LX.—*Traces of a New Tin-group Element in Thorianite.*

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IN the course of an examination of the iron residues separated from 5 cwt. of the cubical Ceylon mineral belonging to Sir William Ramsay (compare O. Hahn, *Proc. Roy. Soc.*, 1905, **76**, A, 115; Dunstan and Blake, *ibid.*, 760), it was found that about 1 per cent. of the material was formed of sulphides of the silver, copper, and tin-group elements which had escaped precipitation in the proper place.

A preliminary examination showed this sulphide precipitate to be mainly due to lead, of which thorianite contains nearly 3 per cent. as oxide (Dunstan and Jones, *ibid.*, **77**, A, 546, and others); the rest, about 10 per cent. of the sulphides as it proved, was a mixture of sulphides of the copper and tin metals which are found only as traces in the mineral itself (Büchner, *ibid.*, **78**, A, 358).

During the separation of these sulphides into groups in the ordinary course of analysis colorations were observed which could not be accounted for and, since further inquiry led to the conclusion that these colorations were due to some substance associated with the tin

metals, an examination of the thorianite residues containing this group was determined on.

The material used in the investigation amounted altogether to about 2·5 kilos. of mixed sulphides; 1 kilo. of this was laboriously collected from 80 kilos. of the iron residues as already indicated (this was particularly rich in tin-group sulphides), and the rest was part of the lead residues of the 5 cwt. of thorianite. Rather more than 6 per cent. of the whole proved to be sulphides of the tin group; this was separated with sodium hydroxide by fusion in a nickel crucible. A portion of the 150 grams so obtained was analysed, but, although only arsenic, antimony, tin (stannic), and selenium were detected, it was evident from the colour of the filtrates that some soluble brown sulphide (?) was also present, and search was made for a method of separation.

Eventually this brown sulphide was isolated with arsenious sulphide, which it resembles in being insoluble in hydrochloric acid and readily soluble in ammonium carbonate solution; to the latter it gives a characteristic deep brown colour. Like arsenious sulphide it dissolves in nitric acid but the concentrated syrupy liquid has a strong golden-brown colour, and leaves on evaporation at 120° a brown, hygroscopic oxide; this is reduced by hydrogen at 250—300° to a black oxide and then at a higher temperature to a dark grey, non-volatile metal which melts at a bright red heat.

The brown sulphide is attacked only with difficulty by a mixture of hydrochloric acid and potassium chlorate; after this treatment the greater part remains mixed with sulphur, from which it is easily removed by a solution of ammonium carbonate.

After many months of work only about 0·05 gram of the brown oxide has been collected from about one-third of the mixed sulphides and this is not free from arsenic. This corresponds with about 1 part in 1·5 million (less than 1 gram to the ton) of thorianite or 0·005 per cent. of the tin-group sulphides, an amount which would very likely have escaped notice altogether had it not been that the sulphide dissolves in water, which is coloured brown by a very small quantity. This solubility in water greatly increases the difficulty of separation, for the solid is not easily recovered from what appears to be a true and not a colloidal solution; it accounts also for the fact that hydrogen sulphide and acid only partly re-precipitate the sulphide from solutions containing ammonium carbonate.

The determination of the equivalent of the metal has been attempted in two ways: by electrolysis, using Faraday's Law, and by reduction of the brown oxide to metal by heating in hydrogen; the latter method indicates a considerably higher equivalent than that of arsenic.

The electrolysis of a few milligrams of material was carried out with the help of Dr. Brill, who weighed the small platinum electrodes on his balance of the Nernst type. The same current was used to deposit antimony, bismuth, and the unknown element from similar solutions of their chlorides containing gelatin, the standard being silver deposited from a solution of silver perchlorate. There was not more than about 1 per cent. of error in the equivalent found for antimony by this method but the deposit of the unknown element was unsatisfactory.

A preliminary spectroscopic examination revealed no new lines, but it is hoped to make further experiments in this direction.

Incidentally a little more knowledge of the composition of thorianite has been gained. It is now possible to state positively that it contains arsenic, mercury, bismuth, molybdenum, and selenium; several grams of arsenious sulphide have been isolated, and a drop of mercury weighing about 0.5 gram; bismuth, molybdenum, and selenium are present in much smaller amount. The lead residues contain also a quantity of silica, but this may have found its way in from vessels employed in the disintegration of the mineral, although the method used (fusion with bisulphate) scarcely warrants this assumption.

Incidentally also a new triple *oxalate* of thorium, uranium, and ammonium was prepared in considerable quantity. To obtain this the pale green double oxalate formed by adding oxalic acid to a solution containing thorium and a uranous salt was dissolved in ammonium oxalate solution and the solution was then slowly evaporated; it forms large emerald-green crystals which lose ammonia and water on exposure to air. The composition of these crystals, determined in conjunction with Miss K. A. Burke, appears to be $\text{ThU}_25(\text{NH}_4)_2(\text{C}_2\text{O}_4)_{10} \cdot 14\text{H}_2\text{O}$.

Lack of material has for the time brought the investigation to a close, but steps are being taken to continue the search for the supposed new element in other ores of arsenic.

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