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# Galena and associated ore minerals from the cryolite at lvigtut, South Greenland

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Sven Karup-Møller and Hans Pauly

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## Galena and associated ore minerals from the cryolite at Ivigtut, South Greenland

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Karup-Møller, S. & Pauly, H. 1979. Galena and associated ore minerals from the eryolite at Ivigtut. South Greenland. – Meddr Grønland, Geosci. 25 pp. Copenhagen 1979-10-01-

Silver- and bismuth-rich galena concentrates have been produced for more than 70 years as a byproduct in the dressing of the crude cryolite from Ivigtut, South Greenland.

Concentrates from the years 1937 to 1962 contained from 0.44 % Ag and 0.74 % Bi to 0.94 % Ag and 1.93 % Bi. Conspicuous increases in the content of these elements appeared twice within this time interval, namely in 1955 and in 1960. Thus it seems that crude cryolite from specific areas within the mine carried galena high in silver and bismuth. This promoted a detailed study of the common Ivigtut galena and associated sulphides.

An outline of the geological setting of the deposit is given. The deposit is divided into two main bodies – the cryolite body and the quartz body. Both are subdivided into units characterized by their content of siderite and fluorite. Galena samples from these units and from rock types surrounding the deposit have been studied.

Galena from units characterized by siderite follows the compositional pattern found in the galena concentrates, whereas the sparse galena mineralizations from units characterized by fluorite contain much smaller amounts of silver and bismuth, less than 0.2 %. However, within the fluorite-bearing units, two peculiar parageneses reveal high contents of silver and bismuth expressed by the presence of particular minerals such as matildite-aikinite and gustavite-cosalite respectively.

Further trace element studies on selected galena samples emphasize Sn and Te as chemically characteristic of the galena and of the sulphide-carbonate phase of the deposit.

The temperature of formation of the main part of the deposit is placed at 550-400°C, and between 300 and 200°C for certain parts of the fluorite cryolite and the fluorite zone.

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Soon after Giesecke's description of the cryolite deposit at Ivigtut in South Greenland (Giesecke 1822) speculation started about the usefulness of this deposit. Research work was centered on cryolite, but the first attempt at mining in Ivigtut started with galena in 1854 (Tayler 1856). In his publication about this venture Tayler mentions that the galena contains about 45 ounces of silver. However, galena was not present in sufficient amounts for continued mining, which therefore came to an end the following year.

Interest in the galena associated with the cryolite persisted after cryolite mining was started in 1859, mainly because the galena was known to carry rather high silver contents. Although the mineral only appeared in small quantities, it was carefully concentrated as a by-product at the dressing plant in Copenhagen when new production methods were introduced in the 1890's. Mineralogically the Ivigtut galena is interesting because its content of silver is accompanied by nearly equivalent amounts of bismuth. Futhermore, several silver-bearing sulphides are enclosed in the galena. A pronounced increase in the content of silver was recorded for the galena concentrates in the 1950's which promoted a detailed investigation of the galena and associated sulphides.

The present paper describes the Ivigtut galena and its associated accessory minerals. The study is based on samples from most units of the cryolite deposit. A brief description of these units is given below.

## The cryolite-bearing granite stock

The map in Fig. 1 shows the cryolite mass as it occurred in the central part of a small granite stock. This was

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Fig. 1. Geological sketch map of the cryolite stock and surrounding rocks as exposed in 1874 shortly after the mining of the deposit had started. (Compiled by H. Pauly).

intruded into the Ketilidian gneisses during the Gardar period about 1200 m.y. ago. A reconstruction of the profile along the longitudinal section L - L in Fig. 1 of the quarry is given in Fig. 2.

The cryolite deposit (enclosed within the Ivigtut Granite) has been subdivided into the *cryolite body* and the *quartz body*. Within each of these bodies separate units were recognized in the course of mining and by means of diamond drilling. The cryolite body, apart from a minor protuberance towards the east, resembles a plane convex lens nearly circular in horizontal section. The quartz body underlies the cryolite body as a nearly cylindrical mass.

The rocks lying in contact with the cryolite deposit have been transformed into various types of greisen. A horizontal sheet of quartz feldspar pegmatite partly covered the top part of the cryolite body.

The various rock types of the intrusion are cut by mineralized quartz veins which extend a few hundred metres into the surrounding Precambrian gneisses.

#### The cryolite body

This part of the deposit was dominated by siderite cryolite (Pauly 1960), a coarse mixture of cryolite and siderite, the latter present usually in amounts of 10–20 %. The term 'siderite cryolite' and also the term 'fluorite cryolite' used below are old mine terms adopted by

Pauly (1960). The siderite generally forms a network enclosing rounded cryolite masses. A few percent of sulphides (mainly sphalerite, chalcopyrite, galena and pyrite) and similar amounts of quartz are associated with the siderite.

As mentioned in Bøggild (1905), and well illustrated in Baldauf (1910), part of the siderite cryolite showed a well-developed banding. Bands of pure cryolite alternated with bands of cryolite containing variable amounts of siderite which increased downwards. This banding was visible at a few small exposures during the last ten years of the mining.

Brecciation seems to have taken place at different stages during the formation of the cryolite body and indicates that the siderite cryolite is likely to represent the first formed unit within the cryolite body.

A rather peculiar rock type was located in the middle of the siderite cryolite (unit 3 in Fig. 2). It is a siderite cryolite variety, which carries about 10 % idiomorphic reddish-brown fluorite. The fluorite contains about 0.3% thorium but less than 100 ppm uranium. The cryolite in this material is nearly black, presumably due to the radioactivity of the fluorite (Pauly 1962a). A description of the black cryolite has been given by Bøggild (1953). This part was mined around 1900 but stockpiled because its fluorite content caused difficulties in the ore treatment. The samples studied are from these stockpiled materials.



Fig. 2. Longitudinal section through the cryolite deposit. (Compiled by H. Pauly).

A mass of pure, white cryolite ore formed an important unit within the cryolite body (unit 2 in Fig. 2). As it is virtually free of other minerals it is not important for the present study.

The body of pure cryolite was separated from the rocks below and to the west by a shell of fluorite cryolite (unit 4 in Fig. 2). Fluorite cryolite also underlay siderite cryolite in the central part of the deposit. In addition to cryolite it is composed of up to 20 % fluorite and smaller but variable amounts of microcrystalline topaz, K-mica (known locally as 'ivigite'), weberite, jarlite and others. Siderite is not present in the fluorite cryolite. Sulphides were scarce and in general only pyrite was found. Very rare samples contained small amounts of galena and chalcopyrite, or both. The main sulphides thus differed markedly from those of the siderite cryolite, which was dominated by sphalerite followed by galena, chalcopyrite and pyrite.

However, an unusual sulphide paragenesis composed of variable amounts of galena enclosing matildite and aikinite was found in a cargo shipment of fluorite cryolite materials at the refinery in Copenhagen. Its exact position within the deposit is not known. It is assumed to have been located near S in Fig. 2. A preliminary analysis on one specimen gave 2.5 % silver and 10 % bismuth. A description of the paragenesis is given on page 14-15. Only a few kilograms of this type of sulphide material was gathered.

The fluorite cryolite, or part of it, is clearly later than the siderite cryolite. This is indicated by brecciation and chemical reactions along the contact between the two rock types, for instance at A in Fig. 2.

#### The quartz body

The quartz body is known only from exploration drilling. The quartz zone (unit 7 in Fig. 2) forms the major part of the quartz body. It contains up to 20 % siderite, a few per cent mica and 2 % sulphides, mainly sphalerite with minor chalcopyrite and a little galena.

The quartz zone is transected by the siderite zone (unit 6 in Fig. 2) which lies as a sheet dipping to the south-west. It contains about 60 % siderite, slightly more than 10 % sulphides, and about 30 % quartz. The dominant sulphide is sphalerite accompanied by some chalcopyrite and a little galena.

The fluorite zone (unit 5 in Fig. 2) occurs as a sheet separating the quartz zone from the overlying fluorite cryolite. It is composed of fluorite, topaz and minor amounts of K-mica, weberite and others. Siderite is not present. Sulphides are present only in trace amounts. The zone was formed late, possibly at the same time as the fluorite cryolite.

An unusual sulphide mineralization known as the gustavite-cosalite-galena paragenesis was located as massive lumps near A in Fig. 2 in the brecciated contact zone between the fluorite zone and the siderite cryolite (Karup-Møller 1973). The total sulphide content was around 50 kg. A bulk analysis gave: 2.74 % silver, 15.34 % bismuth and 16.53 % lead. A summary description of its mineralogy and mode of occurrence is given on page 16.

In drill hole A (A in Fig. 2) the uppermost part of the quartz zone is impregnated with fluorite, topaz and K-mica. Galena-matildite-aikinite mineralization simi-

lar to the one located in the fluorite cryolite was present in this material at a depth of 9.0 and 9.6 m (see page 15).

#### Distribution of sulphides

Sphalerite is the most prominant sulphide of the cryolite deposit. It is followed by chalcopyrite and then by galena. The expression "the common Ivigtut galena" is frequently used. It stands for galena associated with siderite, i.e. galena in all units of the deposit, except for the rare galena varieties found in the fluorite cryolite and the fluorite zone, units 4 and 5, Fig. 2. The content of pyrite has not been estimated but it probably corresponds in total amount to that of galena. Mineralogical analyses of drill cores and of samples of crude cryolite have yielded the following weight ratios between the sulphides:

	galena	chalco- pyrite	sphale- rite	total
cryolite body	23	15	62	100
siderite zone	2.5	10	87.5	100
quartz zone total of	1	10	89	100
cryolite deposit	5	13	82	100

The ratio of the three sulphides is characteristically different from one zone to the next. Also in absolute amounts galena is found to have been concentrated in the cryolite body. Of the 12.000 t considered to have been present in the deposit some 9.000 t were situated in the cryolite body.

Another result of the quantitative evaluation of the deposit is the following weight ratios of sulphides to siderite in the three units:

Cryolite body	1:10
Siderite zone	1:5
Quartz zone	1:9

The sulphide to siderite ratio in the cryolite body and in the quartz zone is nearly the same, while the ratio characterizing the siderite zone is twice as big. In the drill cores it is seen that the occurrence of the sulphides in the siderite zone is restricted in many places to layers rarely exceeding a few metres in thickness. The sulphide content of these lavers may often reach 30 %. A similar heterogeneous distribution of layers and sulphides has not been observed within the cryolite body. Sulphide masses in most samples in the siderite cryolite generally vary in size from about one cm up to, although rarely, fifteen cm across. As mentioned in Pauly (1960) part of the siderite cryolite might be named 'sphalerite cryolite' because this material was characterized by the presence of cryolite enclosing black, equigranular marmatite as the dominant sulphide.

