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Cover photo: An exceptionally rare specimen of cryolite with large, well developed crystals. The largest crystal is almost 4 cm and formed as a twin. The specimen is kept at the Geological Museum, University of Copenhagen, Denmark. Photo O. Medenbach

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The Mid-Proterozoic Ivigtut granite pipe enclosed a cryolite deposit of 12.3 million tons with cross-cutting contacts. The deposit was sharply divided into siderite-cryolite, pure cryolite, fluorite-cryolite and fluorite-topaz units which overlay a large siderite-quartz unit.

Stage 1 of the deposit began with violent brecciation of the granite wall rocks surrounding an eastern extension of the deposit. In the siderite-cryolite unit, the siderite and sulphides formed a three-dimensional network texture enclosing cm-sized cryolite masses. This texture together with dm- to m-sized banding/layering probably formed from a lubricated mush of plastic cryolite and solid siderite plus sulphides. The banding/layering may have developed from plastic, glacier-like movements or during the advance of a crystallization front. Although there is no evidence for cryptic changes in the minerals of the siderite-cryolite unit, a residual pure cryolite unit developed and a subsequent deficiency in Na led to the appearance of chiolite-rich material.

In stage 2, Na-poor fluids accumulated in a large residual cavity. Gas-driven explosions led to partial collapse of the cryolite roof and its penetration by cryptocrystalline topaz. Some fluorite was partly mixed with cryolite forming the fluorite-cryolite while the remainder accompanied topaz in the underlying fluorite-topaz unit. An influx of water gave rise to nests of mica whereas Sr-Ba minerals such as jarlite, bøgvadite and barite crystallized later in fissures and pockets. Two breccia chimneys broke through the margin of the deposit.

In stage 3, vertical fissures formed explosively and were filled by fluidized emplacement of prosopite and cryolite. Secondary aluminofluorides formed in cavernous masses and smaller cavities by reactions between trapped H_2O-rich solutions and stage 1 cryolite.

The deposit formed when F-rich post-magmatic fluids from deeper parts of the Ivigtut granite intensively leached, metasomatized and eventually re-mobilized the top, central part of the granite pipe forming a homogeneous supercritical fluoride melt. Prior to any recorded event, this melt may have undergone immiscible separation into upper fluoridic and lower siliceous masses carrying the same dispersed carbonate-sulphide phase.

Key words: Cryolite, breccia, granite, Ivigtut, Gardar, metasomatism, greisen, fluorine, layering, plastic flowage.

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Introduction

For many years, the cryolite deposit at Ivigtut, now Ivittuut, was the richest mineral deposit in Greenland. Natural cryolite was, and synthetic cryolite still is, the only feasible flux in the electrolytic extraction of aluminium from bauxite. The deposit has long been known for its remarkable variety of aluminofluorides (see Table 1 for chemical formulae of rare minerals).

The Ivigtut cryolite deposit was found on the southern shore of the Arsuk fjord, now Ilorput, in SW Greenland, in an exposure which was partly submerged at high tide. Known to the Greenlanders before 1800, it was first visited by a European scientist in 1806 (Giesecke 1822). His short description and that of Rink (1852) formed the basis for the decision to start mining cryolite for the production of soda. In 1854 an attempt was made to mine galena from a mineralization between the cryolite and the surrounding granite (Tayler 1856).

Extraction of cryolite started when a mining expedition took out 133 tons in mid August 1856. A few days earlier on July 30, a French expedition under Prince Napoleon visited the locality (Edmond 1857). In the account of this expedition, a drawing of the site is given as it appeared just before serious mining started (Fig. 1).

MINE DE CRIOLITHE A ARKSUK-FIORD (GROËNLAND).

Fig. 1. The cryolite deposit prior to mining (Edmond 1857). The persons in the foreground are sampling the pure white cryolite exposed in the eastern part of the deposit. In the background Mount Kunnaat, 14 km west of Ivittuut.

Table 1. Rare minerals from the Ivigtut cryolite deposit
(listed according to order in the text).

Aluminofluorides	
Cryolite	Na_3AlF_6
Chiolite	$Na_5Al_3F_{14}$
Weberite	Na_2MgAlF_7
Cryolithionite	$Na_3Li_3Al_2F_{12}$
Jarlite	$Na_2(Sr,Na,\square)_{14}(Mg,\square)_2Al_{12}F_{64}(OH,H_2O)_4$
Bøgvadite	$Na_2SrBa_2Al_4F_{20}$
Ralstonite	$Na_{0.5}(Al,Mg)_2(F,OH)_6.H_2O$
Prosopite	$CaAl_2(F,OH)_8$
Thomsenolite	$NaCaAlF_6.H_2O$
Gearksutite	$CaAlF_4(OH).H_2O$
Pachnolite	$NaCaAlF_6.H_2O$
Carbonates	
Stenonite	$Sr_2Al(CO_3)F_5$
Silicates	
Phengite	$KAl_2(Si,Al_4)O_{10}(OH,F)_2$
Sulphides	
Gustavite	$AgPbBi_3S_6$
Cosalite	$Pb_2(Bi,Sb)_2S_5$
Matildite	$AgBiS_2$
Aikinite	$CuPbBiS_3$
Freibergite	$Cu_6(Ag,Fe)_6Sb_4S_{13}$
Canfieldite	Ag_8SnS_6
Stannite	Cu_2FeSnS_4
Kësterite	$Cu_2(Zn,Fe)SnS_4$

In 1857 and 1858 more than 1000 tons was mined and a permanent work force was established at Ivittuut. In 1859 F. Jacobsen surveyed the quarry and its surroundings and made a map at a scale of 1:480 (Jacobsen 1862).

Mining started in the exposed pure cryolite in the eastern part of the deposit but 6-8 years later this mass of around 10,000 tons was exhausted.

Mining then switched to siderite-cryolite ore (Pauly 1960) composed of cryolite with siderite and a few percent sulphides and quartz. This material, however, had to be upgraded because the factories receiving Ivigtut cryolite had based their soda production on crude ore containing 85% or more cryolite. The "upgrading" was mainly carried out by selective mining and masses with less than about 80% cryolite were rejected as waste. This waste, which was used to reinforce and widen the shore, and for dam construction, was reclaimed when quarrying finished in 1962.

Following the introduction of the Hall-Héroult process for electrolytic smelting of bauxite in the late 1880's, there was a slowly increasing use of cryolite as a flux by the smelting factories.

Up to the 1890's, only siderite-cryolite was exposed at Ivittuut. It is clear from Baldauf (1910) that siderite-cryolite was the only crude ore in the quarry when he visited it in 1908. He was told that the quality improved with depth but the significance of the fact that the quarrying around 1900 had exposed pure cryolite in the western quarry floor, 30 m below sea-level, was not fully appreciated. It was only through the first large diamond drilling program in 1912-15 that it was proven that a substantial mass of pure cryolite occurred beneath the siderite-cryolite in the western part of the quarry and extended to the west and north.

Quarrying had to expand beyond the existing west and north walls in order to exploit this mass and, therefore, a new dam - the fourth since 1859 - was constructed in 1919. Supplementary drillings were made in the early 1920's and a first attempt was made to evaluate the deposit.

In 1927 it was realised that the cryolite in the western wall and underlying quarry floor contained fluorite and topaz, impurities which the dressing plants in Copenhagen and Natrone, Pennsylvania, could not tolerate. These parts of the mine were therefore abandoned.

A further drilling program was made around 1930 and led to a new evaluation of the deposit. This, and the drilling program, were based on cut-off grades and quality. The geological boundaries of the deposit were still poorly known.

The structure of the complete deposit became clear when the final, major drilling program was carried out in 1948-58; it aimed to give information about the remaining tonnages and quality of crude cryolite and to establish the boundaries of the various units in the deposit. The possibility of using off-grade ore, in particular the fluorite-carrying cryolite, was investigated.

In order to extract all cryolite-containing material within a short period, a 500 m long inclined tunnel was made from the quarry floor 54 m below sea-level to ground surface east of the quarry. During "large scale mining", crude cryolite was stockpiled according to type and grade.

The results of the final drilling program, geological observations in the quarry and the knowledge of the mining staff led to the evaluation of two main types of material: cryolite with siderite and cryolite with fluorite. Around 1958 these two crude ores each amounted to about 0.5 million tons, whereas a third material - remains of the pure cryolite - was only represented by 70,000 tons.

These different materials were subdivided into various qualities according to their cryolite content. Evaluation was based on mineralogical analyses of the drill cores and of cargoes shipped to Copenhagen, and these were checked against chemical analyses. It was recognised that the three types of cryolite material represented geological units within the deposit.

In order to reconstruct the complete deposit, the data from 1958 was supplemented by information from archives, reports and photographs since the start

Table 2. Mineral composition of the units constituting the cryolite deposit. Alteration products of cryolite (thomsenolite, pachnolite, ralstonite and gearksutite) have been omitted.

	Siderite-cryolite	Pure cryolite	Fluorite-cryolite	Fluorite-topaz	Siderite-quartz	Total
Cryolite	71.9	98	70.0	-	-	20.3
Chiolite	tr.	2	8.0	-	-	0.4
Siderite	19.2	-	-	-	21	18.1
Sulphides	1.9	-	tr.	tr.	3	2.4
Quartz	7.0	-	-	-	73	51.8
Fluorite	tr.	-	12.2	56.7	tr.	2.8
Topaz	-	-	4.5	30.1	-	1.4
"Ivigtite"	-	-	2.9	7.1	3	2.5
Weberite-jarlite	-	-	2.4	6.1	-	0.3
	100.0	100	100.0	100.0	100	100.0
Tons x 10^6	2.3	0.5	0.5	0.5	8.5	12.3

"ivigtite" - local name for a fine-grained, spherulitic mica of phengitic composition; tr. - trace.

of mining in 1859. When the earlier amounts of mined and shipped crude cryolite, together with the rejected but later reclaimed low-grade crude ores, were included, the compilation indicated that the cryolite-bearing mass originally contained 3.8 million tons of material including the fluorite-topaz unit underlying its western part. To this was added an underlying mass of quartz with siderite amounting to 8.5 million tons. Thus the total mineralization present in the deposit, as detailed in Table 2, reached 12.3 million tons.

As a by-product of cryolite refining in the Copenhagen plant, about 500 tons of galena containing 0.48-0.91% Ag and 0.80-1.66% Bi were recovered from 1937 to 1964.

The aim of this monograph is to present the main geological and petrological features of the dominant observable stage of the Ivigtut cryolite deposit - stage 1. The succeeding stages 2 and 3 were described by Pauly (1992) and are only summarised here. An overview of the deposit allows us to make a number of inferences on its origin and early, non-observable history. Where unreferenced, the descriptions and data are based on the observations, assessment of mining archives and laboratory work of the authors.

Geological setting

The Ivigtut cryolite deposit was located within the roof zone of a 300 m wide pipe-like granite intrusion at 61°12'N, 48°11'W on the northwest coast of the Ivittuut peninsula in South West Greenland. The granite belongs to the Mid-Proterozoic cratogenic Gardar alkaline province which has similarities to

modern rift systems such as East Africa (Upton 1974; Emeleus & Upton 1976; Macdonald & Upton 1993).

The Ivittuut peninsula is a distinct sub-province within the broader Gardar province and is defined by the Grønnedal-Íka and Ivigtut central complexes and several regional dyke swarms, as well as a concentration of faults, crush zones and associated minor mineralization. The Grønnedal-Íka complex largely consists of nepheline syenites and a carbonatite plug and, with an age of 1299 +/- 17 Ma, belongs to the Early Gardar period (Emeleus 1964; Blaxland et al. 1978). Minor volumes of regional and local dykes were then intruded. The Mid-Gardar regional "brown dykes", the so-called BD dykes, are olivine dolerites and were emplaced in three generations with intervening wrench fault movements. There was a return to local dyke intrusion of basalt, quartz trachyte and phonolite (Gill 1972) and to fault activity at Grønnedal-Íka before minor volumes of phonolite and trachyte were intruded throughout the peninsula. Subsequent activity was restricted to the Ivittuut area and finished with emplacement of the Ivigtut granite (Berthelsen & Henriksen 1975).

The most reliable Rb-Sr age for the Ivigtut granite (1171 +/- 10 Ma; unpublished data of JCB) is within analytical uncertainty of the K-Ar ages (1185, 1188 Ma; Moorbath & Pauly (1962). This age places the Ivigtut granite close to the spectrum of Late Gardar intrusive centres (1159-1118 Ma; Blaxland et al. 1978) and is in agreement with the relatively youthful age inferred from geological events in the Ivittuut peninsula.
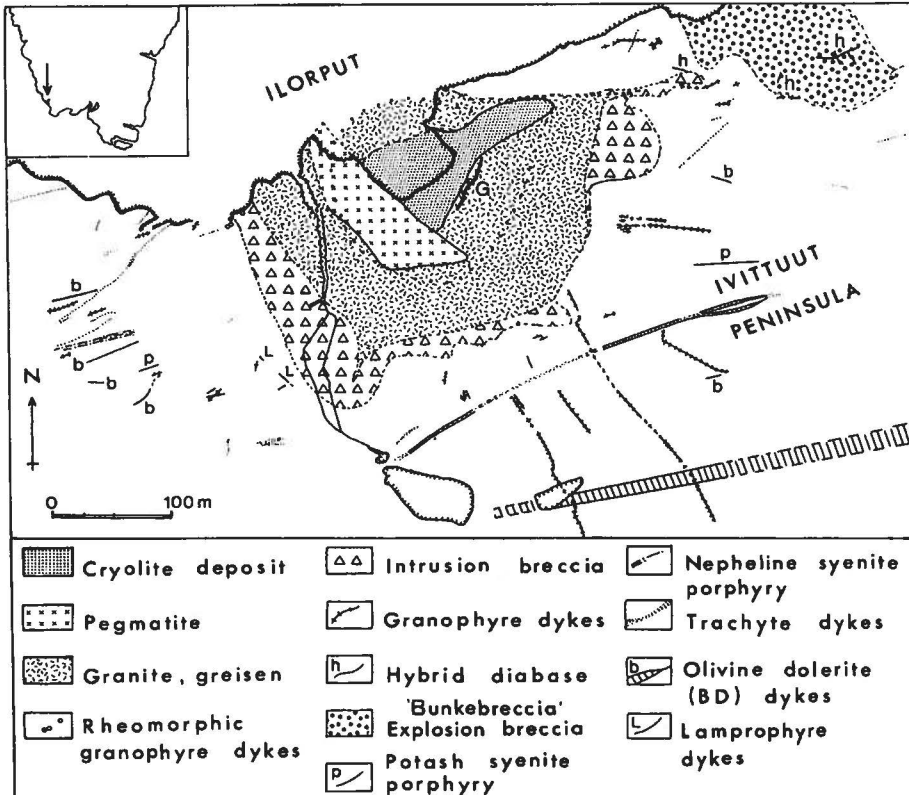

Fig. 2. Geological map of the Ivigtut granite and cryolite deposit, oriented to magnetic north; mainly compiled from F. Jacobsen (1862) and F.L. Jacobsen (1966). The original shore near the deposit is indicated by the heavy line. G - galena mined by Tayler in 1854.

Distinctive Gardar mineralizations are scattered throughout the Ivittuut peninsula (Armour-Brown et al. 1982). Th-U mineralization is located in joints, faults and zones of weakness. Th-bearing veins are more common and contain pyrite, magnetite, rutile and (?)thorite in a gangue dominated by Ca, Mg and Fe carbonates. The few signs of U mineralization occur as narrow veins or inclusions with varying carbonate content. Sulphide mineralizations, such as chalcopyrite-sphalerite plus occasional galena and siderite, again coincide with Gardar trends in the peninsula. Finally, cryolite occurs as a minor phase in two granophyre dykes which trend towards the Ivigtut granite (Jacobsen 1966).

Events at Ivittuut (Fig. 2) began with emplacement of an explosion breccia, the so-called "Bunkebreccia", containing fragments of the older gneisses and Gardar dykes set in a comminuted groundmass of similar material (Berthelsen 1962). The breccia is cut by dykes of hybrid dolerite with microsyenite xenoliths. Subsequent granophyre dykes radiate from the future position of the Ivigtut granite. The thicker ones are 0.5-1 m wide, are first observed about 600 m from the granite/gneiss contact and extend for several km whereas dykes of 5-30 cm width can only be followed for up to 250 m. Minerals representative of the cryolite deposit - cryolite, siderite, fluorite and K-mica - occur in varying amounts within two of the metasomatized granophyres, in one case up to 3 km from the deposit (Jacobsen 1966).

