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CONTRIBUTIONS TO THE MINERALOGY OF ILÍMAUSSAQ Nos 20–21

KØBENHAVN 1971

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- 20 On the mineralogy and paragenesis of tugtupite Na₈Al₂Be₂Si₈O₂₄ (Cl, S)₂ from the Ilimaussaq alkaline intrusion, South Greenland....... H. Sørensen, M. Danø and O. V. Petersen.

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ON THE MINERALOGY AND PARAGENESIS OF TUGTUPITE

 $Na_8Al_2Be_2Si_8O_{24}$ (Cl, S)₂

FROM THE ILÍMAUSSAQ ALKALINE INTRUSION, SOUTH GREENLAND

BY

HENNING SØRENSEN, MARIANNE DANØ

AND

OLE V. PETERSEN

CONTRIBUTION TO THE MINERALOGY OF ILIMAUSSAQ No. 20

WITH 14 FIGURES AND 6 TABLES IN THE TEXT, AND 9 PLATES

KØBENHAVN
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1971

Abstract

Tugtupite, Na₈Al₂Be₂Si₈O₂₄(Cl,S)₂, is colourless to red, tetragonal, pseudocubic and forms triplet twins on {101}. c:a = 1.0269 ± 0.0003 , d = 2.33 g/cm³. $n_{\rm g} = 1.499 \pm 0.001$, $n_{\rm W} = 1.495 \pm 0.001$. $a_{\rm 0} = 8.637 - 8.643$, $c_{\rm 0} = 8.867 - 8.870$, $V_{\rm 0} = 662$ Å³. The description of the crystal structure is taken from Dang (1966). The mineral occurs in hydrothermal veins in the Ilimaussaq alkaline intrusion, South Greenland, and in the Lovozero alkaline intrusion, Kola Peninsula (beryllosodalite). A number of occurrences of tugtupite in Ilimaussaq are described.

Tugtupite is most commonly associated with albite, analcime and Li-mica and is generally secondary after chkalovite. The paragenesis and origin of the mineral and a number of associated beryllium silicates are discussed.

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INTRODUCTION

A new mineral discovered in 1957 by one of the authors (H. S.) in the coastal cliffs of Tugtup agtakôrfia on the north coast of the Tunugdliarfik fjord was described under the provisional name of "beryllium sodalite" in the reports of the International Geological Congress, Norden (Sørensen, 1960). Additional data were published in the discussion volume of the congress (Sørensen, 1963) and it was suggested that the new mineral should be named tugtupite. This is derived from the locality in which the mineral was found first.

Coinciding with the presentation of the new mineral from South Greenland a description of apparently the same mineral was published by Semenov & Bykova (1960) on material from the Lovozero intrusion in the Kola Peninsula. It was demonstrated that the mineral from Lovozero is related to sodalite but that the crystal symmetry is not cubic.

In 1965 The I.M.A. Commission on New Minerals and Mineral Names approved the name tugtupite for the new mineral since the chemical and physical properties of the mineral are distinctly different from those of sodalite.

In 1966 M. Danø described the crystal structure of tugtupite and demonstrated that the crystals are tetragonal with the space group $I\bar{4}$ (Danø, 1966).

Mineralogy

General description

Tugtupite is vitreous, white, pink or carmine red in hand specimen, but the colour is strongly variable. The varieties displaying strong colour preserve this colour under all conditions. The weakly coloured varieties may change colour so that they are pale or white after being kept in darkness, pink when exposed to sunshine. Strong colouration may be produced by, for instance, X-ray radiation, and this colour does not disappear when the sample is placed in darkness.

Usually the mineral forms fine-grained crystalline aggregates which may attain sizes of several centimetres. Locally tugtupite forms small crystals on the walls of cavities in massive tugtupite. The well developed crystals are short prismatic, transparent, colourless to pale pinkish, and range in size from $1 \times 1 \times 1$ mm to $3 \times 2 \times 2$ mm.

Several crystals found lining two small cavities in a sample from Tugtup agtakôrfia were measured on the two circle goniometer. Some of the matt faces could not reflect the light, and their positions were therefore determined on the universal stage. The stereogram fig. 1 gives all the faces found.

The forms developed are: $\{100\}$ matt, $\{001\}$ shiny, $\{110\}$ shiny, $\{101\}$ shiny, $\{2\overline{1}1\}$ shiny, $\{2\overline{1}1\}$ matt and $\{1\overline{1}1\}$ matt). $\{2\overline{1}1\}$ and $\{1\overline{1}1\}$ are represented only by faces measured on the universal stage (table 1).

According to the stereogram (fig. 1) tugtupite belongs morphologically to the crystal class $\overline{4}2$ m. The crystals display positive piezoelectric effect and lack a positive pyroelectric effect (Danø, 1966, p. 813).

The axial ratio, calculated by means of the measured angles (101): $(\overline{1}01)$ and (011): $(0\overline{1}1)$, is c:a 1.0269 ± 0.0003 . (Errors correspond to mean deviation from the mean value of the measured angles (001): $(\overline{1}01)$ and (001): $(0\overline{1}1)$). The ratio determined from X-ray diffraction studies is c_0 : $a_0 = 1.0271 \pm 0.0002$ and 1.0260 ± 0.0002 for red tugtupite (Kvanefjeld plateau) and white tugtupite (Taseq) respectively.

The largest crystals, which show the simplest combinations of faces, are prismatic, bounded by {110} and {001}. The smaller crystals, which are short prismatic, show combinations of tetragonal prisms, pyramid, sphenoid and bisphenoids. Fig. 2 shows a drawing of an idealized crystal ({111} not shown).

Fig. 1. Stereographic projection showing all the faces measured. Open circles shiny faces, black circles matt faces and concentric circles matt faces measured only on the universal stage.