Table 1. Opaque minerals from the cryolite deposit. Decreasing size of spots corresponds to decreasing frequency of corresponding minerals in relation to associated opaque minerals.

sociated opaque miner	rals						enesis	enesis		
	Siderite cryolite	Black cryolite with red fluorite	Siderite zone	Quartz zone	Fluarite cryolite	Fluorite zone	Galena-matildite-aikinite parag	Gustavite-cosalite-galena parag	Mineralized veins and greisen	Pegmatite
Spholerite		•								
Chalcopyrite										
Galena										
Pyrite										
Freibergite				•		-			-	
Te-confieldite										
Stannite / kesterite										
Hexastannite										
Molybdenite										
Bournonite										
Hessite										
Pyrargyrite										
Pyrrhotite	×	•								
Marcasite										
Arsenopyrite										
Argentite										
Native bismuth										
Gustavite / phase X								•		
Vikingite										
Cosolite										
Eskimoite										
Berryite										
Aikinite							•			
Matildite										
Wittichinite										
Emplectite										
Arcubisite										
Mackinowite		•								
Cubanite			•							
Covellite										
Chalcocite										
Native gold										
Volynskite										
Tapalpite									•	
Mineral A										
Mineral B										
Mineral C										
Mineral D										
Wolframite										
Columbite			٠							
Rutile	•		٠						•	
Uraninite										
Coffinite										
Thorite										
Magnetite			•	•						
llmenite										
Hematite				•	•					•
Limonite	•	•	٠	•	•	٠			•	
Cassiterite									•	

		A				В		
	Wt%		Mol ratio		Wt%		Mol ratio	
Cu	14.8 esc	0.3	8.57		17.3 esd	0.8	9.80	1
Ag	32.3	0.8	10.99		27.7	2.0	9.29	
Fe	5.3	0.1	3.55	32	5.0	0.2	3.26	32
Zn	1.6	0.5	0.88		3.2	1.4	1.75	
Sb	26.5	0.3	8.01	ļ	26.6	0.9	7.90	]
S	22.0	0.1	25.26		22.7	0.1	25.56	
Total	102.5				102.5			

Table 2. Microprobe analyses on freibergite. A: 7 grains in polished section 80c and B: 5 grains in polished section 81. esd = estimated standard deviation.

#### Mineral descriptions

This part comprises a description of the accessory ore minerals enclosed in the common Ivigtut galena and those forming the galena-matildite-aikinite paragenesis. Galena is present in relatively small amounts in the gustavite-cosalite-galena paragenesis. The mineralogy of this paragenesis is described in several publications (Karup-Møller 1966, 1970, 1971, 1973 and 1977), and therefore only a brief description of the individual minerals is presented here.

All opaque minerals found in the cryolite deposit are listed in Table 1. Several of these (cubanite, machinawite, covellite, chalcocite, wolframite, columbite, rutile, ilmenite, hematite and magnetite) do not occur as accessory minerals in galena and have therefore been omitted from the present investigation.

#### Freibergite

Freibergite occurs as subhedral to euhedral crystals with an average size of 0.03 mm, rarely exceeding 0.1 mm. They occur isolated or intergrown with one or several of the other accessory minerals identified (Fig. 3). Microprobe analyses on freibergite in two siderite cryolite specimens are listed in Table 2. Similar results were obtained from three other specimens.

#### Te-canfieldite

Te-canfieldite is subhedral to euhedral and the average grain size is 0.05 mm. It occurs in galena, both isolated and intergrown with one or several of the other accessory minerals present (Fig. 3). The reflectance of the mineral is slightly lower than that of freibergite. The

Table 3. Microprobe analyses om Te-canfieldite. A: 6 grains in polished section 81b, B: 8 grains in polished section 82a and C: 5 grains in polished section 78a. esd = estimated standard deviation.

	Α				В			С			
	Wł%		Mol ratio	Wt %		Mol ratio	Wt %		Mol ratio		
Ag	63.5 esd	0.6	8.00	63.5 esd	0.3	8.00	64.2 esd	0.4	8.00		
Sn	9.1	0.2	1.04	8.9	0.2	1.01	9.1	0.1	1.03		
Te	18.4	0.3	1.95	17.5	0.4	1.87	18.5	0.2	1.94		
S	9.9	0.2	4.21	10.0	0.2	4.22	10.1	0.1	4.25		
Tota	100.9			99.9			101.9				





colour is medium to dark grey with a distinct violet tint when compared against the colour of freibergite. With crossed nicols the mineral is isotropic to weakly anisotropic. Microprobe analyses (Table 3) on Te-canfieldite in three polished sections suggest the formula:  $Ag_{8.00}Sn_{1.03}Te_{1.91}S_{4.23}$ .

Varieties with compositions different from that of true canfieldite or Te-bearing canfieldite have been identified. Optically they cannot be distinguished from canfieldite.

Microprobe analyses on two varieties are listed in Table 4. The two compositions poorly fit the canfieldite formula. The (Ag+Sn):(S+Te) mol ratio is smaller than for the Te-canfieldite analyses in Table 3. Furthermore, the S:Te mol ratio in the two varieties is distinctly different. Both ratios are also different from that of the three Te-canfieldite analyses in Table 3.

In polished section no. 27/67 two grains were found to have the compositions: 1) Ag 63.0 %, Sn 20.7 %, Te 0.3 %, S 16.1 % and 2) Ag 51.9 %, Sn 29.8 %, Te 0.2 % and S 15.7 %.

In polished section no. 71/67 a relatively large grain (0.2 mm) had the composition: Ag 41.5 %, Sn 36.8 % and S 22.5 %. The mineral is weakly anisotropic under crossed nicols and displays lamellar twinning.

Te-canfieldite is only known from a few localities. From north-east of Revelstoke in British Columbia the mineral was described by Harris & Owens (1971) who report its composition as: Ag 65.1 %, Sn 10.6 %, Te 8.7 % and S 14.0 %. Te-canfieldite from the Belukinskii wolframite deposit in Eastern Transbaikal, USSR, has the composition: Ag 62.9 %, Bi 0.70 %, Sn 8.20 %, Te 8.60 %, Se 0.40 % and S 9.0 % (Ontoev et al. 1970). Te-canfieldite from these two localities contains less tellurium than the Ivigtut variety.

#### Stannite and kesterite

Stannite and kesterite are common accessory sulphides both in galena and in chalcopyrite from all parts of the cryolite deposit. The two minerals have an average grain size of 0.2 mm. They occur either isolated or intergrown with each other, and sometimes also with other minerals. When associated with each other they formed during penecontemporaneous crystallization.

When compared to iron-poor kesterite, the zinc-poor stannite has a more distinct, light olive-grey reflectance colour, a higher reflectance, a stronger reflectance pleochroism, a stronger anisotropism by crossed nicols and more vivid anisotropism colours. Table 4. Microprobe analyses om Te-canfieldite-resembling mineral. A: 5 grains in polished section 79b and B :3 grains in polished section 27/67. esd = estimated standard deviation.

		А	В				
	Wt%		Mol ratio	Wt %		Mol ratio	
Ag	61.6 esd	2.1	8.00	63.8 esd	1.9	8.00	
Sn	10.6	0.5	1.25	11.9	0.4	1.36	
Te	14.8	0.5	1.63	9.1	0.4	0.97	
S	13.4	0.4	5.85	17.0	0.1	7.17	
Total	100.4			101.8			

Microprobe analyses were made on numerous grains in four polished sections from the siderite cryolite (nos. 1310, 1645, 1638 and 1639) and in one polished section from the quartz zone (no. 331 from drill hole A at a depth of 81.45 m). The results are listed in Table 5. The Fe-Zn ratio of the two minerals varies significantly from one polished section to the next.

In polished section no. 1310 (A in Table 5) stannite with a low content of zinc has been identified, whereas kesterite with small amounts of iron occurs in polished section no. 1645 (B in Table 5). In polished section no. 1638 (C in Table 5), dominated by iron-poor kesterite, a single very zinc-poor stannite grain was detected. This grain occurs in contact with kesterite and the relationships between the two minerals clearly show that they formed penecontemporaneously. In polished sections nos. 1639 and 331 the two minerals lie closer to each other in composition.

Springer (1972) has shown that complete solid solution exists between  $Cu_2FeSnS_4$  and  $Cu_2ZnSnS_4$ temperatures above 680°C. Below this temperature zinc-rich stannite recrystallizes from a high to low temperature modification accompanied by the exsolu-

Table 5. Microprobe analyses on A : 5 stannite grains in PS 1310, B : 7 kesterite grains in PS 1645, C-1 : 6 kesterite grains in PS 1638, C-2 : 1 stannite grain in PS 1638, D-1 : 3 stannite (-kesterite) grains in PS 1639, D-2 : 3 kesterite (-stannite) grains in PS 1639, E-1 : 3 kesterite (-stannite) grains in PS 331 and E-2 : 3 stannite (-kesterite) grains in PS 331. esd = estimated standard deviation.

	С	υ	Fe			Zn	S	n	S		Total
	Wt.%	Esd	Wt.%	Esd	Wt.%	Esd	Wt.%	Esd	Wt.%	Esd	
A	29.2	0.1	10.9	0.5	3.1	0.7	27.0	0.5	30.8	0.2	101.0
В	28.9	0.3	2.9	0.4	11.3	0.3	26.7	0.6	30.1	0.3	99.9
C – 1	28.7	0.2	3.2	0.2	12.0	0.6	27.3	0.6	30.2	0.3	101.4
C-2	29.0		11.9		1.8		27.6		30.7		101.0
D-1	29.5	0.2	7.8	1.4	6.5	0.4	26.9	0.6	30.6	0.3	101.3
D - 2	29.0	1.0	5.3	0.7	10.1	0.7	27.2	0.1	30.5	0.1	102.1
E – 1	29.5	0.2	4.7	0.3	10.4	0.4	27.2	0.1	28.4	0.4	100.2
E - 2	29.7	0.5	8.5	0.6	6.1	0.6	27.5	0.2	29.0	0.2	100.8
Mol.	ratios	(sum a	ofmetals	= 4)							
А	1.98		0.84		0.21		0.98		4.14		
В	1.98		0.23		0.82		0.98		4.09		
C - 1	1.96		0.25		0.79		1.00	ł	4.08		
C-2	1.96		0.92		0.12		1.00	1	4.12		
D – 1	1.99		0.60		0.43		0.97		4.10		
D - 2	1.95		0.40		0.66		0.98		4.07		
E – 1	1.98		0.36		0.68		0.98		3.78		
E – 2	1.98		0.64		0.39		0.98		3.84		

tion of iron-bearing kesterite. These results explain the exsolved kesterite in stannite described by Harris & Owens (1972). It also explains the penecontemporaneous crystallization of kesterite and stannite in the cryolite deposit. Further experimental studies on the stannite-kesterite stability relationships may prove whether or not the two minerals use usefull as a geological thermometer.

#### Hexastannite

This mineral is an hedral with a grain size of less than 0.01 mm.

In reflected light and oil immersion it is reddish brown with a distinct reflectance pleochroism. The anisotropism under crossed nicols is strong and the colours vivid.