An intrusion breccia surrounds most of the Ivigtut granite. It ranges up to 75 m wide but is locally absent on the E side of the granite. The breccia contains xenoliths of the various country rocks set in a microgranitic groundmass. On the W side, the intrusion breccia has locally melted the surrounding gneisses producing rheomorphic granophyre dykes which cut the gneisses (Jacobsen 1966).

The Ivigtut granite pipe penetrated the intrusion breccia, following both its roughly circular shape as well as irregular tongues in the SSW and ENE corners. The pipe is only 300 m in diameter, has been proven in borings to 570 m depth and may be a small apophysis from a larger granite massif. Recent drilling indicates that the granite pipe widens to the northeast where it cuts considerable volumes of hybrid dolerite and syenite (Gothenborg et al. 1988). The granite pipe has a chilled porphyritic microgranite roof which appears to arc over the cryolite deposit and probably acted as a capping to fluids which became concentrated in the top of the narrow pipe. Solidification of the granite was accompanied by strong cupola jointing.

A distinction can be made between a deep granite which is lying below the cryolite deposit and is still present in a core at 550 m depth and a top granite which exhibits concentric but incomplete zones of alteration around the deposit. The petrological character of the two granites indicates that they were both originally part of the same pipe-like intrusion.

The deep granite (Table 3, column 7) is a pink to pale grey, two-feldspar metasomatized leucogranite with strongly greisenized and silicified variants in

Table 3. Chemical analyses of the Ivigtut granite and its metasomatised varieties, a small pegmatite and the bulk cryolite deposit.

	1	2	3	4	5	6	7	8	9
SiO_2	70.37	74.83	75.95	73.13	64.88	75.63	74.19	69.32	53.4
Al_2O_3	13.95	13.13	13.49	13.63	16.66	9.00	13.30	14.81	6.6
Fe_2O_3	0.92	0.40	0.13	0.33	0.39	0.78	0.00	0.83	0.9
FeO	2.48	1.42	1.39	0.95	1.70	3.35	0.97	2.03	10.7
MgO	<0.01	0.01	0.01	0.02	<0.01	0.23	0.06	0.09	0.1
CaO	1.06	0.51	0.23	0.72	6.10	2.33	0.10	0.32	2.0
Na_2O	4.69	3.77	4.16	5.88	0.09	0.97	4.42	4.96	9.2
K_2O	4.59	4.60	4.03	3.37	5.42	2.91	4.61	5.58	0.3
P_2O_5	0.054	0.013	0.007	0.013	0.012	0.005	0.005	0.003	0.004
H_2O^+	0.43	0.30	0.24	0.10	1.85	0.70	0.17	0.33	0.2
H_2O^-	0.14	0.07	0.03	0.02	0.18	0.10	0.03	0.07	0.1
CO_2	0.27	0.20	0.44	0.49	0.74	1.21	0.63	0.33	6.8
F	0.31	0.40	0.09	1.35	1.28	2.84	0.82	0.77	13.1
Sum	99.26	99.65	100.20	100.00	99.30	100.05	99.31	99.44	103.3
-O=F	0.13	0.17	0.04	0.58	0.55	1.21	0.35	0.33	5.3
Sum	99.13	99.48	100.16	99.42	98.75	98.84	98.96	99.11	98.0
Cs	1.1	0.9	0.5	1.1	7.9	2.0	0.4	1.4	<0.3
Rb	280	377	260	490	630	420	520	600	298
Ba	330	75	32	8	40	40	85	11	60
Pb	18	26	22	70	43	1390	120	2	3850
Sr	44	27	11	37	300	140	18	17	215
La	110	67	25	21	63	18	14	169	1.1
Ce	210	123	48	70	175	49	32	322	3.9
Nd	95	60	26	51	107	21	15	203	2.4
Sm	17.5	12.8	5.8	18.4	46.1	10.4	7.7	64	0.86
Eu	2.0	0.31	0.44	0.20	1.0	0.25	0.31	0.90	0.06
Tb	2.7	2.1	1.3	4.3	11.6	5.0	4.2	13.9	0.20
Yb	6.8	6.9	4.5	18.3	27.5	66.0	54.0	43.3	0.68
Lu	1.1	0.92	0.54	2.1	3.1	8.4	6.9	4.9	0.08
Y	115	91	65	213	365	320	136	710	10
La/YbN	10.7	6.4	3.7	0.76	1.5	0.18	0.18	2.6	1.1
Ce/Ce*	0.90	0.86	0.88	1.18	1.11	1.21	1.04	0.84	1.31
Eu/Eu*	0.35	0.07	0.21	0.03	0.06	0.05	0.08	0.04	0.19
Th	26	31	18	64	43	260	334	86	2
U	8	8	6	11	16	78	63	29	<1
Th/U	3.2	3.9	3.0	5.8	2.7	3.3	5.3	3.0	-
Zr	550	370	150	880	1100	3520	2890	1020	17
Hf	14	15	6	41	37	160	206	55	0.2
Nb	180	162	81	400	570	1200	1260	448	2
Ta	23	16	8	40	57	160	190	39	<0.1
Sn	6	13	3	9	83	260	9	2	7
Mo	4	3	1	1	1	6	5	2	2
W	1	-	1	1	7	16	10	<1	2
Mn	530	440	180	180	100	630	380	250	2800
Ni	<1	<1	<1	<1	<1	<1	1	1	1

	1	2	3	4	5	6	7	8	9
Li	20	-	80	170	90	70	76	263	22
Ti	1580	660	410	120	180	110	160	600	6
V	2	1	<1	<1	1	1	1	1	4
Cr	19	7	6	2	4	5	17	<1	<1
Sc	2.3	0.2	0.3	0.1	1.3	1.2	1.2	0.1	1.8
Co	0.6	0.2	0.3	0.2	-	2.1	1.0	<0.1	1.7
Ga	24	37	26	40	29	4	55	59	4
Zn	180	225	110	260	470	2300	730	367	7400
Cd	0.24	-	0.16	<0.1	1.35	4.8	2.0	0.1	27
Zn/Cd	750	-	690	-	340	480	365	3700	276
Cu	<1	<1	<1	<1	6	470	11	<1	960
Ag	<1	<1	<1	<1	<1	7	<1	<1	45
As	1	<1	<1	<1	5	4	3	<1	2.5
Sb	0.11	0.14	-	0.20	-	0.22	-	-	0.25
S	120	200	125	80	780	1000	670	10	8100
Cl	360	220	180	90	180	160	150	70	230

Modal analyses

	1	2	3	4	5	6	7	8	9
Quartz	22.4	30.0	36.1	25.8	29.0	51.5	28.4	21.8	51.8
Perthite	70.9	61.1	59.7	-	-	9.3	-	62.2	-
K-feldspar	-	-	tr.	22.3	2.5	6.9	24.9	3.6	-
Albite	1.0	4.3	2.3	44.6	-	1.0	43.2	5.2	-
Olivine	0.3	-	-	-	-	-	-	-	-
Ferroedenite	1.7	-	-	-	-	-	-	-	-
Biotite	2.9	2.9	0.6	1.1	-	-	-	4.9	-
"Ivigtite"	tr.	0.2	0.6	0.9	60.6	21.4	1.5	-	2.5
Zircon	0.1	tr.	tr.	0.5	0.2	0.2	0.7	0.1	-
Columbite	-	-	-	tr.	0.1	tr.	0.2	-	-
Fe-Ti oxides	0.1	0.1	0.1	0.1	0.1	0.1	-	1.2	-
Sulphides	tr.	tr.	-	0.1	0.1	0.3	0.1	tr.	2.4
Fluorite	0.3	0.8	tr.	1.2	5.4	2.1	0.3	0.8	2.8
Siderite	0.3	0.6	0.6	1.5	2.0	3.8	0.6	0.2	18.1
Cryolite	-	-	-	1.9	-	3.4	0.1	-	20.3

1-6 Ivigtut top granite: 1 unaltered biotite-ferroedenite granite (av. 8 samples); 2 pink hydrothermally altered granite (av. 5); 3 white, leached granite (av. 2); 4 albitised granite (av. 3); 5 muscovite-rich greisen (av. 2); 6 quartz-rich mineralised greisen (av. 8); 7 deep granite, leached, albitised and greisenised (av. 16); 8 small pegmatite from granite-greisen Transition Zone; 9 bulk cryolite deposit (also topaz 1.4, chiolite 0.4 and weberite-jarlite 0.3 wt.%).
La/YbN - La/Yb normalised to chondrite; Ce/Ce* - Ce analysed/Ce interpolated from La and Nd; Eu/Eu* - Eu analysed/Eu interpolated from Sm and Tb; "ivigtite" - local name for a fine-grained, spherulitic mica of phengitic composition; modal analyses in vol.% except for bulk cryolite deposit in wt.%.

the 100 m immediately below the deposit. The granite consists of albite laths intergrown with larger subhedral grains of K-feldspar and with scattered pools of sub-poikilitic quartz. Zircon, columbite, phengite, siderite and fluorite are the main accessories whereas cryolite is distinctly rare. Several stages of metasomatism - hydrothermal alteration and leaching which promoted feldspar exsolution, then albitization and greisenization - were followed by microfracturing and took place throughout virtually all the deep granite.

The top granite (Table 3, columns 1-6) which surrounds the cryolite deposit contains areas of unaltered, dark grey sub-porphyritic leucogranite composed of phenocrysts of microcline microperthite and quartz set in a matrix of the same minerals. The most abundant mafic phase in the fresh granite is a biotite which is Fe-rich but Mg-, Al- and Ti-poor. The sparse olivine is a Mn-rich, nearly pure fayalite ($Fa_{98.6}$); it is generally surrounded by a green amphibole which is ferroedenitic in composition. Similar mafic phases are found in other non-orogenic, non-peralkaline granites such as the amphibole-fayalite granites in Nigeria and are indicative of oxygen fugacities close to the FMQ buffer. Zircon, magnetite and ilmenite are early, and fluorite and siderite are late accessory phases.

Phase relations of the unaltered Ivigtut granite and the earlier granophyre dykes suggest they equilibrated at 1 kbar pressure, i.e. at shallow crustal levels (Bailey 1980). Moderately high levels of Zr, Nb and REE (Table 3, column 1), the presence of fayalite and ferroedenite and a molecular (Na + K)/Al ratio close to 1.0 indicate that the granite has alkaline affinities but lacks the enhanced peralkalinity of most other Gardar granites. Its contents of Na and Fe - key components of the future cryolite deposit - were thus relatively low. Contents of Ca are also slightly lower than in most other Gardar granites whereas F is higher; these features may have been critical for the later appearance of cryolite rather than fluorite. Low contents of ferromagnesian elements and negative Eu anomalies in REE patterns indicate that the granite is a product of fractional crystallization.

A tabloid pegmatite body, up to 170 x 60 x 6 m in size, developed in the top granite but it has not been established whether it crystallized contemporaneously with the granite or was intruded later. The pegmatite crystallized before the later metasomatic activity; its central part rested on the future cryolite deposit. Microcline and milky quartz, up to 0.5 m long, occurred in about equal amounts; microcline margins sometimes contained columbite while milky quartz was accompanied by cassiterite; black biotite and (?)zircon were also early. The later appearance of scattered patches and veins of transparent quartz can be linked to imposed greisenization and was accompanied by fluorite and accessory amounts of siderite, phengite, galena, pyrite, chalcopyrite, sphalerite, molybdenite and arsenopyrite. A number of these accessory sulphides were concentrated in a layered lens or vugh, 1.5-2 m across, which was dominated by fluorite, siderite, weberite, phengite and arsenopyrite.

The southern end of the pegmatite body was apparently faulted down

about 30 m and reappeared as a smaller pegmatite sheet which rested on the cryolite deposit and which eventually died out as scattered dm-sized blocks of microcline. The fault zone - the 5 m thick so-called Transition Zone which defined the granite-greisen contact in the west quarry wall - was composed of late intrusions (Table 3, column 8) or (?) recrystallized material of coarse-grained to pegmatitic heterogeneous granite. Some of these pegmatitic patches as well as the smaller pegmatitic sheet have suffered albitization, greisenization and formation of late spots and patches of cryolite, quartz and sulphides. All of these granitic materials have been overprinted by metasomatism and some of the greisens in this zone seemed to show flowage. The northern end of the pegmatite body was possibly also thrown down and was represented by huge blocks of quartz preserved in a breccia chimney of the NW quarry wall.

The earliest of the metasomatized varieties of the top granite surrounding the cryolite deposit (Table 3, columns 2-6) was the hydrothermally altered, pink granite. It shows sericitized and partly exsolved perthites along with increased contents of quartz. Biotite has recrystallized but the other mafic silicates have been replaced. Leaching of many components took place especially in the most leucocratic, white granites alongside mineralized veins. In subsequent albitized granites, albite ranges up to 65 vol.% and replaces quartz and K-feldspar. Some albitized granites contain up to 10% late cryolite. The later, more voluminous greisenized granites may enclose patchy areas of albitized granite; they show only occasional relics of microcline and albite since most feldspars have been converted to a yellowish phengitic mica. There is a significant, later development of mineralized greisens with up to 90% quartz, up to 10% siderite, fluorite and cryolite, and up to 1% topaz, sulphides, zircon, columbite and cassiterite. A single area of greisen contained up to 30% cryolite and was exposed over an area of roughly 30 x 15 m in the NW quarry wall. The later, more intense zones of metasomatism lay closer to the cryolite deposit and occurred around its NW side; they were imposed on materials which had passed through the earlier stages of metasomatism. The high levels of Zr, Nb and REE in the Ivigtut granite are also present in its metasomatic derivatives pointing to the cogenetic, i.e. autometasomatic character of the post-magmatic processes.

Finally, quartz veins containing cassiterite, sulphides, cryolite and siderite cut the Ivigtut granite, greisen and surrounding gneisses, but were themselves cut by the cryolite deposit

The cryolite deposit

The mineral cryolite, with its ice-like appearance (Fig. 3), shows unrestricted plastic deformation above 450°C (Pauly 1985). Due to this high ductility, primary structures of the deposit may have become masked if not obliterated and many phenomena are difficult to understand if the plasticity of cryolite is not taken into account.

The deposit occurred as a sharply delineated body within the top part of the Ivigtut granite intrusion. It was composed of several units differing from each other in mineralogical composition (Table 2, Fig. 4).

Fig. 3. A pool of water on the floor of the quarry showing two pieces of ice-like cryolite, with a pencil between them, and milky white quartz (top of photo) with its large contrast in refractive index to that of water.

The shape of the upper part, the cryolite-carrying part of the body, was a flattened dome resting on a slightly undulating planar base dipping about 10° N. The dome was 70 m high in its central part where it reached to sea-level; its horizontal section was an oval with E-W and N-S diameters around 140 and 170 m, respectively. From its base, an eastern extension projected upwards and had its highest part 5 m above sea-level (Figs. 4 and 5). The steep threshold be-

tween the base of the cryolite-carrying dome and the eastern extension was about 10 m high and extended in a roughly 130 m arc. The width of the eastern extension diminished to c. 20 m at sea-level and it was thus shaped like a funnel. The extension had a number of special features which will be described below.

