On the occurrence of varlamoffite (partially hydrated stannic oxide) in Cornwall.

By Sir Arthur Russell, Bart.

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Characters and mode of occurrence (A.R.).

As long ago as 1906 I had noticed a yellowish clay-like mineral occurring somewhat abundantly at both Cligga mine, Perranzabuloe, and at Bunny mine, St. Austell. From its appearance the mineral did not look particularly interesting, neither did it suggest being one containing a metal, and for these reasons no attempt was made to determine its character. In a paper read before this Society in 1937 I mentioned this yellowish clay-like substance as occurring associated with rashleighite at the Bunny mine.[2] Soon after the publication of this paper in 1948 I received a letter from Monsieur N. Varlamoff in the Belgian Congo saying he had seen my reference to the 'yellowish clay-like substance' (p. 356) and suggested it might possibly be identical with the mineral varlamoffite which he had recently discovered in the Belgian Congo and which had been named after him, his description of the mineral with analysis, mode of occurrence, and localities having been published in 1948.[3] Sure enough, on examination I found both the Cligga and Bunny minerals to contain a high proportion of tin. Through the interest of Professor K. C. Dunham, Dr. E. A. Vincent of Durham University most readily and kindly undertook the full chemical examination of this somewhat remarkable and puzzling material—a quite tricky

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[2] A. Russell, On rashleighite, a new mineral from Cornwall, intermediate between turquoise and chalcosiderite. Min. Mag., 1948, vol. 28, pp. 353–358.

[3] N. Varlamoff, Matériaux pour l'étude du minéral jaune d'étain (varlamoffite): occurrence, géologie et origine du minéral. Ann. (Bull.) Soc. Géol. Belgique, 1948, vol. 72, pp. B41–B46. [M.A. **10**–454.]

task. In the following notes I have attempted to describe its character and mode of occurrence.

Cligga mine (formerly a part of Perran Great St. George mine) Perranzabuloe, Cornwall. (Six-inch Ordnance map, Cornwall, 48 NW., 1908.)—The small granite mass traversed by countless small mineral veins with greisen walls which forms the 300-feet high Cligga Head has been worked for tin from time immemorial, and latterly for both tin and wolfram. The cliff itself is honeycombed by old workings, the visible numbers of which are continually altering in appearance owing to the frequent falls of cliff. The area occupied by the top of the cliff is covered with granitic and greisenized vein-stuff derived from the old workings, and it is here that specimens of varlamoffite may still be found. The largest and best specimens which I have obtained were found during the carting away of one of these old dumps near the cliff top in February 1939, and at the same time, while the mine was still at work, I found the mineral in situ in some of the small veins underground between the surface and the 300-feet level at the base of the cliff; here also a small vein of stannite is still visible in the roof of one of the old levels. During the late working of the mine there is every reason to believe that considerable quantities of stannite and varlamoffite actually went through the mill, though of course the only tin recovered was in the form of cassiterite.

The Cligga mine varlamoffite is a rather soft, somewhat clay-like colloidal mineral, in colour straw-yellow to massicot-yellow to cream-buff (colours of R. Ridgway). Under the microscope the surface of the purest material often shows a waxy glistening lustre resembling that of certain melts; here and there are blebs of colourless quartz of varying size, minute scales of mica, and occasionally small prisms of black tourmaline. In some specimens the mineral forms layers up to an inch in thickness, with quartz, on greisen; in others it occurs as very considerable masses with quartz and is permeated by long blades of wolframite and is associated with stannite, cassiterite, arsenopyrite, greyish-green scorodite, and scales of white gilbertite.

The following is a list of the minerals which I have observed in the greisen veins of Cligga mine. Molybdenite rarely, cassiterite often well crystallized, stannite abundant, varlamoffite, wolframite abundant; and occasionally well crystallized arsenopyrite, scorodite, pharmacosiderite, native copper, chalcopyrite, olivenite, torbernite, topaz well crystallized, lithia-mica crystallized as large plates, gilbertite, andalusite rarely unaltered and pink in the contact-altered slate (killas).

Bunny mine, St. Austell, Cornwall. (Six-inch Ordnance map, Cornwall, 41 SE., 1908).—The Bunny mine varlamoffite differs from that of Cligga mine in being for the most part of an ivory-yellow colour and very occasionally primrose-yellow. It occurs, intimately associated with light blue-green rashleighite and blue turquoise, in layers up to 1½ inches thick in cassiterite and wolframite lodes with greisen walls traversing kaolinized granite, a description of which was given in my paper on rashleighite. The mineral also occurs alone filling crevices in bands of slightly smoky crystalline quartz. Both the varlamoffite and rashleighite occasionally contain small grains of fresh cassiterite and wolframite, associated minerals being stannite rarely, pyrite, arsenopyrite, chalcosine, fluorite, gilbertite, and tourmaline. The Bunny mine specimens of varlamoffite were obtained by digging into the engine shaft dump, and from a vein outcrop a little south of the southernmost of the two old pits.