Microprobe analyses (Table 6) were completed on four grains in polished section no. 1639 present along the contact between galena and enclosed crystals of pyrite. The analyses lie very close to analyses published on hexastannite, stannite jaune and stanoide.

Table 6. Microprobe analyses on 4 hexastannite grains in PS 1639. esd = estimated standard deviation.

	W	<b>.</b> %	Mol. ratio	
Cu	36.5 e	sd 0.9	2.30	
Fe	11.5	0.5	0.82	4.00
Zn	4.6	0.5	0.28	
Sn	17.7	0.2	0.60	}
S	31.2	0.1	3.90	
Total	101.5			

From the literature it appears that the two last mentioned minerals are identical with hexastannite (Ramdohr 1944, Levy 1967, Kato 1969, Springer 1968, and Oen 1970). The following formula for the Ivigtut hexastannite variety has been calculated:

 $Cu_{2.30}Fe_{0.82}Zn_{0.28}Sn_{0.60}S_{3.90}.$ 

## Hessite

Hessite is anhedral to euhedral in shape and has a grain size of less than 0.02 mm. It occurs alone or intergrown with one or several of the other accessory minerals present (Fig. 3).

#### Pyrargyrite

Pyrargyrite is subhedral to euhedral with an average grain size of 0.04 mm. Microprobe analyses on the mineral in polished section no. 27/67 in galena from siderite cryolite showed a content of less than 0.15 % copper and no arsenic.

#### Bournonite

Bournonite is equidimensional to lamellar in shape and has a maximum length of 0.1 mm. The mineral occurs mainly isolated in the galena, but is sometimes intergrown with hessite, freibergite and mineral C. Microprobe analyses on bournonite in polished section no. 71/67 showed a content of less than 0.1 % silver.

#### Tapalpite and volynskite

Microprobe tests on a small mineral aggregate enclosed in the common Ivigtut galena in polished section no. 91 suggested that this was composed of tapalpite (Ag-BiTeS) and volynskite (AgBiTe<sub>2</sub>).

Table 7. Microprobe analyses on A : 12 aikinite grains in the galena-matildite-aikinite- mineral paragenesis from locality S in Fig. 2, B : 9 aikinite grains in the galena-matildite-aikinite mineral paragenesis from locality A in fig. 2 and C : 10 aikinite grains in the gustavite-cosalite-galena mineral paragenesis near locality A in Fig. 2. esd = estimated standard deviation.

	A			В	В			С		
	Wt. %		Mol ratio	Wt. %		Mol ratio	Wt. %		Mol ratio	
Bi	37.2 esd	0.7	1.02	37.0 esd	0.4	1.03	39.5 esd	1.2	1.07	
Рb	35.9	0.3	0.99	35.9	0.3	1.00	33.9	0.5	0.93	
Cu	10.9	0.1	0.98	10.8	0.7	1.00	10.2	0.1	0.91	
Ag	0.1		0.01	nil			0.1		0.01	
S	16.8	0.3	3.00	16.5	0.3	3.00	17.0	0.3	3.00	
Total	100.9		6.00	100.2		6.00	100.7		6.00	

#### Aikinite

The mineral is one of the three major minerals forming the galena-matildite-aikinite paragenesis. It has also been found in small amounts in the gustavite-cosalitegalena paragenesis. It is shaped as subhedral grains with a size of less than 0.2 mm. Microprobe analyses on the mineral (Table 7) have given nearly ideal aikinite compositions.

#### Wittichenite

Wittichenite together with a number of other minerals has formed during the decomposition of aikinite in the galena-matildite-aikinite paragenesis. Due to its fine grain size (less than 0.01 mm) quantitative microprobe analyses could not be carried out.

#### Emplectite

Emplectite occurs in very sparse amounts in the galenamatildite-aikinite paragenesis from the fluorite cryolite. The mineral has a grain size of less than 0.05 mm. Microprobe analyses on six emplectite grains in polished section no. 58a gave: Cu =  $18.5 \pm 0.2$  %, Bi =  $63.9 \pm$ 0.3 % and S =  $19.8 \pm 0.2$  % suggesting the formula: Cu<sub>0.96</sub>Bi<sub>1.01</sub>S<sub>2.02</sub>.

#### Arcubisite

Arcubisite (CuBiAg<sub>6</sub>S<sub>4</sub>) is only known from the cryolite deposit (Karup-Møller 1976). It occurs as rare grains enclosed in the galena-matildite-aikinite paragenesis from drill hole A and from location S in Fig. 2.

#### Argentite

Trace amounts of argentite intergrown with arcubisite crystallized in the galena-matildite-aikinite paragenesis from the fluorite cryolite.

#### Mineral B

Mineral B ( $Ag_4TeS$ ) occurs closely associated with arcubisite in drill hole A in Fig. 2 (Karup-Møller 1976).

#### Mineral C

Mineral C, considered to be a new species, has only been found in a few polished sections from both the siderite-cryolite and the galena-matildite-aikinite parageneses. The mineral occurs either isolated in galena or more commonly intergrown with hessite, Te-canfieldite and/or freibergite (Fig. 3). It ranges in shape from lamellar to irregularly shaped grains.

In reflected light mineral C is light bluish grey with reflectance values estimated to lie slightly above those of freibergite (the small size, in average 0.05 mm, has prevented reliable reflectance measurements to be carried out). Reflectance pleochroism of the mineral is weak in oil, but not visible in air. Under crossed nicols the anisotropism of the mineral is distinct in air, distinct to strong in oil without pronounced anisotropism colours.

Only three grains were sufficiently large to permit quantitative microprobe analyses to be carried out (Table 8). The results are poor due to the small size of the analyzed grains and the easy breaking down of these when exposed to the electron beam of the probe. The following formula is suggested:  $Ag_9Sb(S,Te)_6$ .

#### Mineral D

Mineral D has developed from the alteration of aikinite. The mineral is shaped as platy grains with a length of less than 0.02 mm. Its reflectance colour and its reflectivity are rather similar to those of galena. The reflectance pleochroism is distinct. The anisotropism under crossed nicols is strong but without distinct colours (all observations are made in oil immersion). A microprobe analysis completed on mineral D in the aggregate shown in Fig. 4 gave Ag  $\sim$  15 %, Pb  $\sim$  23 %, Cu  $\sim$  5 %, Bi  $\sim$  45 % and S  $\sim$  17 %, suggesting the formulae (Ag, Cu) PbBi<sub>2</sub>S<sub>5</sub>.

#### Gustavite-phase X

These two mineral varieties were found in the gustavite-cosalite-galena paragenesis (Karup-Møller 1970). They represent the decomposition product of a high-temperature gustavite variety. Both the high

Table 8. Microprobe analyses on 3 mineral C grains in polished section 63/67.

	Wt %	Mol ratio	Wt%	Mol	ratio	Wt %	Mol ratio
Ag	64.8	6.87 1	66.8	7.18		61.7	7.25 80
Sb	11.9	1.13	8.6	0.82	0.00	7.1	0.75
Te	6.1	0.55	12.4	1.12		17.0	1.70
S	13.7	4.89	9.7	3.51		8.8	3.46
Total	96.5		97.5			94.6	



Fig. 4. Alteration aggregate composed of galena (1); mineral D (2) and gangue extend into aikinite from the aikinite-galena grain boundary (stippled). Note the increasing concentration of the gangue mineral towards the aikinite grain.  $\times$  260, one nicol. Oil immersion. To the right the same aggregate with +N.

temperature variety and its decomposition products belong to the lillianite ( $Pb_3Bi_2S_6$ ) – gustavite ( $PbAg-Bi_3S_6$ ) solid solution series proposed in Karup-Møller (1970). On the basis of microprobe analyses and X-ray crystallographic data (Karup-Møller 1977) the high temperature variety is classified as <sup>3.81</sup>Gus<sub>75.1</sub> and the two decomposition phases as <sup>3.77</sup>Gus<sub>86.4</sub> (host) and <sup>3.82</sup>Gus<sub>58.7</sub> (exsolved variety).

#### Vikingite

This mineral is a new species known only from the Ivigtut gustavite-cosalite-galena paragenesis. Its ideal composition is  $Ag_{1.25}Pb_{2.00}Bi_{3.25}S_{7.5}$ . The compositions of the mineral in three polished sections (Karup-Møller 1977) are plotted in Fig. 5.

#### Eskimoite

This mineral, like vikingite, is known only from the Ivigtut gustavite-cosalite-galena paragenesis. Its ideal composition is  $Ag_{1.75}Pb_{2.50}Bi_{3.75}S_9$ . The compositions of the mineral in two polished sections (Karup-Møller 1977) are plotted in Fig. 5.

#### Cosalite

At Ivigtut cosalite has only been found in the gustavite-cosalite-galena paragenesis (Karup-Møller 1973). It is enclosed in vikingite and gustavite. Its composition (Karup-Møller 1977) is plotted in Fig. 5.

#### Berryite

Berryite occurs in small amounts in the Ivigtut gustavite-cosalite-galena paragenesis (Karup-Møller 1966), Berryite is a rare mineral in the galena-matildite-aikinite paragenesis present in drill hole A at 9.00–9.60 m.

#### Mineral A

Mineral A  $(Ag_2Cu_3Bi_6Pb_9S_{20.5})$  is known only from the cryolite deposit (Karup-Møller 1971). It occurs in extremely small amounts exsolved from the galena in the gustavite-cosalite-galena paragenesis.

#### Gold

A few grains of gold were found in the gustavite-cosalite paragenesis (Karup-Møller 1973).



Fig. 5. The small dots in the bottom right part of the figure represent microprobe analyses on galena in samples Ol-1 to 10 (Table 10) from the galena-matildite-aikinite paragenesis while the crosses represent the bulk galena-matildite composition in the same samples determined by X-ray fluorescence. Microprobe analyses on the major minerals forming the gustavite-co-salite-galena paragenesis are plotted at top left in the figure. 1: Gustavite before its breakdown into the two low temperature gustavite varieties represented by 2 and 3. 4: Vikingite, 5: eskimoite, 6: cosalite associated with vikingite, 7: cosalite associated with gustavite, 8: galena and 9: bulk composition of one randomly selected sample weighing about 100 grams. The microprobe analyses are published in Karup-Møller (1977).

#### Coffinite

Coffinite occurs in sparse amounts in the gustavite-cosalite-galena paragenesis (Karup-Møller 1973). Microprobe analyses on the mineral gave in addition to U, 0.8-4.3 Wt. % S, 2.7-6.4 % Bi, 7.3-15.4 % Pb, 1.6-4.3 % Cl, and less than one per cent of each of the elements Ca, Th and Fe.

### Description of mineral parageneses

#### Accessory sulphides in the Ivigtut galena

The distribution of the sulphides in the major units of the cryolite deposit is presented in Table 1; the mode of occurrence of the major sulphides in the siderite cryolite was described by Pauly (1960). An unusual, and for the cryolite deposit rare, pyrrhotite-marcasite mineralization was described by Oen & Pauly (1967). The mode of occurrence of the accessory ore minerals associated with the common Ivigtut galena is described here.