Fig. 4. E-W longtitudinal section through the cryolite deposit based on mining and drilling records; no vertical exaggeration. The -60 m level was close to the final depth of the quarry. The original extent of the pure cryolite unit is indicated by a dotted line.
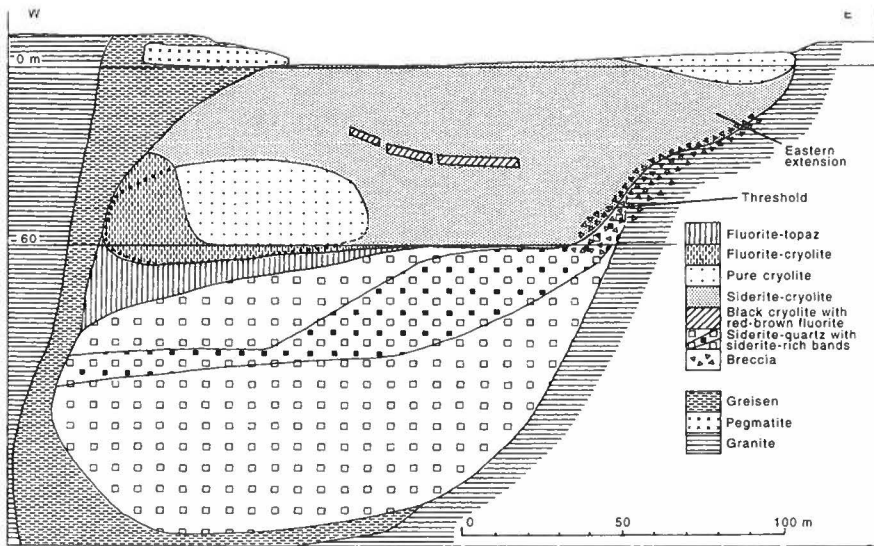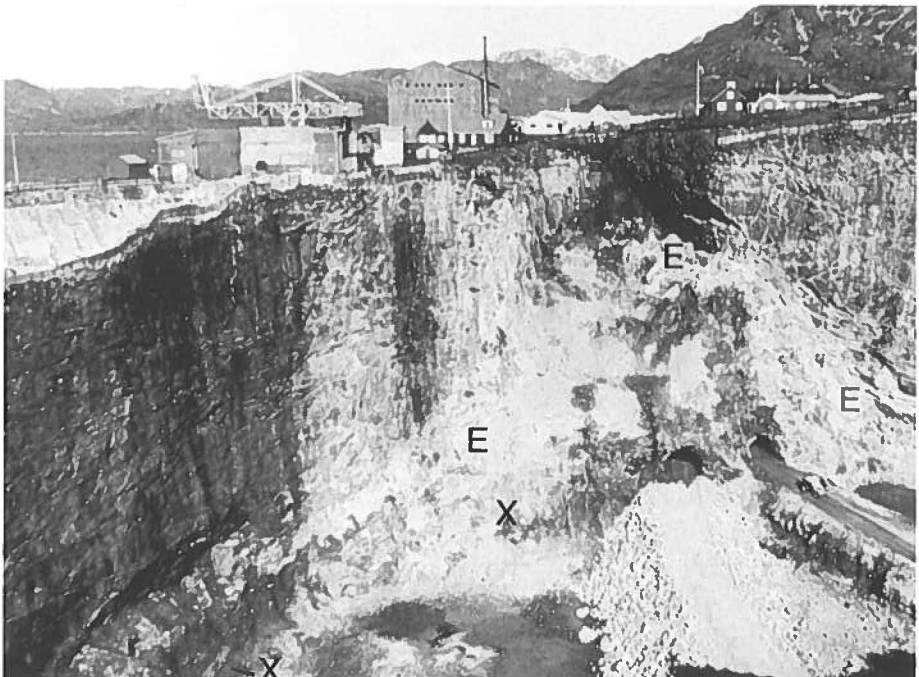

Fig. 5. A 1962 view of the Ivigtut cryolite quarry looking E and showing the mined-out eastern extension (E) of the deposit. At the level of the two transport tunnels, the arc-shaped threshold between the eastern and main part of the deposit contains m-sized xenoliths of granite (X) set in nearly massive siderite.

The major part of the dome and eastern extension consisted of siderite-cryolite. Sweeping around its western and lower part, fluorite-cryolite formed an envelope which rested on a cryolite-free unit dominated by fluorite and topaz. Between the fluorite-cryolite and siderite-cryolite occurred a body of pure white cryolite which was 150 m long SW-NE and, on average, 40 m wide and 25 m thick.

The remaining part of the deposit lay beneath these four units; diamond drillings revealed the presence of a cryolite-free siderite-quartz body reaching down to 150 m below sea-level.

Siderite-cryolite

Banding/layering

The minerals throughout most of the siderite-cryolite were arranged in bands approximately 1 m thick. Locally, modern observations allow us to use the term "layering" (Figs. 6, 7). Other localities clearly display irregular ban-

Fig. 6. Layered siderite-cryolite showing network texture; the pipe tamper is 10 cm long.
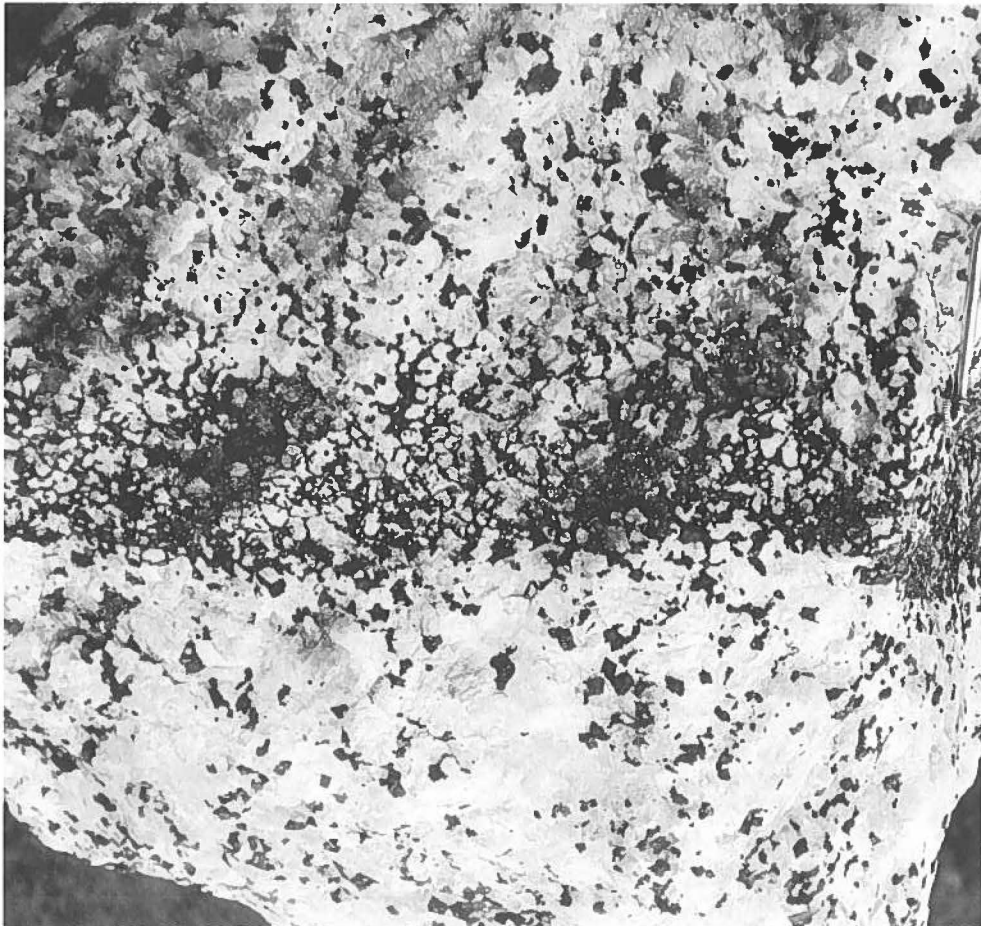
ding (Fig. 8) while archival photographs (Fig. 9) which were not supplemented by geological observations can only be described by the more neutral term "banding".

The individual layers of Figs. 6 and 7 consisted of cryolite with downwards-increasing concentrations of siderite from roughly 0 to 30 vol.%. A long-distance photograph indicates that about 30 bands could be distinguished in the full thickness of the siderite-cryolite unit (Fig. 9). These bands were conformable to the upper surface of the dome-shaped body, i.e. the contact with the overlying granites (Bøggild 1905; Baldauf 1910; Steenstrup 1911). The sketch given in Baldauf (1910) illustrates in principle the pattern as seen in the south quarry wall when the vertical exposure of siderite-cryolite was 25 m high and 80 m long. The photograph of the north quarry wall in 1931 also shows persistent, generally regular banding (Fig. 9) though here a few white bands,

Fig. 7. Layering of siderite-cryolite close to the north wall of the eastern extension of the deposit; width of photograph about 8 m; a close-up is given in Fig. 6.

Fig. 8. Irregular banding near the eastern margin of the deposit at the base of the siderite-cryolite unit; c. 30 m below sea level, SE part of the quarry. This pillar (no. 2 of the old workings) is c. 6 m wide. Photograph by R. Bøgvad 1932.

Fig. 9. Banding in siderite-cryolite, N quarry wall. Typical layers - a black band plus a white band as in Fig. 6 - are about 1 m thick; note that a few white bands of nearly pure cryolite (C) are slightly discordant and the lower right area shows cross-cutting contacts. Photograph by R. Bøgvad 1931.

highly enriched in cryolite and with sharp partly discordant contacts, stand out against the more persistent and diffusely defined banding. Banding had already been observed in 1880 (Holst 1886) and remains of it were still visible

in 1955 close to the eastern margin of the deposit (Fig. 7). Mining records indicate that the banding was parallel to the curving inner border between the siderite-cryolite and pure cryolite units. Thus banding characterised most of the siderite-cryolite unit and was parallel to its outer and inner borders.

The behaviour of the banding at the western and eastern ends of the main mass of siderite-cryolite has not been clearly established. The sketch of Baldauf (1910) suggests that, in the central part of the mass at the western end of the south wall, the upper bands of the mass curved down parallel to the enclosing granite and joined smoothly with the lower bands which curved upwards. However, our interpretation of a 1937 photo of this south wall certainly indicates local discordance and perhaps even major discordance between the downward and upward curving bands. As for the north wall, photos made by R. Bøgvad in 1938 also show bending downwards of the upper bands as they approach the eastern extension. Some bands were tilted whereas others were curved but, apart from such signs of disturbing movement, nothing more can be discerned.

Banding in the main mass was easily followed over a few m (Fig. 7), and nearly always over tens of m (Fig. 9), with only minor changes in thickness or mineral proportions. However, near the eastern margin at the transition between banded siderite-cryolite and the underlying massive siderite, less regular banding was present (Fig. 8). Here, wispy to well-defined lenses, a few m to dm long and a few cm to dm wide, were roughly concordant with the overlying layered siderite-cryolite. Some lenses consisted of pure cryolite surrounded by cm-sized or even dm-sized siderite crystals; others were siderite-rich but contained vein-like bands of cryolite. Irregular masses of pure cryolite up to 1 dm across also occurred. Discordances between lenses were generally <5° but often reached 5-20°. In the more central parts of the siderite-cryolite, in the north quarry wall of 1931, groups of bands showing cross-cutting contacts with angles up to c. 20° were visible (Fig. 9). These last discordances resemble the cross-bedding seen in the Skaergaard intrusion, although the groups of bands in the north quarry wall reach up to c. 8 m whereas the groups at Skaergaard only amount to c. 0.5 m in thickness (Wager & Brown 1968, Plate VIII). Irregular lensoid banding is also known from layered intrusions (McBirney & Noyes 1979, Plates 2, 4A and 5D). Similar features, however, have been observed in glaciers.

Network texture

Throughout normal banded siderite-cryolite, the siderite occurs as mm- to cm-sized aggregates forming a three-dimensional network with rounded masses of cryolite up to several cm across in the interstices (Fig. 6 and Pauly 1960, Figs. 1, 2). The network is less obvious at high proportions of cryolite or siderite but the interrelations of the two minerals are basically the same. This network texture appears to be a primary feature; it occurred between m-sized xenoliths in the early intrusion breccia of the eastern extension and it characterised the delicate layering of Figs. 6 and which we regard as a primary structure.

Critical features of this primary texture are (a) occasional blebs of cryolite - but no other minerals - totally enclosed in single grains of siderite, (b) the intimate association of sulphides with the siderite, (c) smoothly rounded contacts of the cryolite masses against the siderite, sulphides and quartz, (e) the non-oriented character of cryolite masses even when ovoid rather than spheroid, (f) the presence of a single, though twinned crystal within each cryolite mass (g) the absence of optical/structural continuity between neighbouring cryolite masses even when in physical contact and (h) the absence of voids. The crystallization sequence is discussed below.

Having emphasised the primary character of the network texture, we must also note that many samples show secondary features. In these cases, fragments of cleaved siderite, sulphides and quartz, all occasionally with one curved side preserved from the primary texture, are seen to form the network between the cryolite masses. The fragments may be finely comminuted or range up to several cm in size (Fig. 10). The interstitial masses of cryolite show no
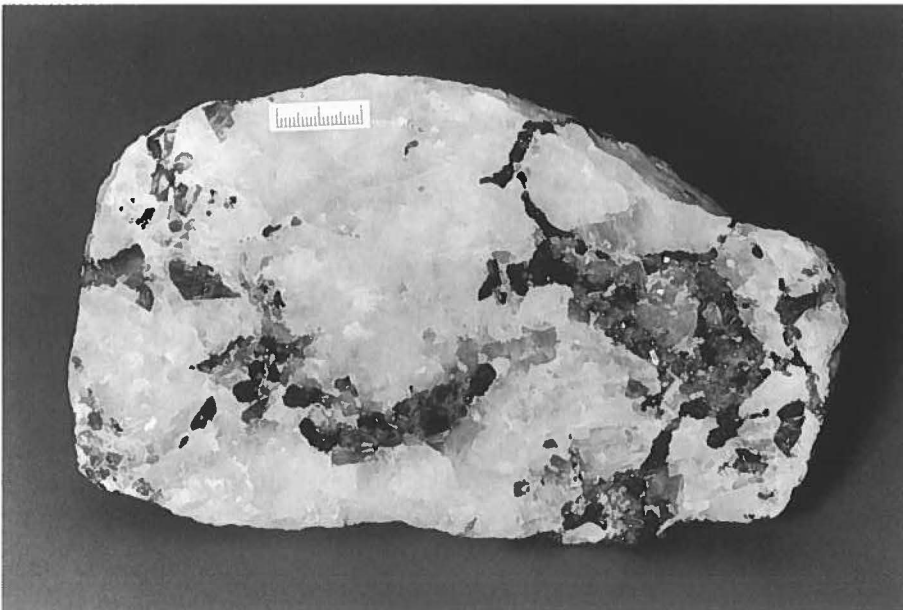

Fig. 10. Siderite-cryolite showing a transition from well-preserved to broken-up network texture with black sphalerite and siderite lying interstitially between rounded cryolite crystals. The scale is 2 cm long.

signs of brecciation or plastic deformation and have clearly consolidated later. Cryolite must have undergone deformation along with the other phases but apparently it subsequently recrystallized as healed crystals thereby pushing intermixed solid fragments of siderite, sulphides and quartz out to the new cryolite grain boundaries and establishing the secondary network texture. Similar recrystallization is observed along shear zones in glaciers where inclusions of rock fragments are pushed to the margins of newly formed, large ice crystals (Shumskii 1961).

Finally, we note that even later brecciation can disrupt both the above types of network texture (Pauly 1985, Fig. 8).

An unusual sub-facies of siderite-cryolite, which was totally surrounded by the main facies, was exposed when the bottom of the quarry was about 28 m below sea-level in 1889. The siderite-cryolite was found to carry cm-sized crystals of zoned red-brown fluorite averaging around 10% in abundance but ranging up to 20%. Due to the presence of about 0.3% Th in this fluorite, the surrounding cryolite was rendered smoky to black by irradiation. In each 5-50 μm wide zone of the fluorite the Th content increases outwards, and between zones there are micron-sized minerals rich in REE, Th, Ca and Sr. This material, termed "black cryolite with red-brown fluorite", formed a sheet 40 x 30 x 3-5 m in size dipping to the east and weighing 1-2 x 104 tons. Towards the eastern end, it was broken into m-sized blocks and displaced to lower levels. In 1894, a 3 m long granite xenolith was reported from the eastern part of the sheet, 33 m below sea-level. The texture of the black cryolite with red-brown fluorite shows idiomorphic discrete crystals or aggregates of fluorite which are overgrown by quartz crystals and set in aggregates of siderite plus the

Fig. 11. Black cryolite (grey) enclosing red-brown fluorites which are rimmed by quartz. The scale is 2 cm long.
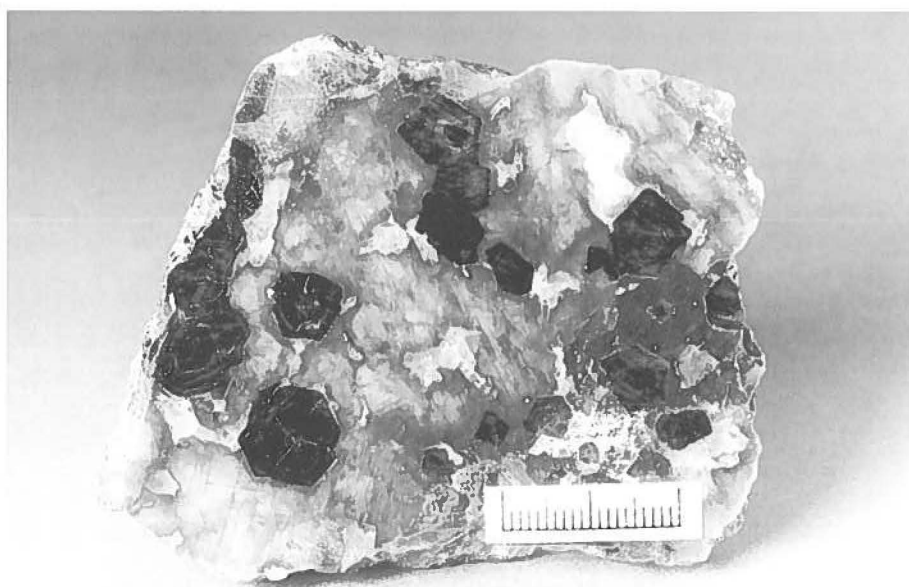
usual sulphides; cryolite is interstitial (Fig. 11)(Pauly 1986a; Pauly & Petersen 1997). The texture is thus similar to that in siderite-cryolite.