Kit Hill Great Consols mine, Stokeclimsland, Cornwall. (Six-inch Ordnance map, Cornwall, 29 NE., 1907.)—The numerous cassiterite and wolframite veins with greisen walls which traverse the granite of Kit Hill seemed a likely locality for varlamoffite and I was rewarded by finding it here in May of this year (1951). The specimens were obtained from one of the many small dumps in an old open-cut on an east and west lode, north-east of the summit.

The varlamoffite is cream-buff to brownish-yellow in colour and exhibits a much more coarse colloidal structure than that from Cligga and Bunny mines. It forms layers up to ⅝ of an inch thick on quartz enclosed by greisen walls, and here again on two of the specimens a very small patch of unaltered stannite is visible in the quartz underlying the varlamoffite. A little black cassiterite, arsenopyrite, scorodite, mica, and tourmaline are also present in the quartz directly adjacent to the varlamoffite.

It may not be out of place to record here the localities in Cornwall at which stannite has been found:

Botallack mine, St. Just (H. S. Boase, 1822).
St. Michael's Mount, Marazion (W. Phillips, 1819).
West Wheal Providence (Wheal Conqueror), St. Erth (A. Russell, 1949).
Dolcoath mine (New Roskear shaft), Camborne (E. H. Davison, 1927).
Carn Brea mine, Illogan (J. Garby, 1947).
South Crofty mine, Illogan (T. M. Hall, 1868).
East Pool mine and Wheal Agar, Illogan (J. H. Collins, 1871).
Wheal Scorrier (Scorrier Consols mine), St. Agnes (R. Jameson, 1816). Requires confirmation.
Wheal Rock (afterwards part of West Kitty mine), St. Agnes (R. E. Raspe, 1785).
Wheal Kine (afterwards part of Polberro mine), St. Agnes (Alfred Fox colln.).

Cligga mine (formerly a part of Perran Great St. George mine), Perranzabuloe (A. Russell, 1939).

Stenna Gwyn mine, St. Stephen in Brannel (W. Gregor, 1800).

Bunny mine, St. Austell (A. Russell, 1944).

Kit Hill Great Consols mine, Stokeclimsland (A. Russell, 1951).

Barrier mine, Gwennap; Wheal Primrose, St. Agnes; and Lanescot mine, Tywardreath, are all mistakenly given as localities for stannite by J. H. Collins, 1871.

CHEMICAL AND X-RAY EXAMINATION (E.A.V.).

A complete chemical analysis has been made of the material from the Cligga mine, and confirmatory qualitative tests made upon the material from the Bunny mine and a sample of varlamoffite from the Belgian Congo.

TABLE I. Chemical analyses of varlamoffite.

	I.		*Ia.*	II.		III.
SnO_2	65·8	H_2SnO_3	37·79	59·22	Sn	25·8
Fe_2O_3	9·23	SnO_2	31·50	25·55	SiO_2	25·8
FeO	0·37	$FeAsO_4.2H_2O$	14·31	—	Fe	8·9
CuO	0·63	Cu_2FeSnS_4	1·51	—	H_2O	11·89
As_2O_5	7·13	SiO_2	1·07	1·68	SO_4, As, Sb also present;	
S	0·44	Al_2O_3	2·14	2·22	17·2 % Sn sol. in HCl;	
$H_2O+105°$	6·26	Fe_2O_3	4·31	9·45	$SnO_2.xH_2O$ 21·85 %	
$H_2O-105°$	4·53	FeO	0·11	—		
SiO_2	1·07	CuO	0·08	—		
Al_2O_3	2·14	MgO	0·66	—		
MgO	0·66	WO_3	1·27	—		
CaO	nt. fd.	Bi_2O_3	0·77	—		
WO_3	1·27	$H_2O-105°$	4·53	2·12		
Bi_2O_3	0·77		100·05	100·24		
TiO_2	nt. fd.			SnO_2 78·45		
MnO	trace			Sp. gr. 2·52–3		
	100·30					
Less O for S*	0·17					
	100·13					
Sp. gr.	3·13					

I, Material from Cligga mine, Cornwall. Analyst, E. A. Vincent.
Ia, Analysis I partially and tentatively recalculated.
II, Varlamoffite, Belgian Congo, average of three analyses. (N. Varlamoff, 1948; S. Gastellier, 1950.)
III, 'Souxite' (varlamoffite), Potosí, Bolivia. (R. Herzenberg, 1946 [M.A. **10**–8].)
* Assuming all S present in stannite, Cu_2FeSnS_4.