Freibergite and Te-canfieldite are the two most common accessory minerals. Hessite and bournonite

are less common whereas pyrargyrite and mineral C are rare. The minerals occur alone or intergrown with each other in aggregates of two or more minerals (Fig. 3). Freibergite has been found in relatively large quantities in galena from the fluorite cryolite.

Stannite and kesterite occur either separated from each other or intergrown in aggregates. The two minerals are mainly contained in chalcopyrite and are here sometimes associated with sphalerite. They also occur in galena near chalcopyrite grains, either alone or intergrown with freibergite.

Cassiterite occurs as clusters of crystal fragments in galena, chalcopyrite and sphalerite. The cassiterite is often surrounded by a narrow rim of stannite/kesterite. The rim is considered to be the reaction product between earlier cassiterite crystals and mineral fluids.

Hexastannite is rare. It has been found along the contact between galena and both chalcopyrite and pyrite. In galena from the fluorite cryolite zone (specimen no. 35) it occurred in peculiar, less than 0.1 mm large, aggregates composed of freibergite, galena, arcubisite and mineral C, see Fig. 6.

Small amounts of primary, very fine grained matildite have been found enclosed in galena associated with chalcopyrite from the quartz zone.

Molybdenite is a common accessory mineral in galena in certain areas of the deposit where relatively high temperatures of formation have prevailed. Such areas are the eastern breccia zone of the siderite cryolite, the



Fig. 6. Aggregate of freibergite (1), arcubisite (2), mineral C (3), hexastannite (4) and fine grained galena in galena. The black dots in the arcubisite grains have been caused by the microscope light.  $\times$ 760. Oil immersion.

greisen (unit 9 in Fig. 1) and the pegmatite (unit 12). At the last named locality the mineral is rather common. Associated minerals here are columbite and cassiterite with a crystal size of up to 1 cm. Abundant fine grained stannite/kesterite is contained in the cassiterite. Haematite, partly altered to magnetite, occurs as laths in siderite.

#### The galena-matildite-aikinite paragenesis

The paragenesis in the fluorite cryolite. In the early 1950's fluorite cryolite specimens mineralized with up to 25 % fine grained galena, matildite and aikinite were found in the crude ore at the refinery in Copenhagen. The fine grain size of the sulphides clearly distinguished these from the coarser common Ivigtut galena associated with chalcopyrite and sphalerite in the siderite cryolite. The sulphides also attracted attention because they occurred in fluorite cryolite materials which generally are free of sulphides. Only a few of the specimens contain macroscopically visible pyrite and chalcopyrite. At the refinery all sulphide-rich samples were systematically handpicked for separate treatment. Allthough careful attention was paid to fine grained materials only about 50 specimens were found containing altogether a few kilograms of sulphides. It may therefore be concluded that no more than 50 kg sulphides are likely to have been present in the deposit. The unusual sulphide mineralization may have been confined to a narrow horizon in the fluorite cryolite and its most probable location is near S in Fig. 1.

The proportion between galena, matildite and aikinite varies significantly from one specimen to another. Galena is always present and may occur without one, or both of the two other sulphides. A characteristic feature is the complete absence of both sphalerite and freibergite.

Two matildite generations have been identified. One of these has exsolved from galena and is the most common. The other is considered to have crystallized penecontemporaneously with galena.

The exsolved matildite grains occur regularly distributed as very fine-grained blebs (average size 0.002 mm) and rarely as irregularly elongated laths or stringers following a single direction in the galena.

The other variety occurs in aggregates randomly distributed in galena with the exsolved matildite (Karup-Møller 1976: Fig. 1). Within these aggregates elongated grains of galena lie between the individual matildite grains. The aggregates are present in substantial amounts in a few specimens and may locally coalesce to form larger sized areas with numerous inclusions of galena, Fig. 7.

Emplectite occurs in specimens containing abundant matildite and aikinite. The mineral generally lies along the boundary between sulphides and non-opaque minerals. Emplectite grains may also occur isolated in galena or within matildite aggregates. In the latter case



Fig. 7. Heterogeneous aggregate of matildite (light grey to white) with interstitial galena (black stringers) in galena (dark grey).  $\times 260$ . Oil immersion. +N.

they resemble the individual matildite grains of these aggregates in their mode of occurrence.

Rounded aggregates of hessite in graphic intergrowth with galena occur in sparse amounts enclosed in galena with exsolved matildite. Sometimes a matildite grain lies across the galena-hessite boundary without disturbing its trend. The part which lies within the hessite aggregate then occurs, like the galena, in graphic intergrowth with the hessite.

Small aggregates composed of one or several of the minerals hessite, Te-canfieldite, mineral C, matildite and galena lie enclosed in matildite-bearing galena. Due to their extremely fine grain size and complex intergrowth positive identification of each mineral, even with the microprobe, was not always possible.

In one specimen of galena with small amounts of aikinite and exsolved matildite, a 0.02 mm thick rim of argentite intergrown with arcubisite occurred along part of the contact between galena and cryolite (Karup-Møller 1976).

Aikinite occurs as well rounded equidimensional grains with a size of up to a few millimetres. Primary formed minerals have not been found within this mineral.

In a few specimens, partial to complete decomposition of aikinite has taken place resulting in the formation of a number of secondary minerals: galena, chalcopyrite, native bismuth, secondary aikinite, wittichenite, matildite and mineral D.

The secondary minerals occur mainly in two different

associations. One is characterized by chalcopyrite, native bismuth, matildite, galena, wittichenite and gangue and the other by galena, secondary aikinite, mineral D and gangue (Fig. 4). Grain size, texture and mineral proportions vary significantly even within the same aggregate. Areas composed of a homogeneous mixture of all sulphides, except chalcopyrite, may grade into banded aggregates dominated by chalcopyrite.

Formation of the secondary minerals has started along the contact between aikinite and both galena and gangue minerals without disturbing the shape of these (Fig. 4). The contact between secondary minerals and host aikinite may either be smooth or irregular. Unreplaced remnants sometimes lie enclosed in the secondary minerals.

The presence of most of the secondary minerals shows that redistribution of iron and silver must have taken place during the aikinite decomposition process.

The galena-matildite-aikinite paragenesis in drill hole A. In drill hole A galena, chalcopyrite and pyrite were found disseminated in gangue minerals at a depth of 9.0 to 9.6 m. Small amounts of aikinite, matildite, arcubisite, mineral B (Ag<sub>4</sub>TeS) and others (Table 1) occur enclosed in the galena (Karup-Møller 1976). The gangue minerals, quartz and siderite, were to some extent replaced by fluorite, topaz and K-mica. This locality is situated a few metres below the brecciated contact between the fluorite and the quartz zones. The late minerals and the sulphides are considered to have formed when the fluorite zone developed.

Galena contains the same two matildite generations as identified in the related sulphide paragenesis from the fluorite cryolite described above. Aikinite occurs as well rounded grains less than 0.1 mm in size. Alteration of the mineral has not taken place.

Arcubisite occurs either alone or associated with the other minerals present in accessory amounts. It may enclose grains of mineral B, sometimes surrounding this as a thin rim. Aggregates of arcubisite, matildite, galena, hessite, chalcopyrite and/or gangue occur isolated in galena, in aikinite or between grains of these two minerals, matildite and berryite. Rare grains of Te-canfieldite and argentite have also been identified.

The gustavite-cosalite-galena paragenesis

The mineral suite was found in situ in 1961 at a few metres distance from drill hole A. Small, irregularly shaped lumps of fine grained fluorite and topaz intergrown with gustavite, vikingite eskimoite, cosalite, galena and small amounts of other sulphides (Table 1) were found enclosed in a heterogeneous mixture of fluorite, topaz, weberite and K-mica, typical of the fluorite zone. These materials occurred as a pocket enclosed in massive siderite with a few percent cryolite. The siderite belongs to a siderite sheet which at this location forms the bottom part of the cryolite body. The pocket occurred near the brecciated contact between this siderite sheet and the underlying fluorite zone.

A general description of the paragenesis is given in Karup-Møller (1973). It was then assumed that the major sulphides in the paragenesis were the two gustavite varieties <sup>3.77</sup>Gus<sub>86.4</sub> (gustavite) and <sup>3.82</sup>Gus<sub>58.7</sub> (phase X) representing the decomposition product of an original high temperature gustavite variety (<sup>3.81</sup>Gus<sub>75,1</sub>). However, recent microprobe and X-ray crystallographic work has revealed the presence of the two new minerals vikingite and eskimoite (Karup-Møller 1977). In general the distinction between these two minerals and gustavite is not possible in the ore microscope. Vikingite may be as common as gustavite but eskimoite considerably less so. Vikingite and gustavite may both enclose cosalite, while eskimoite occurs as host for berrvite. aikinite and pyrite. The composition of vikingite, eskimoite, gustavite and cosalite in different polished sections are plotted in Fig. 5. The following minerals are present in trace amounts: native bismuth, mineral A, chalcopyrite, sphalerite, native gold and coffinite.

### Geochemistry

A major objective of the investigation was an attempt to determine, if any correlation existed between the content of silver and bismuth in the Ivigtut galena and the location of this mineral within the deposit. The study is based upon: 1) analyses of galena concentrates completed during the period 1937 to 1961 and 2) microprobe and bulk chemical analyses (X-ray fluorescence, atomic absorption, neutron activation and emission spectrographic techniques) on selected galena samples from different units of the deposit. The content of trace elements in a few of these samples has also been determined.

Samples and analytical methods

Galena in hand specimens has been obtained from the units 1, 3, 9 and 11 marked on Fig. 2.

Cores from the large drilling programme carried out during the period 1948 to 1958 have enabled us to obtain galena samples from the fluorite, the siderite and the quartz zones. In a drill core from 1914 galena was obtained from siderite cryolite near location O in Fig. 2.

Material representing the fine-grained galena-matildite-aikinite paragenesis (location S, Fig. 2) and the gustavite-cosalite-galena association (location A, Fig. 2) have also been included in the present study.