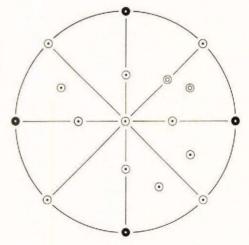


Table 1. Interfacial angles measured and calculated. The calculations are based on the axial ratio determined by direct measurement of the angles $(101):(\bar{1}01)$ and $(011):(0\bar{1}1)$

	Measured angles	Calculated angles
(100):(010)	90°00′00′′ ± 60′′	
(100):(001)	90°00′00′′ ± 60′′	
(001):(011) (001):(101)	$45^\circ 45^\prime 38^{\prime\prime} \pm 30^{\prime\prime}$	
(001):(211)	$66^{\circ}28'00'' \pm 60''$	66°28′02′′±23′′*
(110):(211)	29°36′00′′ ± 60′′	$29^{\circ}34'12'' \pm 18''$
(101):(211)	$30^{\circ}00'40'' \pm 60''$	29°59′34″ ± 2″

^{*} Margin of error corresponding to the mean deviation from the mean value of the measured angles (001):(101) and (001):(011), assuming that the crystals are tetragonal.

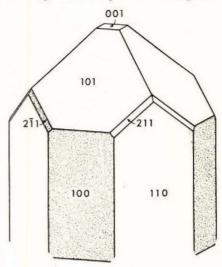


Fig. 2. Drawing of an idealized crystal of tugtupite, see the text.

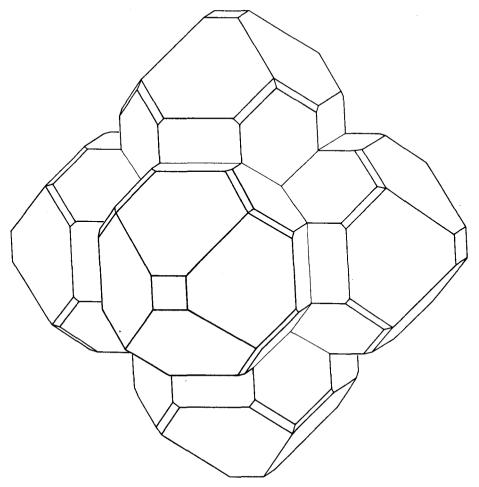


Fig. 3. Drawing of an idealized pseudocubic triplet, twin planes {101}.

The density has been determined to be 2.33 ± 0.01 g/cm³ for both red and white tugtupite. The density calculated from the chemical analysis and the unit cell volume presented in table 4 is 2.35 and 2.34 g/cm³ for red and white tugtupite respectively.

Optical properties

Under the microscope the mineral is transparent and colourless. There is a distinct cleavage parallel to {101} and a fair cleavage parallel to {110}, corresponding to the {110} cleavage in sodalite.

The mineral displays an intricate penetration twinning (figs 3 and 4), which in some samples is rather coarse, with the individuals attaining sizes of 1 mm. The twin plane has been measured to be (101). In other



Fig. 4. Penetration triplet in tugtupite (no.64750,1; Kvanefjeld) 17.8 x, + nic. Twin planes are {101}. The microphotograph has been taken with crossed nicols, $\lambda = 491 \, \mathrm{nm}$ and with addition of a phase difference of app. 440 nm to make the (001) section nearly black but the (100) and the (010) sections different. (H. MICHELSEN phot.).

samples the twinning is of a rather gritty type, the individuals being visible only at high magnification (plate 8, fig. 1). In the coarsely twinned grains the single individuals display an irregular extinction which may be a result of a submicroscopic twinning. This problem is undergoing a special study.

The mineral is optically positive and is uniaxial or has a small axial angle (up to about 10°).

The refractive indices of red and white tugtupite were measured by means of the λ -T variation method (Michelsen, 1957) by Mr. R. Waagstein. No measurable difference in the refractive indices n_{α} and n_{β} has been observed in the biaxial varieties.

Table 2 gives the refractive indices of a number of samples of tugtupite and of the beryllosodalite described by Semenov & Bykova (1960).

Table 2. Refractive indices of tugtupite from three different localities in Ilímaussaq and of beryllosodalite from Lovozero

	Red tugtupite, Kvanefjeld plateau		White tugtupi- te, Tugtup ag- takôrfia (Sø- RENSEN, 1960)	Beryllosodalite, Lovozero (Semenov & Bykova, 1960)	
$n_{\gamma} = n_{\varepsilon} \dots \dots $ $n_{\alpha} = n_{\beta} = n_{\omega} \dots $ $n_{\varepsilon} - n_{\omega} \dots \dots $	$ \begin{aligned} 1.499 &\pm 0.001 \\ 1.495 &\pm 0.001 \\ 0.005 &\pm 0.002 \end{aligned} $	$ \begin{aligned} 1.499 &\pm 0.001 \\ 1.495 &\pm 0.001 \\ 0.005 &\pm 0.002 \end{aligned} $	$ \begin{aligned} 1.502 \pm 0.002 \\ 1.496 \pm 0.001 \\ 0.006 \pm 0.002 \end{aligned}$	~1.495	

The birefringence of the red tugtupite from the Kvanefjeld plateau seems to be slightly higher than that of the white tugtupite from the Taseq slope.

X-ray diffraction

X-ray powder diagrams of red tugtupite from the Kvanefjeld plateau and white tugtupite from the Taseq slope were taken in a Guinier-Hägg camera. Quartz was used as internal standard.

In the final calculations the reciprocal lattice constants were adapted by the least-squares method to the observed $\sin^2\theta$ values. These calculations were carried out on the GIER computer, made available to the Copenhagen Observatory by the Carlsberg Foundation. A programme (REFBASE-2) made by Mr. E. S. Leonardsen, head of the X-ray laboratory of the Mineralogical Institute of the University of Copenhagen, was used.

