Stanniferous Argyrodite from Bolivia: The Identity of the so-called "Crystallised Brongniardite" with Argyrodite-Canfieldite.

By G. T. Prior, M.A., F.G.S., and L. J. Spencer, M.A., F.G.S.,
Assistants in the Mineral Department of the British Museum.

[Read February 1st, 1898.]

THE occurrence in Bolivia of minerals containing the rare element germanium has been recently noted by Prof. S. L. Penfield. One of these minerals from Potosi, described by him in 1893,[1] has the chemical composition of the Freiberg argyrodite (the original source of germanium), but was determined to be cubic, and not monosymmetric, the system to which argyrodite was originally referred. To the supposed new mineral the name canfieldite was given, but when Weisbach's re-examination showed that the Freiberg argyrodite was possibly cubic, the name was transferred by Penfield to another mineral containing germanium, which he described in 1894.[2] This new mineral, Canfieldite, which came from La Paz, occurs as octahedra modified by dodecahedral planes, and is almost identical with argyrodite in all its physical properties, but differs from it chemically in that it contains tin isomorphously replacing germanium. The formula of argyrodite, as modified by Penfield's analyses of both the Bolivian and the Freiberg mineral, is $4Ag_2S.GeS_2$; that of canfieldite proper is $4Ag_2S.SnS_2$. The material actually analysed by Penfield was an isomorphous mixture of the two, containing about 7 per cent. of tin and nearly 2 per cent. of germanium. To such isomorphous mixtures he proposes that the name argyrodite or canfieldite should be given according as the germanium or the tin molecule predominates.

---

[1] "Canfieldite, a new Germanium mineral, and on the Chemical Composition of Argyrodite." *Amer. Journ. Sci.*, 1893, XLVI, 107–113; Abstract, *Min. Mag.* X, 336.

[2] "On Argyrodite and a new Sulphostannate of Silver from Bolivia." *Amer. Journ. Sci.* 1894, XLVII, 451–4; Abstract, *Min. Mag.* XI, 40. Under this title Penfield's two papers are united in *Zeits. Kryst. Min.* 1894, XXIII, 240–8.

The material now to be described is interesting crystallographically on account of the twinning, and chemically in giving a different ratio of tin and germanium from that found in the original canfieldite. It is also found to be identical with the cubic crystals which Damour, in 1854, referred to brongniardite, a massive sulph-antimonite of silver and lead which he had previously described.

STANNIFEROUS ARGYRODITE FROM AULLAGAS, BOLIVIA.

In 1894 Mr. Jacobo Aillon presented to the British Museum two specimens as examples of red silver from the mines of the Colquechaca Company at Aullagas,[1] a mining village, 15,500 feet above sea level, in the province Chayanta, of the department Potosi.

The specimens consist mainly of a cavernous mass of pyrargyrite, showing on the free surfaces short prismatic crystals which are generally rounded and indistinct, but sometimes exhibit the forms $a\{10\bar{1}\}$ and $e\{110\}$. Intermixed with the pyrargyrite is some massive brown blende, one or two thin plates of barytes, a few specks of iron pyrites, and a little grey powdery kaolin, while on one of the specimens there is a considerable quantity of stephanite, both massive and in bright crystals.[2]

The main interest of the specimens, however, is derived from the fact that encrusting the pyrargyrite, as a later growth, are numerous small dull black cubic crystals, which on analysis were found to be stanniferous argyrodite.

Crystallographic Characters.—The crystals are very symmetrical and regular, and for the most part are isolated and almost completely developed on all sides, though occasionally several are grouped together. Many of them, however, especially those of type (2) described below,

---

[1] Aullagas is close to the town of Colquechaca, and lies east of the great lake Aullagas (or Poopó) and north of the town of Potosi. The mines here are noted for their very rich ore, consisting mainly of red silver and native silver. They have been described by H. Reck, *Petermann's geograph. Mitth.* 1867, 247; R. Peele, Junr. "The Silver Mines of Colquechaca, Bolivia," *Engineering and Mining Journal*, New York, 1894, LVII, 78, 100 (abstract, *Zeits. prakt. Geol.* 1894, 215); A. W. Stelzner, *Zeits. deutsch. geol. Ges.* 1897, XLIX, 89.

