MEDDELELSER OM GRØNLAND

UDGIVNE AF

KOMMISSIONEN FOR VIDENSKABELIGE UNDERSØGELSER I GRØNLAND Bd. 169 \cdot Nr. 9

STENONITE

A NEW CARBONATE-FLUORIDE FROM IVIGTUT, SOUTH GREENLAND

BY

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(X-ray by Mrs. M. Danø, chemistry by Mrs. E-L. Mortensen)

WITH 3 FIGURES IN THE TEXT AND 2 PLATES

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bianco lunos bogtrykkeri a/s 1962

Abstract.

In the revised edition of the Mineralogia-Groenlandica (The Mineralogy of Greenland, O. B. Bøggild (2)) Bøggild mentions the occurrence of small grains of an unknown mineral in a baryte-jarlite sample from Ivigtut. The sample was given to the Mineralogical Museum in 1926. Additional finds of small grains of the mineral were made in 1953 by the author.

In 1955 the mineral was found in cm sized specimens in a matrix of jarlite, and during the summer of 1961 many pieces were collected in the Ivigtut cryolite mine, where the mineral also was found in situ.

The composition of the mineral as calculated from the chemical analysis is ${\rm Sr_2AlCO_3F_5}$. It crystallizes monoclinically—presumably ${\rm P2_1/m}$ —, it has three directions of cleavage, along the basis and two prism faces. It is vitreous, colourless (white). The specific gravity is 3.86 and the hardness nearly $3^1/_2$. The refractive indices are 1.452 and 1.538 for the lowest and highest indices, respectively. The axial angle has been measured at $-2{\rm V}=43^\circ$.

The mineral has been named after the famous Danish scientist Nicholaus Stenonis (Nicholaus Steno or in Danish Niels Ste(e)nsen) (1638-1686) and given the name of *Stenonite*.

Stenonite belongs to a paragenesis developed in the contact-zone between siderite-cryolite (common cryolite ore) and masses rich in fluorite, underlying the ore body in the eastern part of the mine. Cryolite has been replaced by jarlite, weberite and stenonite. The original sulphides have recrystallized and the siderite is partly altered to pyrite and hematite. The temperature interval for these processes seems to have been from about 200°C. and below.

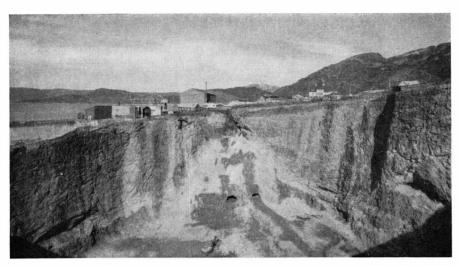


Fig. 1. Ivigtut cryolite quarry as seen from the west. The entrances of the old and the new transportation tunnel are seen just under the middle of the picture. The driving path ends where the new tunnel starts. The stenonite paragenesis was observed a few metres under the entrance of the old tunnel and in the south wall a few metres from the bottom of the pit exactly under the vertical shadow seen in the picture.

INTRODUCTION

The new mineral to be described on the following pages, has already been mentioned in the literature. O. B. Bøggild (2) gives a short note on some observations of a hitherto not identified mineral from Ivigtut:

In an aggregate of jarlite and baryte were found small grains of a mineral with a remarkably high birefringence and with refractive indices 1.46 and 1.54. The mineral proved to be optically biaxially negative. Its optics seemed to indicate that the mineral was a carbonate, but Bøggild finds this to be in contrast to the resistivity which the mineral shows to acids. It does not seem to be attacked by hot acid. The mineral is described as colourless and Bøggild remarks that it is apparently very pure.

In the course of the winter 1952–53 the author found the mineral as small grains in a material mainly consisting of quartz, siderite, and albite together with some jarlite. About fifty milligrams were isolated successfully, and on this material Mr. A. H. Nielsen, chemist at the laboratories of Kryolitselskabet Øresund A/S., carried out a quantitative analysis with the following result:

Sr.Ca: 41%, Ba: 3%, Mg: 1%, Al: 7%. Alkalis counted as Na: 7%.

The latter determination was regarded as not reliable by A.H. NIELSEN and a flame-photometrical determination and a spectrochemical analysis were undertaken with the result that total alkalis hardly could amount to more than one per cent. These determinations were carried out at the laboratories of the Boliden Company, Sweden. The chemical examination further showed the presence of both fluor and carbon dioxide.

The author had an opportunity to discuss these results with the late professor Bøggild. On this occasion Bøggild handed over his material to the author. This material was given to the Mineralogical Museum of the University of Copenhagen 1926 by A/S Kryolith Mine og Handels Selskabet. (The company which at that time undertook mining of cryolite in Ivigtut).

In May 1955 the author found the new mineral in cm-sized specimens in samples of crude cryolite at the plant in Copenhagen, where it was brought with a cryolite cargo from Ivigtut. During the summer of 1961 some large blocks of siderite-cryolite were observed to contain stenonite together with weberite and other minerals. Civil Engineer NIELS LAURSEN, assistant manager of the Ivigtut cryolite mine, with whom the find of these blocks in the stockpile was discussed, informed me that the material in question had been mined in the eastern part of the quarry; see fig. 1. With the relatively large amounts of material from 1955 a better basis for the examinations of the new mineral was established. The nature of the new compound, however, caused that the examinations took a fairly long time before they were brought to an end, and meanwhile other works have likewise caused some delay in the completion of the examinations. A preliminary note was, however, given already in 1955 when a short lecture on the new find was given in the Danish Mineralogical & Petrological Club (Pauly (6)).

In naming the new mineral it had been quite natural to attach O.B.Bøggild's name to it, Bøggild being the first to observe it. At the time when the present author found new samples with the unknown mineral, Bøggild, however, was honoured with the naming of another mineral in that the Na₂Sr₂Al₂(PO₄)F₉ found by Bøgvad (3) by the latter was called *bøggildite*. (See also Nielsen (5) and Pauly & Møller (8)).

