# ART. XV.—*On Canfieldite a new Germanium Mineral and on the Chemical Composition of Argyrodite;* by SAMUEL L. PENFIELD.

IT is with great pleasure that the author is able to announce the discovery of a new mineral containing germanium and to record the occurrence of this rare and interesting element from a new locality. The credit of this is due in great measure to the keen mineralogical interest of Mr. Frederick A. Canfield of Dover, N. J., to whom, while on a business trip in Bolivia, South America, some specimens of this mineral were given as samples of a rich and unknown silver ore, by friends connected with the mining industry. These were brought to the writer for identification and he takes great pleasure here in acknowledging his indebtedness to Mr. Canfield and in expressing his

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*Törnebohm, A. E.: Melilitbasalt fraan Alnö; Geol. Fören i Stockholm Förhandl., 1882, vi. No. 76, p. 240.

thanks to him for the liberality with which he has placed an abundant supply of this valuable material at his disposal. It is in acknowledgment of these services that the mineral has been named after him.

It is unfortunate that at the present no further information can be given concerning the exact locality and mode of occurrence, but from inquiries that have been set on foot by Mr. Canfield it is hoped that full data concerning these points will be given later.

When the mineral was brought to the writer, attempts made to identify it at once showed that it was not one of the ordinary silver minerals. Thus in the open tube it gave a reaction for sulphur but no sublimate. In the closed tube with a Bunsen burner flame only a slight sublimate of sulphur, but at a higher temperature with a blowpipe flame the sulphur increased, while nearer the assay a pale yellow sublimate formed, which became lighter on cooling. On examining this with a lens it was found to consist of minute globules most of which were nearly colorless but some were yellow. Boiling concentrated nitric acid was found to attack and oxidize the mineral very slowly. On charcoal in the oxidizing flame it fused readily and gave almost immediately a pure white sublimate near the assay, but no color to the flame. On continued blowing this sublimate moved farther out, assuming a color which varied from greenish to brownish yellow, for the most part lemon yellow, while the assay changed to a pure silver bead. On examining the coating more minutely with a lens it was seen to have a peculiar smooth appearance, as if it had fused on the surface of the charcoal, while scattered about nearer the assay were numerous small transparent to milk white globules, along with minute globules of silver. These tests led to the suspicion that the mineral might possibly contain germanium and a comparative test, made with argyrodite on charcoal, gave exactly the same results. It is to be noted here that while Richter* describes very minutely the reactions which argyrodite gives on charcoal he does not mention the smooth surface of the coating or the formation of the fused globules which form so characteristic and useful a test for the identification of germanium. In order to prove beyond all doubt the identity of the element thus indicated with germanium the properties of the element as given by Winkler† were studied, a series of careful qualitative tests were made together with the formation of most of the important compounds mentioned by him. Thus a sulpho-salt, soluble in alkaline solutions like those of the tin, arsenic and antimony group, was prepared,

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* Quoted by Weisbach, Jahrb. f. Min., 1886, ii, p. 67.

† Journ. f. prakt. Chem., xxxiv, 1886, p. 177.

from which solution the addition of acid, especially in large excess, precipitated a white sulphide. On heating some of this sulphide in a tube through which a current of hydrogen was passed, small glittering scales of GeS, in luster resembling hematite, were formed just beyond the ignited material. These on examination with the microscope in transmitted light were found to be dark brown in color. Although not mentioned by Weisbach* it was noted that these were strongly pleochroic, the direction of greatest absorption being at right angles to the longest axis of the plates. By continued and higher heating a still further reduction took place and metallic germanium was deposited as a crystalline sublimate on the walls of the tube. Microscopic examination showed this sublimate to consist of small gray-white octahedral crystals of magnificent metallic luster. They were found to be insoluble in hydrochloric acid but were readily dissolved by aqua regia. These results agree exactly with those given by Winkler and the identity was still further confirmed by the entire behavior of the element and by other results which will be given in the course of this article.

The physical properties of this new mineral are as follows: Crystallization isometric. Among the specimens furnished by Mr. Canfield were two which were well crystallized. One of these consisted of a group of unmistakable octahedral crystals, averaging about $7^{mm}$ in axial diameter, but which were too rough for measurement on the goniometer. Their edges were sometimes truncated by the dodecahedron, while some were twinned about an octahedral face. The other specimen contained equally large but less isolated crystals, the luster of whose faces was good and one of the crystals, showing the four upper faces of an octahedron, with edges truncated by the dodecahedron was measured on the reflecting goniometer as follows:

| | | | |
|---|---|---|---|
| $111 \wedge \bar{1}11 =$ | $70°\ 0'$ | | |
| $\bar{1}11 \wedge \bar{1}\bar{1}1 =$ | $70\ 29$ | | |
| $\bar{1}\bar{1}1 \wedge 1\bar{1}1 =$ | $70\ 14$ | $111 \wedge \bar{1}\bar{1}1 =$ | $108°\ 57'$ |
| $1\bar{1}1 \wedge 111 =$ | $70\ \ 8$ | $1\bar{1}1 \wedge \bar{1}11 =$ | $109\ \ 3$ |
| Calculated, | $70\ 32$ | Calculated, | $109\ 28$ |