About 0.3 gram of material was used by the X-ray fluorescence, atomic absorption and neutron activation bulk chemical methods, but only about 10 mg was necessary for the emission spectrographic analyses. The galena to be analyzed was carefully hand picked under a

## Table 9. Ag and Bi analyses on the common Ivigtut galena.

		r		1					
		ATOMIC #	BSORBI	ION (A)		MICRO	PROBE A	NALYSI	E S
SAMPLE NUMBER	SEA	X-RAY FL	& UORESC	ENCE (R)					
å	LEVEL	AI AI	ALYSE	°					NO
LOCATION					An		Bi		DETER
	0.0 m				111. 0		11/4 0	£	DETER-
		1			11.1 . /		111 · 30	630	MINA-
									TIONS
A. SIDERITE CRYOLITE	alder i der der de			0	0 00 04 190				
( ) D// O 101/	E				0.43	0.02	1 20	0.00	(0)
Sc-1 DH. 0. 1914	- 5				0.03	0.03	1.29	0.09	(9)
2 DH. O. 1914	- 2 5				0.36	0.05	0.62	0.0/	(9)
3 Hoist pillar	- 5 0	0.85	1.42	(A)	0.73	0.06	1.92	0.24	(7)
4 East quarry	- 3 5				0.55	0.06	1.12	0.08	(9)
5 South wall	-54	0.75	1.70	(A)	0.68	0.06	1.41	0.12	(11)
6 Black cryolite with reddish	-25			1	0.83	0.10	1.59	0.21	(10)
7 brown fluorite (unit	-25	1			0.89	0.06	1.77	0.10	(10)
8 3 in fig 2)	-25	1			0.90	0.09	1.82	0.08	(10)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	- 25	0.67	0 05	(4)					1
10 Secole and level level	2.5	0.07	1 42		0 77	0 08	1 55	0 37	(16)
To sample not localized		0.74	1.02		0.77	0.00	1.35	0.07	(10)
		0.88	1.54	(K)		0.05		0.00	(10)
1) Sample not localized		0.18	0.04	(A)	0.18	0.09	U.40	0.22	(10)
12 do		0.19	0.04	(A)					
13 do		1.33	2.55	(A)					
14 do		1.10	1.87	(A)	1.25		2.64		
		1.17	2.17	(R)					
15 do					0.71	0.14	1.51	0.27	(9)
16 do					0.69	0.06	1.30	0.34	(9)
17 do					0.40	0.07	0.79	0.22	(10)
17 40					1 00	0.11	2 20	0.20	(0)
18 00					1.07	0.11	2.30	0.20	(7)
19 do		0.00	1.21	(A)	0.81	0.11	1.17	0.15	(9)
	10	0.65	0.92	(R)					
Border zone. Tayler 1856	+ 3	0.14							
Cryolite ore. Hagemann 1876		0.5							
Upper part cryalite body. Jorl 1909.		0.7							
Lower part cryolite body. Jarl 1909.		0.4							
		-							
FLUORITE CRYOLITE									
Fc-1 Sample not localized		0.45	0.05	(A)					
2 d o					0.09		0.09		
3 do		0.12	0.04	(A)					
4 d o		0.15	0.04	(A)					
5 do		0.11	0.10	(R)	0.06	0	0.11		
C.FLUORITE ZONE									
Fz-1 DH. J-4 of 28.00 m	-78				0.03	0.02	0.08	0.06	(10)
D, SIDERITE ZONE									
	(14.14.14)		1913 - 2014						
Sz-1 DH. Z ot 160.40 m	-72	1.07	1.60	(A)					
2 DH. A at 9.60 m	-64				1.54	0.18	3.34	0.44	(5)
3 DH. 154 of 21.15 m	-68	1.53	3.10	(A)					
4 DH. 154 at 37.28 m	-76	0.85	1.10	(A)					
5 DH. 154 of 37.78 m	- 76				0.68	0.08	1.54	0.10	(10)
6 DH. 139 at 20.48 m	-46	0.41	0.80	(A)					
7 DH. 139 at 38.18 m	- 53	1,14	2.12	(A)					
E. QUARTZ ZONE									
0-104 13 -1 (0.00	1.1.2	0.07			0.0.	0.10		0.00	(10)
	-116	0.86			0.86	0.10	1.55	0.09	(10)
2 DH. J-4 at 69.90 m	-107				0.71	0.04	1.33	0.15	(10)
3 DH, J-4 at 77.73 m	-118				1.73	0.14	3.46	0.30	(9)
4 DH. A ut 81,44 m	-135	2.06		(A)	1.79	0.11	3.60	0.44	(9)
5 DH. A at 81.45 m	-135				2.15	0.24	4.30	0.41	(10)
F. MINERALIZED VEINS GREISEN & PEGMATITE									
		125							
Mv-1 DH, J-9 at 39.80 m	- 5 4	0.87	1.60	(A)					
2 Profile 75	-18	0.81	1.37	(A)					1
3 Minerolized greisen	?	1.50	2.78	(A)	1.43		1.35		
4 Mineralized greisen senolite	?	0.67	1.23	(A)	0.66		1.35		2
5 Sample collected by Weber, 1862	?	0.18	0.06	(A)					
6 Sample collected by Thomsen, 1869	?	0.09	0.06	(A)					
7 Pegmatite, (unit 13 in fig. 2)	- 2	0.14	0.04	(A)	0.11	0.06	0.22	0.15	
terr revent 0.01 0. € at 0.25			Assettion ()				and the second		

Table 10. O1–1 to O1–10 : specimens from the galena-matildite-aikinite mineral paragenesis. Fc-5 : specimen from the fluorite cryolite. Sc-10, -14, -19 and -20 : specimens from the siderite cryolite. Mv-3 : specimens from greisen. Gus-1 and -2 : Specimens from the gustavite-cosalite-galena paragenesis. Esd = estimated standard deviation.

	Mic	roprob	e ono	lyses	X -	ray flu	oresce	nce or	alyses	Ne	utro	on acti	vation	analy	ses	S	bect	ral o	nalvs	r \$
		(Wt.	%)				(W1.9	6)				(F	opm)				(	ppm)		
Spl.				- August August				-				_	-					-		100273
no	Ag	Esd	Bi	Esd	Ag	81	Cu	Fe	Zn	Sb	As	Te	Se	Αυ	La	Co	Ni	Sn	Mo	W
01-1	1.13	J. 08	2.10	0.24	0.98	1.71	0.23	1.80	0.019	4	< 5	<1100	500	1.6	10	10	10	10	-	sp
01-7	1.28	0.05	2.31	0.12	1.18	2.12	0.07	0.10	0.019	26	< 6	< 500	<300	0.2	30	60	sp	30	sp	3300
01-3	1.79	0.31	3.33	0.37	2.17	3.81	0.04	1.62	0.017	nd	nd	n d	nd	nd	nď	20	-	10	~	sp
01~4	1.61	0.21	2.95	0.26	2.43	4.32	0.07	0.16	0.022	2	< 2	600	400	12.7	2	50	sp	sp	sp	-
01-5	1.65	0.19	2.80	0.25	2.63	4.30	0.07	0.53	0.016	3	< 4	200	300	1.7	12	-	-	10	sp	
01-6	nd		nd		3.66	7.06	0.23	0.16	0.017	9	3	<1200	< 700	0.6	1	15	-	sp	-	-
01-7	1.79	9.16	3.46	0.17	4.71	13.75	2.47	0.15	0.014	15	9	<\$800	<600	0.6	1	50	-	sp	*	sp
OI-8	1.42	0.27	2.40	0.64	5.26	13.64	1.41	0.35	0.018	nd	nd	nd	nd	nd	nd	10	-	sp	\$P	sp
01-9	1.04	0.21	2.27	0.44	5.32	10.83	0.58	0.21	0.016	2	< 7	< 600	500	2.2	1	-	sp	-	-	-
01-10	0.90	0.19	2.15	0.35	6.87	12,31	0.05	0.33	0.016	5	<6	< 800	600	1.0	1	40	-	۶p	20	40
Fc - 5	0.06		0.11		0.10	0.10	0.05	0.15	0.041	600	<7	700	<400	0.3	1	50	-	30	sp	1800
Sc-10	0.77	0.08	1.55	0.37	0.88	1.54	0.04	0.06	0.028	400	<3	300	200	0.1	1.2	10	-	20	-	
Sc - 14	1.25		2.64		1.17	2.17	0.05	0.67	0.017	300	<2	400	400	0.3	1	25	-	15	-	10
Sc-19	0,81	0.11	1.17	0.15	0.65	0.92	0.04	0.06	0.017	100	2	200	200	0.3	0.5	20	-	25	20	sp
1900 Pb	S conc	entra	e		0.82	1.37	0.50	1.81	0.160	100	30	0 < 200	200	0.6	6	8	15	130	360	sp
Mv - 3	1.43		2.75		n d	2.42	0.05	0.11	0.016	90	2	400	500	0.5	0.2	-		20	20	
Gus-1					5.96	34.23	0.73	0.30	0.017	200	<7	< 2400	< 900	4.2	10	10	-	15	10	30
G J 1 - 2					5.91	30.69	0.44	0.77	0.032	100	<4	< 700	< 500	1.5	6	÷	15	15	40	sp

binocular microscope avoiding all visible mineral impurities. Accessory minerals enclosed in the galena could not be avoided.

The galena intergrown with matildite and aikinite and the galena intergrown with gustavite and cosalite could not be isolated from the associated sulphides. Bulk analyses were therefore carried out on sulphide material free of visible gangue impurities.

All the samples were analyzed for silver and bismuth (Table 9). Three galena samples from the siderite cryolite, one from fluorite cryolite and one from the surrounding greisen together with bulk samples representing the galena-matildite-aikinite and the gustavite-cosalite-galena parageneses have been analyzed for all metals present in detectable amounts (Table 10). One sample representing the galena concentrate produced in 1960 has also been analyzed.

Galena in polished sections has been analyzed for silver and bismuth using the electron microprobe (Table 9). The composition of accessory minerals enclosed in the galena has been determined by the microprobe.

The following is af brief description of the analytical methods used:

The *microprobe analyses* listed in Tables 2–6 and 8 were completed at the Technical University of Denmark using an ARL model EMX microprobe; the analyses listed in Tables 7 and 9 were completed at the Institute of Mineralogy, University of Copenhagen using a HITACHI microprobe model XMA-5B. Acceleration voltage was 30 kV with the ARL microprobe and 20 kV with the HITACHI microprobe. Standards used were pure metallic Ag, Bi, Cu, Sn, Te, Sb and natural galena and chalcopyrite. Corrections were made using a programme written by Springer (1967). In general several grains were analyzed during an analytical sequence. Measurements on standards were taken before and after each sequence and the average values were used for the computations. The spread of the analyses is given as 'esd' (estimated standard deviation) in the tables.

The emission spectrographic analyses were made at the Institute of Petrology, University of Copenhagen using a large HILGER quartz spectrograph. Standards were synthetic sulphides and »SULPHIDE ORE, ASK nr. 3«. Elements determined and detection limits in ppm were: Co (5), Ni (3), Sn (10), Mo (8), W (10), Cd (20) and In (20). The latter two elements were not present in detectable amounts.

The X-ray fluorescence analyses were completed at the Geological Institute, University of Århus, using a Philips PW 1220 X-ray fluorescence spectrometer (60 kV, 24 mA, fine collimator, LiF crystal 220). Standards were synthetic sulphides. Elements determined were Ag, Bi, Cu, Fe and Zn. The atomic absorption spectrophotometric analyses were completed at the Mineralogical Institute, Technical University of Denmark, Lyngby using a Perkin-Elmer atomic absorption spectrophotometer, model 303. Elements determined were Ag and Bi.

The neutron activation analyses were made at the Research establishment, Risø, as described in Gwozdz & Rose-Hansen (in prep.). Standards used were the same as used for the X-ray fluorescence analyses. Elements determined were Sb, As, Te, Se, Au and La.

