

# Thalcusite from Nakkaalaaq, the Ilímaussaq alkaline complex, South Greenland

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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  $\text{Tl}_{1.89}\text{K}_{0.08}\text{Cu}_{2.86}\text{Fe}_{1.34}\text{S}_{4.00}$ . Secondary tenorite–Sb oxide aggregates are developed along cleavages. Tarnish products are essentially pure  $\text{Cu}^+$  sulphide. All three layered thallium sulphides from the Ilímaussaq complex, thalcusite, chalthallite and rohaite, contain K substituting for Tl. Varieties with  $\text{K} > \text{Tl}$  were not found in the massif.

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Three primary thallium sulphides have been found in the Ilímaussaq alkaline complex: chalthallite, rohaite and thalcusite (Semenov *et al.* 1967; Karup-Møller 1978a; Kovalenker *et al.* 1978; Makovicky *et al.* 1980). Chalthallite 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 (Dobrovolskaya *et al.* 1984; Dobrovolskaya & Nekrasov 1994), Rajapura-Dariba, Rajasthan, India (Mookherjee *et al.* 1984) and Mont Saint-Hilaire, Quebec, Canada (Mandarino & Anderson, 1989).

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

Thalcusite,  $\text{Tl}_2(\text{Cu},\text{Fe})_4\text{S}_4$ , has been found at three localities within the Ilímaussaq complex: in ussingite veins on the Taseq slope containing chalthallite 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

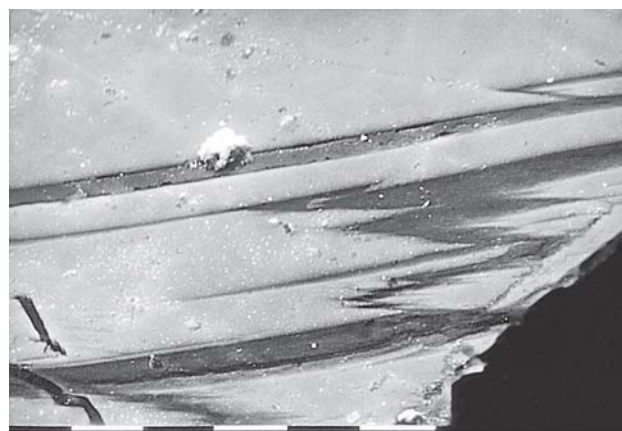


Fig. 1. Polished thalcusite aggregate with tenorite (**dark**) along the open cleavage planes. SEM image; scale division 10  $\mu\text{m}$ . Sample GM 2001.1 (Geological Museum, Copenhagen).

Table 1. Microprobe analyses of thalcosite

	Thalcosite		Mol. ratio	Tarnish*	Supergene alteration	
	Av. wt%	St. dev.			Av. wt%	St. dev.
Tl	50.10	(138)	18.60	11.2	0.4	(2)
K	0.43	(10)	0.83	0.15	0.02	(2)
Cu	23.49	(38)	28.05	53.3	74.8	(39)
Fe	9.68	(18)	13.15	2.6	0.4	(1)
Sb	0.07	(4)	0.05		5.1	(17)
Cl	0.02	(3)	0.04	1.1–2.7*	0.7	(1)
S	16.60	(36)	39.28	11. –13*	0.03	(3)
	100.38		100.00		81.4	

\* Limiting values for the tarnishing product of thalcosite 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).

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 thalcosite from the Taseq slope, as judged from the photographs of Kovalenker *et al.* (1978). On the Taseq slope thalcosite occurs intergrown with cuprostibite and gudmundite. The mode of occurrence also recalls that of chalthallite (Semenov *et al.* 1967; Makovicky *et al.* 1980).

## Experimental

X-ray identification of thalcosite was made with a Gandolfi Camera, using  $\text{CuK}\alpha$  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  $\text{Cu}_3\text{SbS}_4$  for Cu, Sb and S, synthetic FeS for Fe, and natural  $\text{TlAsS}_2$  and KCl for Tl, K and Cl. Wavelengths used were  $\text{CuK}\alpha$ ,  $\text{SbL}\alpha$ ,  $\text{SK}\alpha$ ,  $\text{FeK}\alpha$ ,  $\text{TlL}\alpha$ ,  $\text{KK}\alpha$  and  $\text{ClK}\alpha$ . Detection limits for all seven elements were *c.* 0.2 wt%.