The calculated $\sin^2\theta$ values are compared with the observed values in table 3. Table 3 also presents $\sin^2\theta_{\rm obs.}$ and hkl given by Danø (1966). The lattice constants determined from these sets of $\sin^2\theta$ values are presented in table 4. It can be seen from table 3 and table 4 that there are small but in no way significant differences between the red and the white tugtupite. In fact three other powder diagrams show that the variation inside the red and the white tugtupites is of at least the same order of magnitude.

According to Danø (1966) tugtupite is tetragonal, space group I4. The crystal structure of tugtupite is very closely related to that of sodalite. Cl is placed in the corners and the centre of the unit cell, tetrahedrally surrounded by Na. Al, Si and Be are surrounded by slightly distorted oxygen tetrahedra which share corners. The arrangement can most easily be visualized in the following way: On (or very close to) each face of the unit cell are 4 Al, Si or Be atoms, connected with oxygen to make 8-rings. Two of the oxygen atoms are above the plane, two below. The "free" O-atoms belonging to such a ring are shared with metal

Table 3. The table shows $\sin^2\theta_{obs.}$ and $_{calc.}$, $^dhkl_{obs.}$ and hkl of two slightly different tugtupites (see also table 4), red and white tugtupite from the Kvanefjeld plateau and the Taseq slope respectively, and $\sin^2\theta_{obs.}$ and $_{calc.}$ and hkl of white-pink tugtupite from Tugtup agtakôrfia given by Danø (1966)

Red	tugtupite from the Kvanefjeld plateau White tugtupite from the Taseq slope			е			pite from Tu Danø, 1966)	ıgtup					
Int.	$\sin^2\! heta_{ m obs}$.	$\sin^2\!\theta_{ m calc.}$	dhkl _{obs} .	hkl	Int.	$\sin^2 \theta_{ m obs.}$	$\sin^2\theta_{ m calc}$.	dkhl _{obs} .	hkl	Int.	$\sin^2\! heta_{ m obs.}$	$\sin^2\! heta_{ m calc.}$	hkl
7	0.01556	0.01552	6.179	101	9	0.01553	0.01551	6.187	101	s	0.0158	0.0157	101
4	0.01593	0.01593	6.107	110	5	0.01596	0.01591	6.103	110	vw	0.0162	0.0161	110
4	0.03023	0.03021	4.434	002	5	0.03028	0.03023	4.430	002	w	0.0306	0.0306	002
3	0.03190	0.03187	4.316	200	4	0.03183	0.03183	4.321	200	vvw	0.0323	0.0323	200
7	0.04615	0.04615	3.589	112	10	0.04615	0.04614	3.589	112	m	0.0467	0.0467	112
10	0.04740	0.04739	3.541	211	10	0.04740	0.04734	3.541	211	vs	0.0480	0.0480	211
					i					vvw?	0.0630	0.0628	202
2	0.06387	0.07374	3.050	220	2	0.06377	0.06365	3.053	120	vvw	0.0647	0.0645	220
4	0.07598	0.07594	2.797	103	4	0.07600	0.07598	2.796	103	vw	0.0770	0.0769	103
4	0.07923	0.07926	2.739	301	5	0.07938*	0.07916	2.736	301	vw	0.0803	0.0802	301
3	0.07965	0.07967	2.732	310						vvw	0.0808	0.0807	310
5	0.09390	0.09395	2.516	222	7	0.09391	0.09388	2.516	222	m	0.0952	0.0951	222
4	0.10789	0.10781	2.347	213	5	0.10782	0.10780	2.348	213	w	0.1093	0.1091	213
4	0.10986	0.10988	2.326	312	4	0.10981	0.10979	2.326	312	w	0.1113	0.1112	312
4	0.11105	0.11112	2.313	321	5	0.11097	0.11099	2.314	321	w	0.1126	0.1125	321
					2	0.12700*	0.12730	2.164	400?				
4	0.13684	0.13678	2.084	114	5	0.13682	0.13684	2.084	114	w	0.1384	0.1384	114
5	0.13959	0.13968	2.063	303	7	0.13957	0.13963	2.063	303	w	0.1413	0.1414	303
		0.14299		411			0.14281		411			0.1448	411
5	0.14300*		2.039		7	0.14300*		2.039		m	0.1451		
	ļ	0.14341]	330		Į.	0.14321		330			0.1452	330
3	0.15758	0.15768	1.942	402	4	0.15754	0.15753	1.942	402	vw	0.1595	0.1596	402
						İ				vvw	0.1612	0.1613	420

Table 3 (cont.)

Red tugtupite from the Kvanefjeld plateau					7	White tugtup	ite from the	e Taseq slop	e			pite from Tu Danø, 1966)	
Int.	$\sin^2 \theta_{ m obs.}$	$\sin^2\!\theta_{ m calc.}$	dhkl _{obs.}	hkl	Int.	$\sin^2 \theta_{ m obs.}$	$\sin^2\!\theta_{ m calc}$.	dhkl _{obs.}	hkl	Int.	$\sin^2\theta_{ m obs.}$	$\sin^2\!\theta_{ m calc.}$	hkl
3	0.17136	0.17155	1.862	323	4	0.17134	0.17145	1.862	323	vw	0.1738	0.1737	323
2	0.18451	0.18458	1.795	224	3	0.18454	0.18458	1.795	224	vvw	0.1868	0.1869	224
3	0.18922	0.18955	1.772	422	4	0.18941	0.18935	1.771	422	vw	0.1918	0.1919	422
					2	0.20066	0.20049	1.721	314	vvw?	0.2026	0.2030	314
					2	0.20332	0.20327	1.710	413	vw	0.2062	0.2059	413
		0.20673		501			0.20646		501				
4	0.20656*		1.696		5	0.20659*		1.696					
	i	0.20673		431			0.20646		431	w	0.2093	0.2093	431
				İ	2	0.22875	0.22873	1.612	215	vvw	0.2314	0.2315	215
												0,2403	512
	1				1					vvw?	0.2410		}
					3	0.23811	0.23828	1.580	521			0.2416	521
4	0.24823	0.24832	1.547	404	5	0.24822	0.24822	1.547	404				
2	0.25510	0.25495	1.526	44 0	4	0.25458	0.25459	1.528	440				
					3	0.26050	0.26055	1.510	305			-	
		0.26715		503			0.26692		503				
3	0.26715*		1.491		4	0.26693*		1.492				İ	
		0.26715		433			0.26692		433				
					1	0.27207	0.27209	1.478	006		•		
3	0.28018	0.28019	1.456	424	4	0.28003	0.28005	1.457	424				
3	0.28526	0.28516	1.443	442	4	0.28479	0.28482	1.445	442				
1	0.28678	0.28681	1.439	600					Į į				
3	0.29255	0.29239	1.425	325	4	0.29236	0.29238	1.426	325				
3	0.29919	0.29902	1.409	523	4	0.29880	0.29875	1.410	535				
3	0.30100	0.30109	1.405	532		0.30081	0.30074	1.406	532				