The reflections of the signal were moderately good and considering a slight rounding of the faces the measurements agree as closely to those of the octahedron as could be expected. The dodecahedral faces were too uneven to yield a distinct reflection. These crystals were tested and found to give the characteristic reactions for germanium. The fracture is irregular to small conchoidal. Extremely brittle. Hardness about 2·5. The specific gravity of two distinct, massive fragments,

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* Quoted by Winkler, loc. cit., p. 215.

weighing about five and six grams each, carefully taken on a chemical balance after boiling in distilled water, was found to be 6·2662 and 6·2657 respectively, the temperature being 25° C. The specific gravity of the fragment containing the crystal that was measured and weighing over 22 grams was found to be 6·270. The luster is brilliant metallic. The color black with a blueish to purplish tone. The streak is grayish black, somewhat shiny. The chief pyrognostic properties have already been given. In addition the fusibility at about 1½ to 2 should be noted. The fused transparent globules which were observed on charcoal are probably $GeO_2$. Some of the oxide separated from the quantitative analysis was tested on charcoal as follows: In the oxidizing flame it fused with bubbling to a transparent, glassy globule, giving no coating. By continued heating in the reducing flame it darkened and gave slowly a pure white sublimate. The yellow coating obtained on charcoal from the mineral was probably a mixture of oxide and sulphide of germanium. The fused globules, which were observed near the assay in the closed tube are $GeS_2$ or possibly some oxysulphide. Argyrodite, when tested in the closed tube, gives at first a black sublimate, which as stated by Richter,* looks exactly like mercuric sulphide and undoubtedly is that substance. On intense heating before the blowpipe there formed farthest up on the tube a sublimate of sulphur, next followed the black ring of mercuric sulphide, neither of which increased perceptibly by continued heating, while nearest the assay the nearly colorless globules of $GeS_2$ were deposited. On breaking off the lower end of the tube, driving off the sulphur and mercuric sulphide by gentle heat and then roasting the globules in a current of air, $SO_2$ was given off while the germanium oxide collected into a fused mass but was not volatilized. Regarding the association of canfieldite with other minerals, all that can be said is that the specimens are remarkably pure, only slight quantities of pyrite, sphalerite and kaolin being attached to them.

It having been shown that the mineral was essentially a sulpho-salt of germanium and silver, the following method was adopted for analysis. A weighed quantity, about two grams, was oxidized by concentrated nitric acid, the operation requiring from one to two hours on the water bath. After the oxidation was complete the excess of nitric acid was removed by evaporation. The residue was then dissolved in warm water slightly acidified with nitric acid, and after filtering off a slight trace of insoluble residue the silver was precipitated by hydrochloric acid, filtered and weighed. In the

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* Quoted by Weisbach and Winkler. Loc. cit.

filtrate the sulphur was precipitated as barium sulphate, which was purified by fusion with sodium carbonate, reprecipitated and weighed. For the determination of germanium another portion of two grams was oxidized by nitric acid with the addition of a little sulphuric acid. After removal of the large excess of nitric acid by evaporation, the residue was dissolved in warm water, with addition of some nitric acid if necessary, the silver precipitated with ammonium thiocyanate and removed by filtration. The filtrate contained the germanium together with no acid which forms with it a volatile compound. It was evaporated in a platinum dish, the nitric acid present serving to completely destroy the ammonium thiocyanate, and the excess of sulphuric acid was finally driven off by heating. The residue thus obtained was covered with a little strong ammonia into which hydrogen sulphide was conducted. Under this treatment the germanium oxide dissolved, while all heavy metals, except those which form sulpho-salts soluble in ammonium sulphide, were left undissolved. In this particular case a very small quantity of a black sulphide remained; it was filtered off, ignited and weighed. It is assumed to be a mixture of zinc and iron oxides, resulting probably from admixed sphalerite and pyrite. The filtrate containing the germanium was collected in a weighed platinum crucible and evaporated on the water bath. The residue was oxidized by strong nitric acid, the excess of which was removed by evaporation. The crucible, placed inside of a porcelain one, was then ignited, gently at first, finally to the full extent of a ring burner, then weighed and the germanium determined as $GeO_2$. On further ignition the weight was found to be constant, nor did it change by heating to full redness. When heated in a current of ammonia and air, to remove sulphuric acid, the weight diminished very little; thus in one experiment it fell from 0·1535 to 0·1525 grs., showing that a gentle ignition is sufficient to practically expel all of the sulphuric acid. By heating to a bright redness in a current of ammonia and air the germanium oxide suffered reduction to the metallic state. To show that the germanium oxide was pure and especially to prove the absence of arsenic and antimony the following tests that were made may be mentioned. Rather large quantities of the mineral, when roasted in the open tube gave no sublimate. An acid solution of the oxide gave upon addition of hydrogen sulphide a white precipitate, which when collected on a filter showed only a pale tinge of yellow. Also the oxide obtained in the analysis when dissolved and brought into a Marsh apparatus gave only a most minute and unweighable blackening on the walls of the tube, which on ignition in the air changed to a scarcely perceptible white oxide resembling antimony. As the mineral dissolves completely in nitric acid tin cannot be present. These results therefore showed that the germanium was satisfactorily pure. Another method of analysis in which everything was determined in one portion is as follows: Solution of the mineral in nitric acid, precipitation of the silver with hydrochloric acid, of the sulphur with barium nitrate, removal of the excess of chlorine and barium in one operation with silver nitrate and sulphuric acid, final removal of the silver by ammonium thiocyanate and determination of the germanium in the filtrate as above.