Marginal and contact features

In the south wall at the southern end of the threshold below the eastern extension, a delicately defined cauliflower-shaped arch, some 6 x 4 m in size, was composed of dm-sized siderite crystals curved around an area of siderite-cryolite (Fig. 12). A layer rich in quartz crystals occurred on top of the siderite arch and immediately passed upwards into siderite-cryolite with abundant xenoliths of greisenized granite. Such a delicate reef-like mass of siderite crystals must have crystallized under extremely quiet conditions and must have avoided the plastic deformation inferred elsewhere in the cryolite deposit. Similar structures have occasionally been noted in layered intrusions (McBirney & Noyes 1979, Plate 5C).

Quartz crystals lying on a siderite substrate were also seen at the northern end of the threshold. Here, the massive cm-sized siderite locally formed dm-

Fig. 12. Cauliflower-shaped arch of massive siderite (S) surrounding siderite-cryolite (S-C); c. 50 m below sea-level, S quarry wall, S end of the threshold. The arch is c. 3 m high. Note the overlying seam of quartz crystals (Q) and the presence of granite xenoliths (X) in the overlying siderite-cryolite.

Fig. 13. Pocket of pure cryolite (C) in massive siderite (S); c. 50 m below sea level, N quarry wall, N end of threshold. The chisel is 20 cm long. Note the accumulation of quartz crystals (Q) resting on the lower boundary of the pocket.

Fig. 14. Upper boundary of the massive siderite unit (S) against pure cryolite (C) and siderite-cryolite (S-C); c. 50 m below sea level, N quarry wall, N end of threshold. The exploration tunnel in the top centre of the photo is 2 x 2 m. Note the quartz crystals (Q) resting on the massive siderite.

sized siderite rhombohedra enclosing m-sized pockets of pure cryolite lined by occasional quartz crystals (Fig. 13). The massive siderite was overlain by tens of metres of the normal, banded siderite-cryolite but the lowermost metre consisted of lenses and pockets of pure cryolite enriched in quartz crystals resting haphazardly on the massive siderite (Fig. 14). The quartz-bearing lenses, like the quartz crystals which grew on the earliest siderite crystals and greisen xenoliths of the eastern extension (see below), are considered to have crystallized in situ and, like the underlying siderite reef, have escaped later deformation.

Most of the threshold was composed of massive siderite containing numerous xenoliths (see below).

Here and there along the contacts of the siderite-cryolite unit with the surrounding rocks, a quartz-rich lining was found. A prominent example was exposed in 1864 along part of the north wall of the eastern extension. It was 30 m long, up to 10 m wide and 5 m thick. Due to the high content of quartz this part of the quarry was abandoned and the material was not extracted until 1960. The layered siderite-cryolite shown in Figs. 6 and 7 lay below this quartz-rich lining while above it came a mass of pure cryolite. In the lining, quartz was present as 3-5 cm long crystals or aggregates of such crystals growing out from and enclosing siderite cleavage fragments. Here, cryolite filled the interstices between the other minerals.

In another example, several m of siderite-cryolite containing 30-50% quartz lie above massive siderite in core J7 which passes through the southern part of the threshold. The network texture here seems reworked since the network consists of comminuted fragments of siderite, sulphides and quartz; these are overgrown by mm- to cm-sized quartz prisms projecting into the cryolite masses. Isolated quartz crystals sometimes occur in the cryolite masses. It was quartz-rich areas such as the two described here which raised the long-term average quartz content of siderite-cryolite cargoes from the normal 1-2% to 7% (Table 2).

At some contacts between the siderite-cryolite and the surrounding granite, Baldauf (1910) and Steenstrup (1911) reported coarse-grained siderite which we consider as characteristic of crystallization under quiet conditions.

Mineralogical composition

Considering the siderite-cryolite unit as a whole, the percentage of cryolite varied considerably. In the lower eastern part of the dome-shaped body it was about 50%. Here, nearly 50 m below sea-level, siderite-cryolite rested on the massive siderite of the threshold; this siderite carried 10-20% cryolite. The main mass of siderite-cryolite had a content of around 70% cryolite and in the western part of the quarry the content rose to 80-90% where it approached the pure cryolite unit.

As noted above, the sulphides in normal siderite-cryolite are intimately associated with the siderite. The main sulphides are sphalerite, chalcopyrite and Ag-,Bi-rich galena, generally in the weight ratios 62:15:23; pyrite is similar in abundance to galena and some 20 accessory sulphides have also been reported (Karup-Møller & Pauly 1979). Occasional grains of green Th-rich fluorite, usually with a halo of black cryolite, are also associated with the siderite. Cryolithionite occurs as exceptionally rare, single crystals (Pauly 1986a). Quartz was <2% in normal siderite-cryolite but locally, especially in marginal areas as mentioned above, contents rose to 30-50%.

Geothermometry

Consolidation of siderite-cryolite took place below the α/β transition of quartz, c. 600°C at 2 kbar (Pauly 1960). Sulphide pockets entrapped in massive siderite indicate consolidation from 550-200°C (Oen & Pauly 1967) in broad agreement with the more primary fluid inclusions which homogenise at 555-335°C (Prokof'yev et al. 1990), and with the evidence for plastic flowage of cryolite which points to temperatures around 500°C or higher (Pauly 1985). While we consider the network texture of siderite-cryolite to have developed above 500°C, consolidation of the cryolite masses must have continued below 470°C at which temperature the ubiquitous twin lamellae of cryolite finally become stable (Yurk et al. 1973). Furthermore, the occasional presence of fissures which disrupt the twinning in cryolite (Pauly 1985) and the widespread occurrence of fluid inclusions homogenising at <200°C (see below) are reflections of even later events.

Pure cryolite

The unit of pure cryolite occurred as an elongate mass which stretched 150 m through the deposit in a SW-NE direction at depths of more than 30 m below sea-level (Fig. 4). The sharp boundary to the overlying siderite-cryolite was plotted in the profiles of the regular mine surveys from the 1920's and 30's and was concordant with the banding in this unit.

At its NE end, the pure cryolite unit had sharp contacts to the overlying siderite-cryolite and the underlying massive siderite. Quartz crystals, 1-2 m in length, occurred in the pure cryolite along the lower contact. Below came layers of siderite (15 cm), sulphides (5 cm) and then pure cryolite (5 cm) resting on the massive siderite (Fig. 14).

According to Bøggild (1905), who visited Ivittuut in 1900 when the quarry floor was 35 m below sea-level, a few cryolite crystals measured 6 m. Cryolithionite was found in the pure cryolite in 1902 (Ussing 1904) and chiolite was detected in 1908 (Bøggild 1953). Both minerals occurred as individuals up to

dm sizes. Chiolite was found later on in large amounts 60 m below sea-level at the lower western part of the pure cryolite (Bøggild 1953).

The presence in brecciated pure cryolite of pseudo-cubic forms (see below) points to temperatures above the thermal transition to monoclinic structure (520-470°C; Yurk et al. 1973).

Here and there in the earlier siderite-cryolite unit, there were veins of pure cryolite up to roughly 1 m wide. These, and the pure cryolite veins in two breccia chimneys (see below), may have been derived from the pure cryolite unit.

Fluorite-cryolite and fluorite-topaz

Right from the first appearance of the fluorite-cryolite, it was referred to as a breccia. It was found beneath and west of the pure cryolite unit. Adjacent to this unit, its cryolite content was above 90% with fluorite and topaz each about 2%. Five to ten m away the cryolite content diminished to around 80% while fluorite and topaz both increased to 5-10%. Further away grades with 50-70% cryolite accompanied by 10-20% fluorite and 5-10% topaz rested on the underlying fluorite-topaz unit.

In the high-grade material bordering the pure cryolite, the brecciation which characterised the fluorite-cryolite was merely developed as fissuring of the cryolite. The 10µm- to mm-wide fissures filled by cryptocrystalline topaz formed a three dimensional network enclosing cm- to dm-sized cryolite lumps (Fig. 15). Broken blocks of this material often exhibited large planar surfaces covered by a thin layer of topaz. The planar surfaces represent pseudo-cubic cleavage planes in the cryolite (Pauly 1992). Fluorite occurred in scattered irregular nests in this material.

Mineralogical analyses on cargoes of around 100,000 tons shipped to Copenhagen in 1957-63 showed 75% cryolite and 9% chiolite. Sections along the west wall of the quarry in 1951-2 revealed 40% cryolite and 43% chiolite in an area estimated to represent 10,000 tons of fluorite-cryolite. Clearly, substantial amounts of chiolite were included in these brecciated materials.

Cryolite and in particular chiolite appeared as xenoliths in the fluorite-cryolite with the remaining minerals occurring as intergranular material. Only cryolite and chiolite were coarse, ranging from cm- to dm-sized grains. Fluorite occurred in cm- to dm-sized aggregates showing a colloform texture made up of mm-sized individuals. Topaz, both in the mm-wide fissures and in cm- to dm-wide veins cutting the lower-grade varieties of the fluorite-cryolite, was invariably cryptocrystalline like flint. The veins were essentially monomineralic and the larger veins showed multiple brecciation (Pauly 1992). These features were also valid for the cryolite-free compact fluorite-topaz unit (Fig. 16) on which the fluorite-cryolite rested.

Scattered through the two fluorite-bearing units were veins and irregular aggregates containing microcrystalline spherulites of the phengitic mica "ivig-

tite". Weberite and jarlite-bøgvadite-strontian barite occurred in aggregates of well crystallized mm-sized individuals constituting irregular masses or vein fillings. They are occasionally associated with ralstonite, stenonite and celestite (Pauly 1962, 1992; Pauly & Petersen 1988). In the fluorite-topaz unit, the ratios to fluorite of the accompanying minerals - weberite, jarlite and "ivigtite" - decreased by a factor close to two as compared to the fluorite-cryolite whereas the topaz ratio increased by a factor of 1.4. Higher than average concentrations of weberite, jarlite and "ivigtite" were found in the west wall of the quarry

Fig. 15. Fluorite-cryolite, breccia of light smoky cryolite cemented by topaz. The scale is 2 cm long.
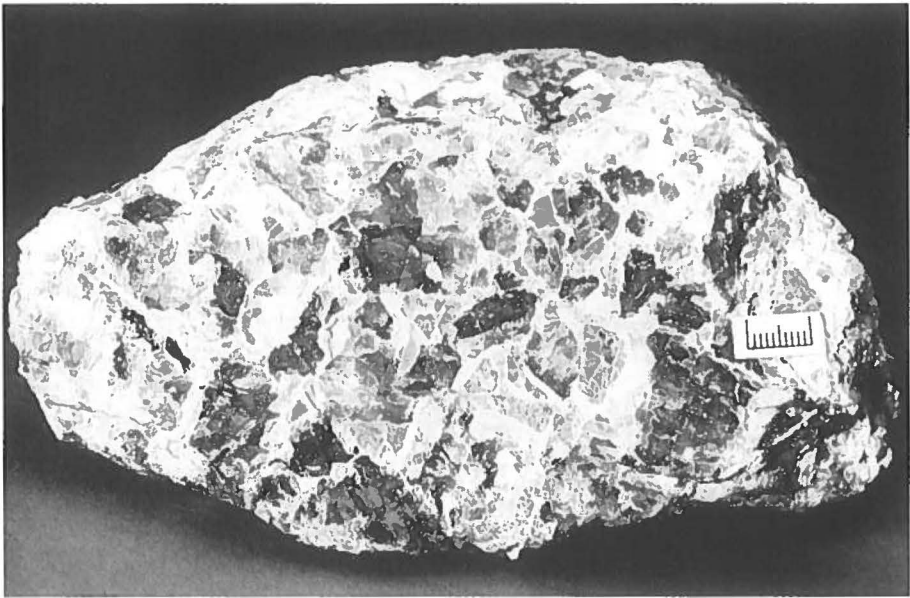
Fig. 16. Fluorite-topaz, aggregates of colloform fluorite repeatedly re-brecciated and cemented by topaz. The scale is 2 cm long.
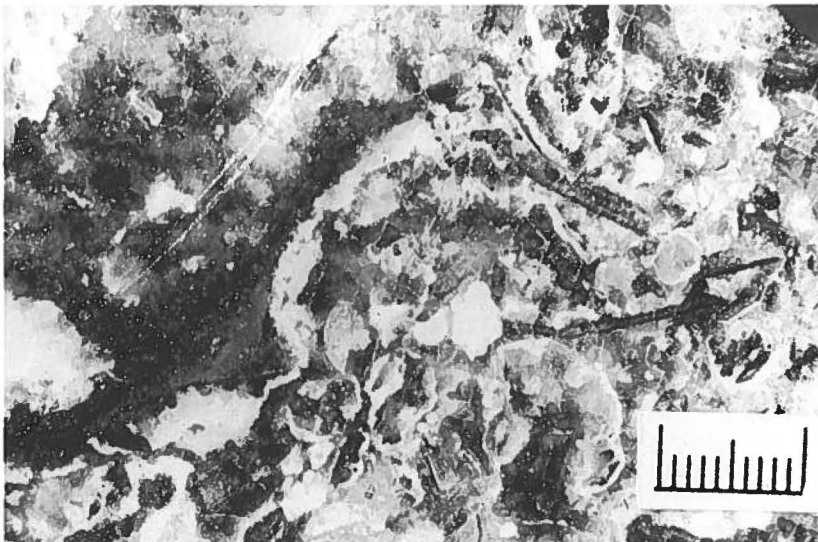
in the mineralogically analysed sections mentioned above. These minerals were obviously enriched in the upper parts of the fluorite-cryolite.

Sulphides in the two fluorite-rich units were virtually absent and largely limited to pyrite. But in two small pockets at the border to siderite-cryolite, Ag-, Bi-poor galena was found in assemblages of gustavite-cosalite-galena and galena-matildite-aikinite (Karup-Møller 1973, 1976; Karup-Møller & Pauly 1979).

Siderite-quartz

Under the units containing cryolite and other fluorine minerals lies a cryolite-free unit composed mainly of quartz and siderite (Fig. 4). This unit was not mined and is still extant. It is known from 36 diamond drillings with a total length of 944 m of which nine drillings passed through the unit to the underlying rocks of the granite intrusion at depths around 150 m below sea-level. The average thickness of the unit in vertical drillings was 85 m.

The composition of the unit varies so as to give three distinct subunits. The dominant one, in 400 m of cores, carries 90% quartz with only a few percent siderite. Its quartz, as in the other subunits, occurs in aggregates of crystals 3-5 cm long and 0.5-0.75 cm wide. Cavities are often seen between the crystals and, in one case, make up 4 vol.%.

Siderite contents of 10-20% were found in 300 m of cores, and concentrations of 40-90% in 200 m of cores. The latter seems to constitute a coherent mass containing 64% siderite and 20% quartz; the sulphides - mainly sphalerite - make up 13%. It is particularly observed in drillings beneath the northern and eastern part of the quarry. Its upper end joined with the massive siderite containing 80-90% siderite which was exposed in the threshold. Interpreted as a
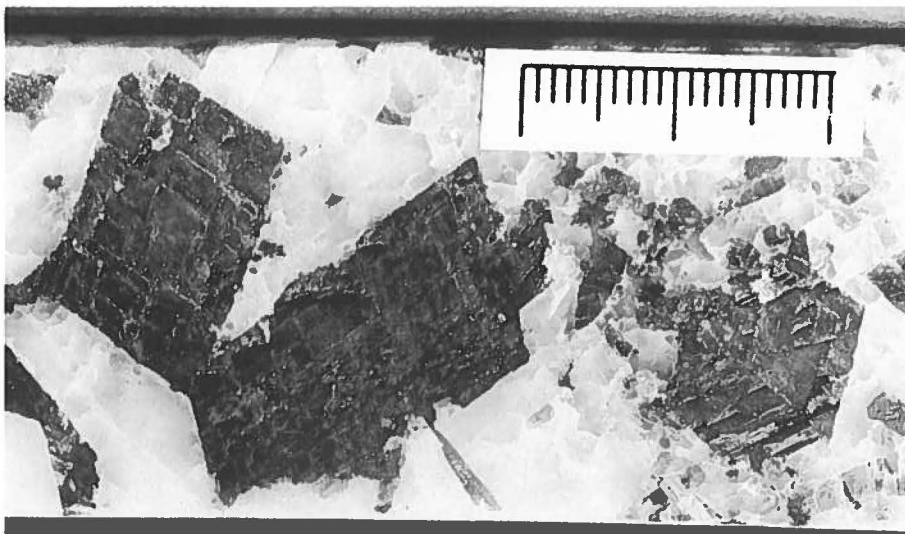

Fig. 17. Siderite-quartz, cataclastic texture with cleavage fragments of siderite. The scale is 2 cm long.

sheet, it dips north and west; its thickness decreases from 20 m to less than 10 m in the west (Fig. 4).