#### Silver and bismuth in galena concentrates

Analyses on galena concentrates are available from the period 1937 to 1964. The annually produced concentrate was collected and stored in several batches and each of these was analyzed independently. A number of concentrate analyses were thus obtained each year. A time gap of 2 to 3 years is judged to have existed between mining of the galena and analyzing the corresponding concentrates. Tracing back a particular batch of galena concentrate to a location in the mine was therefore only possible in a very general way. Galena made up about 0.25 % of the crude ore treated in the dressing plant. Processing about 40.000 t was thus necessary to produce about 100 tons of concentrate. The galena concentrate was produced from middlings roughly one year after the crude ore was processed.

The average values, determined on the galena con-

centrates during the period 1937–1964 (Table 11) were, as mentioned in Pauly & Siemes (1973):

$$Pb = 76.83$$
 %  
 $Ag = 0.7361\%$   
 $Bi = 1.3486\%$ 

These values correspond roughly to 88.7 % PbS, 2.4 %  $AgBiS_2$  and 8.8 % impurities. The impurities were mainly pyrite with a little chalcopyrite, sphalerite and small amounts of other minerals. Recalculated the values correspond to 97.2 % PbS, 2.7 % AgBiS<sub>2</sub> and 0.1 % Ag<sub>2</sub>S. Optical and X-ray examinations of galena failed to detect the presence of distinct Ag-Bi-bearing minerals. It is concluded that the amount of 2.7 % matildite is dissolved in the structure of galena substituting for lead (Ag<sup>+</sup> + Bi<sup>+++</sup>  $\leftrightarrow$  2Pb<sup>++</sup>).

In Fig. 8 the silver content in galena from all analyzed concentrates is plotted. Each point represents the analysis of an individual batch. The average values are plotted at A in Fig. 9. A distinct rise from 0.7 to 0.9 % silver was recorded during the 1950's. The average content of silver in galena from 1953 to 1964 was 0.83 %

The silver and bismuth rich galena-matildite-aikinite paragenesis found in fluorite cryolite in the early 1950's and the gustavite-cosalite-galena paragenesis found in fluorite materials in 1962 were each judged to be present in amounts of less than 50 kg. The Bi:Ag ratio by

Table 11. Galena concentrate analyses recalculated, A : Mol. values of metals = 100.0 %, B : Ag:Bi mol. ratio, C : Wt. % Bi and Ag assuming all dissolved in galena structure and D : Wt % surplus of Ag in galena structure.

Year	РЬ	D :					
		DI	Ag		Bi	Ag	
1964	96.510	1.742	1.753	1.006	1.535	0.797	5
1963	95.989	2.007	2.003	0.998	1.767	0.910	-2
1962	96.366	1.736	1.897	1.093	1.530	0.863	74
1961	96.461	1.692	1.846	1.091	1.490	0.840	71
1960	96.551	1.720	1.731	1.006	1.512	0.787	7
1959	96.447	1.744	1.807	1.036	1.537	0.821	28
1956	96.266	1.827	1.906	1.043	1.610	0.865	34
1955	96.108	1.887	2.004	1.062	1.665	0.910	51
1953	96.368	1.737	1.894	1.090	1.528	0.860	72
1952	96.660	1.587	1.752	1.104	1.400	0.800	78
1949	97.152	1.265	1.582	1.251	1.110	0.720	147
1948	97.087	1.343	1.569	1.168	1.180	0.715	106
1940	96.707	1.560	1.732	1.110	1.375	0.785	75
1938	97.199	1.316	1.483	1.127	1.160	0.675	76
1937	98.028	0.917	1.054	1.148	0.800	0.480	67
Average	96.660	1.605	1.734	1.089	1.415	0.789	59



Fig. 8. Galena concentrate analyses recalculated assuming that all silver present is contained in the galena, i.e. Ag + Bi + Pb + S = 100.0 wt. %.

weight of the gustavite-cosalite-galena paragenesis is roughly 5:1, while that of the other paragenesis is lower, perhaps between 2 and 3 to 1. No significant change in the Bi:Ag ratio of the galena concentrates showing the distinct rise in content of silver from 0.7 to 0.9 % has taken place. This confirms the scarcity of the two parageneses.

It is therefore concluded that the recorded increase has been caused by variations in the amount of silver and bismuth dissolved in the structure of the common galena from different parts of the cryolite body.

Silver and bismuth in selected galena samples

The silver and bismuth content determined on selected Ivigtut galena samples by the microprobe, X-ray fluorescence and atomic absorption methods are listed in Table 9 and plotted at B and C in Fig. 9.

The analyses listed in Table 9 can be grouped as follows:

- 1. Ag below 0.2 %
- 2. Ag between 0.3 and 0.6 %
- 3. Ag above 0.6 % with a few exceeding 1.5 %.

Galenas with low silver contents are present in samples from the surroundings: the pegmatite and two old samples collected in 1862 and 1869 presumably from mineralized veins in the wallrock of the quarry, i.e. outside the cryolite body. The galena mined in 1854-56 was also low in silver (Tayler 1956). This galena occurred along the contact between the cryolite body and the overlying rocks in the south east part of the exposed cryolite mass, (see Fig. 1).

Galena in the few fluorite cryolite samples is also poor in silver, except for sample no. Fc-1. The relatively high silver content in this sample can be accounted for by the abundant freibergite enclosed in the galena analysed.

Two samples of galena from siderite cryolite contained less than 0.2 % silver. This was a surprise, because in general galena derived from siderite cryolite contained around or above 0.6 % silver. The galena concentrates for instance contained from 0.6 to 0.9 % of the metal and by far the largest amount of galena in the concentrates was derived from the treatment of siderite cryolite. The two siderite cryolite samples, from where these silver-poor galenas were taken, differ in no visible way from the common siderite cryolite.

The possibility of having siderite cryolite with galena low in silver obviously calls for examination of samples localised within the siderite cryolite body. This, however, was difficult to obtain as nearly 90 % of the siderite cryolite was already mined out when these problems were taken up during the last 10 years of mining in Ivigtut. Therefore only af few localized samples were secured. In addition galena in drill core samples from 1914 were also obtained. None of the localized galena samples contained less than 0.4 % silver.

A few galena samples contained between 0.3 and 0.6 % silver. Jarl (1909) mentions that galena mined around 1909 only contained around 0.4 % silver. Two galena samples in siderite cryolite (sample Sc-2 from



Fig. 9. A: Galena concentrate analyses. B: Stars represent microprobe analyses on the common Ivigtut galena (Table 2) and squares represent microprobe analyses on galena from the galena-matildite-aikinite mineral paragenesis in the fluorite cryolite (Table 3). C: X-ray fluorescence analyses on the common Ivigtut galena (Table 2).

drill hole O at -25 and sample Sc-17) gave similar low silver values. Sc-17 was collected prior to 1939 and may well represent materials from similar levels in the mine investigated by drill hole O which was completed in 1914.

Galena in all siderite cryolite samples collected after 1950 and a few collected before 1939 contain from 0.6 to 1.3 % silver. Galena from the black cryolite with redbrown fluorite also contains silver values lying within this range.

The silver content in galena from the surrounding greisen and from the quartz body (except in sample Sz-6) likewise fall within this range. Galena samples Qz-4 and Qz-5 from drill hole A in the quartz zone contained 1.75 and 2.15 % silver. Clusters of very fine grained matildite were enclosed in this galena.

Microprobe analyses for silver and bismuth completed on galena from 10 samples representing the galena-matildite-aikinite association are listed in Table 10. X-ray fluorescence analyses carried out on bulk sulphide materials from the same samples are also listed in Table 10. The content of matildite varies strikingly from one sample to the next. Samples nos. Ol-7, 8 and 10 contain significant amounts of aikinite while this mineral is either absent or present only in small amounts in the other samples. It is assumed that all aikinite has the average composition of A and B given in Table 7. On this basis the amount of silver, bismuth and lead tied up in matildite and galena associated with aikinite in the three mentioned samples has been calculated.

The microprobe analyses are plotted in Figs 9 and 5. The X-ray fluorescence analyses representing the matildite-galena bulk composition are plotted in Fig. 5, because most of these fall outside Fig. 9. In Fig. 5 the bulk composition of the gustavite-cosalite-galena paragenesis and the average composition of the major sulphides within this have also been plotted.

Since the microprobe analyses only give the amounts of silver dissolved in the galena structure these analyses must in principle be lower than or equal to those obtained by the other bulk methods used on the same material. In a few cases this is not so. However, the differences observed lie within the analytical error which in general is less than 10 % relative. Still, most of the analyses listed in Table 10 show such differences that they may have been caused by silver added from minerals enclosed in the galena, probably mainly freibergite and some hessite. A complete list of the accessory minerals enclosed in the galena is given in Table 1. The silver surplus is evident when the microprobe plots (stars) at B in Fig. 9 are compared with those at A and C in the same figure. The differences are also evident from the average Ag:Bi ratios listed in Table 12. The average Ag:Bi ratio obtained on bulk sulphide materials by the atomic absorption and the X-ray fluorescens analytical methods is higher than that obtained on galena by the microprobe and is nearest to the matildite ratio.

The matildite content dissolved at room temperature in galena from the galena-matildite-aikinite paragenesis ranges from approximately 0.9 to 1.8 % (Table 10) corresponding to 2 - 4 mol per cent AgBiS<sub>2</sub>. These galenas all contain variable amounts of exsolved matildite. Many of the common Ivigtut galenas contain similar amounts of silver and bismuth (Table 9). Matildite has not exsolved from any of these.

Galenas with up to 7 mol per cent  $AgBiS_2$  without exsolved matildite have been described by Ontoev et al. (1960), Czamanske & Hall (1975) and Karup-Møller (1977). Due to sluggish reaction rates it is difficult to determine experimentally how much  $AgBiS_2$  may remain dissolved in the galena structure at room temperature. At 170°C Van Hook (1960) synthesized galena with 10 mol per cent  $AgBiS_2$ . The ability of galena to

Table 12. Silver: bismuth ratios in analyzed galenas.

Wt. % ratio	Mol.% ratio	Average of
0.546	1.089	galena concentrate analyses (table 1)
0.611	1.183	atomic absorbtion and x-ray fluores- cence analyses (table 2)
0.493	0.955	microprobe analyses (table 2)
0.531	1.029	microprobe analyses (table 3-)
0.516	1.000	ideal matildite (AgBiS <sub>2</sub> )

retain silver and bismuth in its structure at room temperatures thus varies considerable.

#### Trace elements in selected galena samples

The content of trace elements (Table 11) has been determined on the following samples from different parts of the cryolite deposit: Five samples of the common Ivigtut galena, ten samples representing the galena-matildite-aikinite paragenesis, two samples representing the gustavite-cosalite-galena paragenesis (samples Gus-1 and -2), and one sample from the 1960 galena concentrate.

