

Villamaninite, a new mineral.

By W. R. SCHOELLER, Ph.D., and A. R. POWELL.

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EARLY in 1914 a parcel of copper-nickel-cobalt ore, weighing several tons, was received in London for valuation from the 'Cármenes mine, Spain'. This somewhat vague statement of locality refers without doubt to the group of mines in the district of Cármenes, province of León, situated about 6 km. E.N.E. of Villamanín, a station on the railway from Gijón to León and about 40 km. N. of the latter city. The ores of these mines are described as consisting of sulphide minerals of copper, cobalt, and nickel in a gangue of dolomite.¹

Having observed an unusually high content of sulphur in the ore, we secured a quantity of 8 lb. for a mineralogical investigation. The specimens received contain a black mineral—to which we have applied the name *villamaninite*, after the locality—disseminated plentifully and more or less evenly through a matrix of white crystalline dolomite. On fractured surfaces the ore has a mottled appearance with a general resemblance to a fine-grained diorite. A few specks of copper-pyrites and iron-pyrites are visible, and quartz is also present in small amounts. A few lumps contained only iron-pyrites and copper-pyrites in a gangue of dolomite; these were discarded.

The black mineral, as shown on the fractured surfaces of the ore, is seen to be granular and crystalline; but distinctly developed crystals could not be recognized. Most conspicuous, however, are small nodular masses with a radially fibrous structure and bright spherical surfaces. These always appear to be not more than sectors of spheres, generally less than 5 mm. and never reaching 1 cm. in diameter. A concentric structure is not prominent, but the nodules are sometimes broken concentrically, showing both concave and convex surfaces. Films of

¹ S. Calderón, Los Minerales de España. Madrid, 1910, vol. 1, pp. 124, 134, 147, 150, 214, 239; vol. 2, p. 53. J. Revilla, Riqueza minera de la Provincia de León. Madrid, 1906, pp. 68-74, Maps No. 1 and 6. C. A. Tenne and S. Calderón, Die Mineralfundstätten der Iberischen Halbinsel. Berlin, 1903, p. 38.

copper-pyrites and of dolomite are sometimes enclosed radially or concentrically in the nodules.

The morphological characters of the mineral are much better seen on the material which was isolated for analysis by dissolving the dolomite matrix in warm, dilute hydrochloric acid. This material shows small groups of rough crystals which are either irregularly intergrown, or grown together in parallel or subparallel grouping with a repetition of small faces. Recognizable forms are the regular octahedron and the cubo-octahedron; but owing to the roughness of the faces, only approximate measurements could be obtained on the goniometer. The angle between the cube and the octahedron faces $a(100) : o(111)$ gave readings $53^{\circ}-57^{\circ}$, the mean of which is not far from the calculated cubic angle $54^{\circ} 44'$; and between adjacent octahedron faces $69^{\circ}-73^{\circ}$ (calc. $70^{\circ} 32'$). The cube faces always show a peculiar rounding, and it is these faces that form the bright spherical surfaces of the nodules. All stages from single crystals (the largest $\frac{1}{2}$ cm. across) to the more typical nodular sectors could be traced, clearly indicating that the latter are due to a radial (subparallel) grouping of individuals. The spherical (concave and convex) surfaces of separation in the nodules perhaps mark different layers of growth.

The system of crystallization of the mineral is therefore cubic. No faces of a pentagonal-dodecahedron were detected; and there are no indications to suggest that the mineral is pseudomorphous after iron-pyrites. There is no distinct cleavage, and the fracture is uneven. The mineral is not brittle, but is readily reduced to a sooty powder with the knife. Hardness $4\frac{1}{2}$. The colour is iron-black with a dull metallic lustre, and the streak is sooty black. The weathered material on the surface of the pieces of ore and the acid-cleaned material present quite a dull, sooty black appearance. On the rounded cube faces and the spherical surfaces of the nodules the lustre is brighter. The smallest fragments crushed in oil are quite opaque under the microscope.

The powdered mineral is soluble in nitric acid, giving a greenish-blue solution and a globule of sulphur; addition of ammonia to the acid liquor produces a deep-blue solution (copper) and a brown precipitate (iron). Heated in the closed tube, it yields a copious sublimate of sulphur and a less pronounced one of selenium. On being heated in the open tube, the powder burns with a blue flame; the fumes smell of sulphur dioxide and selenium. The same smell is obtained on charcoal before the blow-pipe, the mineral fusing to a globule. Heated with soda in the reducing flame, it gives grey metallic particles soluble in nitric acid with green

colour which turns deep blue on addition of ammonia. The phosphate and borax beads are deep blue in the oxidizing or reducing flame (cobalt).

The analysis of villamaninite was carried out in the following manner :

1. For the determination of silica and selenium, one gram was dissolved in nitric acid and potassium chlorate, and the acid expelled on the water-bath. The residue was evaporated three times with hydrochloric acid on the water-bath to decompose nitrates and chlorates, taken up with dilute hydrochloric acid, and the silica filtered off, ignited, and weighed. The filtrate was strongly acidified with hydrochloric acid and saturated with sulphur dioxide. After standing overnight, the treatment with sulphur dioxide was repeated ; the selenium was collected on a tared filter, washed, dried, and weighed.

2. Sulphur, copper, and iron were determined by dissolving 0.5 gram as before, and evaporating three times with hydrochloric acid. The residue was taken up with very dilute hydrochloric acid, the liquid made ammoniacal, and filtered from the precipitate in which, after solution and reprecipitation, the iron was determined volumetrically with permanganate. The combined filtrates were just acidified with hydrochloric acid and precipitated with barium chloride, the barium sulphate being filtered off, ignited, and weighed. The filtrate was saturated with hydrogen sulphide, the precipitated copper sulphide dissolved in nitric acid, and the copper determined volumetrically with potassium iodide and sodium thiosulphate.

