

ART. LVI.—*On Argyrodite and a new Sulphostannate of Silver from Bolivia*; by S. L. PENFIELD.

IN the August number of this Journal, 1893, page 107, the author described as a new species a germanium mineral from Bolivia, to which the name canfieldite was given. It was shown that the mineral was identical with argyrodite in chemical composition, but differed apparently in crystallization, canfieldite being isometric while argyrodite was monoclinic, according to the description of Weisbach.\* The discovery of the isometric mineral was communicated by letter to Professor Weisbach, and soon after the publication of the author's article a reply was received from him, in which it was stated that

\* Jahrb. f. Min., 1886, ii, p. 67.

better crystals of the Freiberg argyrodite than those originally described had been examined, and the results had shown that they were isometric and tetrahedral. These conclusions have since been published.\* The forms *m* and *o* of Weisbach† are regarded as the dodecahedron (110), *f* and *k* as the tetrahedron  $\alpha(111)$ ,  $\frac{1}{2}$  and *v* as the negative pyramidal-tetrahedron  $\alpha(3\bar{1}1) - \frac{3}{2}z^3$ . Argyrodite being isometric it is evident that the Bolivian mineral is not a new species and the name canfieldite is therefore withdrawn. For the sake of simplicity it is a satisfaction to have the Bolivian mineral identical with that from Freiberg, and it is regretted that the isometric character of argyrodite was not made known before the publication of the canfieldite paper. It was hoped that by the present time some definite information could be given concerning this new occurrence of argyrodite, but as yet no data have been received other than that it is a well known silver ore in the mines at Potosi.

There has also recently come into the authors possession, through the kindness of Mr. Wm. E. Hidden of New York, a specimen from La Paz, Bolivia, which was supposed to be argyrodite. Its total weight was a little over seven grams and it consisted of a few attached octahedrons, modified by dodecahedron planes, the largest crystal measuring 13<sup>mm</sup> in axial diameter. The only visible impurity was a very little metallie silver in wire form, deposited in a few places on the outside of the crystals. The mineral is almost identical with argyrodite in all of its physical properties. The luster is brilliant metallic. Color black with the same bluish to purplish tone observed on argyrodite. The fracture is irregular to small conchoidal. Very brittle. Hardness  $2\frac{1}{2}$ –3, specific gravity 6.276, that of argyrodite from Bolivia being 6.266. Heated before the blowpipe on charcoal at the tip of the blue cone the mineral fuses at about 2 and yields a coating of the mixed oxides of tin and germanium. This is white to grayish near the assay, tinged on the outer edges with yellow. By continued heating a globule of silver results but this is covered by a scale or coating of tin oxide. If the coating on the charcoal is scraped together and fused in the reducing flame with sodium carbonate globules of tin are formed. In the closed tube sulphur is given off and at a high temperature a slight deposit of germanium sulphide, which fuses to globules, is formed near the assay. In the open tube sulphur dioxide is given off but no sublimate is deposited.

The following method was adopted for the analysis. The mineral was oxidized by concentrated nitric acid and the excess

\* Jahrb. f. Min., 1894, i, p. 98.

† Compare figure in Dana's Mineralogy, sixth edition, p. 150.

of the latter removed by evaporation. The residue after moistening with nitric acid was digested with boiling water for some time and the insoluble meta-stannic acid filtered off. This was transferred while still moist to a beaker and treated with strong ammonia into which hydrogen sulphide was conducted until the meta-stannic acid had gone into solution. A slight insoluble residue was filtered off at this point which contained about 0.10 per cent of tin and 0.40 per cent of silver. From the ammonium sulphide solution the tin was precipitated by addition of a little sulphuric acid and weighed as oxide. The filtrate from the stannic sulphide was evaporated and yielded a little germanium which had not been separated from the tin by the nitric acid treatment. In the original filtrate from the meta-stannic acid silver was precipitated by means of hydrochloric acid and weighed as chloride. The sulphur was next precipitated by barium nitrate, and after purifying by fusion with sodium carbonate weighed as barium sulphate. Before evaporating the filtrates hydrochloric acid and barium were removed by precipitation with silver nitrate and sulphuric acid. The excess of silver was finally removed by ammonium thiocyanate and the germanium obtained from the filtrate as described in a previous communication.\* The results of the analysis are as follows:

			Theory for $\text{Ag}_8(\text{SnGe})\text{S}_6$ where Sn: Ge = 12: 5.	
Ratio.				
S .....	16.22	.507	5.92	16.56
Sn .....	6.94	.0589	.0842	7.18
Ge .....	1.82	.0253		1.83
Ag .....	74.10	.686	8.00	74.43
Zn and Fe	.21			----
<hr/>			<hr/>	
99.29			100.00	

In this compound tin is undoubtedly isomorphous with germanium, and the two are present in about the proportion 12: 5. The ratio of S: Sn+Ge: Ag in the analysis is very close to 6: 1: 8, indicating that the formula is  $\text{Ag}_8(\text{SnGe})\text{S}_6$  or  $4\text{Ag}_2\text{S} \cdot (\text{Sn} \cdot \text{Ge})\text{S}_2$ . The agreement between the theory and the analysis is satisfactory.

The only sulpho stannates thus far known to occur in nature are the rare species *stannite*,  $\text{Cu}_2\text{S}$ ,  $\text{FeS}$ ,  $\text{SnS}_2$ , *frankeite*,  $5\text{PbS}$ ,  $\text{Sb}_2\text{S}_3$ ,  $2\text{SnS}_2$  and *plumbostannite* a mineral of doubtful composition containing Pb. Fe. Sb. and S, described by Raimondi.† Frankeite has recently been described by Stelzner‡ and in it Winkler was able to identify a small amount of ger-

\* This Journal, xlv, p. 111, 1893.

† Zeitschr. Kryst., vi, p. 632, 1882.

‡ Jahrb. Min., 1893, II, p. 114.

manium, probably about 0.10 per cent. These authors call attention to the fact that since tin and germanium belong to the same chemical group they are isomorphous with one another and suggest the probability of finding in Bolivia a sulpho-stannate of silver isomorphous with argyrodite. The new mineral described in this article corresponds precisely to this idea. As the Freiberg argyrodite has been shown to be isometric, and the name *canfieldite* cannot therefore be applied to the germanium compound, it is proposed now to transfer the name to the new isomorphous tin compound. It is not probable that this will cause confusion as the name as at first applied was not long in use and has never been introduced into any of the text-books or systems of mineralogy, and especially as it is now transferred to a species which is very closely related, and should come next to argyrodite in a natural system of classification. It is probable that various mixtures of argyrodite  $\text{Ag}_8\text{GeS}_8$  and the molecule  $\text{Ag}_8\text{SnS}_8$  will be found and it would seem best to consider this latter as the canfieldite molecule, while the intermediate isomorphous mixtures would be called argyrodite or canfieldite, according as the germanium or the tin molecule predominated.

Regarding the crystallization of the argyrodite and canfieldite from Bolivia the specimens examined by the author, are apparently holohedral. The octahedron faces are equally developed and have the same luster. There is, however, on each of the dodecahedral faces of the canfieldite specimen a distinct furrow or slight depression running in the direction of the longest diagonal. This may indicate a twinning which has given rise to the apparently holohedral form, or the latter may of course have resulted from an equal development of positive and negative tetrahedrons.

Laboratory of Mineralogy and Petrography,  
Sheffield Scientific School, New Haven, April, 1894.