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# CONTRIBUTIONS TO THE MINERALOGY OF ILÍMAUSSAQ Nos 3–7

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KØBENHAVN BIANCO LUNOS BOGTRYKKERI A/S 1967

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#### GRØNLANDS GEOLOGISKE UNDERSØGELSE

I.

THE LOVOZERO MINERALS – NENADKEVICHITE, GERASSIMOVSKITE AND TUNDRITE – FROM ILÍMAUSSAQ, SOUTH GREENLAND contribution to the mineralogy of ilímaussaq, No. 6

> By E. I. SEMENOV, M. E. KAZAKOVA AND R. A. ALEKSANDROVA

WITH 2 FIGURES AND 1 TABLE IN THE TEXT

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П.

CHALCOTHALLITE – A NEW SULPHIDE OF COPPER AND THALLIUM FROM THE ILÍMAUSSAQ ALKALINE INTRUSION, SOUTH GREENLAND CONTRIBUTION TO THE MINERALOGY OF ILÍMAUSSAQ, No. 7

> BY E. I. SEMENOV, H. SØRENSEN, M. S. BESSMERTNAJA and L. E. NOVOROSSOVA

> > WITH 4 FIGURES AND 3 TABLES IN THE TEXT AND 5 PLATES

> > > С РУССКИМ РЕЗЮМЕ

## KØBENHAVN C. A. REITZELS FORLAG

BIANCO LUNOS BOGTRYKKERI A/S

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# CHALCOTHALLITE – A NEW SULPHIDE OF COPPER AND THALLIUM FROM THE ILÍMAUSSAQ ALKALINE INTRUSION, SOUTH GREENLAND

II.

CONTRIBUTION TO THE MINERALOGY OF ILÍMAUSSAQ, No. 7

BY

E. I. SEMENOV, H. SØRENSEN, M. S. BESSMERTNAJA and L. E. NOVOROSSOVA

#### Abstract

The new mineral chalcothallite,  $Cu_3TIS_2$  was discovered in a hydrothermal ussingite vein in poikilitic sodalite syenite (naujaite) in the Ilímaussaq intrusion, South Greenland.

The new mineral is associated with ussingite, analcime, sodalite, epistolite and chkalovite.

The mineral forms lamellar aggregates. The colour is lead grey to iron black with metallic lustre. There are three mutually perpendicular cleavages. The specific gravity is 6.6, the hardness is 61–90 kg/mm<sup>2</sup>.

The chemical composition is: TI - 38.07, Cu - 40.58, Ag - 0.19, Pb - 0.13, Fe - 3.79, S - 12.06, Sb - 3.93, insoluble 1.52; total 100.27.

The d-values of the strongest lines of the x-ray powder diagram are: 3.93, 3.75, 3.49, **3.07**, **2.48**, 2.32, 2.19, 1.930.

Like chalcocite, chalcothallite is easily subject to transformation and recrystallization. There are inclusions of native silver, chalcocite, vrbaite and avicennite (?).

#### РЕЗЮМЕ

Новый минерал халькоталлит (Cu<sub>3</sub>TlS<sub>2</sub>) был открыт в гидротермальной уссингитовой жиле, секущей пойкилитовые содалитовые сиениты (науяиты), слагающие Илимауссакскую интрузию (Южная Гренландия).

Минерал ассоциирует с уссингитом, анальцимом, содалитом, эпистолитом и чкаловитом.

Халькоталлит образует пластинчатые выделения свинцово-серого до желево-черного цвета с металлическим блеском. Спайность ясно выражена в трех взаимноперпендикулярных направлениях. Удельный вес 6,6; твердость 61-90 кг/мм<sup>2</sup>.

Химический состав и процентное содержание компонентов халькоталлита следующие: Tl – 38,07, Cu – 40,58, Ag – 0,19, Pb – 0,13, Fe – 3,79, S – 12,06, Sb – 3,93, нерастворимый остаток – 1,52; всего –  $100,27^{\circ}/_{\circ}$ . Межплоскостные расстояния наиболее четких линий дебаеграммы порошка минерала равны: 3,93, 3,75, 3,49, **3,07, 2,48, 2**,32, 2,19, 1,930.