*Copper* is present in relatively high amounts in the galena-matildite-aikinite paragenesis and this is due to the presence of variable amounts of aikinite. The copper in the samples from the gustavite-cosalite-galena paragenesis is for the major part contained in the minerals cosalite, aikinite and berryite. The copper content in the samples of the common Ivigtut galena may have been caused mainly by accessory freibergite and chalcopyrite. The high value recorded on the 1960 galena concentrate is definitely due to chalcopyrite impurities.

Zinc is remarkably constant in all the analyzed samples. It is present in amounts of less than 0.02 % except in sample Fc-5 which contains 0.04 % of the metal. Sphalerite is an accessory mineral in the common Ivigtut galena and also in the gustavite-cosalite-galena paragenesis, but it has not been observed in the galena-matildite-aikinite paragenesis. Zinc is a major element in the minerals kesterite and stannite (Table 5) which are frequently present as accessory minerals concentrated in the galena near the boundary between this mineral and chalcopyrite.

*Iron* in the samples analyzed has mainly been caused by the presence of pyrite and to a slight extent also chalcopyrite, freibergite and siderite. Supergene limonite on fractures and grain boundaries may also occur.

Antimony occurs in amounts less than 26 ppm in the samples representing the galena-matildite-aikinite paragenesis. This low value is compatible with the lack of antimony-bearing minerals except for very sparse bournonite. Antimony occurs in the samples of the common Ivigtut galena in amounts varying from 100 to 600 ppm and in amounts from 100 to 200 ppm in those representing the gustavite-cosalite-galena paragenesis. The most common accessory mineral in the common Ivigtut galena is freibergite. This mineral therefore accounts for most of the antimony present. The following antimony-bearing minerals have been found only in very small amounts (and their Sb-contribution is negligible): bournonite, pyrargyrite and mineral C (Table 1). The antimony content of the gustavite-cosalite-galena paragenesis is for the major part assumed to be dissolved in the gustavite structure. Gustavite from other localities has been found to contain several percent of this element (e.g. Karup-Møller 1972).

Arsenic is present in amount of less than 10 ppm in all

samples analyzed except in the 1960 galena concentrate. The relatively high value here (300 ppm) is considered to be due to arsenopyrite impurities.

Selenium and tellurium in the common Ivigtut galena samples range in amounts from 0.02 % to 0.04 %. In galena sample Fc-5 from fluorite cryolite the Se and Te contents are 0.04 and 0.06 % respectively. Most of the determinations for the two elements in the samples representing the galena-matildite-aikinite and the gustavite-cosalite-galena parageneses are 'maximum' values. However, the analyses indicate that the content of the two elements is higher in these two parageneses than in the common Ivigtut galena.

Te-canfieldite is a frequent accessory mineral in the common Ivigtut galena. Hessite is present in much smaller amounts while mineral C and a few other Te-bearing minerals (Table 1) are extremely rare. Distinct selenium-bearing minerals have not been identified and this element is assumed to be dissolved in the galena structure. Galenas with up to 0.6 Te and 9.0 % Se have been described by Czamanske & Hall (1975). It is therefore noteworthy that the Ivigtut galena with much smaller contents of Te contains distinct Te-minerals.

Distinct Te- and Se-bearing minerals have not been found in the gustavite-cosalite-galena paragenesis. Only small amounts of Te-canfieldite, hessite, mineral B and mineral C have been located in the galena-matildite-aikinite paragenesis. The two elements are therefore considered to be dissolved in the structure of one or several of the main sulphides. For comparison, gustavite analyzed by Czamanske & Hall (1975) contains 0.1 % Te and 2.0 % Se, confirming this assumption.

Gold has been found in samples of common Ivigtut galena in amounts less than 0.3 ppm. The average content in the specimens of the galena-matildite-aikinite paragenesis is 2 ppm. One sample contained 12.7 ppm. The content in the two samples representing the gustavite-cosalite-galena paragenesis was 1.5 an 4.2 ppm. A few grains of free gold have been found in a single polished sample with gustavite (Karup-Møller 1973).

*Cobalt* is present in amounts less than 60 ppm. No significant differences exist in the distribution of the element between the analyzed samples. Distinct cobalt minerals have not been identified.

Nickel has only been detected in a few samples. The maximum value recorded was 15 ppm.

Tin was found to be surprisingly low in the analyzed samples, less than 30 ppm. In many of the samples representing the galena-matildite-aikinite paragenesis it is present in amounts even less than the detection limit (10 ppm). The major tin-bearing mineral in the common Ivigtut galena and in the galena-matildite-aikinite paragenesis is Te-canfieldite. Stannite, kesterite and cassiterite are important accessory minerals only in the common Ivigtut galena. Hexastannite is rare. However, since most of these minerals occur near the contact between galena and chalcopyrite they are assumed not to be present in any significant amounts in the isolated and analyzed galena samples. Consequently, the major portion of the tin is, like tellurium, assumed to be tied up in Te-canfieldite. The much higher tellurium content determined suggest that either the tin or the tellurium determinations are incorrect or alternatively, a substantial part of the tellurium present is tied up in hessite or in the galena structure.

Molybdenum is absent in most of the samples analyzed and was low in a few (10-40 ppm). Only the sample representing the 1960 galena concentrate contains significant amount of the element (360 ppm) caused presumably by molybdenite impurities.

*Wolfram* has only been detected in a few samples. It is present in amounts of less than 40 ppm in three of these but is present in very large amounts in two (3000 ppm and 1800 ppm). It has not been possible to identify wolfram-bearing minerals in the hand specimens from which these two wolfram-rich samples have been isolated. Wolframite has been observed in the area around location B in Fig. 2. The two wolfram-rich samples come from the area between A and S; wolframite has not been found within this area.

## Discussion

The major units of the cryolite deposit nos. 1, 2, 3, 6 and 7 (Fig. 2) are considered to have crystallized in close succession. (Hans Pauly, unpublished information). Sulphides occur in small amounts in all of these (except unit 2) and they are invariably associated with siderite. The proportion between siderite and each of the major sulphides varies from one unit to another, but the composition of the galena and the type of accessory minerals enclosed in the galena are more or less the same throughout the units. Sulphides and siderite appear to have crystallized unaffected by whether the host was cryolite or quartz. This suggests the presence of a well defined »sulphide-carbonate« phase dispersed throughout the fluid mass from which the cryolite deposit formed. Some chemical characteristics of the sulphide-carbonate phase and the temperature at which it consolidated are summarized and discussed below.

The fluorite cryolite and the fluorite zone (units 4 and 5 in Fig. 1) formed when late fluids reacted with earlier formed rock types (unpublished observations by Hans Pauly). Siderite is not present and the mineralogy of the sulphides differs strikingly from that of the sulphides in the early formed units. The reason for this is discussed below.

#### The primary sulphide-carbonate phase

As pointed out on p. 6 the four predominant sulphides in the cryolite deposit are sphalerite, galena, chalcopyrite and pyrite. Of these only galena contains a relatively large number of accessory minerals. Small amounts of stannite-kesterite and exsolved sphalerite lie in chalcopyrite. Sphalerite contains exsolved chalcopyrite, sometimes in amounts of up to 25 %. Pyrite rarely contains other sulphides. The major part of the trace and minor metals in the sulphide-carbonate phase has thus been concentrated in the galena structure and in the minerals enclosed in the galena. The two most important minor elements in the sulphide-carbonate phase were Ag and Bi, while the most important trace elements appear to have been Sn, Te, Se, Sb and As.

Ag and Bi: The two dominating minor elements associated with the common Ivigtut galena are silver and bismuth. In agreement with experimental results (Van Hook 1960, Salanchi & Moh 1969) galena may contain more bismuth than considerably silver (e.g. Karup-Møller 1977) but only slightly more silver than bismuth. The common Ivigtut galena, originally present in the deposit in amounts of about 12000 t, contained the two metals in nearly equivalent amounts (Table 12). The gustavite-cosalite-galena and the galena-matildite-aikinite parageneses carry a distinct surplus of bismuth over silver, but the total amount of these parageneses was insignificant, possibly less than 100 kg. It is therefore concluded that a distinct feature of the sulphide-carbonate phase was the presence of silver and bismuth in nearly equivalent amounts.

*Tin*: Already in the first description of the cryolite deposit (Giesecke 1822), distinct cassiterite mineralization was recognized in the pegmatite (unit 11, Fig. 2) and in the sulphide-bearing veins surrounding the cryolite deposit. Cassiterite, stannite-kesterite and Te-canfieldite, all tin-bearing minerals, have also been found as common accessory minerals in the galena within the cryolite deposit. Wolfram mineralization, commonly associated with cassiterite, has been found in very small amounts in the eastern part of the deposit. Tin mineralization is thus a characteristic feature of the intrusive Ivigtut granite stock.

Te and Se: The small but distinct contents of tellurium in the sulphide-carbonate phase have mainly resulted in the formation of Te-canfieldite and hessite. Selenium appears to be present in amounts similar to tellurium. In agreement with the general behaviour of selenium (Sendeeva 1964) it has presumably dissolved in the structure of the galena.

Sb: Antimony is for the major part contained in freibergite. The Sb:Bi ratio of the analyzed galena samples is lower than 1:200, which reflects the antipathetic geochemical nature of these two elements. Malakhov (1969) and Panifilov (1972) have compiled Bi and Sb analyses for galenas from a large number of deposits. It was concluded that the Sb:Bi ratio is high in low temperature deposits and low in high temperature deposits. The relatively high temperatures of formation of the cryolite deposit (discussed below) and the low Sb:Bi ratio are in agreement with these results.

As: The content of arsenic is less than 2 ppm in the analyzed galenas. However, arsenopyrite associated

with galena has been observed by Oen & Pauly (1967) and arsenopyrite is a common constituent of the sulphide parageneses associated with the pegmatite and the mineralized veins intersecting the rocks surrounding the cryolite body. The high content of arsenic (300 ppm) recorded on the galena concentrate from 1960 is considered due to arsenopyrite impurities. The original arsenic content of the sulphide-carbonate phase has therefore not been concentrated in the galena or in accessory minerals enclosed in the galena.

## Variation in silver and bismuth content in Ivigtut galena

As pointed out on page 19 the analyzed galenas can be grouped according to their contents of silver and bismuth: (1) galena with less than 0.2 % silver, (2) galena with 0.3 to 0.6 % silver and (3) galena with more than 0.6 % silver, in rare cases reaching 1.3-2.0 %.

Galena within the pegmatite (unit 11 in Fig. 2) contains less than 0.2 % silver. The pegmatite is presumed to have crystallized earlier at higher temperatures than the siderite cryolite. However, this does not imply that the sulphides and associated siderite, which occur interstitially to the major minerals of the pegmatite (quartz and microcline), have crystallized at similar high temperatures. The generally high silver content of the common Ivigtut galena contrasts clearly with the low silver content of the galena from the pegmatite. This may indicate a different composition of the original sulphide source for the two environments. A low value (0.14 %) was recorded by Tayler (1856) on galena from the top part of the deposit, possibly a mineralized zone, where siderite cryolite bordered on to the surrounding rocks. Galena in mineralized veins, collected in the 1860's (samples Mv-5 and -6 in table 4) from surface exposures adjacent to the siderite cryolite contained similar low silver values.

