

## On the occurrence of varlamoffite at the Sardine tin mine, North Queensland, Australia

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**SUMMARY.** A new occurrence of varlamoffite is described, and the results of chemical analysis, differential thermal analysis, and infra-red spectrographic analysis are presented. It is suggested that varlamoffite is of secondary origin resulting from the attack of meteoric waters on stannite.

IN 1946 and 1947 two papers were published recording the existence of a yellow powder associated with tin mineralization. Herzenberg (1946), who described a sample from Bolivia, concluded that it contained a hydrous colloidal tin oxide,  $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ , which he termed souxite. Buttgenbach (1947) reported a similar material from the Belgian Congo that had been named varlamoffite and which, it was considered, had the formula  $\text{H}_2\text{SnO}_3$ . Although it is debatable which name has priority, varlamoffite is now well engrained in the literature, and was justified by Buttgenbach (1950) on the tenuous grounds that the Congo material had been more fully investigated. The name stems from N. Varlamoff (1948), who is reputed to have been the discoverer of the Congo material.

Subsequently, varlamoffite has been reported from several other localities: Cornwall (Russell and Vincent, 1952), Malaya (Bradford, 1957; Alexander and Flinter, 1965; Singh and Bean, 1967), and France (Bonnici *et al.*, 1964). However, its status as a mineral species is not fully established. Niggli (1953) concluded from chemical and X-ray data that it was a valid mineral with the formula  $(\text{Sn},\text{Fe})(\text{O},\text{OH})_2$ , but this has been queried by Alexander and Flinter (1965), who concluded in consultation with Professor C. O. Hutton that pending further work the term varlamoffite be employed for 'cryptocrystalline yellowish material consisting predominantly of Sn and  $\text{H}_2\text{O}$  that may yield a diffuse powder pattern comparable to, or closely resembling, that of cassiterite, but does yield a pattern identical to that of cassiterite after heat treatment to about 1200 °C'.

Early in 1966, one of the authors (R. G. Taylor), in the company of Mr. D. Wyatt, a Queensland Government geologist, visited the well-known Sardine tin mine, which is situated near Ewan, in the Kangaroo Hills mineral field of North Queensland. Mr. Wyatt drew attention to a fairly abundant yellow powder, which, he had noted, seemed

associated with high tin values. Taylor provisionally identified the material as varlamoffite, and samples were collected for laboratory investigation. Subsequent chemical and X-ray data confirmed his initial diagnosis.

*Mode of occurrence.* The Sardine tin mine is small and privately owned, and is unique amongst Australian producers in that the bulk of its present output is from stannite-rich ore. Its general features are described by Connah (1952) and Wyatt (1961), whilst its mineralogy was discussed by Edwards and Baker (1954). Basically the orebodies consist of a series of small fissure veins and pipes within a 50-ft wide crushed zone of early Palaeozoic phyllites and quartzites. The ore shoots are small, with the stannite-rich bodies occurring at the northern end of the workings in the form of irregular pipes. Edwards and Baker studied the main pipe, and recorded the following primary mineral assemblage: stannite, chalcopyrite, cassiterite, with lesser amounts of pyrite, marcasite, rutile, native bismuth, matildite (?), bournonite, and galena. This sulphide assemblage appeared at a vertical depth of approximately 170 ft from the surface. Above this level, the ore is extensively oxidized. Minerals recorded by Edwards and Baker from the oxidized zone are: limonite, kaolin, azurite, malachite, cuprite, tenorite, together with both primary and secondary cassiterite.

The varlamoffite occurrence is located in a small vein in the oxidized zone directly above the region of the stannite pipes. The vein was found in a stope above no. 4 level, near the foot of the raise to no. 3 level; access is by the raise just north of no. 5 winze in the mine. The vein is 1–2 ft wide, and consists of an ocherous brown-yellow iron-stained mass, the dominant components of which are iron oxides and kaolin-like clay minerals. Malachite, azurite, cassiterite, and some fine-grained secondary quartz are also present. The vein has been followed and stoped for a distance of 50–60 ft, and was extracted for its cassiterite content.

The varlamoffite occurs at several points in the stope as a canary-yellow clay-like powder, coating and permeating masses of white to grey kaolin. Under a binocular microscope it displays a waxy lustre and is often closely intermixed with fine-grained, granular quartz.

*Chemical analysis.* Isolation of the varlamoffite for detailed investigation proved difficult, owing to contamination from intermixed fine-grained quartz and a kaolin-like clay. By repeated decantation, the sample was purified as much as possible, though it proved impossible to eliminate all the clay and fine-grained silica. Microscopic examination of the final concentrate revealed that it contained between 2 and 5% clay. On analysis it gave SnO<sub>2</sub> 60.0%, SiO<sub>2</sub> 10.4, Al<sub>2</sub>O<sub>3</sub> 5.25, Fe<sub>2</sub>O<sub>3</sub> 9.25, FeO 0.07, MgO 0.08, CaO 0.03, Na<sub>2</sub>O 0.11, K<sub>2</sub>O 0.59, H<sub>2</sub>O+ 5.65, H<sub>2</sub>O– 3.35, CO<sub>2</sub> 0.20, TiO<sub>2</sub> 0.93, P<sub>2</sub>O<sub>5</sub> 0.02, MnO < 0.01, S 0.12, As<sub>2</sub>O<sub>3</sub> 0.79, CuO 2.80, PbO 0.16, ZnO 0.03, Bi<sub>2</sub>O<sub>3</sub> 0.45, WO<sub>3</sub> 0.02, total 100.31. The analysts also found 25 ppm of Ag. (Analysts: R. B. Oliver, C. N. Robinson, A. Jorgenson, and G. R. Holden, Australian Mineral Development Laboratories, Adelaide.)