The methods used in the chemical analysis of the Cligga mine material were largely based upon those given by Kallmann.[1] Decomposition by

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[1] S. Kallmann, Importance, composition, and analysis of Bolivian tin concentrates. Indust. Engin. Chem. (Anal. Edit.), 1943, vol. 15, no. 3, pp. 166–174.

means of the low-temperature sodium peroxide frit, as described by Rafter[1] proved effective for preparing a solution of the material for general analysis. The value given for SnO_2 in the analysis is an average of four determinations—two iodimetric and two gravimetric—made upon rather small amounts of material, and though the agreement between these determinations is fair, the writer does not feel justified in quoting the average to two places of decimals. Copper was determined colorimetrically, and bismuth both colorimetrically and gravimetrically as BiOCl, the figure quoted being again the mean of the two results, which were in good agreement.

A qualitative spectrographic examination of a small fragment of the material was kindly made by Dr. L. Lund, of the Department of Geology, University of Leeds. In addition to the elements tabulated above Dr. Lund finds a small trace of silver, but no evidence for antimony, zinc, molybdenum, or vanadium.

The result of the analysis shows that the material is obviously not a definite mineral species, but a complex mixture, in which stannic oxide is the principal ingredient. Qualitative tests indicate also that the arsenic is present in the original material as arsenate. Because of this, and in view of the fact that the material occurs in association with stannite, an attempt has been made (column I*a*) to recalculate part of the chemical analysis.

If all the sulphur is combined with copper, ferrous iron, and tin in the stannite molecule, it is seen that this would account for most of the copper and ferrous iron in the analysis. It seems reasonable, also, to suppose that the arsenate ion may be combined with some of the abundant ferric iron in some form of ferric arsenate. It has been conventionally calculated as scorodite, $FeAsO_4.2H_2O$, though there is no evidence that this mineral exists as such in the mixture. The residual 'combined' water (given off above 105° C.) has been calculated into metastannic acid, H_2SnO_3, and the remaining tin left as stannic oxide. The degree of hydration of the stannic oxide in these materials is clearly indefinite. It is possible that some of the water given off below 105° C. may be loosely associated with more of the stannic oxide, but, in the absence of any precise evidence on this point, it is deemed best to state the 'hygroscopic' water separately. Some water will doubtless also be associated with the ferric iron and alumina remaining in the analysis.

In columns II and III of the table, analyses of varlamoffite from the

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[1] T. A. Rafter, Sodium peroxide decomposition of minerals in platinum vessels. Analyst, 1950, vol. 75, pp. 485–491.

Belgian Congo and from Bolivia are reproduced for comparison. These appear to be simpler substances than that from the Cligga mine. Attention may be drawn in passing to the similarity in the values for silica, alumina, and ferric iron in the Congo and Cligga mine analyses. A small amount of arsenic was detected by the writer, using the Gutzeit test, in a sample of the Congo material sent by N. Varlamoff to Sir Arthur Russell.

No quantitative determinations have been made upon the small amount of picked material available from the Bunny mine, St. Austell, Cornwall. Qualitative tests show the presence of a high proportion of tin, and the total absence of arsenic. These tests, together with the evidence of the X-ray powder photographs, indicate that this material also consists mainly of partially hydrated stannic oxide, and is likely to be more closely comparable with the varlamoffite from the Belgian Congo than with the material from the Cligga mine.

X-ray powder photographs.

X-ray powder photographs have been taken of the partially hydrated stannic oxide materials from the Cligga, Bunny, and Kit Hill mines, Cornwall, and, for purposes of comparison, of the type varlamoffite from the Belgian Congo, a specimen of Cornish cassiterite from the mineral collection in the Durham Colleges' Department of Geology, and of air-dried 'metastannic acid' (prepared by dissolving pure metallic tin in dilute nitric acid and digesting the solution on the hot-plate). These photographs, in the form of positive prints, are reproduced in fig. 1. All were taken under identical conditions in a camera 9 cm. diameter, using Cu-$K\alpha$ radiation.

It is of interest to compare the resolution and the sharp definition of the lines in the cassiterite pattern (no. 5) with the broadened and ill-defined lines of the remainder. These remaining five patterns appear to consist of the most prominent lines of the cassiterite pattern; there are, perhaps, a few minor differences in spacing, but the essential identity of all the patterns is clear enough. No quantitative measurements have been made on the films.