^{*} Values which enter into the final calculations with the weight 0.0.

Table 4. Unit cell parameters of red tugtupite from the Kvanefjeld plateau, white tugtupite from the Taseq slope, and white-pink tugtupite from Tugtup agtakôrfia (Danø, 1966)

	Red tugtupite, Kvanefjeld plateau	White tugtupite, Taseq slope	White-pink tugtupite, Tugtup agtakôrfia (Danø, 1966)
a ₀	$8.637 \pm 0.001 \text{Å} \\ 8.870 \pm 0.002 \text{Å} \\ 1.0271 \pm 0.0002 \text{Å} \\ 662 \text{Å}^3$	$\begin{array}{cccc} 8.643 \pm 0.001 & \text{\AA} \\ 8.867 \pm 0.001 & \text{Å} \\ 1.0260 \pm 0.0002 & \text{Å} \\ 662 & \text{Å}^3 \end{array}$	$8.583 \pm 0.004 \mbox{\AA} \\ 8.817 \pm 0.004 \mbox{\AA} \\ 1.0273 \pm 0.0006 \mbox{ Å} \\ 658 \mbox{ Å}^{3}$

atoms of an 8-ring on another face. In holes between the rings there are Cl atoms with 4 Na around them. In tugtupite the rings on (001) are pure Si-O rings while the rings on (100) and (010) have 1 Be, 1 Al and 2 Si alternating in agreement with the tetragonal symmetry. There is thus an ordering of Si, Al and Be, as was suggested by Semenov & Bykova (1960).

The following bond lengths were determined by Danø (1966).

Be
$$-0 = 1.608 \pm 0.012$$
 Å
Al $-0 = 1.762 \pm 0.014$ Å
Si $-0 = 1.601 \pm 0.008$ Å

Chemistry

The chemical analyses of tugtupite from Ilímaussaq and Lovozero are reproduced in table 5. Apart from the high content of water in the sample from Lovozero the two analyses are practically identical, although the Lovozero sample is richer in Al₂O₃ and poorer in SiO₂, Na₂O and Cl than the sample analysed from Ilímaussaq.

The formula of the mineral is calculated as

which when compared with the formula of sodalite

$${
m Na_8Al_6Si_6O_{24}Cl_2}$$

indicates that there is a substitution of BeSi for AlAl in the sodalite structure. This accounts for the lower symmetry of the tugtupite.

Table 5. Chemical analysis of tugtupite from Ilímaussaq, metal atoms in 100 g as presented by Danø (1966), and chemical analysis of beryllosodalite as presented by Semenov & Bykova (1960).

	Tugtupite from	Beryllosodalite from Lovozero		
	Weight percent	Metal atoms in 100 g	Weight percent	
SiO ₂	51.58	0.861	50.45	
Al ₂ O ₃	11.15	0.219	12.56	
Fe ₂ O ₃	tr			
Ga ₂ O ₃	(0.035)*		0.043	
BeO	5.40	0.216	5.30	
MgO	0.20	0.005	war.	
CaO	-		0.50	
Na ₂ O	25.52	0.822	23.26	
K ₂ O	0.12	0.002	0.40	
H ₂ O+			1.50	
H ₂ O	0.03		1.51	
s ⁻	0.33	0.010		
C1	7.28	0.205	6.04	
$-0 = Cl_2, S \dots$	1.80		1.40	
Total	99.81		100.16	
Analyst	ME MOURITZEN	•	A. V. Bykova	

^{*} Determined in the laboratories of IMGRE, Moscow.

Differential thermal analysis and thermogravimetric analysis

The differential thermal analysis of red tugtupite from the Kvane-fjeld plateau shows a weak exothermal reaction at about 190°C (peak temperature about 240°) and a distinct endothermal reaction at about 990°C (peak temperature about 1040°C), the latter corresponding to the melting of the mineral.

According to Danø (1966, p. 813) X-ray powder diagrams showed no change in symmetry when the mineral was heated to the melting point.

The thermogravimetrical analysis of red tugtupite indicates a loss of Cl and S, starting at about 890°C and continuing up to at least about 4020°C.