Подобно халькозину, халькоталлит легко подвергается превращениям и перекристаллизации. Халькоталлит содержит включения самородного серебра, халькозина, врбаита и авиценнита (?).

#### INTRODUCTION

In the summer of 1964, while examining the nepheline sodalite syenite massif of Ilímaussaq, an unknown ore mineral was discovered by E. I. SEMENOV. The detailed examination of the samples carried out at IMGRE revealed that this mineral is a new copper-thallium sulphide with the approximate formula  $Cu_3TIS_2$ . The mineral is named chalcothallite after its chemical composition.

The name chalcothallite has been approved by the Soviet-Russian and the I.M.A. Commission on New Minerals and Mineral Names (10th of february, 1966). The mineral may be related to the tetradymite or chalcocite mineral groups.

The material examined is kept in the Mineralogical Museum of the Academy of Sciences, Moscow, in the Museum of IMGRE and in the Mineralogical Museum of the University of Copenhagen.

The visit of E. I. SEMENOV to Ilímaussaq was made possible by a grant from the Rask-Ørsted-Foundation, Copenhagen.

Mrs. A. DEMIN has translated the Russian part of the text into English. The material was collected during the investigations in the Ilímaussaq intrusion being carried out by Grønlands Geologiske Undersøgelse (the Geological Survey of Greenland) under the direction of H. SøRENSEN. The authors wish to thank the Director of the Geological Survey of Greenland, K. ELLITSGAARD-RASMUSSEN, for permission to publish this report.



Fig. 1. Simplified geological map of the Ilimaussaq alkaline intrusion after JOHN FERGUSON (Medd. Grønland 172, 4, 1964).

#### MODE OF OCCURRENCE

Chalcothallite was found on the north-west slope of Nákâlâq at an altitude of 525 m (fig. 1 at the co-ordinate 5.15 and fig. 2). This slope is often called the Taseq slope. The mineral occurs in limited amounts in veins of ussingite intersecting poikilitic sodalite syenite (naujaite).

The mineral forms small dark spots in the ussingite and is generally surrounded by thin zones of green products of alteration.

The ussingite veins are up to 2 m thick and may attain lengths of 20 m, or more. The thickest veins strike NW-SE to N-S and are vertical. At their ends the veins branch and pass into networks of thin veins which intersect the naujaite in an intricate way.

Lujavrite is restricted to a network of thin veins of fine-grained black arfvedsonite lujavrite. The number of these veins is largest at a level immediately below the thickest veins of ussingite. The lujavrite contains angular inclusions of naujaite.

The naujaite is furthermore cut by thin green veins of felt-like ægirine (cf. Sørensen, 1962).

The ussingite veins cut veins of lujavrite and felt-like ægirine but may also occupy the central part of ægirine veins so that these veins have marginal zones of ægirine and central zones of ussingite. The feltlike ægirine was formed in zones of deformation in naujaite and also in augite syenite, that is after the consolidation of these rocks. The ussingite veins are therefore considerably later than the naujaite and are most probably genetically connected with the lujavrite. This age relation is supported by the fact that lujavrite and ussingite veins may be contiguous. In places ussingite veins appear to be formed in fractures along lujavrite veins and may enclose acmitized fragments of the latter.

The central parts of the hydrothermal veins are composed of coarsegrained aggregates of white or pink ussingite with scattered crystals of chkalovite up to 30 cm across and with large plates of epistolite partly altered into gerassimovskite. In places there are clusters of large cubic crystals of white or transparent analcime up to 10 cm across. Other constituents are natrolite, microcline, Li-mica, tugtupite (in very small amount), sphalerite, molybdenite, galena and red aggregates of niobophyllite. The chalcothallite is mainly enclosed in ussingite.



Fig. 2. The Taseq slope seen from Kvanefjeld. The locality in which the chalcothallite was found is indicated. (Јонк Накsen phot.).

The marginal parts of the veins often are rich in large crystals of yellow sodalite and may, as mentioned above, be rich in ægirine. Steenstrupine is a scarce constituent in the border zones.