The broadening of the prominent lines in the varlamoffite patterns, and the failure of the finer ones to be resolved at all, is presumably to be ascribed to the partly colloidal nature of these ochreous materials, which might be interpreted as mixtures of cassiterite and hydrated stannic oxide, with other impurities, in a very fine state of subdivision. In particular, the 'metastannic acid' prepared in the laboratory has given very

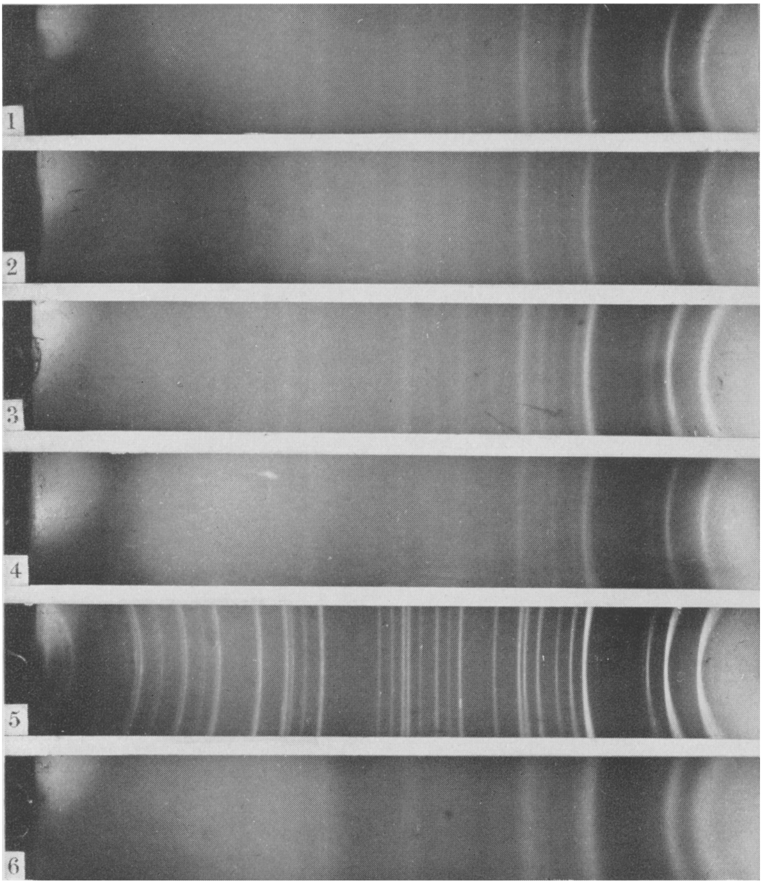

FIG. 1. X-ray powder photographs of stannic oxide materials. 1. Varlamoffite, Kalima, Maniema, Belgian Congo. 2. Arsenic-bearing varlamoffite, Cligga mine, Cornwall. (Analysis in table I.) 3. Varlamoffite, Bunny mine, Cornwall. 4. Varlamoffite, Kit Hill mine, Cornwall. 5. Cassiterite, Redmoor, Cornwall. 6. Hydrated stannic oxide ('metastannic acid') prepared in the laboratory.

broad and diffuse bands. It is stated in Dana's 'System of mineralogy' (7th Edition, 1944, p. 579) that 'Gels or sols of hydrous stannic oxide are formed by precipitating stannic salts with alkalies, and in other ways, and on aging give the X-ray diffraction pattern of cassiterite'.

Of the other patterns, that of the Bunny mine material is perhaps rather better defined than those of the Congo or the Cligga mine materials.

As far as can be made out, the pattern of the analysed material from the Cligga mine shows no lines which are not part of the cassiterite pattern. It is scarcely to be expected that the minor ingredients would have any effect upon the X-ray powder pattern, but some manifestation of the presence of ferric arsenate might have been anticipated. This substance, if present, does not therefore occur as the well-crystallized mineral scorodite, but in a colloidal form which seems to have no effect other than to cause a more or less uniform scattering of the X-rays.

Conclusions.

Some degree of hydration of stannic oxide, then, does not cause a rearrangement of the cassiterite crystal structure, and it seems probable that the 'combined' water in these materials is held by a tenacious surface adsorption on to particles of stannic oxide of almost colloidal dimensions consisting of aggregates of relatively small numbers of cassiterite unit cells. It would appear to be difficult on theoretical grounds to accommodate water molecules into the rather compact body-centred tetragonal lattice of cassiterite without causing considerable disruption.

No study has been undertaken to determine the precise nature of the hydration, or to determine which of the various possible hydrated stannic oxides are in fact present.