Luminescence and colour

POVARENNYKH, PLATOV, TARASHCHAN & BELICHENKO (in press) have examined the visible region of the spectral absorption curves and

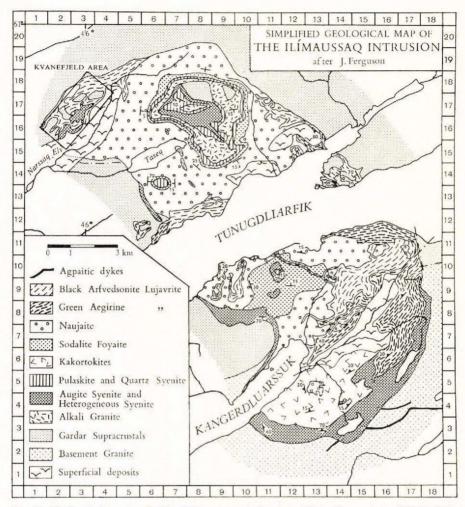


Fig. 5. Geological map of the Ilímaussaq intrusion after Ferguson (1964). The coordinates of the localities are: Tugtup agtakôrfia 8,12; Head of Kangerdluarssuk 12,7; Kvanefjeld 3,16; Taseq region 5,15.

the luminescence spectrum of tugtupite from Ilímaussaq. It is suggested that the luminescence is caused by S_2^- molecular ions occupying the position of the Cl ions in the crystal structure. These ions are also responsible for the colour of the mineral, but other, thermally less stable, radiation centres may also play a role.

Mode of occurrence

Tugtupite has been found in many places all over the Ilímaussaq intrusion (fig. 5). The mineral is confined to hydrothermal veins inter-

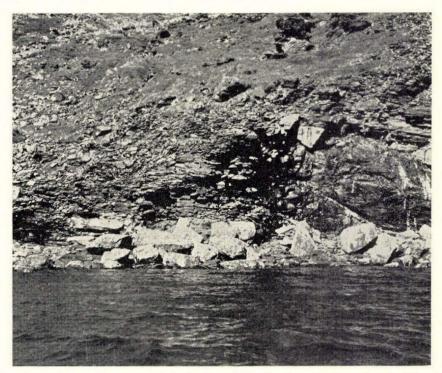


Fig. 6. Tugtup agtakôrfia. Inclusions of naujaite (white) in laminated and schistose lujayrite.

secting poikilitic sodalite syenite (naujaite) and syenite. The mode of occurrence has been studied in a number of localities, namely Tugtup agtakôrfia, the head of Kangerdluarssuk, Qeqertaussaq, Kvanefjeld and the Taseq plateau.

1. Tugtup agtakôrfia

Tugtup agtakôrfia, a small point on the north coast of the Tunugdliarfik fjord, is the type locality of tugtupite.

The point is made up of black lujavrite with big inclusions of naujaite (fig. 6). Tugtupite occurs as a granular mass in a vein of albitite, 30–50 cm thick and practically vertical, intersecting one of the bodies of naujaite (Sørensen, 1960 and 1962). The vein does not intersect the lujavrite overlying (and enclosing) this body of naujaite (figs 7 and 8).

Albite is the predominant mineral of the major part of the vein. It is either sugary or cleavelanditic. In the latter case the laths are set at right angles to the vertical contacts. In cavities there are small tabular crystals of albite.



Fig. 7. Two vertical veins of albitite (centre and centre right) in naujaite enclosed in lujavrite. Tugtup agtakôrfia. The tugtupite locality is found in the uppermost part of the left vein (see also fig. 8). The dark rims are of acmite + steenstrupine.

Scattered through the granular albitite are grey patches of microcline which are partially replaced by albite. Accessories are epistolite, yellow sodalite, Li-mica, schizolite, steenstrupine, sphalerite, acmite and arfvedsonite, all of which may occur in large concentrations around patches of analcime. The borders of the vein are enriched in acmite and steenstrupine. Ussingite and tetragonal natrolite have been found in one sample of the border zone (Andersen, Danø & Petersen, 1969).

The uppermost part of the vein is made up of brown masses up to 20 cm across of analcime which display a distinct cubic cleavage. There are also aggregates of white, brown or transparent icositetrahedra of analcime up to 1 cm across, often in vugs. In the analcime there are small "screens" of white albite. Yellow sodalite, sphalerite and prismatic crystals of schizolite are found in the cavities partially filled with crystals of analcime. These crystals have white films of tetragonal natrolite. Tugtupite is confined to the lowermost part of this analcime rock, and is found about 70 cm below the upper contact of the vein (figs 8, 9 and 10).

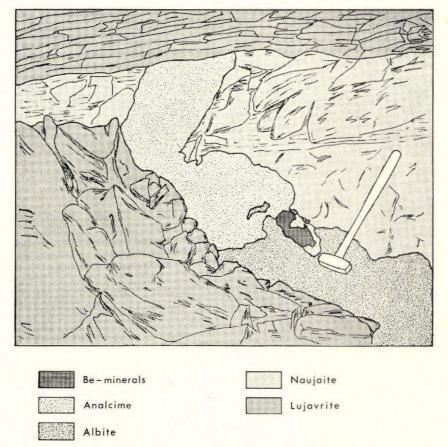


Fig. 8. Tugtupite-bearing part of albitite vein at Tugtup agtakôrfia. Hammer handle about 40 cm long. The lujavrite in the left foreground is not in place but consists of boulders.

This almost pure analcime rock is underlain by albitite with scattered analcime and is separated from the overlying lujavrite by a black zone of arfvedsonite, 1 cm thick.

The uppermost part of the analcime rock is clearly formed at the expense of naujaite since it contains corroded and altered remnants of naujaitic sodalite, microcline and eudialyte. The poikilitic structure is well preserved.

This analcime-rich part of the vein has inclusions of acmite and steenstrupine near the contact with the naujaite, indicating that the acmite-steenstrupine marginal zone of the albitite has been partially replaced by the analcime.

