fairly rapid), small weighed crystals of melanterite suspended by threads being employed as nuclei for crystal-growth. It is noteworthy that, however large the number of faces on the complex crystals of melanterite employed as nuclei, the resulting crystals of pisanite are invariably simple, showing only the four prism-faces with the two basal planes. With small percentages of copper (up to 4½ %) the prisms are green and short. With increased percentages of copper they become more and more blue, instead of green, and much longer.

The experiments were performed in quadruplicate or more, that is, at least four or more crystals were obtained from each mixed solution, and one of these was broken up for analysis, only the ends being taken,

¹ A similar occurrence of epsomite was also noticed by the author in the iron mines of Sierra Alhamilla in the province of Almeria.

so as to eliminate the melanterite nucleus. The following table summarizes the results obtained :

Series mark.	Composition of Solution.			Composition of Crystals.		
	By weight.		Molecular ratio.	By weight.		Molecular ratio.
	% Cu.	% Fe.	Cu : Fe.	% Cu.	% Fe.	Cu : Fe
E	0.18	7.10	1 : 44	0.64	19.57	1 : 34.6
G	0.73	7.00	1 : 10.8	2.10	18.24	1 : 9.8
N	1.46	6.62	1 : 5.14	3.43	17.00	1 : 5.6
A	2.46	5.79	1 : 3.72	4.45	16.09	1 : 4.1
X	record missing		1 : 2.51	4.87	15.69	1 : 3.65
B	3.98	3.94	1 : 1.2	8.24	12.67	1 : 1.74
C	5.11	2.86	1 : 0.53	10.23	10.87	1 : 1.2
Y	see note		1 : 0.53	10.69	10.42	1 : 1.1
O	5.94	2.11	1 : 0.40	12.21	9.06	1 : 0.84
XX	6.20	1.93	1 : 0.35	14.65	6.85	1 : 0.53

Note. In experiment XX small crystals of chalcantite formed on the sides and bottom of the jar simultaneously with the pisanite. The crystals of pisanite XX were redissolved in a minimum of water, and the resulting saturated solution was that utilized for experiment Y. Specimens of artificial pisanite belonging to each of the above series, except the last, have been presented to the British Museum.

Although the ratio of copper to iron in the solutions is always higher than that in the resulting crystals, no definite relationship between the two ratios appears to be established by the above figures. It is interesting to note that the crystals containing the highest proportion of copper, namely, 14.65 % with 6.85 % iron, correspond with a composition of 65.95 % $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ and 33.85 % $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. J. W. Retgers,¹ as the result of his experiments, found that the maximum proportion of $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ that could enter pisanite was 53.17 %, which is a little less than that in the author's crystals of series O. H. Leitmeier,² however, in describing specimens of pisanite from Lading in Carinthia, quotes three analyses of this mineral by Herz which show from 17.45 % to 18.81 % of CuO (= 13.93 to 15.01 % Cu). These confirm the author's figures of a maximum of 14.65 % Cu . It may be concluded that while stalactites or stalagmites of pisanite may possibly be found containing more than 15 % Cu (because such need not necessarily be of homogeneous composition) the highest percentage of copper that can enter definitely crystallized pisanite is, as found by the author, about

14.65 % Cu (= 18.35 % CuO , or 65.95 % $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$).

As regards the colour of pisanite, Leitmeier (loc. cit.) states that up

¹ J. W. Retgers, Zeits. Physikal. Chemie, 1894, vol. 15, p. 562.

² H. Leitmeier, Centralblatt Min., 1917, pp. 321-331 [Min. Abstr., vol. 1, p. 347].

to a content of 8% CuO it is green, then blue from 8% up to 15.36%, bluish-green again at 17.64%, and again blue at 18.81% CuO; and he suggests that at the last of these percentages a definite double salt is formed with the composition $\text{FeCu}_2(\text{SO}_4)_3 \cdot 21\text{H}_2\text{O}$. The author's experiments show that the crystals of mixed sulphates turn bluish-green at a content of about 4.4% Cu (= 5.5% CuO, instead of 8% quoted by Leitmeier), and from that point up to a content of 12.2% Cu (= 15.1% CuO) they become gradually and more definitely blue. Unfortunately, the crystals with 14.65 Cu (= 18.35% CuO) were not preserved, but utilized for a further experiment (Y of the table); the author's recollection is that in colour they were precisely similar to those with 12% Cu.

Artificial Chalcanthite.—Simultaneously with the above-recorded experiments on artificial pisanite, carried out in the year 1888, the author attempted to determine the maximum amount of iron that could be induced to enter into chalcanthite in the form of $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$. A saturated solution of CuSO_4 was prepared, containing 7.65% of copper, and in measured volumes of this, different weights of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved. The mixed solutions were allowed to crystallize by natural evaporation, small crystals of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, suspended by threads, being employed as nuclei. The following table summarizes the results obtained:

Series mark.	Composition of Solution.			Composition of Crystals.		
	By weight. % Fe.	% Cu.	Molecular ratio. Fe : Cu.	By weight. % Fe.	% Cu.	Molecular ratio. Fe : Cu.
D.	0.27	7.65	1 : 25	0.19	25.19	1 : 118
H	0.67	7.45	1 : 9.79	0.23	25.15	1 : 97
F	1.35	7.45	1 : 4.88	0.46	24.89	1 : 48
J	1.85	7.34	1 : 3.5	0.59	24.75	1 : 37
Q	2.21	6.51	1 : 2.59	0.84	24.48	1 : 25.7

Like the artificial pisanite before referred to, specimens of each of the above series of artificial chalcanthite are now lodged in the British Museum. The highest percentage of iron, viz. 0.84%, corresponds to 3.64% of $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ crystallized isomorphously with the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the triclinic system. According to Retgers (loc. cit.) the maximum amount of $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ that can crystallize with the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is 5.12%, but the author obtained a maximum of only 3.64% even when employing a solution in which the ratio of Cu : Fe was as 1 to 2.59. Beyond that proportion pisanite forms simultaneously with chalcanthite.