After some considerations the astonishing fact was faced that the famous scientist Nicholaus Stenonis (Niels Steensen used this latinized form of his name; he is, however, often mentioned as Nicholaus Steno) had never got his name connected with a mineral. Following discussions partly with other Danish geologists, partly with people

studying Steno's life, etc., it became settled that we could allow ourselves to attach his name to the new mineral found in the cryolite deposit in Ivigtut. To a Danish mineralogist it is of course a great pleasure to be able to honour one of the most prominent Danish scientists within geology. It is fully justified that he has been named one of the founders of geology, especially crystallography, so it is quite natural that his name should be included in the list of minerals named after honourable persons. It is only necessary to point out that he was the first to call attention to the fundamental law for crystals of the constancy of interfacial angles.

In forming the mineral name it was a question whether it should be cast over the Danish form of Steno's name: Steensen as he himself at least once wrote it, or it should be the form Stenonis which should be the basic form. It was, however, decided that the latinized form Stenonis which he himself used on his publications was the safest root and the name of the mineral therefore was finally decided to be

STENONITE.

(At the XXI. International Geological Congress held in Copenhagen in August 1960 the mineral was shown under the label of *Steensenite*).

MINERALOGICAL DESCRIPTION

Fig. 2 shows the new mineral as it was found in jarlite material in 1955. The illustration shows one of the largest individuals of the mineral, about 4 cm in length and about 1 cm wide, the mineral is thought to penetrate several centimetres into the sample, because one finds an individual with the same orientation on the back of the sample.

The mineral is white or colourless, in mm-sized grains it can be quite limpid. The lustre is glassy. Small grains of the mineral often indicate three different cleavage directions through which the pieces attain a parallelepipedic shape resembling the rhombohedral shape seen by carbonates, this is at least valid at a superficial view of the material.

The optical examinations seem to show that the mineral crystallizes monoclinically and that it has the base (001) and two prism faces {120} as directions of cleavage. Goniometer measurings undertaken by H. MICHELLSEN, M.Sc., gave the following results:

(120)
$$\wedge$$
 (1 $\overline{2}$ 0) = 100°45′
(120) \wedge (001) = 102°
 β = 98°10′ ± 20′
a:b = 0.62 ± 0.01.

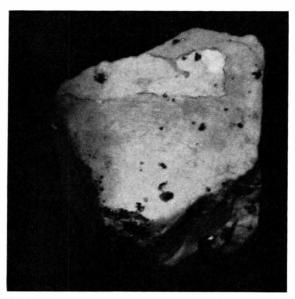


Fig. 2. Massive jarlite with pyrite crystals. Light area, borderline drawn with pencil, is one individual of stenonite 4 cm in length.

The two specimens used for the goniometer measurements have better basal cleavage than prismatic cleavage. This is not, however, in agreement with the observations in the microscope of the frequency of the different interference figures on the faces mentioned; powder preparations have, of course, been used for this examination.

The hardness of the mineral is between 3 and 4, closer to 3 than to 4. The specific gravity (determined on a piece weighing .4149 g by means of a pycnometer) is G = 3.86, with an uncertainty of ± 2 per cent.

The refractive indices for stenonite have been determined by the immersion method. γ was judged to be quite near to ω for quartz, whereas α is less than $^{1}/_{100}$ under the refractive index of the liquid glycerine (ordinary trade quality with ab. 12 per cent water):

$$\begin{array}{c} n_{\gamma} = 1.538 \\ n_{\beta} = 1.527^{1} \\ n_{\alpha} = 1.452 \\ n_{\gamma} - n_{\alpha} = 0.086 \\ -2 \text{ V} = 43^{\circ} \\ c \wedge \gamma = -32^{\circ 1} \\ \alpha = b^{1} \end{array}$$

¹ Determined by H. MICHELSEN, M. Sc.

The carbonate-like character of the mineral, indicated by the cleavage, is likewise remarkable in the microscope, partly due to the rhombic shape of many of the grains, partly due to the high birefringence of the mineral.

X-RAY EXAMINATIONS OF STENONITE

Single crystals as well as crystalline powder of the mineral have been examined by X-rays. In Table I the values of $\sin^2\theta$ for the powder lines are given with their corresponding intensities. This table should be useful for identification purposes. (See Table I).

The Weissenberg and the Precession method have been used to determine the approximate values of the lattice constants. These have been refined by means of the powder technique, using a Guinier camera in order to reduce the high background of the Debye-Scherrer film and

Table I. Diffraction Pattern of Stenonite.

Radiation: CoK_{\alpha}

Camera: 19 cm Bradley type.

No	I	$\sin^2 \theta_{ m obs}$	No	I	$\sin^2 \theta_{ m obs}$	No	I	$\sin^2\theta_{ m obs}$
								,
1	VW	.0597	22	W	.2192	43	vw	.4537
2	S	.0697	23	m	.2291	44	m	.4743
3	W	.0758	24	w	.2359	45	vvw	.4864
4	w	.0805	25	vw	.2387	46	vvw	.4922
5	w	.0819	26	vvw	.2454	47	w	.5023
6	w	.0851	27	m	.2501	48	vvw	.5136
7	vw	.0896	28)	1:00	(.2587	49	vvw	.5388
8	vw	.0964	29	diff.	.2633	50	diff. vw	.5484
9	vw	.1105	30	W	.2743	51	diff. vw	.5536
10	vw	.1156	31	vw	.2799	52	vvw	.5783
11	vvw	.1241	32	vw	.2841	53	w	.6010
12	vw	.1290	33	m	.2887	54	vvw	.6278
13	vvw	.1321	34	diff. vw	.3137	55	vvw	.6333
14	vw	.1352	35	diff. vw	.3229	56	vw	.6980
15	m	.1590	36	diff. vw	.3406	57	W	.7104
16	m	.1645	37	diff. vw(?)	.3809	58	vw	.7241
17	S	.1706	38	w	.3988	59	w	.7374
18	m	.1747	39	m	.4083	60	W	.7426
19	vvw	.1988	40	vvw	.4197			
20	vvw	.2055	41	S	.4326			
21	m-s	.2158	42	vvw	.4422	· .		

