Thalcusite from Nakkaalaaq, the Ilímaussaq alkaline complex, South Greenland

Sven Karup-Møller and Emil Makovicky

Thalcusite from a new locality in the Ilímaussaq complex, the Nakkaalaaq mountain, occurs in a coarse ussingite–aegirine vein and is associated with sphalerite and cuprostibite. The empirical composition is Tl$_{1.89}$K$_{0.08}$Cu$_{2.86}$Fe$_{1.34}$S$_{4.00}$. Secondary tenorite–Sb oxide aggregates are developed along cleavages. Tarnish products are essentially pure Cu$^+$ sulphide. All three layered thallium sulphides from the Ilímaussaq complex, thalcusite, chalcothallite and rohaite, contain K substituting for Tl. Varieties with K > Tl were not found in the massif.

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Three primary thallium sulphides have been found in the Ilímaussaq alkaline complex: chalcothallite, rohaite and thalcusite (Semenov et al. 1967; Karup-Møller 1978a; Kovalenker et al. 1978; Makovicky et al. 1980). Chalcothallite and rohaite are only known from the Ilímaussaq complex, whereas thalcusite occurs at four other localities: the type locality Talnakh, Noril’sk region, Polar Siberia, Russia (Kovalenker et al. 1976), the Murun massif, Aldan Shield, Yakutia, Russia (Dobrovol’skaya et al. 1984; Dobrovol’skaya & Nekrasov 1994), Rajapura-Dariba, Rajasthan, India (Mookherjee et al. 1984) and Mont Saint-Hilaire, Quebec, Canada (Mandarino & Anderson, 1989).

At Ilímaussaq chalcothallite has been found in ussingite-bearing hydrothermal veins on the Taseq slope, and rohaite in sodalite–analcime veins on the Kvanefjeld plateau. Cuprostibite and a few common sulphides are present at both localities. See Sorensen (2001, this volume) for a map of the localities mentioned in the text and a brief description of the complex.

Thalcusite, Tl$_2(Cu,Fe)_4$S$_6$, has been found at three localities within the Ilímaussaq complex: in ussingite veins on the Taseq slope containing chalcothallite and cuprostibite, disseminated in naujaite at the head of the Kangerluarsuk fjord in the southern part of the complex and recently also on the top plateau of the Nakkaalaaq mountain in the northern part of the complex.

Mode of occurrence

The thalcusite-bearing sample from Nakkaalaaq measures seven by five centimetres. It is composed of coarse ussingite containing a few up to several centimetres long aegirine crystals and opaque mineral aggregates. One such aggregate is composed of sphalerite intergrown with thalcusite and partly altered cuprostibite, and another is composed of only thalcusite. In the latter opaque cluster, thalcusite forms a platy aggregate half a centimetre in cross-section and about one

Fig. 1. Polished thalcusite aggregate with tenorite (dark) along the open cleavage planes. SEM image; scale division 10 µm. Sample GM 2001.1 (Geological Museum, Copenhagen).
millimetre in thickness. The individual grains of the aggregate are split and partly crumpled along the basal cleavage plane (001) (Fig. 1). Alteration of the aggregate has resulted in loss of much of the aegirine and in malachite staining. The sample is assumed to come from nearby unexposed ussingite-bearing hydrothermal veins; such veins are exposed elsewhere on the plateau.

This mode of occurrence appears similar to that of thalcusite from the Taseq slope, as judged from the photographs of Kovalenker et al. (1978). On the Taseq slope thalcusite occurs intergrown with cuprostibite and gudmundite. The mode of occurrence also recalls that of chalcothallite (Semenov et al. 1967; Makovicky et al. 1980).

Experimental

X-ray identification of thalcusite was made with a Gandolfi Camera, using CuKα radiation. Microprobe analyses were carried out with a JEOL Superprobe 733 using wavelength dispersive mode with an on-line correction program supplied by JEOL. Standards used were synthetic Cu3SbS4 for Cu, Sb and S, synthetic FeS for Fe, and natural TlAsS2 and KCl for Tl, K and Cl. Wavelengths used were CuKα, SbKα, SKα, FeKa, Ti-La, KKa and ClKα. Detection limits for all seven elements were c. 0.2 wt%.

Chemical composition of thalcusite

Fifty-four point analyses of the thalcusite aggregate gave consistent results (Table 1). The resulting molar ratios give the empirical formula \( \text{Tl}_{1.89} \cdot \text{K}_{0.08} \cdot \text{Cu}_{2.86} \cdot \text{Fe}_{1.34} \cdot \text{S}_{4.00} \). The quality of the analysis is influenced by the condition of the weathered aggregate. Cl and Sb are present only in trace amounts. Thalcusite at Nakkaalaq is richer in iron and thallium than thalcusite from Taseq which, according to Kovalenker et al. (1978), has the formula \( \text{Tl}_{1.41} \cdot \text{K}_{0.07} \cdot \text{Cu}_{3.10} \cdot \text{Fe}_{1.11} \cdot \text{S}_{4.00} \). Both differ in composition from thalcusite at the head of Kangerluarsuk which is K-free, \( \text{Tl}_{1.91} \cdot \text{Cu}_{3.01} \cdot \text{Fe}_{1.04} \cdot \text{S}_{4.00} \) (Makovicky et al. 1980). At the last-named locality the mineral is associated with galena, troilite and djerfisherite and is partly altered to covellite and chalcopyrite.

In spite of its crystallisation in Na-rich environments, thalcusite has a Tl- and K-based structure. These cations are eightfold co-ordinated by sulphur. Being a smaller cation, Na⁺ does not fit this co-ordination and structure type; it is octahedrally co-ordinated as, e.g., in NaCu₅S₃ (Effenberger & Pertlik 1985).