The result of the analysis gave the following figures:

| | | | | Average. | Deducting impurities. | Theory for $Ag_8GeS_6$ |
|---|---|---|---|---|---|---|
| S ..... | 17·03 | 17·04 | | 17·04 | 17·10 | 17·06 |
| Ge.... | 6·51 | 6·52 | 6·61 | 6·55 | 6·57 | 6·42 |
| Ag . . | 76·01 | 76·09 | | 76·05 | 76·33 | 76·52 |
| Fe, Zn | ·14 | ·16 | ·10 | ·13 | | |
| Insol. . | ·29 | | | ·29 | | |
| | | | | 100·06 | 100·00 | 100·00 |

The formula of the mineral is evidently $Ag_8GeS_6$ or $4Ag_2S . GeS_2$. The agreement of the analysis with the theory as will be noticed is reasonably close.

Winkler made the following analysis of argyrodite, from which he derived the formula $Ag_6GeS_5$ or $3Ag_2S . GeS_2$.

| | Analysis by Winkler. | Theory for $Ag_6Ge_5S_5$ | Theory for $Ag_8GeS_6$ | Atomic weights. |
|---|---|---|---|---|
| S.... | 17·13 | 18·21 | 17·06 | 32 |
| Ge .. | 6·93 | 8·23 | 6·42 | 72·32 |
| Ag .. | 74·72 | 73·56 | 76·52 | 107·7 |
| Hg .. | ·31 | | | |
| Fe .. | ·66 | | | |
| Zn .. | ·22 | | | |
| | 99·97 | 100·00 | 100·00 | |

It will be noticed that Winkler's analysis agrees much more closely with the theory for $Ag_8GeS_6$, especially in respect to the sulphur and germanium, than with the formula advanced by him. It seems probable, therefore, that the two minerals have the same chemical composition, but since Weisbach has shown that argyrodite is monoclinic and since canfieldite is isometric, they cannot be identical.

In order to investigate this point more closely it seemed desirable to make a new analysis of argyrodite by the same methods which had been used for canfieldite. The material was very carefully selected from an excellent specimen of the

Freiberg argyrodite in the collection of Prof. Brush. The specific gravity was determined in two ways. Some larger fragments, weighing about two grams, gave on the chemical balance in distilled water 6·149 and the smaller ones gave by use of the pycnometer 6·162. These results, though somewhat higher than those given by Winkler and Weisbach, which were 6·085–6·111, are still considerably lower than the specific gravity of canfieldite. The result of the analysis is as follows:

| | | | Average. |
|---|---|---|---|
| S | 16·97 | | 16·97 |
| Ge | 6·67 | 6·62 | 6·64 |
| Ag | 75·57 | 75·53 | 75·55 |
| Hg | ·34 | | ·34 |
| Fe, Zn | ·24 | | ·24 |
| | | | 99·74 |

It will be seen that this analysis agrees remarkably well with that of Winkler, the only essential difference being that the silver is somewhat higher and the iron and zinc are lower. This suggests that these latter are impurities, resulting from the presence of a slight admixture of pyrite and sphalerite, both of which are associated with the mineral. In regard to the mercury, since this element has never been known to occur otherwise at Freiberg, it is probable that it replaces silver. If we now recalculate these analyses, excluding the iron and zinc with sufficient sulphur to form pyrite and sphalerite, and replacing the mercury by its equivalent in silver, we obtain the following:

| Canfieldite. | Argyrodite, Winkler. | Argyrodite, Author. | Theory for $Ag_8GeS_6$ |
|---|---|---|---|
| 17·10 | 16·56 | 16·83 | 17·06 |
| 6·57 | 7·05 | 6·69 | 6·42 |
| 76·33 | 76·39 | 76·48 | 76·52 |
| 100·00 | 100·00 | 100·00 | 100·00 |

From the consideration of these results there can be no doubt that canfieldite and argyrodite have the same chemical composition, which is $Ag_8GeS_6$. It is evident therefore that we have here a case of dimorphism, for both the crystalline forms and the specific gravities indicate that the minerals are distinct.

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