Radiation: Co K $_{\alpha}$ +

No	I	$\sin^2 \theta_{ m obs}$	$\sin^2 heta_{ m ealc}^{++}$	hkl	$\sin^2 heta_{ m calc}^{++}$	hkl
1	vvw	.0132	.0154	011		
2	w	.0191	.0190	002		
3	vw	.0291	.0289	$10\overline{1}$		
4	w-m	.0361	.0358	101		
5	VW	.0384	.0383	$\overline{1}10$		
6	w	.0398	.0395	$11\overline{1}$		
7	VW	.0475	.0465	111	.0473	021
8	vvw	.0506	.0503	$11\overline{2}$		
9	m	.0597	.0600	$10\overline{3}$		
10	vvs	.0704	.0701	120		
11	m	.0757	.0759	004		
12	m –	.0809	.0807	103		
13	m	.0824	.0822	$12\overline{2}$		
14	m	.0854	.0865	014	.0852	023
15	vvw	.0961	.0960	$\overline{1}2\overline{2}$		
16	w-m	.1106	.1105	200		
17	W	.1158	.1157	$20\overline{2}$		
18	vw	.1244	.1245	$13\overline{1}$		
19	w	.1292	.1292	015	.1290	105
20	vw	.1324	.1314	131	.1321	$12\overline{4}$
21	W	.1352	.1353	$13\overline{2}$		
22	vvw?	.1555	.1555	$13\overline{3}$		
23	w	.1588	.1588	$20\overline{4}$		
24	w-m	.1600	.1599	124	.1611	025
25	w-m	.1648	.1647	221		
26	w	.1697	.1699	040	.1697	$21\overline{4}$
27	m	.1710	.1708	006		
28	vvw?	.1731	.1742	115		
29	w-m	.1751	.1749	$\overline{2}23$.1763	133
30	vvw	.1889	.1889	042	.1883	116
31	vvw	.1986	.1988	$14\overline{1}$		
32	vvw	.2056	.2052	$\overline{2}15$.2058	141
33	vvw	.2127	.2130	134		
34	vvw	.2141	.2141	204		
35	s	.2168	.2165	223	.2178	231
36	vw	.2208	.2202	$12\overline{6}$		
37	vvw?	.2241	.2245	$13\overline{5}$.2247	214
38	m	.2299	.2299	$14\overline{3}$.2298	116
00	1-1-7	0971	∫ .2359	$10\overline{7}$		
39	w dobb.	.2371	.2370	225		
40	vw	.2400	.2399	$20\overline{6}$		
41	vvw	.2429	.2430	$30\overline{1}$.2431	017
42	vw	.2459	.2458	044		
43	m	.2506	.2506	143	.2504	216
44	vw	.2602	.2602	$30\overline{3}$.2591	135
45	vw	.2618	.2617	126		
46	vw	.2641	.2638	301	.2664	036
47	vvw?	.2699	.2709	$31\overline{3}$.2996	233
48	vw	.2752	.2750	027	.2744	311
49	vw	.2802	.2804	240	.2823	226
50	vvw	.2851	.2844	107	.2856	242
51	v-m	.2896	.2894	$32\overline{2}$.2912	320

 $^{^+}$ The actual radiation was ${\rm CuK}_\alpha,$ but the values of $\sin^2\!\theta_{\rm obs}$ have been changed to the $^{++}$ ${\rm Sin}^2\theta$ is calculated from $\sin^2\!\theta=0.02763\,h^2+0.01062\,k^2+0.004745\,l^2+0.00346\,hl.$

⁺⁺⁺ The intensity values marked with * are from Precession film, the rest from Weissen-

Indexing of Stenonite.

Camera: Guinier type.

$\sin^2 \theta_{ m calc}^{++}$	hkl	hkl	I+++	hkl	I+++	hkl	1+++	
		011	vvw					•
		002	w					
		$10\overline{1}$	vw					
		101	vw					
		Ī10	vvw					
		$11\overline{1}$	w					
		111	vvw	021	w			
		$11\overline{2}$	vvw	0_1				
		$10\overline{3}$	w					
		120	vs					
		004	w-m					
		103	w					
		$12\overline{2}$	m					
		014	w	023	m			
		$\overline{1}2\overline{2}$	vw	0.00	***			
		200	m					
		$20\overline{2}$	w-m					
		$13\overline{1}$	m*					
		015	w	$10\overline{5}$	W			
		131	vvw	$12\overline{4}$	w			
		$13\overline{2}$	m-s*					
		$13\overline{3}$	w*					
		$20\overline{4}$	w-m					
		124	m	$02\overline{5}$	vvw			
		221	m					
		040	m*	$21\overline{4}$	vvw			
		006	\mathbf{m}					
		115	vw*					
		$\overline{2}23$	\mathbf{m}	133	vvw*			
		042	m*	$11\overline{6}$	vw			
		$14\overline{1}$	w*					
.2061	230	$\overline{2}15$	vw	141	vw*	230	w*	
		134	w*					
		204	w					
		223	m	231	w*			
		$12\overline{6}$	m					
		$13\overline{5}$	wm*	214	vvw			
.2280	$23\overline{3}$	$14\overline{3}$	s*	116	vvw	$23\overline{3}$	_	
		$10\overline{7}$	m					
		$22\overline{5}$	m					
		$20\overline{6}$	w					
		$30\overline{1}$	vw	017	vw			
	-	044	vs^*					
		143		$21\overline{6}$	m			
		$30\overline{3}$	m	135	w*			
		126	m					
		301	m	036	w-m			
.2702	051	$31\overline{3}$	vvw	233	_	051	w*	
		027	m-s	311	vw*			
		240	s*	$22\overline{6}$	m			
	052	107	w	$24\overline{2}$	w*	052	w*	
.2845	052	101	YY.	212				

corresponding values for CoK_{α} .

oerg film.

to improve the resolution. As the unit cell is rather large we have many more or less overlapping powder lines. Our Guinier camera registers only powder lines with $\sin^2\theta$ values up to 0.5000, but the indexing is very uncertain for the higher values anyway.

Table II gives measured values of $\sin^2\theta$ up to 0.2900. $\operatorname{CuK}_\alpha$ radiation has been used for exposure, but $\sin^2\theta$ has been recalculated to $\operatorname{CoK}_\alpha$ radiation to make comparison easier between the two tables. The lines have been indexed and the corresponding values of $\sin^2\theta$ calc. are given. We have made use of single crystal films in order to decide between the many possibilities for indexing a powder line. The last columns of the table give the intensities of the single crystal reflexes. (The values from the Precession films are starred and are perhaps not quite so reliable as the rest). It should be kept in mind that only intensities within the same film can be directly compared and that a powder line will be composed of reflexes with the same spacing, but not always the same intensity. (See Table II).