8. For the determination of nickel and cobalt, 0.5 gram was dissolved in nitric acid and potassium chlorate, and the residue of nitrates treated according to the iodide method worked out by us and published in 'The Analyst', 1919, vol. 44, p. 275.

The first analysis was made on hand-picked nodular fragments obtained by pounding the ore in a mortar (see column 1 below). The yield was poor, only 4 grams of clean mineral being obtained.

In order to secure a larger quantity of clean material and to examine the sulphide mineral other than nodular, about 5 lb. of ore, coarsely broken, were heated with dilute hydrochloric acid until effervescence had ceased. The residue was washed with water followed by alcohol, and dried : the dry sulphides were then screened through a sieve having eight apertures per linear inch, for convenience in hand-sorting. The oversize weighed 54.8, the undersize 194 grams.

The oversize was sorted by hand into nodular pieces (11.1 grams ; see column 2) and black crystalline material not showing nodular structure (16.7 grams ; see column 3).

The remainder of the oversize (27 grams) containing a little silica as well as fragments slightly contaminated with yellow pyritic material, was crushed to 8-mesh, mixed with the undersize, and analysed as 'acid-cleaned unsorted' (221 grams; see column 4).

	1		2		3		4
	Hand-picked nodular.		Acid-cleaned nodular.		Acid-cleaned crystalline.		Acid-cleaned unsorted.
Sulphur	... 49.00	...	49.18	...	49.68	...	47.27
Selenium	... 1.54	...	1.44	...	0.88	...	0.88
Copper	... 17.65	...	18.51	...	22.18	...	19.48
Nickel	... 18.19	...	18.24	...	15.94	...	15.58
Cobalt	... 7.45	...	7.24	...	6.80	...	6.79
Iron	... 4.89	...	4.17	...	5.11	...	6.00
Silica	... 0.88	...	0.84	...	0.22	...	8.80

	99.10	...	99.07	...	100.21	...	99.75
Spec. grav.	4.488	...	4.528	...	—

The similarity in composition shown by these analyses is close enough to justify the assumption that the nodular and the crystalline material are different forms of the same mineral species. As regards the unsorted material, both its appearance and chemical composition show that it consists chiefly of villamaninite contaminated with subordinate quantities of pyrites and quartz. A qualitative analysis on 20 grams proved the absence of tellurium, thallium, indium, and gallium; traces of arsenic, bismuth, and lead were detected, while the reaction for zinc was a little more pronounced.

The analytical data are in fair agreement with the composition of a disulphide MS_2 , like iron-pyrites, in which selenium replaces part of the sulphur and the metals copper, nickel, cobalt, and iron are vicarious: $(Cu, Ni, Co, Fe)(S, Se)_2$. Thus, the atomic ratio $(S + Se):(Cu + Ni + Co + Fe)$ for analyses No. 1, 2, and 3 works out at 1.958, 1.986, and 1.904 respectively. In this connexion it should be mentioned that the hand-picked specimen first analysed, which had not been dried by heat, shows the highest sulphur ratio; with samples 2 and 3 a faint smell of sulphur was noticeable when they were withdrawn from the oven.

Though the chemical constitution of villamaninite is not fully established by the analyses reproduced above, we propose its inclusion in the pyrites group; this seems to us legitimate on account of its form of crystallization and its high sulphur content. The percentage of sulphur found by analysis does not quite satisfy the amount calculated for a disulphide; but the same may be said of laurite, which Dana classes in

the pyrites group, although differences of opinion exist as to the formula of that mineral: some regard it as a disulphide, others as a sesquisulphide. Again, it may be objected that copper cannot vicariously replace nickel or cobalt in a disulphide, on the ground that it is always univalent in sulphide minerals except covellite, in which it is bivalent. We think it, however, inadvisable to theorize too much upon this point in view of our ignorance as to the constitution of native sulphides and arsenides such as pyrites, mispickel, realgar, molybdenite, patronite, &c. The fact remains that villamaninite, though very rich in copper, contains practically two atoms of sulphur to one of metal. The disulphides of nickel and cobalt themselves have so far not been found in nature except in cobaltnickel-pyrite,¹ in which approximately half the iron is replaced by nickel and cobalt. Higher sulphides of copper, such as Cu_2S_3 and Cu_3S_4 , have been prepared artificially.²

Summary.—The description of the new mineral may be summarized as follows:

Villamaninite, a sulphide of copper, nickel, cobalt, and iron, rich in selenium; probably a disulphide $(\text{Cu}, \text{Ni}, \text{Co}, \text{Fe})(\text{S}, \text{Se})_2$. Copper 19, nickel 18, cobalt 7, iron 4, sulphur 50, selenium $1\frac{1}{2}$ per cent. Crystalline system cubic. Occurs disseminated in crystalline dolomite as small, iron-black crystals, also as small, nodular aggregates. Lustre dull metallic. Opaque; streak sooty black. Hardness $4\frac{1}{2}$. Sp. gr. 4.4–4.5. In the closed tube, gives a sublimate of sulphur and selenium. Soluble in nitric acid, leaving a globule of sulphur. Locality: Cármenes district, near Villamanín, Prov. León, Spain.

In conclusion, we desire to acknowledge our indebtedness to Mr. L. J. Spencer, who determined most of the physical characters of the new mineral, and gave valuable help in the preparation of the manuscript. Selected specimens have been presented to the Mineral Department of the British Museum (Natural History).

¹ M. Henglein, *Centralblatt Min.*, 1914, p. 129.

² F. Bodroux, *Compt. Rend. Acad. Sci. Paris*, 1900, vol. 180, p. 1897.