[2] On the crystals of stephanite the following forms were observed (the letters and indices are as given by Dana, *System of Mineralogy*, 6th edition, 1892):—

(i.) $c\{001\}$, $b\{010\}$, $m\{110\}$, $\pi\{130\}$, $q\{114\}$, $M\{113\}$, $P\{111\}$.
(ii.) c, b, $t\{023\}$, $k\{011\}$, $d\{021\}$, q, M, $h\{112\}$, P.
(iii.) c, b, m, t, k, M, P. All these crystals are twinned on $m(110)$.

Partial measurements of minute crystals implanted on an octahedron of the stanniferous argyrodite gave—

(iv.) c, b, $s\{012\}$, t, d, etc.
(v.) c, b, t, d, $\delta_1\{071\}$, etc.

are only shells of material implanted upon a nucleus of pyrargyrite, specks of which mineral they also sometimes enclose. These shells are easily detachable, and their inner surfaces show impressions of other crystals, and are sometimes encrusted with minute crystals of iron pyrites, and with extremely minute acicular crystals of an undetermined black metallic mineral. The habit of the crystals varies considerably. The following types can be distinguished :—

FIG. 1.

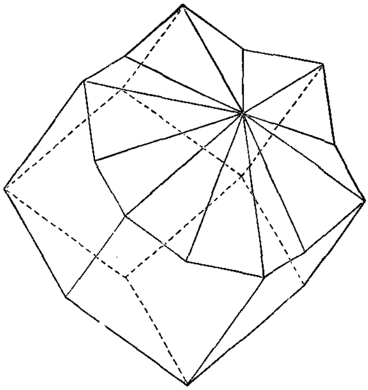
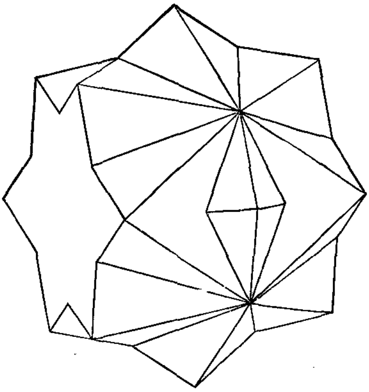


FIG. 2.



(1). *Simple* (i.e. *not twinned*) *octahedral crystals,* $o\,\{111\}$, *usually with narrow dodecahedral planes,* $d\,\{110\}$.

(*a*) Small, bright, and smooth crystals, with the dodecahedral planes very narrow or absent. These crystals, which do not exceed 0·5 mm. in diameter, occur only on the blende. On one crystal was measured $oo' = 70^\circ 25'$, $70^\circ 42'$; $od = 35^\circ$ approx.

(*b*) Larger crystals, with dull, rough and pitted surfaces; dodecahedral planes are always present, and are occasionally more largely developed than the octahedral planes. These crystals average 1·5 mm. in diameter; the largest measures 5 mm. along the octahedral edge.

(2). *Dodecahedral crystals,* $d\,\{110\}$, *always twinned and never with octahedral planes.*

In size and surface characters these resemble type (1)*b*. The twin axis is perpendicular to $o\{111\}$. The following varieties can be distinguished, all of which occur with geometrical regularity :—

(*a*) Contact twins, showing no trace of the plane of junction. This twin occurs on gold, and is figured in most treatises on crystallography.

(*b*) Interpenetrating dodecahedra, with the two interpenetrating individuals at one end only of the twin axis, and at the other a simple crystal (fig. 1). Similar twins have been described by Sadebeck for blende.[1] The argyrodite "trilling" figured[2] by Weisbach is explained by these interpenetrating dodecahedra.

(*c*) Two interpenetrating dodecahedra, with re-entrant angles at both ends of the twin axis, as occur in sodalite.[3]

(*d*) Three interpenetrating dodecahedra, with two of the individuals twinned on two octahedral planes of the third individual (fig. 2). Here one pair of parallel planes is common to the three crystals, and four pairs are common to two crystals. A similar trilling, but far less regular, has been described by Sadebeck as occurring on blende.[4]

(*e*) Apparently simple dodecahedra, but on closer inspection showing numerous small projections on the faces due to small crystals in twin position.

(3). *An octahedron twinned according to the spinel law.*

Only one small indistinct crystal of this type was observed, this being on the specimen with the stephanite; all the other crystals on this specimen were of type (1)*b*. The re-entrant angle was measured as 37°—38½° (calculated 38°56′). This crystal was not examined chemically.

The difference between types (1) and (2) is very striking, and when considered in connection with the fact that twinning is mentioned in the two previous descriptions of argyrodite (from Freiberg and Bolivia), whilst Penfield's crystals of canfieldite were apparently simple, it would suggest that there is a difference in chemical composition. A separation of the two types for quantitative analysis was scarcely practicable, but as mentioned below (p. 10), both tin and germanium were found in the twinned as well as in the untwinned crystals, while the colour, fracture and streak were the same for all.

