THE
AMERICAN JOURNAL
OF
SCIENCE AND ARTS.

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THIRD SERIES.

VOL. XV.—[WHOLE NUMBER, CXV.]

Nos. 85—90.

JANUARY TO JUNE, 1878.

WITH TWO PLATES.

NEW HAVEN: EDITORS.
1878.

ART. XLIV.—*On the chemical composition of Guanajuatite, or Selenide of Bismuth, from Guanajuato, Mexico;* by J. W. MALLET, University of Virginia.

THIS mineral seems to have been first noticed by Señor Castillo in March, 1873, and was by him partially described[*] as a sulpho-selenide of bismuth.

In the Guanajuato journal "La Republica" for July 13, 1873, Fernandez[†] published a full description, giving to the mineral the name Guanajuatite, and stating that it is solely a selenide of bismuth, a small amount of sulphur found being attributed to admixture with a little pyrite. In the same year or 1874 Rammelsberg[‡] obtained as the result of a partial examination on a very small quantity,

Selenium	16·7
Bismuth	65·4
	82·1

and suggested the presence of zinc. The mineral was more fully examined by Frenzel,[§] whose analysis yielded,

Selenium	24·13
Sulphur	6·60
Bismuth	67·38
	98·11

whence the formula has been deduced—$2Bi_2Se_3 . Bi_2S_3$.

In the 2d Appendix to the 5th edition of Dana's Mineralogy[‖] the name Frenzelite was proposed for the species, but this has subsequently been retracted[¶] in favor of the prior claim of the name Guanajuatite given by Fernandez.

The above are up to this time, I believe, the only published notices of the mineral in question. They leave two doubts in regard to its composition, namely, whether sulphur is really a constituent or only found from accidental admixture, and whether zinc is present or not.

At the Philadelphia Exhibition of 1876, my friend Señor Mariano Bárcena, of the Mexican Commission, was kind enough to give me authentic specimens of this mineral, partly in the original condition as found, and partly reduced to powder. I have availed myself of the opportunity thus afforded of at-

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[*] Naturaleza, ii, 174 (1873); Jahrb. Min. (1874), 225.

[†] Quoted in this Journal, April, 1877, p. 319.

[‡] 2d App. to 5th ed. Dana's Mineralogy (March, 1875), p. 22.

[§] Jahrb. Min. (1874), 679.

[‖] Loc. cit.

[¶] This Journal, loc. cit.

tempting to settle the above questions by careful repetition of the chemical analysis. The already pulverized specimen was chiefly used, but was supplemented by a portion of the other—neither was altogether free from the hydrous silicate of aluminum which constitutes the gangue.

The method employed was the following. Water having been driven off by careful heating in a slow stream of carbon dioxide gas, collected and weighed, the mineral was mixed with ten times its weight of potassium cyanide and fused in an atmosphere of hydrogen. The mass on cooling was treated with water, and the solution filtered; the residue on the filter dried and again fused with the cyanide to ensure complete decomposition, repeating the treatment with water and filtration. From the mixed filtrates selenium was thrown down by addition of hydrochloric acid in excess, filtered after thirty-six hours on a weighed filter, cautiously dried and weighed; it was then burned, and a minute amount of silica left behind was determined. The solution from which the selenium had been precipitated was treated with potassium per-manganate as long as decolorization took place, and barium chloride then added; from the weight of barium sulphate thrown down sulphur was determined. The remaining solution was then evaporated to dryness at 100° C., the residue moistened with hydrochloric acid and treated with boiling water, leaving a further trace of silica; manganese (from the per-manganate used) and aluminum were now precipitated by ammonium sulphide, and separated by barium carbonate, the alumina being determined. The original residue of bismuth, left on the filter when the selenio-cyanate of potassium was filtered off, was dissolved in nitric acid, evaporated to dryness to separate a further portion of silica, redissolved, the bismuth thrown down by hydrosulphuric acid, filtered off, and a further portion of alumina (with a trace of ferric oxide) recovered from the filtrate. Lastly, the bismuth sulphide was carefully reduced by fusion with potassium cyanide, and weighed as metal.

The results were,

Selenium	31·64
Sulphur	·61
Bismuth	59·92
Alumina	2·53
Ferric oxide	*trace*
Silica	3·47
Water	1·46
	99·63

Zinc was specially looked for, both in the general analysis and using a separate portion for this purpose alone, but none could be found. Possibly, as Rammelsberg had but a very small quantity of material on which to work, he may have been led to suspect the presence of zinc by a precipitate of aluminum hydrate derived from gangue.

No evidence, physical or chemical, could be found of the presence of pyrite; the trace (unweighable) of iron appears to belong to the gangue.

It is stated that this gangue is galapectite (Halloysite); if the amount of such mineral present be calculated from the alumina the above figures represent the specimen as composed of—

Guanajuatite		92·17
Gangue	Halloysite	6·72
	Quartz	·56
Moisture		·18
		99·63

and the Guanajuatite in the pure state would consist of

Selenium	34·33
Sulphur	·66
Bismuth	65·01
	100·00

Hence we have the atomic ratio,

$$Bi : Se : S = 310 : 432 : 21,$$

or, uniting the sulphur with selenium,

$$Bi : Se = 310 : 453 = 2{\cdot}000 : 2{\cdot}922,$$

a close approximation to 2 : 3, justifying of course the formula Bi_2Se_3.

The quantity of sulphur present is too small to warrant the assumption that it bears a simple atomic proportion to the selenium, but the former element certainly is present, and not as pyrite. One can scarcely suppose that in Frenzel's analysis nearly six per cent of iron was overlooked, as it must have been if pyrite were the cause (as suggested by Fernandez) of the occurrence of the sulphur found.

It seems clear that the mineral in question must be viewed as sesqui-selenide of bismuth, with isomorphous replacement to a variable extent of selenium by sulphur.

It is also mentioned (this Journal, April, 1867) that Fernandez has described a second selenide of bismuth from the same locality, and has derived from his analyses of more or less pure specimens the formula Bi_3Se. This formula is very improbable, since it involves the presence of an odd number of perissad atoms. Perhaps there may have been an admixture of native (metallic) bismuth.