We have found the following lattice constants.

$$\begin{array}{lll} a &=& 5.447 \, \pm \, 0.002 \; \mathring{A} \\ b &=& 8.688 \, \pm \, 0.004 \; \mathring{A} \\ c &=& 13.14 \, \pm \, 0.01 \; \mathring{A} \\ \beta &=& 98^{\circ}20' \, \pm \, 5' \\ V &=& abcsin\beta = 615.0 \; \mathring{A}^3 \end{array}$$

The number (z) of molecules in the unit cell is given by

$$z = \frac{N \times V \times d}{M} = 4.005,$$

where

$$\begin{array}{ll} N = Avogadro's \ number = 0.6023 \times 10^{24} \\ d = density & = 3.863 \ g/cm^3 \\ M = molecular \ weight & = 357.2 \end{array}$$

(The ideal formula Sr₂AlCO₃F₅ has been used for calculating M, not the composition given by the chemical analysis).

As reflexes hol with 1 uneven or h uneven are not extinct, there is no c- or a-glide plan in the structure. The lattice cannot be centred, as we find reflexes hkl with h+k and k+l uneven. Possible space groups are then P2, P2₁, Pm, P2/m and P2₁/m.

From Precession films of okl it is seen that the only oko reflex (including 050) not extinct is 040, so a 2₁-axis is very likely. A Weissenberg film of okl and hko would contain more oko reflexes and would

therefore give a more definite answer. No piezoelectric effect is found, so $P2_1/m$ is a likely space group.

We hope to be able to make a complete structure determination and thus determine the space group with certainty.

CHEMICAL ANALYSIS OF STENONITE

The material selected for the chemical analysis was optically judged to contain nearly 3 per cent of the mineral jarlite. Other impurities were judged negligible.

1	2	3	4	5	6
	Wt. º/o	Corr. for jarlite Wt. ⁰ / ₀	Rem. Wt. ⁰ / ₀	4. recal. to 100 °/ ₀	Ion fractions
Sr	47.08	1.19	45,89	47.48	0.542
Ba	1.09	0.03	1.06	1.10	0.008
Ca	0.01	0.01	0.00	0.00	
Na	0.58	0.11	0.47	0.49	0.021
Al	7.73	0.36	7.37	7.63	0.282
F ¹	27.13	1.29	25.84	26.74	1.407
CO ₃ ²	16.00		16.00	16.56	0.276
он	n.d.	0.09			
	99.62		96.63	100.00	

Table III. Analyst: E-L. Mortensen.

	Ion fractions	Dispersions	Number of ions
$Sr + Ba + Ca + Na$ Al F CO_3	$0.571 = 2 \times 0.285$ $0.282 = 1 \times 0.282$ $1.407 = 5 \times 0.281$ $0.276 = 1 \times 0.276$	1.39/0	2 1 5 1

 $^{^1}$ Found through melting with $\rm Na_2CO_3$ followed by distillation with $\rm H_2SO_4$. In the distillate precipitation with PbClF and F-calculation is based on the determined Cl.

In addition to the chemical analysis of stenonite above the following results have been obtained through spectrographical examinations of

 $^{^2}$ The sample is disintegrated in diluted HCl. The generated CO_2 absorbed on soda asbest and calculated as weight increase of it.

	Wt. $^{\rm o}/_{\rm o}$	Equivalents
Sr	47.08 1.09	1.075 0.016
Ca	0.01 0.58	0.016 0.001 1.975 0.024
Al	7.73 27.13	0.859
$\mathrm{CO_3}$ OH 1	16.00 0.09	1.533 1.972 0.011
	99.71	0.011

Table IV. Calculation of equivalents.

the material. These examinations were carried out at the spectrographic laboratory of the Mineralogical Museum by Mr. Ib Sørensen, Civil Engineer:

As appears from what precedes, the material for analysis was rather pure. The only impurity to occur in noticeable amounts was jarlite and it is not directly seen in the analytical values. After deduction of the main elements for this mineral according to its analysis the formula for stenonite can be calculated and, as is seen, the result is $\mathrm{Sr}_2\mathrm{AlCO}_3\mathrm{F}_5$. This formula immediately reveals the singular character of the new mineral. The known fluo-carbonates parisite ($\mathrm{Ce}_2\mathrm{Ca}(\mathrm{CO}_3)_3\mathrm{F}_2$), cordylite ($\mathrm{Ce}_2\mathrm{Ba}(\mathrm{CO}_3)_3\mathrm{F}_2$), synchisite ($\mathrm{Ce}(\mathrm{Ca}(\mathrm{CO}_3)_2\mathrm{F})$), bastnäsite ($\mathrm{Ce}(\mathrm{Co}_3)\mathrm{F}$) and ancylite, remarkable by its content of Sr , can all be regarded as irrelevant material for comparison in respect of stenonite. This is also valid for the various compound halides.

In Ivigtut the mineral bøggildite was found some years ago. It was shown to be a phosphate fluoride Na₂Sr₂Al₂(PO₄)F₉, but it is also not comparable to stenonite. Judging from the optical characteristics there is no doubt about the carbonate character of the new mineral. Hence it seems reasonable to classify it as a carbonate fluoride. It seems to

¹ Calculated after deduction of 3 per cent jarlite.

constitute a new group among compound halides. Whether there is a connexion to the fluo-carbonates can only be decided by future examination of the material.

THE PARAGENESIS OF STENONITE

The composition of the new mineral in the Ivigtut assemblage clearly places it together with the minerals jarlite and bøggildite. Because the latter has to be characterized as a mineral belonging to a very special paragenesis, dependent on the presence of certain elements in its formation, it is of no great interest in this connexion. As to jarlite we first and foremost have to note that stenonite occurs together with this mineral.

The latest published formula for this mineral is NaSr₂Al₂F₁₁. Whether this is the correct formula and the final answer to the jarlite question or not, has not yet been found out. The occurrence of jarlite together with stenonite, however, shows that the new mineral occurs together with a mineral where besides Sr and Al also alkalis belong to the main constituents in contrast to stenonite, where no alkalis enter the formula.