Tugtupite forms an irregular, fine-grained mass up to 40 cm across, which appears to send a network of thin veinlets into the adjacent

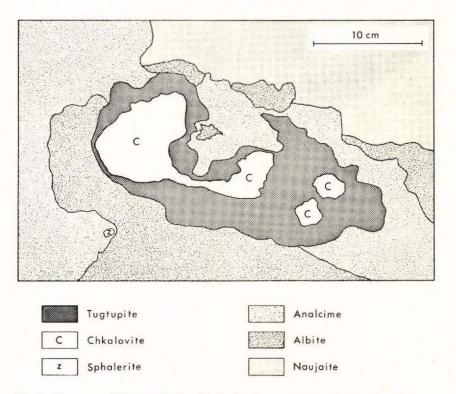


Fig. 9. Close-up of the tugtupite-chkalovite intergrowth at Tugtup agtakôrfia.

analcime-albite rock. The tugtupite contains large masses of chkalovite up to 10 cm across, and there are also scattered areas of analcime, often in the form of discrete crystals. The chkalovite is intersected by veinlets of fine-grained tugtupite. These veinlets, which may be only a millimetre thick, swell to thicknesses of several centimetres, in which cases there often are cavities containing small crystals of tugtupite.

Under the microscope (sample nos. 21059 A and B) it can be seen that the grains of chkalovite enclosed in tugtupite are deformed (undulatory extinction) and are intersected by zones of crushing in which the chkalovite forms small rounded grains. These zones are partially replaced by tugtupite (plate 1, fig. 2).

The chkalovite is generally enclosed in the tugtupite, but scattered grains of chkalovite have been found in analcime-rich areas in albitite (sample nos. B 1 and B 3). The age relation between chkalovite and albite is difficult to determine. Inclusions of albite of corroded appearance and of microcline and analcime in the chkalovite may be due to a "thin section effect" since the grains of chkalovite enclosed in albite are of amoeboid outline. The chkalovite is in places in direct contact with albite



Fig. 10. Same as fig. 9. The pencil (16 cm long) is placed on the tugtupite-chkalovite. The white mineral is albite, the grey is analcime (note crystals to the left), the black (top and bottom) is acmite-steenstrupine margin of vein.

while in other places it is separated from that mineral by granular masses of tugtupite. Chkalovite appears to be corroded by analcime, which may contain inclusions of albite.

The areas of analcime in the albitite adjacent to the tugtupite-rich area contain corroded grains of albite and appear to be formed later than the albitite. The analcime areas are surrounded by a branching network of thin veinlets of analcime and natrolite which penetrate into the albitite. There may be patches of tugtupite along the margins of the "geodes" of analcime.

Tugtupite occurs as granular masses in which the grain size varies from 0.5 mm in the thin veinlets to about 1 mm in the thicker masses with gradual transitions. The tugtupite grains are generally of irregular outline and thus display an interlocking type of intergrowth (plate 2, fig. 1).

The tugtupite contains aggregates of small flakes of Li-mica, and there are inclusions of chkalovite, albite, microcline (plate 2, fig. 2), sodalite, analcime, epistolite, schizolite, arfvedsonite, sphalerite, aegirineaemite and steenstrupine.

The veinlets of tugtupite intersect not only the chkalovite but penetrate into the albite and microcline of the enclosing albitite. The twin lamellae of the albite are intersected by these veins.

The relations between tugtupite and analcime are less clear. The two minerals have straight or faintly lobate mutual boundaries. There are inclusions of analcime in the tugtupite, and tugtupite crystals are found in interstices between analcime crystals, favouring the view that tugtupite is later than analcime.

When considering the age relations of the minerals it should be mentioned that the chkalovite enclosed in tugtupite often shows signs of deformation, while that enclosed in albite is undeformed. The laths of albite are also undeformed.

2. The head of Kangerdluarssuk

Danø & Sørensen (1959, fig. 3) and Sørensen (1962, p. 28 and p. 111) have described a one metre thick vertical vein intersecting crumbling naujaite near Lilleelv at the head of the fjord. The vein is composed of fine-grained aegirine and albite with minor amounts of analcime, sodalite and natrolite.

Patches of the vein are composed of crystals of aegirine and steenstrupine up to 1 cm or more across in a fine-grained groundmass of albite, microcline, ussingite, aegirine needles, sodalite, analcime and natrolite. Accessories are lovozerite, sphalerite, galena, chkalovite, tugtupite, Limica, igdloite, britholite, schizolite and, along the margins of the vein, eucolite.

The coarse-grained patches have been studied in sample nos. 18468 and 21149. The ussingite clearly replaces microcline. Fractures in the eucolite and the interstices between the aegirine crystals are mainly occupied by ussingite and, to a lesser extent, by Li-mica, albite and microcline. As albite is predominant around the eucolite and aegirine grains, this may indicate that the ussingite was formed earlier than the albite. This is difficult to establish in the matrix because albite and ussingite have interlocking boundaries.

Large grains of sodalite are set in a fine-grained groundmass of albite, aegirine, steenstrupine and lovozerite, and they are penetrated by ussingite and albite.

Chkalovite occurs as large and small grains with rounded or irregular outlines. They are generally surrounded by thin zones of fine-grained tugtupite, although chkalovite has been observed in direct contact with albite, ussingite and microcline. There is most often a rim of fine-grained albite between the tugtupite-chkalovite and the ussingite. The zone of tugtupite is thicker at these places than where the albite rim is lacking.

Chkalovite borders on eucolite and aegirine and is penetrated by prismatic crystals of schizolite. The tugtupite rims contain inclusions of eucolite, aegirine, microcline, albite, sphalerite (partly altered into hemimorphite), lovozerite, steenstrupine, Li-mica and britholite. Small needles of aegirine are orientated as in the adjacent green rock.

A few metres to the west of the above-mentioned vein, in the gravel covering the crumbling naujaite, there is a train of boulders of albitite. Even if polygonal structures (patterned ground) with cross sections up to two metres are well developed in this gravel, the train of albitite boulders has been traced with very few interruptions and practically without displacement for more than 100 m.

The vein appears to be about 20 cm thick and is mainly made up of albite, sugary as well as cleavelanditic.