At location O and B in Fig. 2 galena in the siderite cryolite contains around 0.4 and 0.5 % silver (this study and Benzon 1875). According to Jarl (1909) galena from the upper western part of the deposit near location O carried 0.7 % silver and galena from deeper parts within this area about half of this value. This area was mined before 1909. Galena in the central part of the deposit, between locations A and E in Fig. 2 contained 0.7 to 1.3 % silver. This area of the deposit was mined during the period 1937 to 1964.

The silver and bismuth content of the common Ivigtut galena has thus increased from the marginal areas towards the central areas of the deposit. Within the central areas increases of the two metals in the mineral might have taken place with depth.

The analyzed galenas from the quartz body contains from 0.86 to 2.15 % silver. The number of samples available do not permit any conclusions about possible systematic changes in the content of silver and bismuth in galenas from this part of the deposit.

#### Temperatures of formation

According to Pauly (1960) all quartz found in the siderite cryolite was formed as low quartz which suggests temperatures of formation below 600°C. The same is also valid for the quartz in the quartz zone. According to Oen & Pauly (1967) sulphide pockets entrapped in massive siderite indicate consolidation in the temperature interval between 550° and 200°C; the galena in these pockets crystallized early but recrystallization of the mineral took place at just above 400°C. Below this temperature galena did not form.

These observations suggest that the major part of the sulphides in the deposit crystallized at temperatures between say 550°C and 400°C.

If consolidation of the deposit started from the outside moving inwards, then the top and the protruding eastern part consolidated first, presumably at higher temperatures, whereas the central and deeper parts consolidated later and at lower temperatures, though still within the temperature interval of 550–400°C. This suggests smaller silver-bismuth contents for galena formed in the upper range than in the lower range of this temperature interval.

#### Formation of the sulphides

The mode of occurrence of the fluorite cryolite and the fluorite zone shows that the consolidation of these two units was completed later than the siderite cryolite, the quartz zone and the siderite zone (Hans Pauly, unpublished information). Mineral parageneses within the fluorite cryolite comprising jarlite, prosopite and other late minerals indicate that the formation of the fluorite cryolite took place over a range of temperatures down to distinctly less than 200°C. (Pauly 1962b). Fluid inclusion studies on associated fluorite suggest that the gustavite-cosalite-galena paragenesis began to crystallize at temperatures below 300°C (Karup-Møller 1973). The relationships between matildite and galena within the galena-matildite-aikinite paragenesis (Karup-Møller 1976) show that the temperature of formation of these sulphides was less than 230°C.

Crystallization temperatures between 300° and 200°C thus appear to be characteristic for materials within the fluorite cryolite and the fluorite zone.

Pyrite is the most frequent sulphide in the fluorite cryolite though present only in small amounts. In many places it is assumed to have formed through reactions between siderite and the late mobile material which gave rise to the formation of the fluorite cryolite and the fluorite zone. (Hans Pauly, unpublished information).

Reactions between siderite-cryolite and fluorite-carrying materials involved remobilization of the sulphides in the siderite cryolite (Pauly 1962 b). Together with the reprecipitation of the sulphidic material, redistribution of the involved metals may have taken place. The observed silver-bismuth poor galena samples from fluorite-cryolite materials might thus be regarded as the counter parts to the extremely silver-bismuth rich parageneses characterized by gustavite-cosalite and matildite-aikinite respectively. Unfortunately neither the latter nor the matildite-poor galena from fluorite cryolite have been found in situ. The relations between the two type materials therefore remain speculative.

Some of the trace elements contained in the original galena and minerals enclosed in this may also have been redistributed. Antimony was concentrated in the silver and bismuth poor galena resulting in the formation of relatively abundant freibergite, while the element is virtually absent from the aikinite-matildite-galena paragenesis. Tellurium, selenium and gold appears to have been slightly enriched in the two silver-bismuth parageneses.

## Conclusion

Galena, sphalerite, chalcopyrite and pyrite represent the predominant sulphides of the cryolite deposit and they invariably occur together with siderite throughout the major units nos. 1, 3, 6 and 7 in Fig. 2. The common Ivigtut galena contains up to 4 mol. % AgBiS, dissolved in its structure. A number of accessory sulphides are enclosed mainly in this galena. They are characterized by one or several of the elements: Sn, Te, Sb, Ag and Bi. Of these the most significant are the tin-bearing phases cassiterite, stannite/kesterite and Te-canfieldite. Cassiterite is a relatively abundant mineral in the pegmatite (unit 11, Fig. 2) and in the mineralized veins surrounding the cryolite deposit, but the mineral is only present in insignificant amounts within the cryolite and the quartz bodies of the deposit. A characteristic feature of the cryolite deposit as a whole, therefore is the distinct Sn-mineralization and the relatively high silver and bismuth contents of the common Ivigtut galena, i.e. galena associated with siderite in the cryolite and quartz bodies.

The temperature of formation of the sulphides in the siderite and in the quartz body (Fig. 2) may have ranged between 550° and 400°C. Within the siderite cryolite a general increase in the content of AgBiS<sub>2</sub> in the galena structure took place towards the central and deeper parts accompanied presumably by decreasing temperatures of formation within the interval  $550 - 400^{\circ}$ C. This increase, follows the assumed path of the progressing crystallization of the siderite cryolite body.

The sulphides in the late formed fluorite-cryolite and fluorite zone (units 4 and 5 in Fig. 1) differ from those in the remaining part of the deposit. Galena, present in sparse amounts, contains less than 0.2 mol. % AgBiS<sub>2</sub>, but may occasionally carry silver-rich freibergite. The unusual gustavite-cosalite-galena and galena-matildite-aikinite parageneses, which have contributed several new minerals (gustavite, vikingite, eskimoite, berryite, arcubisite, mineral A and mineral B), have only been found within these two units of the deposit. They are considered to have formed when the common Ivigtut galena was remobilized. When this happened, silver and bismuth was concentrated in pockets leading to the crystallization of the two parageneses while a silver-bismuth poor galena crystallized elsewhere. The temperatures of formation may have ranged between 300° and 200°C.

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## Greenland Geoscience

1979.

1. C. K. Brooks:

»Geomorphological observations at Kangerdlugssuaq, East Greenland«.

The Kangerdlugssuaq area is mainly comprised of two contrasting rock groups: on the one hand the easily-eroded lavas and sediments of late Mesozoic to early Tertiary age and on the other the highly resistant Precambrian gneisses. Intermediate between these two types in terms of behaviour with respect to erosion are the Tertiary plutonic complexes and the basaltic areas along the coast which have been intruded by intense dyke swarms.

In the late Mesozoic the area was a peneplain, and low relief apparently persisted throughout the volcanic episode as there is good evidence that the lava plateau subsided during its formation. During this period ocean-floor spreading gave rise to the embryonic Danmark Stræde. Shortly after the volcanic episode the Kangerdlugssuaq area became the centre of a massive domal upwarping which has been a dominant feature of the land-forms up to the present day. The original surface of the dome has been reconstructed on the basis of topographic and geological evidence to show that it was elliptical in form with a major axis of at least 300 km in length and a height above present sea-level of about 6.5 km. However, subsequent isostatic effects are not considered in deriving these figures. The updoming is estimated to have occurred about 50 m.y. ago.

Several kilometres thickness of sediments and lavas were eroded off this dome at an early stage exposing the gneissic core, which still stands in alpine peaks up to about 2.7 km altitude in the central part, and dumping ca. 50000 km<sup>3</sup> of sediment on the continental shelf. The erosion was ettected by a radial, consequent drainage system, relicts of which can still be found. Kangerdlugssuaq itself may owe its origin to a tectonic line of weakness formed in response to doming, but there are also good arguments for its being purely erosional. The erosion of the dome was probably fluviatile but all trace of this stage has been obliterated by the subsequent glaciation.

In the period between the Eccene and the early Miocene, possibly around 35 m.y. ago, the entire area underwent epeirogenic uplift raising the undeformed parts of the original lava plateau to around 2.5 km above sea-level. At present this plateau is undergoing dissection from the seaward side, but considerable areas are still preserved under thin, horizontal ice-caps.

A brief description of the various types of glaciers, an impermanent, ice-dammed lake and the areas of ice-free land is given. In the Pleistocene, the Kangerdlugssuaq glacier was considerably thicker than at the present time and extended far out over the shelf, excavating a deep channel here. Finally some observations on the coastlines are presented.

2. Svend Karup-Møller and Hans Pauly:

»Galena and associated ore minerals from the cryolite at Ivigtut, South Greenland«. 25 pp.

#### Greenland Bioscience

1979.

1. Erik L. B. Smidt:

»Annual cycles of primary production and of zooplankton at Southwest Greenland«. pp.

Annual hydrographic observations, measurements of primary production, and sampling of zooplankton were undertaken in Southwest Greenland waters in the 1950s and -60s. In the coastal area and at the entrance to Godthåbsfjord winter cooling normally extends to the bottom, resulting in a vertical mixing of the water and an effective replenishment of nutrients at the surface. The subsequent production rate is, therefore, high with an average annual gross production calculated to about 160 g C m<sup>2</sup>. In the inner fjord regions the stratification is normally much more stable with persisting warm bottom water, and the production is, therefore, lower here than in the coastal area. The seasonal variation in the relations between daylight, primary production, phosphate, and quantity of zooplankton is, presumably, representative of the coastal waters at SW Greenland. A maximum in primary production in spring is normally followed by another maximum in late summer. The number of animals in the microplankton samples from the upper 30 m (the productive layer) is at its maximum simultaneously with the second maximum of the primary production, while the maximum of the macroplankton biomass (taken by stramin net) extends until late autumn in the coastal and outer fjord regions.

A maximum of the macroplankton biomass during winter in the deep water layers in the inner Godthåbsfjord, caused by inflow of warm bottom water, stable stratification and cooled outflowing surface water acting as a barrier to the ascent of the animals, is assumed to be normal to the open, non-threshold, W Greenland fjords.

Seasonal vertical migration of the zooplankton is indicated by Hensen net hauls from different depths. There is a concentration of zooplankton in the upper water layers in April–September and a deeper concentration from autumn to spring.

Annual cycles of various animal groups are described for holoplankton and meroplankton, separately. Holoplankters are normally dominant, copepods being the most numerous group. Meroplankters, especially bottom invertebrate larvae, are relatively numerous in the microplankton in spring and summer with *Balanus* nauplii dominant in spring and lamellibranch larvae in the following months. In a special section on fish eggs and larvae it is shown *1.a.* that cod eggs and larvae are normally concentrated in the upper 50 m, where they are much exposed to temperature variations, while eggs and larvae of American plaice occur also in deeper water. This may partly explain why the cod stock is more vulnerable to low temperatures.

It is shown that the epipelagic plankton fauna in the survey area in terms of growth and mode of development is more similar to the arctic than to the boreal fauna. It could therefore be termed subarctic, which also corresponds to the environmental conditions in the area.

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