In all samples stenonite has been found together with jarlite, the most important Sr-mineral in Ivigtut, but in addition to this, the following minerals have also been observed in the material here treated:

* Pyrite	st Cryolite	o Thomsenolite	\mathbf{Baryte}	Topaz
* Sphalerite	Stenonite	o Pachnolite	Barytoce-	Ivigtite
			lestine	
* Chalcopyrite	$\mathbf{Jarlite}$	o Ralstonite	* Siderite	Albite
* Galena	Fluorite	o "Cubic Minerals"	Hematite	Muscovite
	Weberite	o Prosopite	Magnetite * Quartz	

As is seen, it is a numerous and variegated mineral assemblage in which stenonite occurs. All these minerals can, however, be arranged in groups. The first group includes minerals which have been replaced to some degree or recrystallized during the processes giving rise to the stenonite paragenesis. Minerals of the first group have been marked with an asterisk. The minerals formed during the following processes might be divided in a group of earlier minerals, water-free, and a later group, minerals containing water. The minerals belonging to the former group

are principally jarlite, weberite, and fluorite, besides stenonite, and minerals belonging to the latter series are principally thomsenolite, ralstonite and prosopite. The latter group has been marked with o in the list of minerals. Minor constituents of the assemblage of minerals are the sulphates and silicates together with some of the sulphides. They belong either to one or more of the groups mentioned. Pyrite for instance occurs together with minerals of all groups. Ivigitite, the greenish K-mica, seems to occur together with pyrite, but it is more frequent in such parts of the specimens as seem to represent the later stages of formation, the stage characterized by formation of minerals containing water.

Plate I, fig. 1 and fig. 2 are photos of two sides of the same sample. Conspicuous in both pictures are the white rectangular areas lined by a narrow black sulphide rim. In appropriate light the rectangular area on Plate I, fig. 2 can be seen to consist of one individual of stenonite (for the main part of the area at least). It therefore seems reasonable to suppose that the shape of the area has been created by the growth of the stenonite crystal. It was the reflexes of light in this particular piece of material which drew attention to the unusual paragenesis and caused the author to collect it in the heaps of crude ore just arrived at Copenhagen in 1955.

In Plate I, fig. 1 jarlite constitutes the main part of material inside the double rectangular area pictured. Stenonite, however, constitutes a noticable amount of the material present. It seems possible that jarlite has replaced stenonite, a phenomena rather often met with in thin sections of this material. The shape of the area might therefore also in this case originally have developed through the growth of the new mineral.

From the observation of the sample in the picture it should be noted that the Sr-bearing minerals jarlite and stenonite form a clearly defined zone between, on the one hand, surrounding cryolite and, on the other, a rather fine-grained intergrowth of fluorite and weberite. In the latter new-formed quartz (maybe also recrystallized quartz is present), some topaz, jarlite, etc., are present. Weberite and fluorite constitute the main components. Sulphides are found mainly within the Sr-bearing minerals and only as a minor constituent outside this zone. Pyrite dominates, but some sphalerite occurs, too.

The dark triangular area in Plate I, fig. 2 to the right of the white rectangular area represents a rather fine-grained aggregate of quartz, siderite, and a little hematite, it seems to indicate original siderite, now replaced by quartz and a little hematite together with some recrystallized siderite. Along the borderline of this dark area occur small pyrite crystals indicating that some of the iron of the original siderite has been converted into this iron sulphide. In other places of the same sample corresponding

areas are to be found. They show varying amounts of siderite to be present. The dark colour is mainly due to the presence of hematite together with or intergrown with the quartz.

It seems worth noting that siderite occurs together with the other minerals of the paragenesis. Whether the siderite recrystallized or simply has been preserved through the whole formation of the stenonite paragenesis is of less importance. The main thing is that siderite could exist in the environment where stenonite formation took place. As the temperature indications we have for this assemblage seem to indicate temperatures at or below 200° C, the existence of siderite only points to partial pressure of CO_2 at about a few mm Hg.

The material just described constitutes the primary minerals within the stenonite paragenesis. The fluorides are water-free and on the whole they form compact masses. In the material from this find there are, however, several pieces containing minerals characteristic of the so-called secondary minerals in Ivigtut: thomsenolite, pachnolite, ralstonite, prosopite, etc. Plate I, fig. 3, illustrates this.

In the picture one can observe a partly concentric structure in the material. It consists of weberite with a good deal of fluorite besides some sulphide grains, both pyrite and sphalerite. Along the border of the concentric figure several larger pyrite crystals occur. They are all surrounded by thomsenolite. From the look of the piece it is clear that this part of it represents formations in or at a void or open space. Thomsenolite and the other fluorides containing water dominate this environment and in many cases can be seen to form a "box-work" structure. Such a structure is in other places of the cryolite deposit taken as evidence of secondary replacement of cryolite. There is no reason for not accepting the same view here, but at the same time it seems reasonable to place the thomsenolite-forming processes at the end of a series of processes which in their beginning gave rise to the formation of stenonite, followed by jarlite together with weberite and fluorite.

In the lower part of Plate I, fig. 3, can be seen an inclined thin vein which mainly consists of prosopite with minor amounts of thomsenolite, ralstonite, etc. This vein intersecting the whole mass certainly represents the product formed latest in the present material. This is also in good agreement with observations elsewhere in the deposit, where prosopite is found to fill cracks and line fissures in cryolite.

Here and there in the samples crystal-lined cavities occur. Most crystals in these cavities are thomsenolite and other minerals of that kind, such as ralstonite. But in several cases one can observe crystals or crystal aggregates of jarlite. Such aggregates may be compared with stilbite in the way they are built up and the term sheaf-like aggregates may be appropriate here. In contrast to the common development of

jarlite these sheaf-like aggregates may reach cm or half-cm size, the common type only attaining sizes of the order of one or two mm. Pyrite is often found close to the cavities and always with well-developed crystal faces. In several cases nicely developed crystals of sphalerite may be observed in the cavities. Stenonite has never been found developed as free crystals in this environment. The formation of the latter mineral obviously took place before the formation of minerals also crystallizing into the cavities, and formation of free crystals of jarlite in cavities are only seen in a number of the samples some distance away from places where thomsenolite is dominating. Weberite and fluorite have not developed free crystals in cavities. The build-up of specimens into certain zones, stenonite-jarlite zone and weberite-fluorite zone, seems to favour the view that the latter was formed at an earlier stage than the former, in which way also an explanation of the absence of crystals of weberite and fluorite seems to be given. It should be kept in mind that fluorite also seems to have been formed at some later stage together with thomsenolite, because in a few samples thomsenolite seems to have grown to a large size, several cm across, poikilitically including fluorite and other minerals.