In the marginal part of the vein and in the adjacent naujaite there are large masses of yellow sodalite which contain corroded remnants of naujaitic minerals and thus partly replace that rock. This sodalite is intersected by veins of felt-like aegirine branching out from a dense green rock which occurs between the sodalite and the albitite of the central part of the vein. The sodalite is also cut by thin veins of albite with varying, sometimes high, contents of microcline in the cores. These veins occupy cleavage fractures in the sodalite (plate 3, fig. 1).

The marginal dense green rock is composed of interlocking fibres of aegirine with interstitial arfvedsonite, albite and igdloite. This rock is partly replaced by albite and is cut by veinlets of albite from the central part of the vein.

The partly replaced dense green rock was studied in thin section nos. 66131, 66132, 66134 and 66135. In addition to aggregates of irregularly shaped grains of albite and numerous needles of aegirine, which are sometimes bent, there are scattered laths of microcline and amoeboid areas of analcime up to 0.5 cm across. The latter may have cores of sodalite (plate 3, fig. 2). The analcime in places forms a very irregular interstitial network in the albitite. This albite-analcime rock contains scattered grains of chkalovite which have rounded, strongly corroded outlines. They are enclosed in albite-analcime; there are spots of very fine-grained tugtupite (?) along their margins.

This marginal part of the vein furthermore contains steenstrupine, lovozerite, epistolite, Li-mica, schizolite, britholite and pseudomorphs after eudialyte. It is cut by veinlets of natrolite and tugtupite (?).

The contact relations between the marginal fine-grained albiteanalcime rock and the cleavelanditic albite of the central part of the vein are difficult to establish. There may either be an interfingering of the two rocks across the contact, or the cleavelanditic albitite may pass into the fine-grained albite-analcime rock. There is no analcime in the cleavelandite. The analcime of the adjacent fine-grained albite-analcime rock forms elongated areas which are arranged parallel to the contact (plate 4, fig. 1).

The albite laths of the cleavelanditic albitite are "foliaceous" (cf. Vlasov, Kuzmenko & Eskova, 1959, p. 189) and are generally oriented at right angles to the contact, except in the marginal, fine-grained parts. There are inclusions of aegirine felt, scattered Li-mica and cavities with flat crystals of albite. The albite is intersected by white veins of natrolite and by veins of light pink tugtupite. The latter generally have a wavy course.

The veinlets of tugtupite (no. 66133) are generally bounded by flakes of Li-mica, often bent, small and large flakes occurring together (plate 4, fig. 2). In the Li-mica there are small flakes of epistolite, a little neptunite and small grains of a monazite-like mineral. There are patches of tugtupite in the Li-mica. The tugtupite of the veinlets forms fine-grained masses of equigranular grains which are less than 0.1 mm across. There are rare interstitial grains of albite.

The veinlets branch out from larger aggregates of granular tugtupite with a grain size of 0.1 to 3 mm. In these masses there are curved flakes of Li-mica and small interstitial grains of albite. Many of the tugtupite grains have wavy extinction, and the gritty type of twinning is widespread.

In the border between naujaite and albite there is in places a rather coarse-grained albitite composed of laths of albite a few mm long which are intergrown in such a way that there are numerous interstitial pore holes. The albitite appears to pass into the more massive cleavelanditic albitite in which the albite laths are in parallel orientation. The porous albitite partly replaces a rock rich in eudialyte and aegirine prisms and partly the marginal aegirine-rich border zone of the veins. It contains patches of tugtupite.

This type of albitite was examined in thin sections of sample nos. B.2 and 66135. The albite laths have few twin lamellae and foliaceous outlines. The albitite is intersected by numerous veinlets of very fine-grained natrolite which cut across the albite grains or are situated along their cleavages and along grain boundaries. The veinlets are up to 0.2 mm wide (plate 5, fig. 1).

The areas of tugtupite, which are made up of small grains of tugtupite of fairly polygonal outlines, are not intersected by the natrolite veinlets and thus appear to have formed later than these. Short apophyses of tugtupite occupy interstitial areas in the albite adjacent to the masses of tugtupite. They may occupy the central parts of natrolite veinlets. There are scattered inclusions of albite in the marginal parts

of the tugtupite aggregates. There are no large flakes of Li-mica in association with this type of tugtupite.

The largest masses of tugtupite, up to several centimetres across, are associated with light yellow sodalite. These masses often display hexagonal outlines and may be up to 20 cm across. Sodalite generally forms the margins of these areas while tugtupite occurs in the central parts. The tugtupite aggregates are scattered in an irregular way over the sodalite and often have thin marginal rims of fine-grained Li-mica. There are also irregular patches of albitite and ussingite in the sodalite, and there are small cavities lined by crystals of tugtupite.

The sodalite appears to be enclosed in albite and also borders on the aegirine rock of the vein margin. The albite is partly cleavelanditic, partly sugary. It has intergranular fine-grained natrolite and is intersected by veinlets of Li-mica.

Ussingite forms large aggregates which are penetrated by a fine network of natrolite veinlets up to 0.2 mm wide. The natrolite veinlets do not intersect the albite laths, indicating that the albite was formed later than the ussingite and natrolite (plate 5, fig. 2). The ussingite contains inclusion of aegirine, sodalite, schizolite, igdloite, epistolite and sphalerite.

The tugtupite of this association was examined in thin sections of specimen nos. 64901 and 77227. The aggregates of tugtupite consist of equidimensional grains with straight or irregular mutual boundaries. The grains often show wavy extinction. The individual grains may be up to 5 mm across. There are scattered inclusions of aegirine, Li-mica, albite, granulated sodalite and ussingite. The enclosed ussingite is intersected by veinlets of fine-grained natrolite. The inclusions in the tugtupite areas generally occupy interstitial positions. Along the margins of the tugtupite aggregates there are often thin zones composed of sodalite (plate 5, fig. 2) or of numerous small flakes of Li-mica (plate 6, fig. 1) with cloudy plates of epistolite. The latter mineral is partially replaced by a fine-grained aggregate possibly consisting of gerassimovskite.