In this connexion, it may be as well to state briefly Varlamoff's observations and conclusions concerning the origin of the varlamoffite in the Belgian Congo. Here, he writes (loc. cit., 1948, p. B 45), it is often found filling geodes lined with cassiterite, and moulded upon this mineral. These cassiterite crystals retain perfectly smooth and polished faces, proving that the earthy yellowish varlamoffite does not originate from alteration of cassiterite. Further, he records that stannite is traversed by veinlets of the yellowish material, which has obviously been formed at the expense of the stannite, replacing it along cracks. Similar yellowish material has also been found to replace other sulphides, such as chalcopyrite.

Finally, in the Belgian Congo occurrences, tetrahedral zonary growths of varlamoffite are found, which are regarded as pseudomorphs after stannite.

Since varlamoffite in the Cornish occurrences is associated again with stannite and wolframite in greisen veins, while scorodite and arsenopyrite are also present locally, it seems likely that a similar origin can be envisaged for the material in the Cligga, Bunny, and Kit Hill mines. A process of oxidation and hydration of stannite, perhaps with arsenopyrite or scorodite, seems far more probable than any direct hydration of such a stable mineral as cassiterite. Tiny specks of a sulphide mineral, identified as stannite, have been noted by Sir Arthur Russell in the Kit Hill material, and he also records scorodite.

ADDENDUM.

Since the above paper was written, Dr. C. F. Davidson, of H.M. Geological Survey, has kindly drawn the authors' attention to two further papers, published in 1950, concerning the varlamoffite from the Belgian Congo.

In the first, H. Buttgenbach[1] discusses the naming of these hydrated stannic oxide materials, concluding that, although there is some doubt as to whether the Bolivian 'souxite' of R. Herzenberg[2] or the Congo 'varlamoffite'[3] of the late R. De Dycker has priority, the available descriptions of the latter are so much more complete and authentic that the name varlamoffite should be retained. He remarks also that X-ray patterns obtained from the Congo varlamoffite were identical with those of synthetic metastannic acid. (The X-ray photographs are not illustrated.)

The second paper, by S. Gastellier,[4] gives an account of the chemical composition and properties of the Congo material. This investigation is more complete than that which we have attempted on the Cornish examples, and evidence is given which seems to indicate the presence of actual metastannic acid, H_2SnO_3, in the mixtures. It is further suggested that some of the ferric iron may exist in some sort of combination with stannic oxide.

It is apparent that our work with these Cornish varlamoffites has led to much the same results as were obtained by the workers on the Belgian Congo material. Clearly, the X-ray photographs of the Cornish material, which are discussed above, must be similar to those obtained by Prof. E. Niggli and M. Lambot, and mentioned by Buttgenbach.

Arsenic, bismuth, tungsten, and other elements were sought in the Congo material, but not found. The presence of considerable arsenic in

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[1] H. Buttgenbach, Souxite et varlamoffite. Bulletin des Séances, Inst. Roy. Colonial Belge, 1950, vol. 21, no. 2, pp. 409–411. [M.A. **11**–416.]

[2] R. Herzenberg, Nuevos minerales de Bolivia. Boletín Técnico, Fac. Nac. Ingeniería, Univ. Técnica, Oruro, 1946, no. 1, reprint 11 pp. [M.A. **10**–8.]

[3] H. Buttgenbach, Les minéraux de Belgique et du Congo Belge. Liège and Paris, 1947, p. 182. [M.A. **10**–354.]

[4] S. Gastellier, Note sur un minéral jaune trouvé par M. Varlamoff. Bulletin des Séances, Inst. Roy. Colonial Belge, 1950, vol. 21, no. 2, pp. 412–419. [M.A. **11**–416.]

our analysed material remains of interest. Even if some or all of this element were combined with ferric iron, as suggested above, the possibility that some of the iron might also be combined with stannic oxide in some way would not be ruled out.

The fact that all these materials so far analysed contain comparable amounts of ferric oxide may have some significance, and the authors agree with S. Gastellier that further researches would be desirable in order to try to confirm the existence of natural metastannic acid, either in the free state or in combination.

Acknowledgements.—In conclusion, the authors wish to record their gratitude to Monsieur N. Varlamoff (evidently a very attentive reader of this Magazine) for sending a specimen of the Belgian Congo varlamoffite; to Dr. Lars Lund, of the University of Leeds, for making the spectrographic examination of the material from the Cligga mine; to Dr. C. F. Davidson for drawing their attention to the latest accounts of the Belgian work on varlamoffite; and to Professor K. C. Dunham for his interest and encouragement in the work.