The very imperfect crystals of the Freiberg argyrodite, after being described originally as monosymmetric and later as orthorhombic, have, in consequence of Penfield's observations, been recently given as cubic

---

[1] *Zeits. deutsch. geol. Ges.* 1869, XXI, pp. 634, 636; figs. 10, 11, Plate XVII.

[2] This figure is reproduced in Dana's *System of Mineralogy*, 6th edition, 1892, p. 150, fig. 2.

[3] C. F. Naumann, *Lehrb. d. Kryst.* 1830, II, p. 232, fig. 621. This figure is given in Dana's *System*, p. 429.

[4] *loc. cit.* p. 634, fig. 19.

and tetrahedral.[1] In the crystals at present described there is, however, nothing that suggests hemihedral development.

Physical Characters.—The mineral is opaque and of a dull iron-black colour. Crystals, when bright, as in the first habit (1)*a*, have a metallic lustre with a very faintly perceptible purplish tinge on the natural faces The streak is black and shining.[2] The fracture is even, with a finely granular appearance and a dull metallic lustre. The hardness is between that of gypsum and calcite. The mineral is somewhat brittle, but not extremely so. The specific gravity (weight of 1 cc.) is 6·19 at 18°C. as determined on 1·1021 gram of the material collected for analysis.

Chemical Characters.—In collecting material for analysis much care had to be exercised owing to the intimate association of the mineral with pyrargyrite. Each crystal was broken open and examined in bright sunlight under the lens, and also under the microscope. By the indications of streak and the character and colour of the fractured surfaces, pyrargyrite could be easily detected, and was then scraped away, whilst fragments which had a gritty feel under the knife, owing to the presence of pyrites, were rejected. The material so collected consisted of crystals of types (1)*b* and (2), with perhaps more of the latter. It was all taken off the specimen, on which no stephanite was found, since, in colour and streak, this mineral might have been confused with that which we were examining.

Heated in the closed tube, the mineral gives a sublimate of sulphur, and on intense ignition before the blowpipe, a pale lemon-yellow transparent gummy-looking sublimate of germanium oxide. When heated on charcoal before the blowpipe, a silver bead is left, and a white sublimate tinged with yellow is formed far out on the charcoal, while nearer the assay minute transparent fused globules of germanium oxide may be detected under the microscope.

Apart from these blowpipe tests, however, the identity of the mineral with stanniferous argyrodite was indicated by the following method of qualitative analysis:—

Two or three of the small crystals were introduced into a piece of hard glass tubing drawn out at one end and connected at the other with a hydrogen apparatus. On heating to redness in a slow current of the gas, the mineral yielded on both sides of the assay a deep reddish brown

---

[1] A. Weisbach, *Neues Jahrb. für Min.* 1894, I, 98.

[2] The shining streak is obtained when a fragment of the mineral is crushed with a knife point on biscuit porcelain or on hard smooth paper; when the mineral is crushed on soft paper of loose texture, the streak is dull black, with a sooty appearance.

and black sublimate of germanium sub-sulphide and metallic germanium. The sublimate was dissolved in nitric acid, the solution evaporated to dryness, and the residue treated with a little ammonia into which sulphuretted hydrogen was conducted until it just dissolved. In this solution, on addition of a large excess of sulphuric acid and saturation with sulphuretted hydrogen, a bulky pure white precipitate of germanium bisulphide was produced. The residue in the combustion tube after the ignition in hydrogen was treated with nitric acid, and the tin separated from the silver as metastannic acid. This was dissolved in ammonium sulphide, and the tin precipitated as yellow sulphide on addition of acid. From the sulphide, spangles of metallic tin were obtained by reduction on charcoal before the blowpipe. In the filtrate from the metastannic acid, the silver was precipitated by hydrochloric acid. When examined by the above method, crystals of the two principal types, the twinned and the untwinned (see p. 8), were found to behave in a similar way, and to show the presence of both tin and germanium. In the case of the twinned crystals, 36 milligrams of material yielded about a milligram of oxide of tin, corresponding to about 2 per cent. of tin in the mineral.