The texture of siderite-quartz is often defined by cleavage fragments of siderite surrounded and overgrown by quartz (Fig. 17), i.e. similar to the texture in quartz-rich margins of siderite-cryolite. The same four sulphides found in siderite-cryolite (sphalerite, chalcopyrite, Ag-,Bi-rich galena and pyrite) are again associated with siderite. Galena contains the same accessory ore minerals, notably freibergite, Te-canfieldite and stannite/kësterite (Karup-Møller & Pauly 1979).

Breccias of the deposit

Already in the first years of mining, xenoliths of the host granite intrusion were found embedded in pure cryolite in the top northern part of the eastern extension of the deposit. They were later found along the southern wall of this eastern extension where the xenoliths were embedded in siderite-cryolite with network texture.

When the cryolite-bearing masses in the eastern extension were mined out in 1960-62, the remaining lower surface of the extension was seen to have a brecciated contact. At higher levels, the breccia was several m thick and contained dm-sized, cm-thick flaky xenoliths of various granitic rocks (Fig. 18). Lower down, at the threshold to the main part of the deposit, similar flaky xenoliths lay on m-sized blocky xenoliths. These blocks were scattered through most of the arc of massive siderite but were particularly numerous below the eastern extension, around the entrances to the transport tunnels (Fig. 5).

The xenoliths in the threshold and along the margins of the eastern extension were generally composed of the pink, least altered granite but with lesser amounts of greisen or pink granite altering to greisen. Such varieties and proportions can be matched with the wall rocks of the eastern extension and are quite unlike the more intensely greisenized and mineralized wall rocks elsewhere around the deposit. None of the xenoliths showed a reaction rim against the host materials. Siderite occurred in the host material but also filled cracks in the xenoliths. In some examples, quartz crystals grew on one side of a xenolith - presumably the original wall of the deposit - but elsewhere all sides of a xenolith were overgrown by quartz which had clearly crystallized after brecciation. A granite and greisen xenolith at the SE corner of the eastern extension had a mineralized quartz vein along one side and a dm-wide seam of flaky xenoliths on the opposite side where it had been adjacent to the deposit. By rotating through 150° and moving it some 5 m higher, the xenolith could be matched with wall-rock granite having an identical vein.

Xenoliths elsewhere in the deposit were rare. A m-sized xenolith at the foot of the north wall 30 m below sea-level had along one side a piece of a mineralized quartz vein in which an aggregate of wolframite crystals was present.
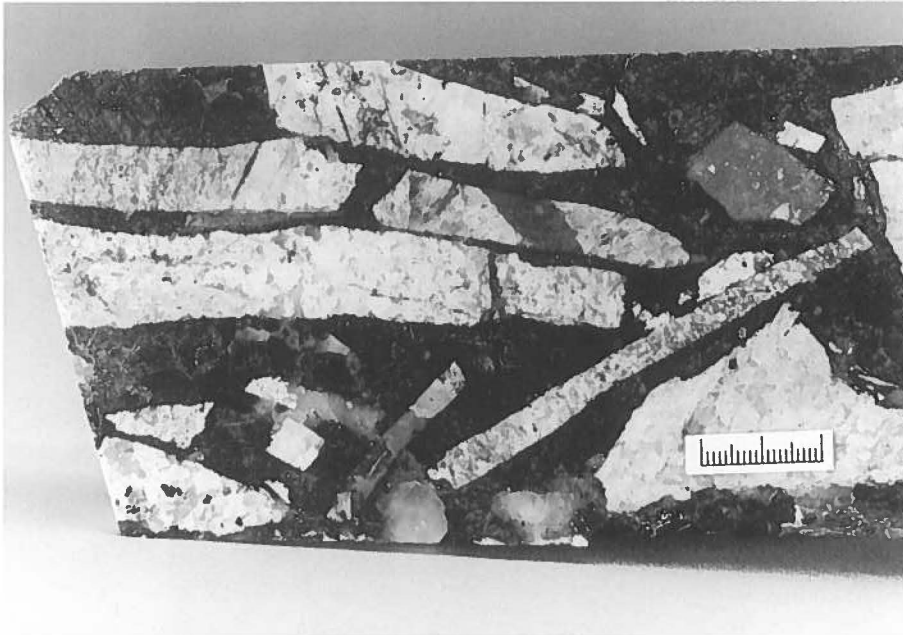
A 3 m long xenolith was reported in 1894 from the eastern end of the black cryolite with red-brown fluorite. A few cm-sized, altered fragments of pegmatitic microcline were found in cores from the siderite-quartz zone.

Two late breccias, of a different character, were exposed in the western half of the deposit in the south and northwest walls when the quarrying had advanced to within 20 m of the margin of the cryolite body.

The south wall breccia had a chimney form; it was shaped like an inverted funnel - c. 50 x 30 m at its base on the quarry floor, at 55 m below sea-level, but tapering upwards for at least 65 m. The lower part of the breccia broke through the banded siderite-cryolite but did not displace it visibly. Laterally, where it extended outside the deposit, the breccia was composed of densely packed greisen xenoliths together with some m-long slabs of quartz-feldspar pegmatite. Pure cryolite veins filled the space between, and penetrated mm-wide fissures in, the xenoliths but there were no alteration rims at the contact (Pauly 1982). A m-wide vein along the west side of the breccia ended in a lump of pure cryolite weighing several hundred tons and lying 15-20 m above the cryolite body (Fig. 19).

A similar breccia chimney, 50 x 30 m at its base and extending upwards for some 65 m, occurred in the northwest wall of the quarry. In 1959 it appeared as in Fig. 20. This chimney stood in and included xenoliths from the fluorite-cryolite unit, though the xenoliths were not markedly displaced. It was also associated with a m-wide vein which ended in a 1000 ton mass of pure cryolite.

Veins of pure cryolite, near the foot of the >100 m long west wall, connected the two breccias and indicate that they were emplaced contemporaneously.

Fig. 19. The south wall of the quarry with the funnel-shaped breccia chimney (BC) cutting siderite-cryolite (S-C) and overlying granite (G). Photograph by R. Bøgvad, 1945.
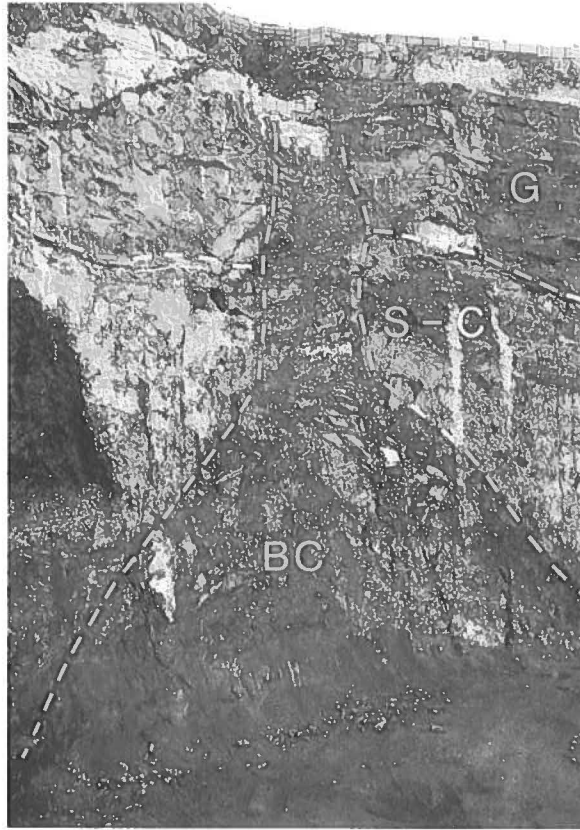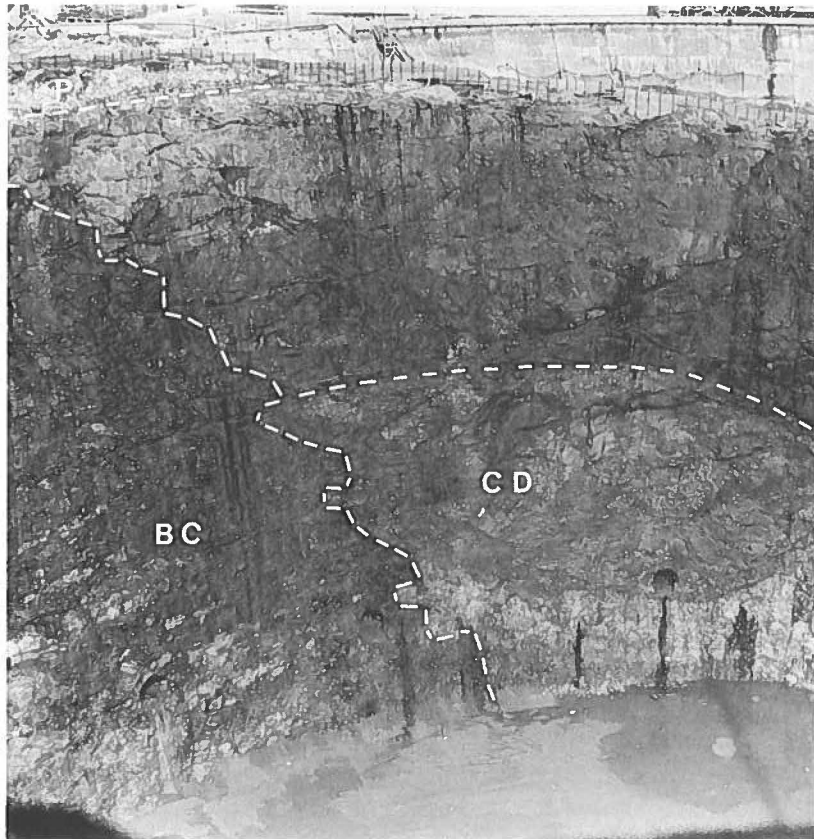

Fig. 20. The breccia chimney (BC) in the northwest wall in 1959. The border between the cryolite deposit (CD) and the enclosing rocks, mainly greisens, is indicated. In the upper left corner, just beneath the fence, the remains of the pegmatite body (P) are seen as a 30 m long, tapering area.

Late fissures and cavities

In the outer western part of the deposit, more than 20 vertical fissures containing prosopite have been observed (Pauly 1992). These fissures were up to several cm wide and extended over some 30 m height in a zone in the outer parts of all the cryolite-bearing units. Within the fissures was a brecciated mixture of fragmented minerals corresponding to the host rock. Prosopite only occurred as aggregates of micron sized crystals between the densely packed mineral fragments. A second type of fissure showed sedimentary layering with layers composed of varying proportions of cryolite and prosopite. Within these fissure fillings, some cryolite underwent recrystallization and cryolite crystals were occasionally developed. Both types of fissures are cut or flanked by thin veins of thomsenolite.

Thomsenolite and prosopite were major constituents of cavernous masses in fluorite-cryolite. The cryolite was replaced by thomsenolite which was followed by ralstonite; both minerals were veined by prosopite with the bulk of prosopite occurring as light blue dense masses; the prosopite was accompanied by agate-like crusts of fluorite; residual solutions in cavities crystallized varied assemblages - thomsenolite or jarlite or gearksutite.

The common thomsenolite of the deposit, which replaced 2-3% of all cryolite-bearing units, occurred in boxwork structures derived from the parting directions of the former cryolite. Less commonly, the thomsenolite was accompanied by crystals of ralstonite and pachnolite or by powdery gearksutite. Only rarely, in the upper part of the deposit, were there fissures lined by crystals of cryolite.

Geological evolution of the cryolite deposit

The evolution of the cryolite deposit can be divided into three observable stages (Pauly 1992). Certain inferences on its mise en place and earlier history can also be made. Stages 1 (11.3 10^6 tons) and 2 (1.0 10^6 tons) are represented by particular units within the deposit whereas stage 3 (only 0.08 10^6 tons) is represented by features breaking through or replacing the older units.

Stage 1

The first recorded event during stage 1 was the brecciation of the granitic wall rocks around the eastern extension of the deposit and the underlying threshold. During the initial brecciation, flaky xenoliths spalled off the wall rocks into the adjacent cryolite or siderite-cryolite material. Xenolith formation may be compared to rock bursts in mines where the unsupported walls of a gallery spall off flakes due to stress from the load of overlying rocks. Such xenoliths thus imply an (?explosive) release of pressure, probably through the roof of the cryolite deposit. During the succeeding climax of brecciation, m-sized blocks were detached from the walls. Both the flaky and the blocky xenoliths were scattered through a viscous mass of siderite and/or cryolite rather than accumulating on the floor of a low-viscosity hydrothermal fluid body. Locally, lenses of cryolite lined by siderite +/- quartz grew between the xenoliths after the brecciation. Quartz crystallised from fluids both before and after brecciation, and some siderite-forming fluids were capable of penetrating cracks in xenoliths. The absence of reaction zones at xenolith and wall-rock margins is consistent with the presence of a generally plastic host material rather than reactive fluids. Overall, then, we consider that emplacement of a plastic mass of siderite and cryolite into the eastern extension led to a two-stage formation of an intrusion breccia around its margins. Local crystallization of siderite, cryolite and quartz continued after the brecciation suggesting that the plastic mass coexisted with small amounts of fluids. These may have acted as a lubricating medium during emplacement.

It appears that, prior to brecciation, all the main mineral components of the deposit were already present. Thus it seems unnecessary to link the onset of their crystallization to the build up of pressure prior to or the release of pressure during brecciation.

It was probably during emplacement into the eastern extension that pre-existing siderites were broken up into the cleavage fragments which are common throughout siderite-cryolite. Only in a few cases - the cauliflower-shaped "reef" of siderite, pegmatitic lenses in the massive siderite and rare rhombohedra within siderite-cryolite - have euhedral, presumably primary crystals of siderite survived. These indicate locally quiet conditions of crystallization. Small amounts of quartz crystallized on granite wall rock prior to brecciation but this may merely reflect a local environment adjacent to the siliceous wall rocks. The bulk of quartz crystallized on xenoliths after brecciation, on cleavage fragments of siderite and on siderite substrates such as the siderite reef or siderite-lined lenses. Crystallization of siderite-cryolite started at temperatures below 600°C, probably around 550°C.

On textural grounds, it is inferred that the idiomorphic crystals of fluorite in the black cryolite with red-brown fluorite formed even before the brecciation in the eastern extension. There is no evidence to suggest how such early, discrete and high-density fluorite crystals became concentrated within the main

mass of siderite-cryolite. Although only 1-2 x 10^3 tons of this fluorite are present, it apparently scavenged a high proportion of the Th and REE from the early "fluids" of the deposit. The amount of Ca removed, however, only constitutes about 0.3% of the total Ca in the deposit and is thus unlikely to have influenced the appearance of cryolite.

The massive siderite zone (Fig. 4) which, on structural and textural grounds, crystallized early, appears to pass without any structural discontinuity into siderite-cryolite above and siderite-quartz below. We are unaware of any evidence that siderite-cryolite crystallized before siderite-quartz or vice versa. This suggests that the fundamental separation of the deposit into a fluoride unit overlying a siliceous unit had already been established prior to the events of stage 1. We return to this point below in our discussion of the proto-cryolite deposit.

Banding/layering

The time of formation of banding/layering in the main mass of siderite-cryolite is not clear but, where it occurs between xenoliths of the eastern extension breccia, it must be considered very early.

Some features in and around the siderite-cryolite unit, e.g. the early reef of massive siderite and local pegmatitic lenses of cryolite and siderite, are indicative of quiet in situ crystallization. However, discordant lens-like features near the margin and local cross-cutting contacts towards the centre of the unit point to disturbing movements. The banding/layering which characterised most of the siderite-cryolite cannot be unequivocally interpreted as forming under quiet or disturbed conditions. Thus the horizontally extensive banding/layering of the main mass combined with the curving round at its western and eastern ends could indicate the quiet inwards advance of a crystallization front parallel to the surrounding walls. Alternatively, these structures may indicate flowage, e.g. in a thermally driven flattened convection cell or in a mush which was mechanically squeezed into the eastern extension (see below). Whether quiet or energetic, it seems clear that discordant mechanical movements took place at a later stage perhaps when the siderite-cryolite mass had largely consolidated.