Fig. 3. Vertical vein of ussingite (in centre). (JOHN HANSEN phot.).

The adjacent naujaite often is penetrated by small stringers from the veins and may be enriched in arfvedsonite, acmite and chkalovite.

The ussingite veins occur in a rather high level in the naujaite contrary to the types of late veins described previously by SØRENSEN (1962). These veins occur in the lower part of the naujaite or in USSING's "breccia zone" which is composed of lujavrite with inclusions of naujaite (USSING, 1912). The hydrothermal veins of this low level occur in naujaite intimately injected by large masses and thick and thin veins of lujavrite. Their predominant minerals are albite, microcline, analcime, natrolite, sodalite, acmite, ægirine and arfvedsonite while ussingite and chkalovite are less conspicuous. Accessory minerals are steenstrupine, pyrochlore, epistolite, Li-mica, schizolite, astrophyllite, niccolite, sphalerite, galena, and others. Steenstrupine and pyrochlore are very conspicuous at this level.

On the Taseq slope the ussingite veins are poor in steenstrupine and pyrochlore, but rich in chkalovite and epistolite.

At a still higher level on the Taseq plateau the naujaite is strongly impregnated by veins of extremely fine-grained albite associated with analcime, neptunite, fluorite, epididymite, eudidymite, genthelvite and

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leucophane (SEMENOV & SØRENSEN, 1966). Steenstrupine is practically lacking. At this level lujavrite veins are few and thin and there is a considerable vertical distance to large bodies of lujavrite. This may indicate, that the mineralogy of the hydrothermal veins is determined by the level of formation. However, the systematic investigation of the hydrothermal mineralization of Ilímaussaq has only begun and may prove or disprove this preliminary interpretation of the distribution of the hydrothermal minerals.

The minerals of the chalcothallite-bearing veins are substantially sodium minerals devoid of thallium.

The high temperature derivates of the nepheline and sodalite syenites—the pegmatites—are rich in microcline, polylithionite and astrophyllite, all of them potassic minerals containing Rb, Cs and Tl. Thus, the Ilímaussaq astrophyllite contains  $0.02 \, {}^0/_0$  Tl (determined by N. Z. KURBANOVA). The sodium minerals of the low temperature derivates —the hydrothermal veins—contain lesser amounts of dispersed thallium, which may explain the presence of chalcothallite—the first proper thallium mineral found in an alkaline massif.

#### MINERALOGY

Chalcothallite forms lamellar aggregates, measuring up to  $3 \times 2 \times 0.5$  cm, in white or pink ussingite. The aggregates split easily into thin leaves. The colour of the mineral is lead-grey to iron-black with metallic lustre and black streak. Cleavage is distinct in three mutually perpendicular directions of which that parallel to the laminae is perfect while the other two cleavages are good or fair. The cleavage parallel to the laminae presents a good plane of gliding with marked granulations (plate 1, fig. 1). The mineral easily splits up into very fine flakes or into rectangular plates when exposed to compression. The small plates are almost entirely covered by an iridescent tarnish, which is similar to that which is typical for many copper minerals (including chalcostibite).

The specific gravity of chalcothallite is 6.6. (determined by hydrostatic weighing by G. G. PROKHOROVA). The hardness is  $61-90 \text{ kg/mm}^2$ which approximately corresponds to 2-2.5 of the Mohs' scale (determination by S. I. LEBEDEVA).

The X-ray powder diagram (table 1) of the mineral is quite specific

no.	intensity	$d_{hkl}$	no.	intensity	d <sub>hkl</sub>
1	4	3.93	16	3	1,626
2	3	3,75	17	1	1,577
3	3	3,49	18	2	1,509
4	2	3,27	19	2	1,443
5	10	3,07	20	2	1,355
6	2	2,94	21	2	1,279
7	2	2,75	22	2	1,238
8	2	2,58	23	1	1,207
9	9	2,48	24	3	1,188
10	3	2,32	25	1	1,087
11	3	2,19	<b>26</b>	1	1,065
12	4	1,930	27	1	0,891
13	3	1,834	28	1	0,856
14	3	1,735	29	1	0,817
15	3	1,684			

Table 1. X-ray powder diagram of chalcothallite radiation:  $\lambda - Cu$ , 2 R = 57.3 mm. Analyst: V.S. LEBEDEV.