In the quantitative analysis a similar method to that described by Penfield was adopted. The mineral was decomposed by prolonged digestion with fuming nitric acid, the liquid evaporated nearly to dryness, and the residue treated with hot water. The insoluble metastannic acid (containing also some germanium, silver and iron) was collected on a filter, and treated with ammonia, into which sulphuretted hydrogen was passed until the sulphides of tin and germanium passed into solution, leaving behind a little sulphide of silver and iron. The tin was then precipitated as sulphide by neutralising with sulphuric acid, and weighed as oxide, while the germanium in the filtrate was estimated as oxide on evaporating to dryness and treating the residue with nitric acid. After weighing, the oxide of tin was tested for germanium by reducing in hydrogen, and as a slight sublimate of germanium was obtained, the tin was estimated as metal.

In the original filtrate from the metastannic acid the silver was precipitated by hydrochloric acid, and the sulphur with barium nitrate. Before evaporating the filtrate, in order to avoid loss of germanium owing to the volatility of the chloride, the excess of hydrochloric acid was removed by means of silver nitrate; and at the same time the excess of barium was precipitated by sulphuric acid. The excess of silver was then removed by means of ammonium thiocyanate, and the filtrate evaporated to dryness. The residue was treated with ammonia into which sulphuretted hydrogen was passed. The solution, containing germanium sulphide, was then filtered from the sulphide of iron, and evaporated to dryness. The residue was oxidised with nitric acid, and the germanium determined as oxide.

In a re-determination of the silver, made on 0·3197 gram from the same sample of powdered material, the mineral was decomposed by ignition in hydrogen, and the silver and tin in the metallic residue separated by means of nitric acid.

The result of the analysis made on 0·7608 gram is as follows (G. T. P.):—

			Atomic Ratios.		Calculated for $5(4Ag_2S.GeS_2)+2(4Ag_2S.SnS_2)$.
Ag	74·20	Mean of 73·89 74·51	·6928	or 8	75·65
Ge	4·99		·0694	1·13	4·59
Sn	3·36		·0284		2·89
S	16·45		·5168	5·97	16·87
Fe	0·68				
Sb	traces				
	99·68				100·00

THE SO-CALLED "CRYSTALLISED BRONGNIARDITE."

Under the name brongniardite, A. Damour in 1849[1] described a mineral from Potosi, Bolivia,[2] having the composition $PbS.Ag_2S.Sb_2S_3$ as determined by these analyses. On this original material no crystals occurred, but Damour considered that the mineral from its chemical composition should be isomorphous with the Binnenthal dufrenoysite ($2PbS.As_2S_3$) which he had recently investigated. At that time, however, having been misled by the association of cubic crystals of binnite with the mineral he had analysed, he was under the impression that dufrenoysite was cubic: he therefore suggested that should crystals of brongniardite be found, they would probably also be cubic. Accordingly when, a few years later, he[3] obtained from Louis Sæmann, a mineral dealer in

---

[1] "Notice sur la Brongniardite, nouvelle espèce minérale." *Annales des Mines*, 1849, [iv], XVI, 227–231; and F. de Castelnau, *Expédition dans les parties centrales de l'Amérique du Sud*, 1851, Vol. V, p. 440.

[2] Not Mexico, as at first stated, and as quoted in the text-books.

[3] "Note sur la cristallisation de la brongniardite, espèce minérale." *Annales des Mines*, 1854, [V], VI, 146–7.

Paris, a specimen, also from Bolivia, of apparently the same massive mineral, in the cavities of which however were small octahedral crystals, he appears to have been somewhat too readily convinced, as the result of a blowpipe examination,[1] that the crystals contained the same elements as the massive material, and that both were identical with the brongniardite he had previously described. The crystals were determined to be octahedra symmetrically truncated on all the edges, and to be consequently cubic. Brongniardite is therefore described in the text-books as a cubic mineral having the composition $PbS.Ag_2S.Sb_2S_3$.

In the British Museum a specimen of "massive and crystallised brongniardite," which was acquired with the Allan-Greg collection in 1859, is accompanied by Sæmann's label giving the locality as Aullagas, Bolivia, and mentioning the results obtained by Damour in 1854. This specimen in external characters agrees precisely with the published description of Damour. Thus it shows small octahedral crystals, with narrow dodecahedral planes, in cavities in a massive mineral; and pyrargyrite and blende, which are mentioned by Damour, are also present in small amount.

The massive material consists for the most part of a mineral (presumably brongniardite) which was found to contain silver, lead, antimony and sulphur, and to have a specific gravity of 5·99. Intimately associated with this mineral is some galena, and in parts also miargyrite, which occurs both massive and as indistinct crystals. It is on the latter mineral that the octahedral crystals occur.