The material in which Bøggild first observed the new mineral was chiefly composed of baryte. It was pronounced porous with an appearance as if some interstitial mass had been dissolved and carried away. Stenonite occurred here as tiny crystals scattered in the sample, only to be observed in thin sections. The baryte is not conspicuous, because this mineral so to say belongs to what can be termed the normal jarlite paragenesis. The porous character of the sample closely corresponds to the "boxwork" structure formed by thomsenolite in stenonite samples and elsewhere, but it should be emphasized that this structure in the case of Bøggild's sample only consists of baryte. As stressed by Bøggild it is interesting to note this skeleton growth of baryte in which one optical orientation governs the whole mass, in other words, showing the presence of a 20 cm-sized baryte specimen. Although the appearance of the specimen reminds of the thomsenolite "box-work", it seems doubtful whether one should see a replacement of cryolite in it.

As mentioned above, siderite can be seen here and there in the stenonite material. Certain samples are even rich in siderite. Of special importance is the marked brecciation exhibited by these pieces, the brecciation followed by a transformation of the siderite into hematite and pyrite. It seems beyond doubt that these pieces illustrate the alterations of siderite and its accompanying minerals through the action of those processes which formed the stenonite paragenesis.

The special character of some samples deserves mentioning. These are the pieces found in 1952–53. They were rich in siderite and albite.

The latter is rather rare in the cryolite ore itself and here it is evidently replacing original cryolite, thus illustrating the intensity with which also silica has taken part in the replacement processes. Ivigtite, which is a ubiquitous mineral in those parts of the cryolite deposit characterized by the presence of fluorite, is also present here. It is a K-mica and mainly because of its compact fine-grained form and green colour it has got a specific mineral name years ago when also analysis of such material wrongly was found to indicate the presence of Na in this mica. In the stenonite material the ivigtite often appears in mm-sized greenish-yellow crystals, only rarely found elsewhere in the deposit. The intermediate refractive index for this type is 1.59 and -2V lies between 30 and 40°.

A sample from a diamond drilling in which were found some stenonite and jarlite, contained a beautifully developed violet mica in cmsized leaves. Spectrographic analysis, carried out at the Spectrographic Laboratory of the Mineralogical Museum, Copenhagen, only indicated Li as traces in the mica. It seems to be a K-mica. X-ray powder examination gave diagrams resembling muscovite.

Thin sections of the compact white parts of material illustrated in Plate II, fig. 1 and 2, reveal how jarlite occurs incorporated in stenonite. Jarlite occurs as embayments in stenonite, as wedge-shaped areas extending into stenonite and as veins through stenonite. In places a mechanical deformation of the stenonite seems to have taken place and the scattered pieces of this mineral are seen to have been moulded together by jarlite. The picture of the two minerals, as seen in the microscope, seems to indicate simultaneous crystallisation, but the formation of jarlite seemingly continued for some time after the consolidation of stenonite.

Observations on the ore minerals in the stenonite paragenesis:

In an attempt at further elucidation of the formation of stenonite and its accompanying minerals some notes concerning the opaque minerals are to be given. The following ore minerals have been observed:

> Pyrite Hematite Sphalerite Magnetite Galena Covelline Boulangerite Chalcosite Chalcopyrite

This mineral assemblage is nothing out of the common. Some of the otherwise common accessory minerals from Ivigtut sulphides (see Pauly 1960 (7)) are even missing.

The more interesting features about these minerals are, however, their mutual relations. Plate II, fig. 3, illustrates this rather well. It is easily seen how the sphalerite is surrounded by a thin mantle of galena. The galena cover on the sphalerite grains is really so thin that it seems justifiable to call it a film on the sphalerite. Examination of polished samples of this material did not reveal sphalerite grains without this "galena-film". In other words, it seems to be a characteristic feature of this material that all grains of sphalerite have been covered by a thin layer of galena. With a lens one can also see that sphalerite grains often have a silvery look due to this coating.

Chalcopyrite mainly occurs as inclusions in the sphalerite, where it often can be seen in nicely developed, oriented intergrowth with the host. In this respect the relations are much like those found in the common cryolite ore (see Pauly 1960 (7)). There are, however, certain discrepancies, of a negative kind. Neither cubanite nor valleriite — or relicts of these mixed crystals between chalcopyrite and pyrrhotite — have been observed in the sulphide minerals in the stenonite material. Even though the sphalerite appears very light, poor in iron, the environments are rich in iron, both as pyrite, siderite and oxides. If one is allowed to draw conclusions on this basis, it seems as if the temperature of formation has not been high enough to allow the formation of the above—mentioned mixed crystals of the copper and iron sulphides. As this temperature is assumed to be as low as 225°C for the stable formation of valleriite it might indicate a temperature of formation for the stenonite paragenesis lower than this, (see Borchert 1934 (1)).

Sphalerite occurs in the compact mass of jarlite and stenonite, it occurs in the weberite, and it occurs together with pyrite in or at the cavities mentioned above. In all cases it has the same appearance. In order to determine the iron content of this sphalerite an amount of it has been taken out from parts of a sample with cavities, where large amounts could easily be collected. The result of the determination is seen in Table V. The temperature indicated by this method is fairly low, about 150°C, but it must be noted that the content of iron is just under the lower limit of the examples given by Kullerud in his paper on temperature indications by iron content in sphalerite, Kullerud (4).

The various ways of estimating the temperature during the processes forming the stenonite paragenesis are rather inconclusive, as is evident from the preceding sections, in spite of this it is the author's opinion that the material as such points to formation temperatures about 200°C. For a majority of the products formation temperatures down to about 150°C should be assumed.

Pressure indications other than the existence of siderite have not been noted. From the existence of siderite we might conclude that a

	Wt. ⁰ / ₀	Wt. ⁰ / ₀ as mono- sulphide	Mol. º/o
Fe	2.3 0.17	3.6 0.26 96.1	4.0 0.28 95.7

Table V. Analyst: C. H. HOLTEN.

partial pressure of carbon dioxide, about a few mm Hg, prevailed during parts of the formation.