The absence of Sb in the mineral shows lack of any potential interlayers with chalcothallite or rohaite compositions, even for thalcusite associated with cuprostibite and gudmundite at Taseq.

Supergene alteration

Along some contorted cleavage planes thalcusite is interlayered with a fine-grained aggregate (Fig. 1) which under the microprobe beam gave a homogeneous set of 14 analyses (Table 1). These data agree very closely with tenorite (CuO) with an admixture of Sb oxides (or even a Cu-Sb oxide) of unknown composition.

The fairly uniform oxide mixture (Sb varies from 2.6 to 8.0 wt%) with the summary formula \( \text{Cu}_{91.2} \cdot \text{Tl}_{9.2} \cdot \text{Fe}_{0.6} \cdot \text{Sb}_{3.4} \cdot \text{Cl}_{1.6} \cdot \text{S}_{0.1} \) cannot be explained as an oxidation prod-

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* Limiting values for the tarnishing product of thalcusite after exposure to air for three years. Numbers in parentheses are standard deviations in terms of the last digit.

All analyses stem from sample GM 2001.1 (Geological Museum, Copenhagen).
uct of thalcusite. It undoubtedly originates from the oxidation of a mixture of cuprostibite and chalcosite, originally deposited between the split thalcusite flakes. The textural evidence (Fig. 2) supports this conclusion: surfaces of thalcusite show signs of primary crystal growth.

Tarnishing of thalcusite

Tarnishing of polished sections is a common but little studied phenomenon. Chen et al. (1980) examined tarnishing of Ag-bearing chalcopyrite and the chalcopyrite–silver pair. The tarnish is an Ag₂S film encroaching upon chalcopyrite. Their investigation of fast tarnishing tennantite (≤ 0.9 wt% Ag) showed secondary products spreading quickly as rims and dendritic coatings over adjacent silicates and epoxy. Microprobe and X-ray diffraction data indicated digenite in the first-stage coating, and dendritic coatings, gradually replaced by chalcosite with time. Both nodular structures and branched dendritic coatings developed.

Mozgova et al. (1994) reported on tarnish products in 10–30 years old sections containing Cu and Ag sulphides and sulphosalts. They found that acantite and Cu sulphides were the principal tarnish product, and they identified the Cu sulphides as chalcosite and djurleite. There was a wide range of starting materials – bornite, Ag, Ag-bearing tetrahedrite, etc. Both Chen et al. (1980) and Mozgova et al. (1994) emphasise diffusion of Ag and Cu from and over the surface of the primary minerals and their reunion with S into simple sulphides. Finally Mozgova & Tsepin (1983) observed growth of Ag₃S dendrites on the surface of Ag-bearing tetrahedrite (4–5 wt% Ag) during prolonged excitation by the microprobe beam.

Tarnish products were observed on thalcusite after the polished section had been exposed to air for three years. They belong to the nodular type (Fig. 3). Lines of globular secondary products outline either cleavage planes of thalcusite or the polishing scratches across its surface. The multiple microprobe analyses reflect the thinness of the coating by yielding mixtures of the compositions of thalcusite and of the new product in variable proportions. The original 23.5 wt% Cu gradually increases to 53.3 wt%, accompanied by a fall in Tl values from 50.1 wt% down to 11.2 wt%, decrease in Fe from 9.7 wt% to 2.6 wt%, drop in K to values of 0.15 wt% and in S from 16.6 to about 11–13 wt%. The analytical totals change to 80.6–85.0 wt% and chlorine appears, reaching up to 1.1–2.7 wt%. The Cu:S ratio is close to 2:1, indicating that the product is Cu₂S, chalcocite, or very close to it. Calculating the weight deficit as oxygen shows that the investigated phase cannot be a sulphate or a sulphite of copper. Tl apparently is not concentrated; the role of secondary chlorine is unclear. Slight repolishing entirely removes the secondary products.

Mineralogical implications

Potassium contents in sulphides are rare and appear confined to alkaline intrusive massifs and to the late products of the Cu–Ni sulphide magmas in the Noril’sk Intrusion. The presence of potassium in the layered
sulphide and sulphide–antimonide structures (thalcusite, chalcothallite and rohaite) appears to be confined to late veins (ussingite or sodalite–analclime) of the Ilímaussaq complex. Thalcusite enclosed in naujaite at Kangeraluarsuk is K-free (Makovicky et al. 1980). The potassium analogue of thalcusite, murunite K$_2$Cu$_3$FeS$_4$ (Dobrovols'kaya & Nekrasov 1994), has not been found in the Ilímaussaq complex. Djerfisherite is the only other K-bearing sulphide present (Karup-Møller 1978b).

Synthetic selenides related to bukovite, Tl$_2$Cu$_3$FeSe$_4$, (Johan & Kvaček 1971), a selenium analogue of thalcusite, Tl$_2$Cu$_3$FeS$_4$, stretch over a rich spectrum of Cu–Tl stoichiometries, most of them being richer in Cu than bukovite (Berger 1987). They may be layered structures (TlCu$_4$Se$_3$, TlCu$_2$Se$_2$) or tunnel structures (TlCu$_6$Se$_5$, TlCu$_2$Se). Berger (1987) has also established that the mineral sabatierite, TlCu$_2$Se$_2$, has a layered structure whereas crookesite, TlCu$_4$Se$_3$, is a tunnel structure. None of these Cu-rich thallium selenides or corresponding sulphides have so far been observed in the Ilímaussaq complex. Instead, their role appears to be taken by chalcothallite, Tl$_2$M$_{6.35}$SbS$_4$ (M = Cu, Fe; Cu/Fe ~ 8/1) and rohaite, Tl$_2$M$_{6.6}$Sb$_2$S$_4$ (M = Cu).

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