Now these dull black octahedra have exactly the appearance of the type (1)*b* of stanniferous argyrodite described in the preceding section (p. 7); the streak, too, and the even fracture, with its granular appearance and dull metallic lustre, are very similar. So striking, in fact, was the resemblance of the crystals, that the specimens presented by Mr. Aillon were at first regarded as brongniardite. Therefore, when the small black crystals on the latter had been shown to be a stanniferous argyrodite, it became necessary also to make a chemical examination of the so-called brongniardite crystals.

For this purpose the amount of material available was very limited. Two or three of the crystals, weighing altogether 23·2 milligrams, were heated in hydrogen and examined in the way described on p. 9. The reddish brown sublimate formed on the combustion tube was dissolved,

---

[1] He noted, however, that the yellow sublimate on charcoal obtained from the crystals was less marked than that furnished by the massive mineral.

and finally yielded a pure white bulky precipitate of germanium sulphide, while in the metallic residue the presence of tin was proved by the production of the yellow sulphide,[1] and that of silver by precipitation as chloride. The weight of the silver chloride amounted to 22·1 milligrams, corresponding to about 72 per cent. of silver in the mineral. No lead or antimony was detected. Thus the result of the above physical and chemical examination is to prove that the crystals which were referred by Damour to brongniardite are really identical with a stanniferous argyrodite.

Through the kindness of Prof. A. Lacroix we have been able to examine fragments from several of the specimens of brongniardite collected by the Castelnau Expedition (1843-7), and now preserved in the Natural History Museum at Paris. One of these (labelled Potosi) shows the small octahedra of argyrodite-canfieldite, and in every detail resembles in appearance the specimen described in this section.

As far as we are aware, the only other mention that has been made of crystallised brongniardite is by L. F. Navarro.[2] A specimen from the Cueva de Plata, Sierra Nevada, now in the Natural History Museum at Madrid, is described as showing cubes resembling argentite in appearance. Further examination would probably prove them to be that mineral.

OCCURRENCE OF SULPHOSTANNATES IN BOLIVIA.

The occurrence at Aullagas of stanniferous argyrodite is of interest as illustrating the wide distribution of sulphostannates in Bolivia. Canfieldite is found at La Paz, stannite[3] at Guanuni and Potosi, franckeite[4] (a sulphostannate and sulph-antimonite of lead) at Chocaya and Aullagas, kylindrite[5] (another sulphostannate and sulph-antimonite of lead) at Poopó, while the somewhat unsatisfactory plumbostannite[6] of Raimondi (which may possibly be identical with franckeite or kylindrite) occurs at Moho, Peru, only a few miles from the Bolivian boundary. Thus

---

[1] The precipitate was only a slight one, indicating that the mineral was in composition nearer to argyrodite than to canfieldite.

[2] *Anales Soc. Española Hist. Nat.* 1895, XXIV, Actas, p. 94.

[3] See Abstract, this vol. p. 46.

[4] A. W. Stelzner, *Neues Jahrb. Min.* 1893 II, p. 114; *Zeits. deutsch. geol. Ges.* 1897, XLIX, p. 141.

[5] A. Frenzel, *Neues Jahrb. Min.* 1893, II, p. 125.

[6] Also mentioned from Trinacria, near Poopó (*Zeits. deutsch. geol. Ges.* 1897, XLIX p. 693); and from Arangaro in Chili (*Bull. Soc. Fran. Min.*, 1895, XVIII, p. 340).

all the five naturally occurring sulphostannates at present known occur within or close to the borders of Bolivia, and, with the exception of stannite, are all peculiar to that region.

As recently emphasised by Stelzner,[1] the mode of occurrence of tin ores in Bolivia is of an exceptional character. Instead of occurring, as is almost invariably the case, in connection with deep-seated granitic rocks and in association with tourmaline, topaz, and other minerals containing boron and fluorine, usually considered as products of fumarole action, the tin ores of Bolivia are found accompanied by metallic sulphides[2] in the ordinary type of mineral veins, and in association with trachytic and andesitic rocks. It is just under such conditions that sulphostannates would be likely to be found.

---

[1] *Zeits. deutsch. geol. Ges.* 1892, XLIV, p. 531; 1897, XLIX, pp. 51–142; Abstr. *Min. Mag.* X, 261.

[2] A case of the occurrence together of cassiterite and andorite is noted by us in the last number of this Magazine (Vol. XI, p 299).