The existence of baryte or celestine in only two samples (O.B. Bøggild and a sample from a diamond drill core) and the total absence of sulphates, whereas sulphides, mainly pyrite, are present in the new stenonite material, seem to indicate that oxidizing and reducing processes obviously do not affect the formation of stenonite.

THE OCCURRENCE OF STENONITE IN THE IVIGTUT DEPOSIT

Most of the stenonite material used for the description has been found as "boulders" in ore shipments to Copenhagen from Ivigtut. As mentioned above, stenonite occurrences were located in the eastern part of the quarry in the summer of 1961. Before that a careful search for the new mineral was carried through in samples from various places in the mine. In this way the presence of stenonite was noted in material from several diamond drillings and in material from a minor area of the south wall of the pit.

In all cases but two the new mineral was observed as minute grains — less than $10\,\mu$ in diameter — and not very frequent either. Due to the optical properties of stenonite it is, however, easily recognized even in such small grains.

The material in which these observations were made consisted mainly of jarlite, but also contained some of the minerals found together with stenonite as described above. A number of the samples were taken from diamond drillings in the south wall of the quarry and chosen because the material had an appearance recalling the stenonite paragenesis:

 $^{\rm 1}$ Baryte has later been found in material from the large block shown on fig. 3. (added in proof).

¹ Calculated assuming sample pure sulphide. Determinations of impurities were not possible due to lack of material.



Fig. 3. Block, about 1 meter in diameter, containing stenonite in large patches together with weberite, jarlite, fluorite and other minerals. The upper right part of the block containing much siderite (dark) with some hematite. Cryolite is present together with the siderite and dominates on the hidden side of the block. White zigzag area to the right of the pencil mainly consists of albite. Stenonite occurs for example immediately under the pencil. Pencil 13 cm long.

White masses of fluorides sprinkled with pyrite crystals. Material from an area in the lower part of the south wall where jarlite had previously been found, exhibited masses with such an appearance and the microscopic work revealed minute grains of stenonite here, too.

As mentioned, two occurrences showed stenonite in visible amounts, the one localized in the summer of 1961 and a diamond drilling from the western part of the quarry. Fig. 1 shows the eastern part of the Ivigtut mine. The entrance to the transport tunnel is seen in the middle of the picture where the driving path on the mine floor ends. To the left the older tunnel-entrance is seen. It is the entrance used up to a few years ago. A few metres below this, material quite similar to stenonite material was found and it was shown to contain the mineral itself just as the boulders hitherto known. Moreover, it was to this part of the mine that Civil Engineer N. Laursen localized some large blocks with plenty of stenonite.

The situation of stenonite in this locality as well as in the other places mentioned is much the same. The surroundings are rich in jarlite and it is close to or in the borderzone of siderite-containing ore and fluorite masses.

The occurrence located by diamond drilling in the western part of the quarry is a little different from the finds mentioned. It was found in the core from about 20 m below the mine floor and more than 100 m away from the localities mentioned, stenonite was found in cm-sized grains together with jarlite, weberite, celestine, and a violet mica, as mentioned above. Just as in the above-mentioned localities stenonite here again has developed near the border of the deposit in the vicinity of an internal boundary between siderite-containing materials and fluorite-bearing masses.

DISCUSSION

The above-mentioned finds strengthen the view already gained from the examination of the stenonite "boulders":

Stenonite belongs to such parts of the deposit where large amounts of Sr is present (indicated by the presence of jarlite).

Stenonite is found close to borderzones where siderite-bearing materials meet fluorite masses.

The picture fig. 3 — block of typical stenonite material — illustrates this very well. Siderite cryolite in the upper right part of the block contains some hematite formed through the conversion of siderite. The lower left part of the block consists of weberite and jarlite, and here and in the middle part of the block stenonite occurs.

The siderite material where stenonite was found (fig. 1) is characterized by bordering on fluorite masses and the occurrence of nests of weberite and jarlite inside the siderite materials. The appearance of these masses clearly demonstrates that later alterations took place in and near the siderite-fluorite borderzone after the siderite formed. The alterations in the siderite materials have given rise to minerals generally found in the fluorite mass, and also to the formation of specific minerals such as stenonite and hematite.

A relation between siderite-cryolite and masses rich in fluorite of which the former is the older, is quite in keeping with observations in other places of the deposit.

The processes giving rise to the paragenesis with the new mineral must have started with the introduction of the elements Sr, Mg, and Ca, the elements necessary in the formation of jarlite, stenonite, weberite and fluorite. The minerals formed at the closing stage of the whole formation indicate addition of K (in the mica), OH, and presumably also some Si. Whether a removal of Na has taken place together with minor amounts of the other elements present in the original mineral assemblage or Na in toto has been bound in the formation of the jarlite, weberite, and albite cannot be decided.

Considering the siderite-cryolite which is thought to represent the original material, it is seen to be much poorer in sulphide than the replacing materials represented in the stenonite paragenesis. At the same time one notes that the proportions between the sulphides in the old and in the new mineral assemblage has been radically altered. In siderite-cryolite (see Pauly 1960 (7)) the dominating sulphides are galena, chalcopyrite, and sphalerite, but in stenonite material pyrite dominates, and sphalerite comes next to it; the other sulphides only form minor amounts here. Siderite-cryolite with dominating sphalerite is well-known, but also this is of quite another character than the stenonite material.

The much larger amounts of sulphides, S mainly represented in pyrite, seem to indicate the introduction of S to the environment, and the altered proportions between the sulphides compared to the original material seem to indicate removal of certain elements, presumably Cu and Ph.

The added sulphur in most cases appears as sulphide in the stenonite material and only in two samples noticeable amounts of sulphates occur. This seems to be of less importance to the occurrence of stenonite itself, but it might be of some interest to note that the common jarlite environment so to say is characterized through the presence of sulphates (as opposed to the so-called metajarlite), but together with stenonite we have jarlite without these sulphates and it must be called jarlite because it has an optical appearance indicating a rather well crystallized state together with the fact that crystal aggregates of the mineral can be seen in cavities in the material.