The regular layering seen in Figs. 6 and 7 might suggest to an igneous petrologist familiar with layering in the Skaergaard intrusion and the ideas of Wager & Brown (1968) that cumulus primocrysts of cryolite settled out from and accumulated within a sideritic host liquid. According to this idea, the onset of a new layer records the arrival of a pulse of settling crystals and is characterised by the concentration of euhedral, often oriented crystals at the bottom of layers. None of these features are present in siderite-cryolite (see Fig. 6). Nor can this idea be reconciled with the local occurrence of quartz crystals growing on the siderite and projecting into the supposedly early masses of cryolite.

In situ crystallization has been proposed as an alternative explanation for igneous layering (Maaløe 1978, McBirney & Noyes 1979). Thus repeated layering in igneous intrusions may arise by oscillatory crystallization at a slowly advancing crystallization front: concentration of certain components leads to the nucleation of one phase but this is followed by the exhaustion of these components and the nucleation of a different phase, the process being repeated many times. Repeated alternations of first-nucleating phases, however, are not immediately consistent with the fixed crystallization sequence in siderite-cryolite and it would be necessary to argue that evidence for such alternations was obliterated during the subsequent stages of primary crystallization or during secondary brecciation. Thus, although layering was probably present throughout the siderite-cryolite, comparisons with igneous-type processes are difficult to make and key textural details may well have been obliterated by later recrystallization (cf. McBirney & Hunter 1995).

In the earlier description of the siderite-cryolite unit, we noted that critical evidence for any continuity between the bands of the main mass and those of the eastern extension is lacking. Thus we can only speculate on an alternative possibility that the banding of this unit was due to "ice-like" or "salt-like" flowage of material from the main mass into the eastern extension at the moment of emplacement when the enveloping intrusion breccia was formed. Plastic flowage was perhaps concentrated along shear planes which were preferentially infiltrated by siderite-bearing fluids; these planes of intense disturbance were blurred by later recrystallization, annealing and further movements and thus developed the delicately varying concentrations of siderite, as seen in Figs. 6 and 7. Locally discordant banding and lenses occurring in the central and marginal areas of the siderite-cryolite mass are, of course, consistent with mechanical flowage but may only be indicative of late and local conditions.

In its mechanical properties, cryolite is comparable to halite (Pauly 1985) but the details of flowage and recrystallization of salt, e.g. in salt domes, have only recently started to receive attention (Richter-Bernburg 1980, Talbot 1998) and analogies with the cryolite deposit must be considered as preliminary. The layering seen in presently extruding salt domes is thought to represent primary bedding intensified by strain and dissolution to varying degrees. In contrast, the Ivigtut layering appears little deformed and more similar to the layering and textures in layered gabbros or bedded evaporites (Chris Talbot, personal communication 1998). We also find it unlikely that the ubiquitous banding/layering in siderite-cryolite could have developed during the period when only 10% of this mass flowed into the eastern extension.

The modal evolution seen in core J7 from the southern part of the threshold appears to provide critical evidence. The core bottomed in granitic wall rock with greisen next to the deposit; the overlying material is (a) massive siderite followed upwards by (b) several quartz-rich zones (presumed to be layers) of siderite-cryolite and then (c) cryolite-rich siderite-cryolite showing network texture and modal variations consistent with layering. Fractional crystalliza-

tion of a melt or more likely of a mush of plastic cryolite set in a fluid which later crystallized siderite, sulphides and quartz would mean that crystallization of the early consolidating siderite and then quartz would produce zones, i.e. layers, successively rich in these minerals and they would be overlain by material rich in cryolite, the last mineral to consolidate. Work is in progress to check whether cryptic variations in the various phases are consistent with fractional crystallization. In a mechanical model of "ice-like" or "salt-like" flowage, the agreement between crystallization sequence and modal evolution could only arise by chance.

Network texture

Our interpretation of the network texture in siderite-cryolite concentrates on the primary examples of the texture. At first sight, a hand specimen showing primary network texture appears to be a mass of rounded cryolite fragments cemented by later siderite and sulphides. However, we consider that, during formation of the network texture, the cryolite - based on its mechanical properties above 500°C (Pauly 1985) - was in a plastic, non-consolidated state. The sequence of crystallization was siderite, sulphides and then, locally, quartz. After this network had crystallized, the cryolite consolidated in the intervening spaces. The occurrence of cryolite blebs in siderite and the frequently rounded surfaces of siderite, sulphides and quartz against the cryolite lead us to infer that cryolite - as rounded and easily deformed plastic masses - was present at an early stage and that the crystallizing siderite, sulphides and quartz were moulded around these masses which presumably gave strength to the whole network. Following solidification of the network, the interstitial masses of plastic cryolite continued their long and complex history of consolidation. Since the twin systems differ for each cryolite mass, each mass was or became structurally independent of its neighbours.

This model suggests that, prior to any crystallization, viscous masses of cryolite coexisted with (?) aqueous-carbonate fluids rich in siderite and sulphide components. Presumably they formed a mush like ice and water. Such a mush may have been periodically subject to flowage similar to the lubricated interior of a glacier or been capable of convective stirring, and these processes may have led to the pervasive development of banding/layering throughout the siderite-cryolite.

Alternatively, it is perhaps more reasonable to argue that the mush developed during the inferred flowage of siderite-cryolite into the eastern extension. Flowage could have broken up larger cryolite masses into the typically 2-5 cm size masses which are observed and could have produced the siderite fragments which, as noted above, are common throughout siderite-cryolite.

At the same time, the presence of siderite veinlets cutting xenoliths around the eastern extension is evidence for the presence of a sideritic fluid phase. The flowage may have been lubricated by this coexisting fluid and, in turn, infil-

tration of this fluid between the plastic masses of cryolite would have been promoted, especially in and close to the most intense planes of movement (see above). Thus the pervasive network texture and banding/layering of the siderite-cryolite may have arisen by the same process: flowage of a mush or lubricated mixture of plastic cryolite and brittle siderite + sulphides into the eastern extension.

In addition to this inferred flowage, secondary imposition of a cataclastic texture on large volumes of network-textured siderite-cryolite has taken place and can be attributed to later movements of the ductile cryolite. If we accept the evidence and arguments for early and secondary disruption of textures, the question naturally arises as to how the delicate gradations in siderite/cryolite proportions seen in the network texture of Figs. 6 and 7 have been able to survive. Furthermore, similarly delicate gradations appear to have been repeated many times throughout most of the siderite-cryolite and to have resulted in persistent and generally regular banding/layering. One of the authors (JCB) sees the delicate banding/layering with network texture as the slightly disturbed relic of primary crystallization processes, whereas the other author (HP) considers it more likely that it resulted from plastic, glacier-like movements above 450°C within the siderite-cryolite. Similar banding has been observed in glaciers from a number of localities including Greenland where shear zones with rock or shell fragments have undergone later recrystallization (Shumskii 1961; Anker Weidick, personal communication 1994).

Although the banding/layering is concordant with the dome-shaped margins of the body which might suggest that a crystallization front steadily advanced from these walls, the old descriptions and photographs of the deposit do not suggest that the central, final bands have in any way become fractionated from the outer, earlier material. To date, the few chemical constituents that have been analysed in galena and cryolite from various localities within the siderite-cryolite unit appear to be remarkably monotonous (Karup-Møller & Pauly 1979; Pauly 1986a). This apparent monotony and the persistence of bands/layers, regardless of their genesis, across virtually the full width of the deposit both suggest that the siderite-cryolite, at an early stage in its history, was present as a homogeneous mass of fluid or mush.

The monotony of mineral parageneses and the apparent absence of cryptic variations in the minerals of siderite-cryolite also suggest that this unit did not evolve by fractional crystallization and accordingly such a process was not responsible for the appearance of the pure cryolite unit. Perhaps these two units arose at an early stage by in situ liquid differentiation or perhaps the siderite-sulphides component of the proposed mush was simply absent from the material which made up the future pure cryolite unit.

Despite these uncertainties in its initial formation, it seems clear that the pure cryolite unit consolidated later than the siderite-cryolite unit since it forms the roof to the large cavity with stage 2 residual fluids and it is the most likely source for pure cryolite veins which cut through the siderite-cryolite

unit. During crystallization of the pure unit of cryolite, Na_3AlF_6, fractionation does seem to have taken place and a slight deficiency of Na relative to AlF_3 developed leading to the appearance of chiolite, $Na_5Al_3F_{14}$, with 0.3% K at the western edge of this unit.

Stage 2

Following the appearance of chiolite, there was an abrupt change in conditions within the western part of the deposit and stage 2 began (Pauly 1992). Na became almost totally exhausted and a large cavity with residual fluids rich in Ca, F and Al, plus some Si, Mg and K and a little Sr-Ba, appeared. Al and Si were probably located in some type of volatile F compound. Extensive gas-driven explosions led to the emplacement of cryptocrystalline topaz in breccias and vein breccias and, contemporaneously and independently, colloform fluorite was precipitated. Together these two minerals formed the fluorite-topaz unit in the deeper part of the deposit. Above, the cryolite roof to the cavity partly but instantaneously collapsed and the topaz-veined fragments, admixed with fluorite, gave rise to the fluorite-cryolite. Chiolite broke down to form cryolite and topaz (Pauly 1986b).

The fractionation of fluids at the end of this fluorite-rich stage became so extreme that cm- to m-sized pockets amounting to thousands of tons crystallized unusual H_2O-bearing assemblages rich in Mg (weberite), K ("ivigtite" mica) and Sr-Ba (jarlite-bøgvadite-barite; Pauly 1993).

The Ag-,Bi-poor galena and the unusual parageneses of Ag-,Bi-rich sulphides probably formed when the common Ag-,Bi-rich galena of earlier units was remobilized by fluids of the fluorite-rich units (Karup-Møller & Pauly 1979).

Consolidation of the residual fluids probably resulted in contractions and shifting of load pressure on the deposit. As a result, explosively released gases may have produced the two breccia chimneys extending upwards some 70 m, i.e. about 30 m above the upper margin of the deposit. Subsequently, cryolite veined and flowed plastically between the xenoliths of the breccia and was squeezed through m-sized pipes to form pockets of pure cryolite >20 m above the cryolite deposit.

The absence of altered margins to fragments in the breccias of both the fluorite zones and the two chimneys suggests a rapid discharge of gases rich in CO_2 rather than H_2O vapour.

Stage 3

Stage 3 of the deposit began after the fluorite-cryolite had consolidated and led to the formation of a variety of fissures and cavities (Pauly 1992). Water vapour pressure built up in pockets in the outer western part of the deposit and

water vapour was released along more than 20 vertical fissures. Fluidized introduction of microcrystalline prosopite and brittle, fragmented cryolite was followed locally by their sedimentary accumulation. Here, the occasional development of cryolite crystals demonstrates that the host fluid was pure water free of Ca and Mg ions; it may have evolved from less pure water collected in cavities below the fissures.

The cavernous masses of secondary aluminofluorides began as pockets of Ca-Mg-rich solutions in an advanced state of transforming cryolite. A sudden drop in pressure caused the solutions to precipitate the dense mass of prosopite and the crusts of fluorite, probably from supersaturated solutions or gel-like masses. In the succeeding quiet period, the remaining solutions varied even between adjacent cavities and this led to crystallization of Ca-rich (thomsenolite, gearksutite) or Mg-rich (ralstonite) assemblages (Pauly 1992).

Most cavities in the cryolite-bearing units contained solutions with Ca^{2+} ions and these reacted with cryolite in the cavity walls to form crystals of thomsenolite, pachnolite and gearksutite. Less commonly, Mg^{2+} ions reacted to form ralstonite and only rarely were such solutions pure enough to form crystals of cryolite itself. Fluids in this final stage must have been H_2O-rich and CO_2-poor (Pauly 1992).

The evidence for violent gas discharge, first through the Bunkebreccia pipe and then intermittently from the evolving cryolite deposit, suggests that the overlying Gardar volcanic landscape was marked by the release of gas streams with intervals of quietness.

Genesis of the cryolite deposit

Preliminary remarks

Although nearly a score of cryolite occurrences have been reported, none of them rival the high concentration and enormous mass of cryolite found in the Ivigtut deposit (Bailey 1980). Regardless of mineralogy, well-defined mineral deposits in granitic environments apparently never attain the size of the cryolite deposit. The main cryolite-bearing unit of the Ivigtut deposit - the siderite-cryolite - was everywhere characterised by banding/layering and a network texture; other deposits lack these features.

A key parameter in understanding the evolution of the cryolite deposit must be its water content: under anhydrous conditions pure cryolite crystallises at c. 1010°C but remains ductile down to c. 450°C; in contrast an aqueous solution of suitable chemistry readily precipitates cryolite at 25°C and 1 atmos. pressure. Although precipitation of cryolite is thought to have taken place in a few hydrothermal environments, the F of most hydrothermal deposits combines with Ca to form fluorite, or is less commonly located in fluorapatite, topaz, tourmaline, micas, clays or Ca-Mg aluminofluorides. Against the background of

this unique array of geological and physicochemical features, the evidence for the genesis of the Ivigtut cryolite deposit is now discussed.

Geological setting

The setting and emplacement of the Ivigtut granite - a 300 m wide granite pipe intruding an older intrusion breccia - is comparable with many shallow-level intrusive complexes controlled by brittle fracturing and explosive release of magmatic gases (Taylor 1979). When the granite magma of a narrow pipe consolidates and contracts, it is likely that the reduction in volume will be taken up by the formation of joints and major voids in its quickly cooled roof zone. Jointing is well developed in the granite roof overlying the cryolite deposit, but there is no evidence to suggest that the cryolite deposit occupied a large contraction void. Note that a number of breccia and granite pipes contain scattered or concentrated mineralized veins, but they lack major bodies such as the cryolite deposit.

The cryolite deposit has sometimes been genetically classified with those granitic pegmatites containing cryolite. As indicated above, however, several stages of metasomatism and a generation of quartz veins intervened between formation of the Ivigtut granite pegmatite and the cryolite deposit. Furthermore, the deposit dwarfed the pegmatitic bodies within the granite and its margins were nowhere defined by coeval pegmatitic material.

The cryolite deposit was exceptionally large - 170 by 140 m in plan and up to 155 m thick. Other mineralized bodies within granitic roof zones are distinctly smaller. The silica cap at Panasqueira, Portugal, is some 50 x 20 m in section and is probably a hydrothermal filling of an open chamber (Kelly & Rye 1979). The "quartz bell" at Sadisdorf in the Erzgebirge is no more than 20 m thick and is a quartz-rich greisen formed by silicification of a pegmatite occupying a contraction void (Baumann 1971). At Climax, Colorado, granite porphyry cupolas enclose a stockwork of molybdenite-bearing quartz veinlets over 1000 m in diameter but large, well-defined hydrothermal bodies are absent (White et al. 1981).

At both Panasqueira and Sadisdorf, the hydrothermal bodies are associated with greisens extending for hundreds of metres. At Climax, the stockwork is associated with pervasively silicified and quartz-topaz-pyrite impregnated zones, and a greisen vein zone, all up to several hundred metres in size. At Ivittuut, greisens were observed to be only tens of metres thick but, in our opinion, they were formerly more extensive and were the immediately preceding materials in a transformation process which led to formation of the cryolite deposit (see below).

Geochemical and mineralogical evidence

A synthetic mixture corresponding to the bulk cryolite deposit was made by combining data on the mineral composition and tonnages of the various units with representative samples of minerals from these units. Analysis of this mixture (Table 3, column 9) indicates that, compared with other mineral deposits, the Ivigtut cryolite deposit is characterised by high contents of Na, Al and Si. Such a combination of components is most likely to be derived from a pre-existing aluminosilicate rock, in this case the Ivigtut granite. The Si/Al ratio of the deposit (6.8), however, is much higher than in unaltered granite (4.5) suggesting that some Si was introduced by post-magmatic fluids as inferred for mineralized greisen (7.4). A number of the elements significantly present in the deposit (notably Fe, Mn, Mg, Ca, Sr and Ba) were released during the early metasomatic breakdown of high-T phases in the Ivigtut granite. Mass-balance calculations indicate that the released tonnages could account for the bulk of these elements in the cryolite deposit. The high Na/K ratio of the deposit may partly reflect the following stage of albitization. However, the molar Na/Al ratio of the deposit (2.1) is much higher than in albite (1.0) and points to selective incorporation of Na from post-magmatic fluids. A number of components such as F, CO_2, S, Zn, Cd, Cu, Pb and Ag are so abundant that they cannot have been be derived from pre-existing granite but must have been introduced in fluids, at various stages, probably from larger volumes of underlying granite. A few elements such as P, Ti and Cr were released during early metasomatic alteration of the Ivigtut granite and left virtually no subsequent record. Potassium was largely retained during the various stages of post-magmatic alteration but has left little record in the cryolite deposit.