	Theoretical	Ilímaussaq sample					
	composition (weight percent)	weight percent	relative number of atoms				
Tl	44.5	38.07	0.187				
Cu	41.5	40.58	0.638				
Ag	_	0.19	0.002				
Pb	_	0.13	0.001				
Fe	· _	3.79	0.068				
S	14.0	12.06	0.377				
$\operatorname{Sb}$	_	3.93	0.032				
insoluble	-	1.52	-				
Total	100.0	100.27					

Table 2. Chemical composition of chalcothallite.

and cannot be correlated with those of known minerals. The chemical analysis of chalcothallite by L. E. Novorossova is presented in table 2.

The result of the chemical analysis was confirmed by means of the electron microprobe KAMEKA in the Bardin Metallurgy Institute (analyst: S. B. MASLENKOV) and by microspectrographic analysis at ZNIGRI (analysed by N. KORENNOVA). The mineral contains Tl, Cu, S and Sb and sometimes Au, As, Bi and Pb.

When examined under the microscope at a magnification of 1000 the aggregates of chalcothallite are practically monomineralic. Foreign inclusions only make up  $2-3 \,^{\circ}/_{0}$  of the aggregates. Most of the inclusions are products of decomposition of chalcothallite and have the same cation bulk composition as the primary mineral. This fact facilitated the deduction of an approximate chemical formula for chalcothallite:  $3 \, \text{Cu}_2\text{S}$ . Tl<sub>2</sub>S or Cu<sub>3</sub>TlS<sub>2</sub>. Antimony is a minor component, while Ag, Fe, Pb and As apparently are less constantly present.

A. YU. MALEVSKY synthesized the compound  $Cu_3TlS_2$  (without antimony). The product of synthesis has a homogeneous appearance and is similar to the natural mineral with regard to optic properties (fig. 4, plate 1, fig. 2 and plate 2, fig. 1).

In polished sections the lamellar structure of chalcothallite is very distinct, the lamellae being elongated and having a pronounced longitudinal cleavage. The transverse cleavage is also distinct but only for short distances, which results in fan-like or step-like fractures (plate 2, fig. 2). Commonly there are deformations (produced by translation) with bending of the lamellae along the cleavage (plate 1, fig. 1). These morphological peculiarities are similar to the mode of occurrence of tellurides of bismuth. The reflectivity of chalcothallite is moderate and is (according Table 3. Average reflectivity of chalcothallite (in air).  $(\times 20. \text{ Aperture } 0.40. \text{ Platinum standard } \text{N} 2).$ 

λnm	440	460	480	500	520	540	560	580	600	620	640	660	680	700
$\mathbf{R}^{\mathbf{I}}$ 0/0	35.4	34.0	32.7	31.8	31.0	30.5	29.7	29.5	29.2	29.1	29.1	29.0	28.9	28.9

to visual observation in white light) a little higher than that of chalcocite (plate 3, fig. 1).

The quantitative measurements of the average reflectivity in air of natural chalcothallite was performed by L. A. LOGINOVA on the FME-1 apparatus of ZNIGRI. The results of the determinations are given in table 3 and in fig. 4. Fig. 4 also shows the reflectivity of the synthetic compound.

The colour of chalcothallite in white reflected light is light grey; when adjacent to chalcocite it acquires a weak pinkish-lavender tint which corresponds to a steepening of the slope of its dispersion curve



thetic compound  $Cu_3TlS_2$  (2), air.

R in the long wave part of the spectrum (fig. 4). A bireflectance is notable in air, the position corresponding to Rg is colourless or weakly bluish, and that corresponding to Rp pinkish-lavender. The anisotropy effects are distinct, the colours being orange brown tints.

The relief of chalcothallite is low, practically identical with the relief of chalcocite or a little lower than that of vrbaite (plate 3, fig. 1 and plate 5, fig. 3).