If the analysis is compared with those of varlamoffite from the Belgian Congo (Varlamoff, 1948; Gastellier, 1950), and from the Cligga mine, Cornwall (Russell and Vincent, 1952), it is immediately apparent that the sample from the Sardine tin mine

contains much more silica and alumina than do the specimens from Cornwall and the Congo—this is presumably due to the clay mineral contamination. There must also be some contamination by very fine-grained silica, because the amount of  $\text{SiO}_2$  is too great to be accounted for by the clay. However, the amounts of ferric oxide and water are comparable with those in the other occurrences. Arsenic is low in the Australian sample when compared with that from Cornwall, but copper is high.

The results of a spectrographic analysis for trace elements are (in parts per million): Co 1, Cr 15, V 40, Mo 3, Be 5, Ga 40, Ba 100, Sr 30, Yt 15, Ni < 5, Au < 3, Cd < 3, Ge < 1, Pd < 10, Pt < 10, Os < 10, Ir < 2, Ru < 2, Sb < 30, Nb < 20, Ta < 100, La < 100, Ce < 300. (Analysts: R. B. Oliver, C. N. Robinson, A. Jorgenson, G. R. Holden, Australian Mineral Development Laboratories, Adelaide.)

An *X-ray powder diffraction photograph* of the suspected varlamoffite revealed a set of rather diffuse, broad lines, essentially the same as the most prominent lines of the cassiterite pattern. This repeats the experience of previous workers (Russell and Vincent, 1952; Niggli, 1953; Bonnici *et al.*, 1964, etc.), and corresponds well with Alexander and Flinter's definition (1965).

A *differential thermal analysis* was carried out by K. R. Burrows, of the Australian Mineral Development Laboratories, Adelaide. The trace showed an endothermic peak at 110 °C. The remainder of the curve, which extends to 1150 °C, is almost completely smooth. Bonnici *et al.* (1964) recorded a weak exothermic peak at 390 °C, and made no comment. Antun (1960) recorded a strong endothermic peak at 130 °C—thought to be due to loss of water. The 110 °C endothermic peak of the Queensland sample is also considered to be due to this cause. Antun also noted a weak exothermic peak at 480 °C, and a weak exo-endothermic undulation at 800–900 °C. The latter is accounted for by the decomposition of muscovite contamination, which Antun was unable to eliminate from his sample. He considers that the exothermic peak at 480 °C is possibly due to conversion of varlamoffite to cassiterite. Antun's work supports, to a certain extent Niggli's (1953) conclusion that varlamoffite has the composition  $(\text{Sn,Fe})(\text{O,OH})_2$ .

The *infra-red spectrum* of the North Queensland varlamoffite (fig. 1) shows a broad OH frequency stretch of  $3300\text{ cm}^{-1}$ , very similar to that of goethite and other related oxyhydroxides as reported by Schwarzmman (1962) and Phillips (1966). This suggests that there are hydrogen bonds. Schwarzmman (1962) has tabulated data of hydrogen bond length and hydroxyl frequency stretches for various inorganic hydroxides and oxyhydroxides and from his data we deduce a hydrogen bond length of  $2.78\text{ \AA}$  in varlamoffite. These infra-red data are evidence in support of the work of Niggli (1953) whose postulates were mentioned above.

*Mode of origin.* Most of the reported occurrences of varlamoffite show a strong spatial association with stannite, and most previous workers have concluded that it is a secondary mineral resulting from the attack of meteoric waters on stannite. Singh and Bean (1967) also suggest that the varlamoffite at Chenderiang Ridge, Malaysia, which corrodes and pseudomorphs cassiterite, may be a hypogene replacement mineral.

At the Sardine tin mine the nature and supergene occurrence of the varlamoffite suggest a secondary origin, and the close proximity of large amounts of primary stannite suggests conditions similar to those suggested by Russell and Vincent (1952), etc.

It is interesting to note that Edwards and Baker (1954) in their study of the oxidation of stannite at the Sardine tin mine conclude 'with the conversion of the stannite to

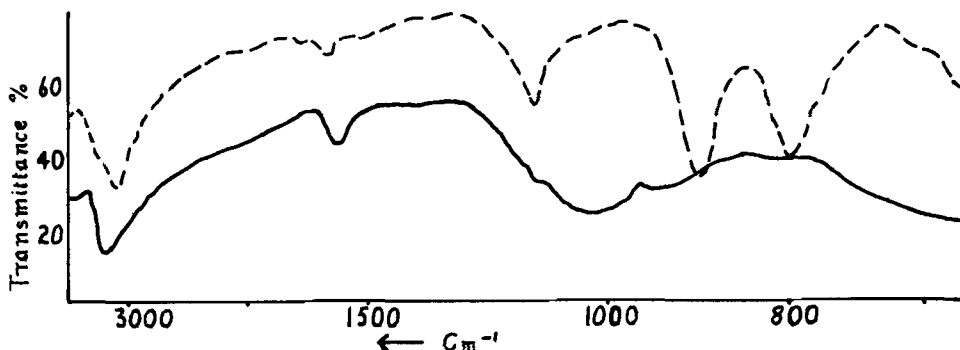


FIG. 1. Infra-red spectra of varlamoffite (continuous line) and goethite (dashed line).

covellite and chalcocite, secondary cassiterite makes its appearance as minute granules and needle-like crystals, precipitated in the veinlets of secondary copper sulphides, or, as outgrowths on the coarser crystals of primary cassiterite. The amount of such secondary cassiterite is not always sufficient to account for the amount of tin set free during the replacement of the stannite, and it is concluded that this additional tin migrated with the iron set free from the stannite, and is not incorporated in the covellite and chalcocite'. This suggests that a supply of tin would be readily available for conversion into varlamoffite under suitable conditions.

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