Calculations and arguments such as those outlined here help us to assign the components of the deposit to particular sources (see Table 4 and text below).

Several trace element ratios are good indicators of post-magmatic conditions in the Ivigtut granite and cryolite deposit (Table 3). Thus ratios of heavy to light REE increase sharply with advancing metasomatism; this is a common feature of metasomatized granites and has been attributed to complex ion formation between heavy REE and F +/- Cl (Bowden & Whitley 1974). Cerium anomalies appear in many REE patterns of samples from the greisens and the cryolite deposit; they reflect the conversion of Ce^{3+} to Ce^{4+} and point to a highly oxidising milieu. Zn/Cd ratios around 700 in the unaltered granite are reduced to around 300 in the metasomatised granites and in the cryolite deposit where Zn and Cd are dominantly held in sphalerite. Th/U ratios cover a narrow range around 3.2 in the fresh granite but range from 1.3-17.5 in the metasomatized granites; separation of these normally coherent elements can again be attributed to the formation of fluoriferous complex ions with different properties. The separation culminates in the cryolite deposit where the ra-

Table 4. Calculations modelling formation of the cryolite deposit from the Ivigtut granite.

	A		B	C	D
SiO_2	53.4	SiO_2	63.2	79.4	70.4
TiO_2	tr.	TiO_2	tr.	tr.	0.3
Al	2.7	Al_2O_3	7.8	9.8	14.0
Al_2O_3	1.4	FeO*	13.7	3.3	3.3
FeO*	11.5	MnO	0.5	0.1	0.1
MnO	0.4	MgO	0.1	tr.	tr.
MgO	0.1	CaO	2.5	1.1	1.1
Ca	1.5	Na_2O	10.8	4.7	4.7
Na	6.8	K_2O	0.4	0.5	4.6
K_2O	0.3	P_2O_5	tr.	tr.	0.1
P_2O_5	tr.	H_2O^+	0.2	0.3	0.4
H_2O^+	0.2	H_2O^-	0.1	0.1	0.1
H_2O-	0.1	F	0.3	0.3	0.3
F	13.1	CO_2	0.3	0.3	0.3
CO_2	6.8	S	tr.	tr.	tr.
S	0.8	Zn	tr.	tr.	tr.
Zn	1.2[1]	Sum	100.0	100.0	100.0[3]
Sum	100.0[2]				

[1] Includes 0.4% Pb and 0.1% Cu; [2] includes 0.2% others (Rb, Sr etc.);
[3] includes 0.2% others (Zr, REE, etc.).

A   Cryolite deposit. Note Al, Na and Ca as elements.

B   Reduction of volatiles (F, CO_2, S and Zn) to levels in granite (-21.3 %); conversion of Al, Na and Ca to oxides; recalculation of non-volatiles to give sum of 100%.

C   Reduction of leached components (FeO*, MnO, MgO and CaO) to levels in granite (-12.3%); reduction of Na_2O to level in granite (- 6.1%); recalculation of unfixed components to give sum of 100%.

D   Reduction of SiO_2 to level in granite (-9.0%); TiO_2 and P_2O_5 were lost during post-magmatic alteration, and K_2O was apparently lost during transformation of greisen to proto-cryolite deposit; these three components are now restored to levels in granite (+4.5%); recalculation of unfixed components to give sum of 100% gives the composition of the Ivigtut granite.

During conversion of granite to cryolite deposit, we consider that volatiles (21.3%), Na_2O (6.1%) and SiO_2 (9.0%) were introduced by post-magmatic fluids. Adding these to the leached components (12.3%), and ignoring the small losses of TiO_2, P_2O_5 and K_2O, leaves 51.3% material assigned to the granite. See text for further discussion.

dioactive, red-brown fluorite contains 3900 ppm Th but only 7 ppm U, giving a Th/U ratio of 560!

The presence of cassiterite in quartz veins in and around the Ivigtut granite led early visiting geologists to compare the cryolite deposit with mineralizations associated with the F-rich orogenic "tin granites" of Central Europe and Cornwall. Later work at Ivittuut has also noted disseminated cassiterite in greisens, and stannite and other Sn sulphides both in veins related to the granite and as inclusions in the sulphides of siderite-cryolite. However, if the high contents of zircon and columbite in the Ivigtut granite and greisens, and of sphalerite relative to other sulphides, are taken into consideration along with the tectonic setting of the Gardar province, a better analogy can be drawn with the cryolite-bearing, non-orogenic "tin granites" of Nigeria (Bowden & Jones 1978).

Pauly (1960) argued that the presence in siderite-cryolite of black Fe-rich sphalerite (marmatite) and of chalcopyrite with sphalerite stars pointed to a hypothermal milieu, though this argument seems less secure in the light of later research on these minerals. Relics of a hypothermal/pneumatolytic stage are seen in the conversion of accessory cassiterite to stannite and in the presence of Sn, Mo, W and Li in the bulk deposit (Table 3). The elevated contents of Ag and Bi in galena are consistent with hypothermal conditions (Schroll 1955). Available geothermometry points to initial temperatures of crystallization between 500-600°C and confirms the hypothermal status of the deposit (Oen & Pauly 1967).

The emplacement of granophyre dykes with cryolite and other minerals characteristic of the cryolite deposit prior to intrusion of the comagmatic Ivigtut granite is strong evidence for a genetic link between the granite magma at Ivittuut and cryolite-rich mineralization. The geochemical and mineralogical features of the Ivigtut granite, its metasomatized derivatives, especially the mineralized greisens, and the cryolite deposit are also consistent with such a linkage. Thus one of the distinctive geochemical features of the deposit - its high Zn/Cu and Zn/Pb ratios - can be traced back to similar features in the Ivigtut granite. It is likely that the sequence of autometasomatic stages recognised in both the deep and top granites reflects the evolving state of post-magmatic fluids rising from a large and comagmatic granitic massif that was parental to the Ivigtut granite pipe. These fluids migrated upwards through the deep granite but became concentrated in the central part of the top granite where the most intensely metasomatized zones are located and where we envisage that a proto-cryolite deposit appeared and underwent a complex evolution.

Isotopic evidence

Rb-Sr and K-Ar studies, respectively, indicate that the age of the Ivigtut granite is around 1171 or 1185 Ma, but these values differ markedly from the Pb-

Pb "model" age and the Pb values clearly require a multi-stage model. Ulrych (1964) proposed a three-stage model beginning with a primary age of at least 2980 +/- 10 Ma representing the age of ordinary lead mineralization. The radiogenic component of these leads was derived from a source which came into existence between 1880 +/- 60 Ma and 1100 +/- 40 Ma. Final emplacement of the anomalous lead was not earlier than 1100 +/- 40 Ma.

Recently obtained Pb isotopic analyses on whole-rock gneisses from the Ivittuut peninsula help to clarify this history (Taylor & Kalsbeek 1986; Feiko Kalsbeek, personal communication 1991). The gneisses yield an age of 3110 +/- 65 Ma and a $^{238}U/^{204}Pb$ value of 7.18 +/- 0.02. Such gneisses were probably developed from or contaminated by low-U/Pb granulite facies rocks in the deep crust beneath the peninsula. The galenas of the cryolite deposit and overlying pegmatite sill yield a relatively imprecise age of about 1170 Ma which can be easily reconciled with the Rb-Sr and K-Ar age determinations. Furthermore, the analysed galenas lie between the Geochron at 1170 Ma and the isochron for the peninsula gneisses at 1170 Ma. This strongly suggests that the Pb isotopes of the galenas arose by contamination of mantle-type Gardar Pb by Pb from the surrounding 3110 Ma gneisses.

Blaxland (1976) presented a relatively imprecise Rb-Sr whole-rock isochron for the Ivigtut granite. Recent work by one of the authors (JCB) with Ole Larsen of Copenhagen University indicates that the imprecision arose because isotopically variable rock populations had been combined. Blaxland's study also highlighted the complexity of the Ivigtut system since the initial $^{87}Sr/^{86}Sr$ ratios of the Ivigtut granite, speculated to be about 0.707-0.704, the interstitial cryolite of albitised granites (about 0.72) and the cryolite deposit (about 0.709) were found to be significantly different. It was argued that the mineralizing fluids which eventually crystallized cryolite had selectively leached considerable amounts of Rb, Sr and ^{87}Sr from large volumes of older continental crust. The recent work with Ole Larsen provides a more reliable initial $^{87}Sr/^{86}Sr$ ratio near 0.705 for the fresh granite. This initial ratio is slightly above the lowest mantle-type Gardar ratios of 0.702-0.704 and suggests that some contamination by the continental crust has taken place. Variable initial ratios among the different, autometasomatized granites confirm that the Ivigtut system was open with respect to radiogenic Sr during the post-magmatic stages.

Sulphur isotopic ratios have been measured by Kulp et al. (1956) and Ault & Kulp (1960) who found that most sulphides from the cryolite deposit showed a tight grouping of $^{32}S/^{34}S$ ratios around 22.1, close to the average for crustal and mantle rocks (22.13). This could be taken to imply that the source rocks for the sulphur were largely unfractionated, homogeneous regions typical of the crust or mantle. However, Ohmoto & Rye (1979) have cast doubt on the suitability of sulphur isotope ratios for assessing the source regions of sulphur and, instead, emphasise the role of oxygen fugacity, temperature and other parameters in controlling these ratios.

Ratios of $^{12}C/^{14}C$ reported by Wickman (1956) show a trend of increasingly light carbon with average $d^{13}C$ changing from -5.9 ‰ in siderites from metasomatized granites to -7.9 ‰ in siderites from the cryolite deposit. The great majority of values fall in the narrow range -3.3 to -8.5 ‰ and are similar to $d^{13}C$ values for primary mantle materials and many crustal materials; only marine limestones and graphite- or organic carbon-bearing rocks can be eliminated as unnacceptable sources. Most hydrothermal deposits show an evolution towards decreasing light carbon and it is possible that the opposite trend for the Ivigtut system reflects an increase in the oxidation state of late fluids.

A preliminary oxygen isotope survey of the Ivigtut system by one of the authors (JCB) revealed a regular increase of $d^{18}O$ values from 7.9 in the fresh granite, to 8.4-9.7 in metasomatised granites to 10.5 ‰ in the bulk cryolite deposit. The fresh top granite is within the range of 7.8-8.3 ‰ for normal granites in the H1 class of Taylor (1968) while the other values are similar to pegmatites and hydrothermally altered granites of the H2/H3 class. Thus, although the Ivigtut system was probably emplaced at relatively shallow levels, there is no indication that it exchanged oxygen isotopes with $d^{18}O$-depleted meteoric groundwater. The data are consistent with the idea that the steadily increasing $d^{18}O$ values simply reflect the falling temperature of the system.

Overall then, the available isotopic data on the Ivigtut system in combination with the petrological results indicate that the magmas were ultimately derived by fractionation of mantle-derived basalts. Minor contamination by radiogenic Sr and major contamination by radiogenic Pb may have taken place during ascent through the crust. Interaction with the surrounding gneisses was intensified during the post-magmatic stages when the fluids responsible for metasomatism and the cryolite deposit picked up radiogenic Sr, probably by selective leaching of minerals in the basement rocks. Leaching did not take place via meteoric waters; cogenetic F-rich post-magmatic fluids derived from the granite massif beneath the Ivigtut pipe are more likely agents.

Fluid inclusion evidence

Preliminary work on fluid inclusions in quartz, cryolite and siderite from the cryolite deposit indicates that these minerals crystallized under a range of conditions (Konnerup-Madsen 1980; Prokof'yev et al. 1990). Although the majority of inclusions homogenise at <350°C, some inclusions that now contain an aqueous solution, liquid CO_2, gas and salt crystals homogenise at 335-555°C to a fluid with high concentrations of both salt components and CO_2. Such a combination requires pressures >1 kbar. Given the repeated brecciation and ductile behaviour of siderite-cryolite, we find it remarkable that such high-temperature fluid inclusions have been preserved and suspect that even

more primary fluid inclusions have escaped detection.

Less saline inclusions homogenise at 240-325°C and formed under pressures of 1.6-2.3 kbar whereas secondary inclusions are more dilute, homogenise at 135-155°C and contain little CO_2. Many of the inclusions homogenising at lower temperatures tend to be rich in either H_2O or CO_2 suggesting they are the result of low-pressure boiling of mixed H_2O-CO_2 fluids.

Analysis of water released from fluid inclusions in siderite revealed 7.17-7.45 wt.% F and 3.82-4.66 wt.% Cl but no other anions. In comparison to most hydrothermal deposits where aqueous solutions commonly contain NaCl, KCl and some CO_2, and assuming no later contamination, the fluids of the cryolite deposit are characterised by exceptionally high F contents.

In some specimens of siderite-cryolite, the salinity of aqueous inclusions in cryolite is higher than in siderite suggesting that the two coexisting minerals crystallized from different fluids.

The shift from relatively high to low pressures in the fluid inclusions agrees with evidence for the release of volatiles from the deposit such as the formation of breccias in the fluorite zones and chimneys.

We are more reluctant to accept the evidence from fluid inclusions that the parental fluids or melts for the cryolite deposit were rich in H_2O. The early, main stages of the cryolite deposit apparently had a H_2O-poor character: blobs of cryolite apparently had the strength of a viscous rather than a fluid mass so that siderite + sulphides were moulded around these blobs; vughs and voids are conspicuously absent. Some of these features, it must be admitted, are also absent from other massive hydrothermal bodies, such as the silica cap at Panasqueira, Portugal (Kelly & Rye 1979), and may have been obliterated at Ivittuut by later movements of the ductile cryolite. Again, cryolite is moderately soluble in pure H_2O (0.30 g/l at 0°C increasing to 0.75 g/l at about 95°C according to Buchwald (1940)) so that the continued passage of hydrothermal solutions through the deposit might be expected to dissolve cryolite. Since there is no sign of dissolution in the early main stages of the deposit, perhaps aqueous solutions were never present. Alternatively, these aqueous solutions may have been saturated in sodium and aluminofluoride ions and were thus incapable of dissolving cryolite.

Experimental and thermodynamic evidence

Although virtually no experimental work has been performed on systems close in composition to the cryolite deposit, comparisons with other F-rich systems can be usefully made (reviews by Bailey 1977, 1980; Dingwell 1988; London 1992). There is experimental as well as natural evidence from fumaroles and metasomatically altered rocks that aluminofluorides may develop by the interaction of aqueous solutions with silicate rocks and minerals, the fluorine being supplied by any of these materials. High levels of F in granite-H_2O sy-

stems are known to lower liquidus (to <800°C) and solidus (to <525°C) temperatures, to raise component diffusivities and lower viscosities and nucleation rates. Quartz tends to crystallize before feldspar, and feldspathic aluminosilicate units in the melt are broken down to form sodium ions and aluminofluoride complex ions. During the cooling and degassing of granite melts, volatiles are preferentially lost in the sequence CO_2, HCl and H_2O whereas F is strongly retained by the melt. F-rich melts may show immiscible separation into a fluoridic alkaline melt and a polymerised silicate melt. Earlier suggestions that F contents of several weight percent lower the solubility of water in granitic melts have not been confirmed (Holtz et al. 1993).

Above 10-12 wt.% F in the granite-H_2O-HF system at 1000 kg/cm², the granite melt and the coexisting hydrous solution coalesce into a supercritical hydrous fluoride melt and a fully molten state persists down to the lowest temperature investigated - 575°C (Glyuk & Anfilogov 1973). The Ivigtut cryolite deposit with 12.9 wt.% F may have corresponded to such a hydrous fluoride melt though the influence of additional components such as Fe and CO_2 remains to be assessed. It is likely that the melt would have been capable of absorbing any Na and F released by underlying granites during their soldification and post-magmatic alteration and that rapid re-homogenization would have accompanied the addition of these and other new components because of their high diffusivity in F-rich melts. According to the experimental work outlined above, it is anticipated that such melts would begin crystallization by precipitating copious amounts of quartz which would grow quickly because of high diffusivity and sink rapidly owing to the low density and viscosity of the system (but see discussion below).

Fluid inclusion studies indicate that cryolite occurrences in various countries have crystallized from hydrothermal solutions over the wide range of 90-480°C, with most inclusions homogenising at 100-300°C. Under these latter conditions, thermodynamic calculations suggest that cryolite formation is favoured over fluorite when the sodium activity exceeds the calcium activity by 2-4 orders of magnitude, and when temperatures are lower and conditions more acidic (Prokof'yev et al. 1987). These calculations ignore the possibility of complex ion formation, e.g. complex aluminofluorides, and may not be relevant to conditions in the cryolite deposit where the Na/Ca ratio was 2.9 (Table 2) and where cryolite formed at >500°C. Thermodynamic calculations on the stability of chiolite and cryolite made by Anovitz et al. (1987) did not consider the influence of H_2O and CO_2.