Like chalcocite, chalcothallite is probably easily subject to transformation and recrystallization. Thus in polished sections subjected to hot cementation, there appear in the mineral patches of fine crystalline structure, along fractures and even along scratches made by abrasives during polishing of the sections. The fine crystalline patches (plate 3, fig. 2 and plate 4, fig. 1) often form polysynthetic transformation twins (plate 4, fig. 2). The polysynthetic twins are usually oriented in a tapering way along the elongation of the mineral, whereas the individual lamellae are of the same thickness and situated perpendicular to this direction. The reflectivity of the mineral did not change during recrystallization.

The microprobe analysis revealed changes in the chemical composition of chalcothallite at places of recrystallization. Generally, the contents of Cu and Sb are constant while the Tl content varies (mostly decreasing to some extent).

In polished sections prepared by cold cementation recrystallized portions were absent.

#### ASSOCIATION (INCLUSIONS AND ALTERATION)

Natural chalcothallite contains inclusions of native silver, chalcocite, vrbaite and avicennite (?) which are mainly situated near the periphery (plate 2, fig. 2) and along the cleavages of chalcothallite. They form composite finely dispersed particles, hundredths, or rarely tenths (up to 0.3), of a millimetre thick. (plate 5, fig. 1) All inclusions are probably products of hypergene alteration of the mineral, and only some of the inclusions of silver may be primary. Compared to common silver, the above mentioned silver has a lower reflectivity (about 70 °/<sub>0</sub>) and hardness (25 kg/mm<sup>2</sup>). The silver inclusions in chalcothallite contain 75-80 °/<sub>0</sub> of silver (determined by X-ray microprobe analysis). The second component of the native silver has not been identified; it is, however, not Cu, Sb or Au, but may be Tl. Thus, the mineral may be an intermediate member in a series between native silver and thallium, for which the above mentioned hardness and reflectivity is characteristic.

In reflected light the inclusions of vrbaite differ from chalcothallite in having bright red internal reflexions and high relief; its reflectivity is however slightly higher than that of chalcothallite in immersion.

Avicennite is thought to be present in the mechanical mixture of powder-like non-transparent minerals (plate 5, fig. 1). A test undertaken on the microspectral apparatus in an atmosphere of argon revealed thallium and oxygen. Green copper minerals are also products of oxidation of chalcothallite.

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## PLATES

#### Plate 1.

- Fig. 1. Chalcothallite with the longitudinal cleavage displaying effects of translation.  $\times$  300, immersion.
- Fig. 2. Synthetized Cu\_3TlS\_ with weekly developed step-like cleavage (upper right).  $\times$  300, immersion.



Fig. 1.



Fig. 2.

#### Plate 2.

- Fig. 1. Mixture of the two phases  $Cu_3TlS_2(1)$  and  $Cu_2S(2)$  obtained by synthesis with a surplus of copper.  $\times$  300, immersion.
- Fig. 2. Plate of chalcothallite with step-like cleavage and traces of hypergene substitution.  $\times$  50, air.



Fig. 1.



Fig. 2.

## Plate 3.

- Fig. 1. Chalcothallite (1) with well pronounced longitudinal cleavage, partly replaced by chalcocite (2).  $\times$  300, immersion.
- Fig. 2. Recrystallized patches in chalcothallite; one nicol.  $\times$  750, immersion.



Fig. 1.



Fig. 2.

#### Plate 4.

- Fig. 1. The same as plate 3, fig. 2. Recrystallized patches in chalcothallite; crossed nicols,  $\times$  750, immersion.
- Fig. 2. Polysynthetic twins in recrystallized patches; crossed nicols,  $\times$  750 immersion.



Fig. 1.



Fig. 2.

#### Plate 5.

- Fig. 1. Chalcothallite with finely dispersed inclusions of secondary minerals.  $\times$  500, immersion.
- Fig. 2. Crushed grains of chalcothallite (1) and native silver (2) in bakelite.  $\times$  750, immersion.
- Fig. 3. Inclusions of vrbaite in chalcothallite.  $\times$  750, immersion, white light.



Fig. 1.



Fig. 2.