The recrystallisation of the sulphides, or more specifically one might say that the mobilization of the sulphidically bound elements caused by the recrystallisation seems to have been followed by a removal of Cu and Pb. Some Cu has, however, been kept together with the sphalerite in which it now forms well developed oriented inclusions, and some of the Pb has been deposited as a thin coating on the earlier formed sphalerite crystals. The chalcopyrite inclusions in the sphalerite are quite similar to the common inclusions found in sphalerite from sideritecryolite. In the latter this intergrowth is taken as a sign of chalcopyrite exsolution in the sphalerite. If the same interpretation can be used for the stenonite material it must be admitted that chalcopyrite exsolves in sphalerite at rather low temperatures in the vicinity of 200°C. One might of course regard the chalcopyrite inclusions as remnants from the original paragenesis, but the sphalerite has a very homogeneous look in the microscope, and because of the occurrence of free crystals developed in the cavities, and the lack of zoning in regard to the placing of the chalcopyrite in the sphalerite grains (no chalcopyrite-free outer zone of the grains), one is apt to regard the sphalerite formation as a total redeposition or recrystallisation not allowing the preservation of relicts from an earlier existence. It is clear beforehand that these considerations in which an attempt has been made to clarify the formation conditions for stenonite must also have validity for the accompanying minerals, such as jarlite, weberite, and part of the fluorite. It seems that these minerals have in part been formed at lower temperatures than stenonite, and minerals such as thomsenolite and ralstonite, etc., have been formed at even lower temperatures. Such considerations have to be in keeping with the formations of these minerals in other parts of the deposit, and there are, indeed, a great many features in common to the stenonite environment and the more frequent occurrences of the other minerals. Further treatment of the common environment of these minerals connected with the fluorite-bearing parts of the deposit will appear later.

June 1961.

Hans Pauly.

ACKNOWLEDGMENTS

Most sincere thanks are given to Kryolitselskabet Øresund A/S for the opportunity to carry through the investigations described above and for the permission to publish the result.

Civil Engineers Mrs. E-L. MORTENSEN and Mrs. M. Danø have given the author most valuable help in his work with the description of this new mineral through their cooperation in the fields of chemistry and structural determinations. For this the author wishes to offer his cordial thanks.

Besides it should be stressed that several of the members of the laboratory staff have given valuable help and inspiring discussion of the various problems of these investigations. The author is much indebted to Mr. C. H. Holten, M. Sc., Mr. H. Buchwald, Civil Engineer and Miss K. Jensen.

Mr. H. Micheelsen, M. Sc., has carried out goniometer measurements, Mr. Ib Sørensen, M. Sc., has made spectrographic determinations, and for this I would like to express my best thanks.

Special thanks are given to Mr. A. H. NIELSEN for his great interest in the problem and for his painstaking work with determination of the chemical composition on the minute quantities which in the beginning of these investigations were at hand.

I also owe sincere thanks to my assistants years ago Miss Mona Hansen, Mr. Aage Jensen, and Mr. Stig Bak Jensen, who took part in the collection of the material from the shipments of raw cryolite.

The revision of the English language of the manuscript was carried out by Mr. Niels Haislund, M.A.

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Plate I.

- Fig. 1. Light-coloured rhombic areas are intergrowths of stenonite and jarlite. On the right above the dark area, mostly pyrite, cryolite is seen. The central part of the specimen mainly consists of jarlite and stenonite, whereas the lower part is built up of fluorite and weberite. The dark rhombic borderline contains sulphides, mostly sphalerite and some pyrite. Specimen 14 cm high.
- Fig. 2. Top of hand-piece consists of cryolite. Dark rectangular line (mostly sphalerite) surrounds white stenonite single individual. Under this area some cryolite is seen. The dark area on the right consists of quartz with hematite and siderite (rather fine-grained). The main part of the specimen consists of jarlite, weberite and fluorite. Scattered pyrite crystals and some siderite are seen as dark spots and patches. Specimen 14 cm high.
- Fig. 3. Concentric figure made up of weberite and fluorite. Jarlite is present mostly outside the concentric figure, where also some stenonite occurs. Black grain in the concentric figure is sphalerite. Pyrite crystals and some thomsenolite make up the outer left part of the sample. Thin vein of prosopite cuts through the sample from the inner corner (right side of sample) to lower left corner of sample. Specimen 12 cm across.



Fig. 1.

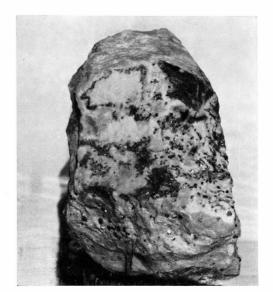


Fig. 2.

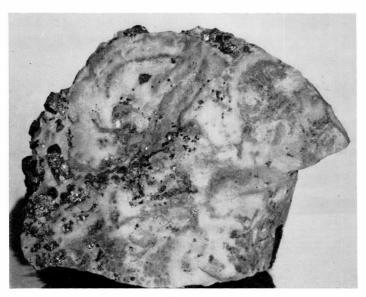
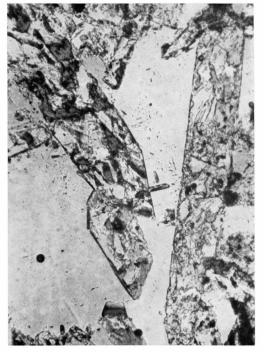


Fig. 3.

Plate II.

- Fig. 1. Thin section, crossed nicols, $120 \times$. Stenonite veined and replaced by jarlite, mechanical fragmentation of stenonite also seems indicated.
- Fig. 2. Thin section, crossed nicols, $35 \times$. Replacing vein of jarlite in stenonite.
- Fig. 3. Polished prep. plane view, $180 \times$. Sphalerite, with neatly arranged inclusions of chalcopyrite and surrounded by a thin mantle of galena, situated in stenonite-jarlite.



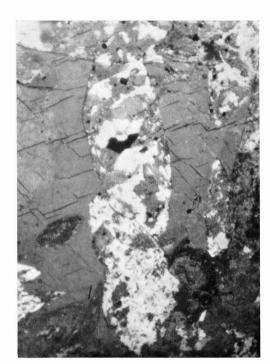


Fig. 1.

Fig. 2.

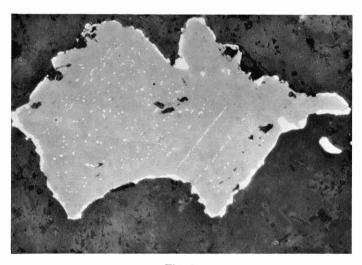


Fig. 3.