Formation of the cryolite deposit

Alternative paths of formation

In the Ivigtut deposit, as in several other cryolite occurrences, the cryolite formed at the post-magmatic stage of granite evolution occurring in pegmatites, metasomatized granites and mineralized bodies (Bailey 1980). This agrees with experimental studies on the F-poor, <10 to <12 wt.% F, part of the granite-H_2O-HF system which reveal that aluminofluorides such as cryolite fail to appear in the magmatic products but occur in dense coexisting vapours (reviews by Bailey 1977, 1980; Dingwell 1988; London 1992). Equivalent fluids are thought to have been trapped in multi-phase inclusions in the Volyn pegmatites, Ukraine, and contain cryolite. These inclusions appear to show a largely continuous evolution from granite melt through dense saline brines to dilute hydrothermal solutions. When such an evolution, with F as the dominant anion in the brine, is integrated with the genesis of natural cryolite occurrences (Fig. 21), it is seen that cryolite-rich bodies such as the Ivigtut deposit could arise by several geological paths.

Firstly, it is conceivable that largely by addition of Na and F a cooling granite system could continuously evolve from granite melt to bulk cryolite de-
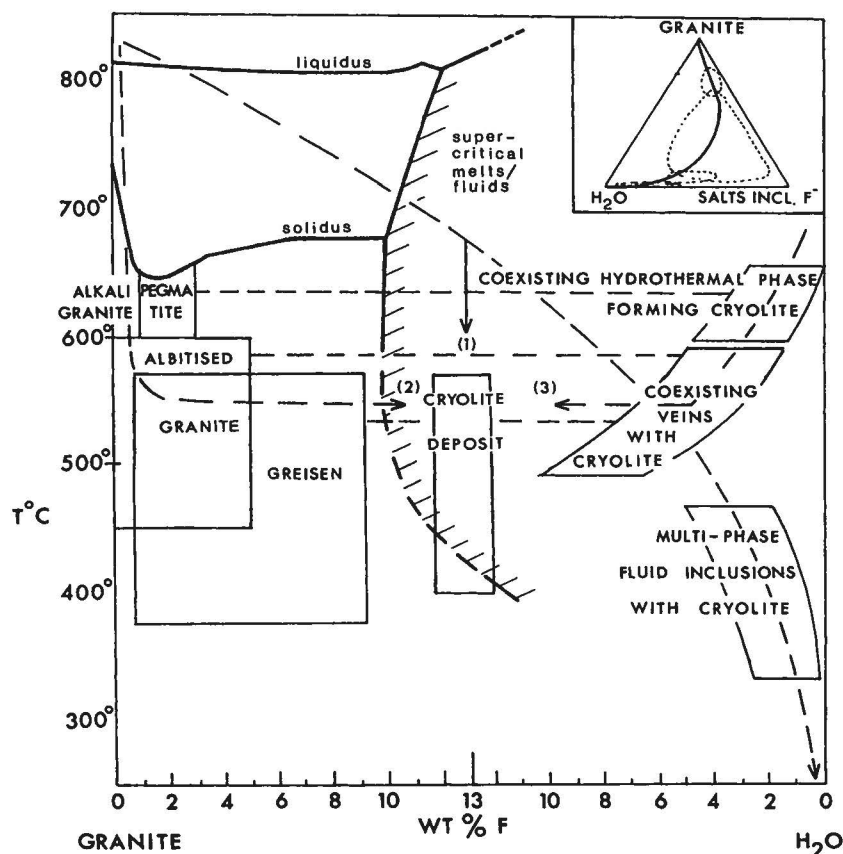

Fig. 21. Schematic diagram of the F-rich granite - H_2O system equivalent to the curving line in the granite - salts - H_2O system (see inset), based on Bailey (1977, Fig. 4) and Bailey (1980). Three geological paths which could lead to formation of the cryolite deposit are indicated and discussed in the text.

posit (path 1 of Fig. 21). Some of the small cryolite-rich pegmatites at Ivittuut could be considered as representing steps in this evolution and it is possible that they preserve melt inclusions indicative of such an evolution.

A second path would allow the Ivigtut granite to solidify, and then pass through a series of post-magmatic metasomatic stages of increasing F before undergoing re-mobilization in an area of maximum F concentration (path 2 of Fig. 21). This model reproduces the observed geological succession in the Ivigtut system, is consistent with the cogenetic character of granite, metaso-matic derivatives and cryolite deposit, and avoids any space problem for the cryolite deposit. After re-mobilization, we envisage the future proto-cryolite deposit as a homogeneous unit composed of a supercritical hydrous alu-minofluoride-rich melt and this is consistent with the well defined margins and textures of the present deposit. Aluminium is a rare element in hydro-thermal deposits but its high contents in the cryolite deposit can be explained by its derivation from pre-existing aluminosilicate rocks. Finally, the model explains why cryolite is exceptionally rare in the granite underlying the cryo-lite deposit but locally abundant in the top granite where it crystallized as the final phase in some albitized and greisenized granites. Cryolite-bearing fluids never ascended through the granite pipe; instead they were formed in situ near the top of the pipe in a proto-deposit by homogenization and remobili-zation of components from several sources.

According to our calculations (Table 4), these components were roughly 50% Ivigtut granite, 35% post-magmatic fluids - rich in volatiles, Na and Si - probably derived from the Ivigtut granite pipe and underlying granite massif, and 15% material released from these same granite sources during post-mag-matic alteration. Some of the radiogenic Sr in post-magmatic fluids and the cryolite deposit was apparently released from the country rocks.

Path 3 would emphasise that cryolite-bearing hydrothermal solutions be-came concentrated in a single locale eventually forming the cryolite deposit. However, the main conduit for such solutions would have to be the deep gra-nite and, as indicated above, there is virtually no evidence for the passage of cryolite-bearing solutions through this granite.

We next explore some of the details and consequences of path 2 which, in our opinion, provides the most realistic model for the formation of the cryo-lite deposit.

Formation and evolution of the proto-cryolite deposit

The clearly delineated character of the cryolite deposit, its sharp, intrusive contacts and coarse grain size relative to the surrounding microgranitic rocks suggest that the deposit at one stage formed a homogeneous fluid mass. We consider that the composition of this fluid mass, allowing for the loss of volatiles such as H_2O and CO_2, is given by the bulk composition of the deposit (Table 3, column 9).

The site of the future cryolite deposit was located beneath the chilled carapace of the Ivigtut top granite and may well have been composed of solidified granite with small pockets of residual pegmatitic material. The three successive facies of the top granite - chilled porphyritic margin, subporphyritic microgranite and the late pegmatite body plus local pegmatitic patches - suggest that a rapidly chilled margin sealed in granite magma whose central areas locally remained molten to lower temperatures. Large volumes of this top granite then underwent alteration and leaching by the first wave of cogenetic post-magmatic fluids which probably rose from the underlying granite massif. These fluids only reacted with the central areas of the top granite. With the breakdown of mafic phases and recrystallization of high-temperature feldspars, considerable tonnages of Fe, Mn, Ca and to a lesser extent Zn, Ba and Sr were released.

It was only during the subsequent albitization of the top granite that significant amounts of cryolite appeared for the first time; Na-F metasomatism produced thousands of tons of albitized granite with 40-60% albite and 5-10% cryolite. Since the intensity of all types of metasomatism increases towards the central areas of the top granite, it is reasonable to suppose that even larger amounts of albite and cryolite formed in the most central areas, the site of the future cryolite deposit.

During subsequent greisenization, large volumes of albite and K-feldspar broke down and abundant Na, K, Al, Si and O were released. In greisens the world over, the released K is fixed in K-mica and Na is lost, but in the Ivigtut system considerable amounts of Na appear to have been retained. Large volumes of Na and Al appear to have combined with the F- and H_2O-rich greisenizing fluids to form a supercritical hydrous aluminofluoride melt. That this melt, even at this stage, was capable of crystallizing cryolite is seen in the thousands of tons of greisen which contain >10% cryolite. The bulk of the aluminofluoride melt, however, remained in the most highly fluxed, central and top part of the Ivigtut granite. We consider that this central area underwent large-scale remobilization forming a new melt chamber, the proto-cryolite deposit.

Samples similar to this proto-fluid mass may be represented by fine-grained m-sized nests rich in cryolite, quartz and siderite which surround dm-sized blocks of microcline just above the deposit in the western wall. Texturally,

these nests show a sequence of metasomatic replacements and did not attain a liquid state. In central parts of the top granite, however, more heavily fluxed nests may have coalesced to form a large and growing fluid mass. The absence of relict, undigested materials within the deposit points to total remobilization; xenoliths are rare and virtually restricted to rock-burst and intrusion breccias around the eastern extension.

Prior to the start of crystallization, the proposed fluid mass may have undergone limited evolution. With cooling, fluids containing a significant proportion of the CO_2, HCl and H_2O in the chamber of the proto-deposit would have escaped and thus enhanced its F-rich character. It is probable that considerable amounts of K, Fe and Ca also escaped in these fluids and were precipitated as phengite, siderite and fluorite in the adjacent and most intensely metasomatized granites. Furthermore, it is likely that later fluids rising up from the cooling granites below had a more normal hydrothermal character and may have contributed significant amounts of H_2O, S and chalcophile elements to the proto-deposit.

It may be possible to locate a distinct generation of veins whose composition corresponds to that of the bulk cryolite deposit.

The margins of the proto-deposit are no longer extant. Where the host rocks around the N, W and S sides of the deposit were cryolite-, siderite-bearing greisens, it can be argued that the proto-deposit and its wall rocks were close to physicochemical equilibrium and that the observed cross-cutting contacts are minor, late movements. However, the pink hydrothermally altered granite surrounding the eastern extension was clearly out of equilibrium and it seems clear that this part of the deposit was mechanically emplaced and crystallized before equilibration with the wall rocks had time to take place. Given a temperature of c. 600°C, cryolite-rich parts of the eastern extension would have been emplaced by plastic flow. The later chimneys which broke through the S and NW margins of the deposit have already been noted. Thus, due to the mobility and explosivity of the deposit at various stages in its history, all original margins of the proto-deposit have been obliterated.

We have argued above that, when the early zone of massive siderite was formed, the deposit was already divided into a fluoride unit overlying a siliceous unit. It seems likely that this fundamental separation came into being during the evolution of the proto-cryolite deposit. But how was it achieved? The experimental evidence from Fe-, Ca-poor granite-H_2O-HF systems (see above) might suggest that formation of the quartz-rich unit was due to early crystallization, sinking and accumulation of quartz crystals from the cooler roof of the chamber. If this took place, we would expect that cm-sized crystals sinking through a chamber nearly 150 m in thickness would accumulate on the chamber floor as a layered, preferentially oriented mass of crystals with the coexisting liquid trapped between the crystals. Instead we observe a jumbled mass of crystals with up to a few percent voids or, in certain zones, large amounts of interstitial siderite with the same sulphides as in the cryolite-bearing units.

Furthermore, quartz is not the earliest phase to crystallize from the cryolite deposit; it was preceded by the rare, Th-rich red-brown fluorite and - in both siderite-cryolite and siderite-quartz - by the abundant siderite. Nor is sinking of low-density quartz through a denser and highly viscous cryolitic melt or mush physically plausible. A preferable mechanism may be the immiscible separation of a fluoridic melt from a siliceous melt. Such a mechanism would probably have been accompanied by dispersion of the same siderite-sulphide component through both the fluoridic and siliceous melts. Immiscibility is widely reported in F-rich silicate melts (e.g. Glyuk & Anfilogov 1973; Gramenitskiy & Shchekina 1993) but further experimental work on compositions closer to the cryolite deposit will be needed to assess this possibility.

The varying evolution of greisens in the different wall rocks around the intrusion may prove a useful monitor of the history of the proto-deposit. Thus it is difficult to understand how greisens in contact with Si-poor siderite-cryolite could have passed through the observed and well-marked stage of silicification. We suspect that the required metasomatic fluids were, in fact, derived from an earlier higher-temperature stage when the proto-deposit was more homogeneous and was thus capable of releasing siliceous fluids to country rocks on all sides. The proposed, later separation into a fluoridic melt above a siliceous melt appears to be consistent with the distribution of the final varieties of greisen, namely greisens with up to 30% cryolite adjacent to siderite-cryolite in the NW quarry wall and greisens with up to 90% quartz adjacent to siderite-quartz immediately below the deposit.

The subsequent geological evolution of the upper, cryolite-rich part of the deposit has been outlined above. The evolution of the lower, siderite-quartz zone is poorly understood.

Finally, we emphasise that the narrowness of the Ivigtut granite pipe and its chilled margins would have provided a powerful means of channelling, concentrating and retaining F-rich fluids rising from the underlying granitic massif and led to the appearance of the world's only economic deposit of cryolite.

Conclusions

(1) The top of the Ivigtut granite pipe underwent a history of magmatic crystallization and consolidation followed by autometasomatism and remobilization leading to formation of a homogeneous hydrous fluoride melt in an independent chamber. The melt from this complex replacement process crystallized to form the cryolite deposit. The deposit was derived from roughly 50% Ivigtut granite, 35% post-magmatic volatiles, Na and Si which were all probably derived from the surrounding granite and underlying massif, and 15% material leached from these same granite sources and from the country rocks.

(2) The components for the three main phases of the deposit - quartz, cryo-

lite and siderite - were already present, and the fundamental division of the deposit by (?)immiscibility into a fluoridic melt overlying a siliceous melt had already been established when the first recorded event in the deposit took place.

(3) The abundance and unique properties of fluorine were the key to the genesis and early evolution of the Ivigtut cryolite deposit: fluorine was readily transported in post-magmatic fluids and became fixed by metasomatic reactions in the roof zone of the granite pipe; aluminosilicate bonds were reconstituted into aluminofluoride bonds; millions of tons of granitic and hydrothermal material were transformed into a Ca-poor supercritical hydrous fluoride melt; immiscibility of this melt in a proto-cryolite deposit may have led to the separation of fluoride and siliceous melt fractions.

(4) In stage 1 of the deposit (11.3 10^6 tons), the intrusion of siderite-cryolite into a small eastern extension of the deposit was accompanied by rock-burst phenomena and violent brecciation of the granitic wall rocks. The two main units of siderite-cryolite and siderite-quartz appear to have crystallized contemporaneously. The siderite-cryolite unit was everywhere characterised by banding/layering and network texture but the origin of these features remains enigmatic. They may eventually be understood in terms of (a) igneous-type in situ crystallization processes or (b) "ice-like" or "salt-like" movements dependent on the plasticity of cryolite. The temperature of consolidation of siderite-cryolite lay between 500 and 600°C. The western part of the siderite-cryolite unit passed into a pure cryolite unit where a subsequent deficiency in Na led to the appearance of chiolite-rich material.

In stage 2 (1.0 10^6 tons), gas-driven explosions led to partial collapse of the pure cryolite roof above a large residual cavity containing Na-poor fluids. This led to crystallization of a fluorite-cryolite breccia unit above a fluorite-topaz unit. Highly fractionated fluids then crystallized unusual H_2O-bearing assemblages rich in Mg (weberite), K ("ivigtite" mica) and Sr-Ba (jarlite-barite-bøgvadite). Two breccia chimneys broke through the margin of the deposit and their xenoliths were cemented by plastically injected cryolite.

In stage 3 (0.08 10^6 tons), the build-up and release of water vapour pressure in the western part of the fluorite-cryolite led to the fluidized emplacement of prosopite and cryolite in fissures. Secondary aluminofluorides - thomsenolite, ralstonite, prosopite, gearksutite, pachnolite and rare cryolite - formed in cavernous masses and smaller cavities by reactions between trapped aqueous solutions and stage 1 cryolite.

(5) The narrow shape of the Ivigtut granite pipe together with its chilled capping led to the channelling and concentration of rising F-rich fluids and resulted in the economic dimensions of the cryolite deposit.

Acknowledgements

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BIOSCIENCE • GEOSCIENCE • MAN & SOCIETY

This book presents the first integrated study on the genesis and evolution of the Mid-Proterozoic Ivigtut cryolite deposit in Southwest Greenland. The three stages in the evolution of the deposit and its main mineralogical, geochemical and isotopic features are reviewed. The deposit formed when F-rich post-magmatic fluids from deeper parts of the Ivigtut granite intensively leached, metasomatized and eventually re-mobilized the top, central part of the granite pipe forming a homogeneous supercritical fluoride melt.

Hans Pauly (1922-1997) was professor in mineralogy, Technical University of Denmark, Lyngby. In a career largely devoted to the geology of the Ivigtut cryolite deposit, he examined in great detail the physical and chemical properties of cryolite and discovered five new minerals.

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