

ART. VIII.—*Sperrylite*,\* a New Mineral; by HORACE L. WELLS.

A SMALL quantity of the remarkable mineral which is the subject of this article was sent to the writer in October, 1888, by Mr. Francis L. Sperry, of Sudbury, Ontario, Canada, chemist to the Canadian Copper Co. of that place. A few tests sufficed to show that it was essentially an arsenide of platinum and consequently of great interest, since platinum has not been found before, at least as an important constituent, in any minerals except the alloys with the other metals of the platinum group.

Since the time mentioned Mr. Sperry has furnished, with great liberality, an abundance of the material for investigation and has given the following account of its occurrence :

“The mineral was found at the Vermillion Mine in the District of Algoma, Province of Ontario, Canada, a place 22 miles west of Sudbury and 24 miles north of Georgian Bay, on the line of the Algoma Branch of the Canadian Pacific Railway. The mine was discovered in October, 1888. A 3-stamp mill was put up for the purpose of stamping the gold quartz. Associated with this gold ore was a considerable quantity of pyrite, chalcopyrite and pyrrhotite. At the contact of ore and rock and occupying small pockets in decomposed masses of the ore, there was a quantity of loose material composed of gravel containing particles of copper and iron pyrites. It was in milling this loose material that several ounces of the arsenide of platinum were gathered on the carpet connected with the stampmill. Through the kindness of Mr. Charlton, the genial President of the Vermillion Mining Co., all of the mineral that was available was generously placed at my disposal.”

It may be mentioned here that Mr. Sperry sent me, a few weeks before sending the arsenide, a minute bead which he had obtained in making a fire-assay for gold on an ore, consisting chiefly of chalcopyrite and pyrrhotite, which came from the same mine where the arsenide was found but which was not the material in which it actually occurred. This bead on examination proved to be composed largely of metals of the platinum group, and, from the color of the precipitate produced by ammonium chloride, it was thought that it contained a large proportion of iridium, but its small size prevented a satisfactory examination. With this bead in mind, I expected that the new mineral would contain a considerable amount at least of iridium, but, strangely enough, none of this metal was found in it. The material as received consisted of a heavy, brilliant sand composed largely of the arsenide; but intermixed with this a considerable amount of fragments of chalcopyrite,

\*Pronounced Sperryl-ite.

pyrrhotite and some silicates could be seen. In order to purify the substance it was treated for a short time with warm aqua regia to remove sulphides, etc.; then it was treated for a long time with hot hydrofluoric acid to remove the silicates. After these treatments the sand possessed great brilliancy, but it was found by microscopic examination to contain some transparent grains which on chemical examination proved to be stannic oxide. Prof. S. L. Penfield kindly examined these grains and found that they corresponded perfectly in their optical properties with cassiterite.

Nearly all the grains of the new mineral showed extremely brilliant crystal-faces, though most of the crystals were fragmentary; in size they were mostly between  $\cdot 05$  and  $\cdot 5^{\text{mm}}$  ( $\frac{1}{20}$  and  $\frac{1}{50}$  inch) in diameter.

The color of the mineral is nearly tin white or about the same as that of metallic platinum; the fine powder is black.

The specific gravity taken twice on the same 8 grams of material, was  $10\cdot 420$  and  $10\cdot 424$  at  $20^{\circ}$ ; this material was the same that was used for analysis, and, correcting the average of these results for  $4\cdot 62$  per cent. of cassiterite, the true specific gravity becomes  $10\cdot 602$ .

The sand is not easily wet by water and shows a marked tendency to float when brought to its surface. By placing a shallow layer of water upon the mineral in a vessel it is easy to nearly cover the surface of the water with a continuous layer of the crystals by inclining the vessel repeatedly so that they are brought to the surface. The phenomenon is not due to any oily substance upon the particles, for they float with equal readiness after being boiled with a strong solution of potash and washed with alcohol and ether. When they are floating upon water it is quite difficult to cause them to sink, and when carried to the bottom by a stream of water they frequently carry down small bubbles of air which they completely surround and hold down by their weight. If ether is poured upon water on which they are floating, they remain suspended between the two liquids, and, by agitation, can frequently be made to sink to the bottom in spherical clusters surrounding globules of ether.

The mineral is only slightly attacked by aqua regia; even when it is very finely pulverized and the strongest aqua regia is repeatedly applied with the aid of heat for several days, the solution is only partial.

*Pyrognostics.*—The mineral decrepitates slightly when heated. In the closed tube it remains unchanged at the fusing-point of glass. In the open tube it gives very readily a sublimate of arsenic trioxide and does not fuse if slowly roasted, but if rapidly heated it melts very easily after losing a part of the arsenic. Perhaps its most characteristic reaction is the follow-

ing: when dropped on red hot platinum foil it instantly melts, gives off white fumes of arsenic trioxide having little or no odor, and porous excrescences are formed in the platinum which do not differ in color from the untouched foil.