## Chemical composition of thalcosite

Fifty-four point analyses of the thalcosite aggregate gave consistent results (Table 1). The resulting molar

ratios give the empirical formula  $\text{Tl}_{1.89}\text{K}_{0.08}\text{Cu}_{2.86}\text{Fe}_{1.34}\text{S}_{4.00}$ . The quality of the analysis is influenced by the condition of the weathered aggregate. Cl and Sb are present only in trace amounts. Thalcosite at Nakkaalaaq is richer in iron and thallium than thalcosite from Taseq which, according to Kovalenker *et al.* (1978), has the formula  $\text{Tl}_{1.41}\text{K}_{0.07}\text{Cu}_{3.10}\text{Fe}_{1.11}\text{S}_{4.00}$ . Both differ in composition from thalcosite at the head of Kangerluarsuk which is K-free,  $\text{Tl}_{1.91}\text{Cu}_{3.01}\text{Fe}_{1.04}\text{S}_{4.00}$  (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, thalcosite has a Tl- and K-based structure. These cations are eightfold co-ordinated by sulphur. Being a smaller cation,  $\text{Na}^+$  does not fit this co-ordination and structure type; it is octahedrally co-ordinated as, e.g., in  $\text{NaCu}_5\text{S}_3$  (Effenberger & Pertlik 1985).

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

## Supergene alteration

Along some contorted cleavage planes thalcosite 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  $\text{Cu}_{94.2}\text{Tl}_{0.2}\text{Fe}_{0.6}\text{Sb}_{3.4}\text{Cl}_{1.6}\text{S}_{0.1}$  cannot be explained as an oxidation prod-

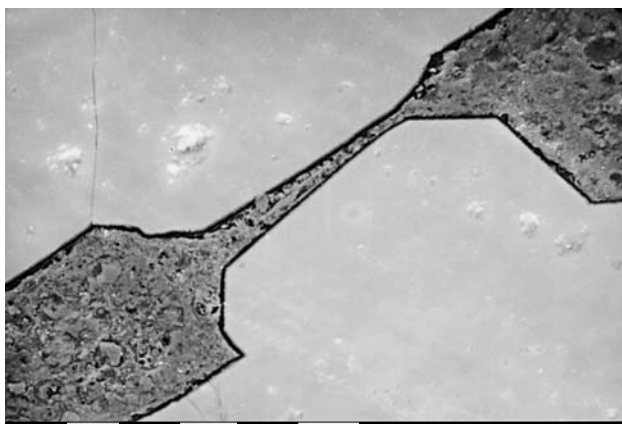


Fig. 2. Euhedral thalcosite growing into a cavity now filled with tenorite (**dark**). SEM image. Scale division 10  $\mu\text{m}$ . Sample GM 2001.1 (Geological Museum, Copenhagen).

uct of thalcosite. It undoubtedly originates from the oxidation of a mixture of cuprostibite and chalcocite, originally deposited between the split thalcosite flakes. The textural evidence (Fig. 2) supports this conclusion: surfaces of thalcosite show signs of primary crystal growth.

### Tarnishing of thalcosite

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  $\text{Ag}_2\text{S}$  film encroaching upon chalcopyrite. Their investigation of fast tarnishing tennantite ( $\leq 0.9$  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 chalcocite 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 chalcocite 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 & Tsepina (1983) observed growth of  $\text{Ag}_2\text{S}$  dendrites on the surface of Ag-bearing



Fig. 3. Secondary  $\text{Cu}_2\text{S}$  growth along polishing scratches and contorted cleavage on the surface of polished thalcosite. Compare with Fig. 1, top centre SEM image. Scale division 10  $\mu\text{m}$ . Sample GM 2001.1 (Geological Museum, Copenhagen).

ing tetrahedrite (4–5 wt% Ag) during prolonged excitation by the microprobe beam.

Tarnish products were observed on thalcosite 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 thalcosite or the polishing scratches across its surface. The multiple microprobe analyses reflect the thinness of the coating by yielding mixtures of the compositions of thalcosite 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  $\text{Cu}_2\text{S}$ , 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, chalthallite and rohaite) appears to be confined to late veins (ussingite or sodalite–analcime) of the Ilímaussaq complex. Thalcusite enclosed in naujaite at Kangerluarsuk is K-free (Makovicky *et al.* 1980). The potassium analogue of thalcusite, murunite  $K_2Cu_3FeS_4$  (Dobrovolskaya & 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,  $Tl_2Cu_3FeSe_4$ , (Johan & Kvaček 1971), a selenium analogue of thalcusite,  $Tl_2Cu_3FeS_4$ , 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 ( $TlCu_2Se_2$ ,  $TlCu_4Se_3$ ) or tunnel structures ( $TlCu_7Se_4$ ,  $TlCu_5Se_3$ ). Berger (1987) has also established that the mineral sabatierite,  $TlCu_6Se_4$ , has a layered structure whereas crookesite,  $TlCu_7Se_4$ , 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 chalthallite,  $Tl_2M_{6.35}Sb_4$  ( $M = Cu, Fe$ ;  $Cu/Fe \sim 8/1$ ) and rohaite,  $Tl_2M_{8.67}Sb_4$  ( $M = Cu$ ).

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