*Chemical analysis.*—The following analyses of the mineral were made after a considerable amount of preliminary work had been done on it, the results of which confirm these figures.

|                  | I.           | II.          | Mean.              | Ratio.   |
|------------------|--------------|--------------|--------------------|----------|
| As               | 40.91        | 41.05        | 40.98 ÷ 75 = .546  | .550 = 2 |
| Sb               | 0.42         | 0.59         | 0.50 ÷ 122 = .004  |          |
| Pt               | 52.53        | 52.60        | 52.57 ÷ 197 = .267 | .274 = 1 |
| Rh               | 0.75         | 0.68         | 0.72 ÷ 104 = .007  |          |
| Pd               | trace        | trace        | trace              |          |
| Fe               | 0.08         | 0.07         | 0.07               |          |
| SnO <sub>2</sub> | 4.69         | 4.54         | 4.62               |          |
|                  | <u>99.38</u> | <u>99.53</u> | <u>99.46</u>       |          |

The composition is consequently represented by the formula PtAs<sub>2</sub>, a small portion of the platinum and arsenic being replaced respectively by rhodium and antimony. In composition this mineral appears to be nearer Wöhler's laurite\* than any other mineral now known. The form of both is isometric,† but their composition is apparently not quite analogous since the formula of laurite is given as RuS<sub>2</sub> +  $\frac{1}{30}$  Ru<sub>4</sub>Os. It is possible that the latter formula is slightly incorrect since Wöhler used an extremely small quantity (.3145 gram) for his analysis and acknowledged the uncertainty of his results. It is also to be noticed that the composition of the mineral corresponds to that of the artificial platinum arsenide made by Murray.‡ The writer has confirmed the composition of this artificial arsenide by heating a known weight of platinum to redness and passing over it vapor of arsenic in a current of hydrogen. The following are the results of the experiments:

|     | Pt. taken. | As. absorbed. | Ratio. |        |
|-----|------------|---------------|--------|--------|
|     |            |               | Pt.    | As.    |
| I   | .3806      | .2922         | 1      | : 2.02 |
| II  | .5725      | .4354         | 1      | : 2.00 |
| III | 1.0757     | .8112         | 1      | : 2.00 |

It was noticed in these experiments that the arsenic combines with the platinum with incandescence and the alloy melts even below a red heat after a part of the arsenic has been taken up. At the end of the operation, however, the fused globule solidifies, throws out peculiar, arboresecent forms and the PtAs<sub>2</sub> remains as a porous and very brittle mass which is neither fused nor changed in composition when heated to bright red-

\* Ann. Ch. Pharm., cxxxix, 116.

† See next article for crystalline form of Sperrylite. ‡ Watt's Dictionary.

ness in hydrogen. In its behaviour with solvents and its pyrognostic properties the artificial compound agrees exactly with the natural mineral.

*Method of analysis.*—The amount of substance taken for each analysis was about 1.5 g. The pulverized substance was gradually heated in a current of chlorine gas and the volatile chlorides were absorbed by water in a receiver.\* This liquid was made ammoniacal after adding a very small quantity of tartaric acid to keep the small amount of antimony in solution and the arsenic was determined as magnesium pyroarsenate. From the filtrate from the ammonium magnesium arseniate, antimony and a trace of platinum were precipitated as sulphides, the sulphide of antimony was dissolved in strong hydrochloric acid, the sulphide was reprecipitated, filtered on asbestos and weighed after proper heating in a current of carbon dioxide, while the trace of platinum sulphide was ignited and the residue was added to the main part of the platinum left by treatment with chlorine. This part was treated with dilute aqua regia; this left an insoluble residue consisting of casiterite and a finely divided black substance which had been found by previous qualitative tests to be rhodium. This residue was fused with sodium carbonate and sulphur, the insoluble rhodium sulphide formed was ignited in air, then in hydrogen and weighed, while the tin was determined as stannic oxide in the usual way. The purity of the rhodium was shown by its complete solubility in fused potassium disulphate, also by finding that it gave no sodium double chloride soluble in alcohol after ignition with sodium chloride at a faint red heat in a current of chlorine. About  $\frac{2}{3}$  of the total rhodium was found here. The purity of the stannic oxide was shown by reducing it in hydrogen and dissolving the metal in hydrochloric acid.

The solution in aqua regia containing platinum with a little rhodium and iron and a trace of palladium was treated for the platinum metals essentially by the method of Claus;† the main variations being a repeated separation of platinum from rhodium and the weighing of platinum as metal. A distinct but extremely small precipitate of palladium cyanide was obtained, but the amount of palladium was too small to sensibly affect the balance when an attempt was made to weigh it.

*The name.*—The writer takes great pleasure in naming this interesting mineral after Mr. F. L. Sperry, to whose efforts this investigation is due.

Sheffield Laboratory, Dec. 12, 1888.

\* Preliminary experiments with the artificial compound,  $\text{PtAs}_2$ , had shown that all the arsenic passes off in this operation if the heat is applied slowly enough so that the substance does not melt after losing a part of its arsenic.

† Rose and Finkener, *analytische Chemie*, 6<sup>te</sup> Aufl., vol. ii, p. 236.