3. Qeqertaussaq

On the small island of Qeqertaussaq there is a number of late veins (Sørensen, 1962, p. 22 and p. 100). Thin veins of felt-like aegirine and black lujavrite are partly replaced by albite.

In the albititic parts of these veins there are grains up to 0.3 cm large of chkalovite surrounded by amoeboid zones of tugtupite with a very intricate penetration twinning of the gritty type.

Accessories in the veins are microcline, arfvedsonite, astrophylite, sphalerite, schizolite, britholite, monazite, steenstrupine and epistolite. Analcime and natrolite are present in small amounts.



Fig. 11. Excavation in tugtupite-bearing vein at Kvanefjeld. Photo taken in July, 1969.

4. The Kvanefjeld area

In the northernmost part of the Ilímaussaq intrusion tugtupite has been observed in a number of places, especially on the Kvanefjeld plateau, but also on the north wall of the Gletscherelv valley below the plateau. This slope in its lower part is made up of naujaite enclosed in and penetrated by lujavrite. In its upper part augite syenite and anorthosite are intersected by lujavrite veins containing small xenoliths of naujaite (cf. Sørensen, Hansen & Bondesen, 1969).

Tugtupite has been found in scattered veins in naujaite and augite syenite, often in spatial association with arfvedsonite lujavrite. These veins are up to 50 cm wide and have been traced for up to 50 m. The width of the generally vertical veins varies along their strike. They often stop abruptly, even where empty joints are continuous with the veins (figs 11, 12, 13 and 14).

These veins are mainly composed of fine-grained albite or coarse-grained analcime. They may be zoned, having tugtupite in the central part, and often have inclusions of felt-like aegirine and of augite syenite.

The augite syenite is strongly deformed in the zones occupied by these albititic veins and may have disseminated tugtupite.

The tugtupite from these veins is the most strongly coloured variety of the mineral found in Ilímaussaq so far. The colour is an intense carmine-red. The tugtupite occurs in angular patches up to 10 cm across, often with cores of chkalovite and clearly replacing crystals of that



Fig. 12. The vein excavated in fig. 11. For explanation see fig. 13. Photo taken in July, 1968.

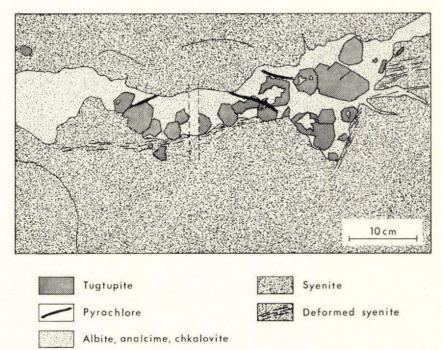


Fig. 13. Same vein as fig. 12. Kvanefjeld.

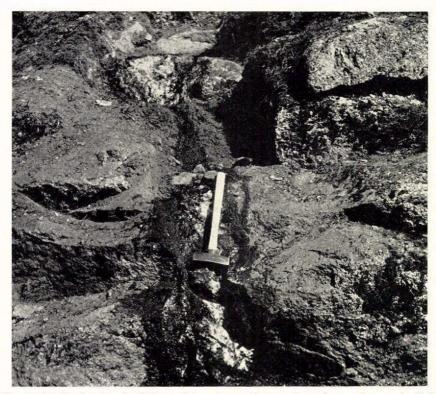


Fig. 14. Vertical vein of albite-analcime in augite syenite a few metres east of the vein shown in figs 11, 12, 13.

mineral. There are, moreover, inclusions of albite, microcline, aegirine and epistolite. Tugtupite also forms branching veinlets in grains of chkalovite and in the albitite. This leaves the impression that the tugtupite impregnates the vein rock (plate 6, fig. 2).

The albititic matrix of the veins has thin streaks of pyrochlore, neptunite, igdloite and fine-grained arfvedsonite. Further constituents seen in hand specimen are yellow sodalite, natrolite and tetragonal natrolite, neptunite, schizolite, patches of pyrochlore, sphalerite, Limica, epistolite and beryllite. The streaks of pyrochlore-neptunite intersect all other constituents, including tugtupite.

The analcime-rich vein rocks are composed of equidimensional grains of analcime with grain sizes of 1 cm or more. There are scattered patches of albite aggregates and of aggregates of microcline penetrated by albite. The analcime appears to penetrate the albite-microcline and may also occur as vermicular inclusions along the margins of albite grains. There are small patches of sodalite in the analcime. Cavities are wholly or partly filled by aggregates of tetragonal natrolite, in places associated with schizolite.

Tugtupite displays lobed boundaries towards analcime. The tugtupite is intersected by zones of brown pigmentation, gelbertrandite (?) and perhaps Li-mica.

Large grains of chkalovite have marginal zones of tugtupite against the enclosing analcime (plate 7, fig. 1) and are penetrated by tugtupite along cracks (plate 7, fig. 2). Thin zones of beryllite in the chkalovite do not penetrate into the tugtupite. The tugtupite contains inclusions of analcime and may be crowded with pigmentary material, aegirine and arfvedsonite needles.

On the Kvanefjeld plateau tugtupite has also been detected in drill holes, for instance in drill hole no. 22 at a depth of 63.92 m below the surface. The tugtupite occurs in a vein in naujaite. The tugtupite is associated with crystals of light pink sorensenite up to 1 cm long, and occurs generally as marginal zones around that mineral.

Under the microscope it can be seen that the matrix of the vein is made up of laths of microcline up to 0.5 cm long. The microcline is strongly corroded by analcime and natrolite. There are small laths of albite, aggregates of fine-grained neptunite, schizolite, arfvedsonite and aegirine, scattered small crystals of monazite and a very few anhedra of steenstrupine. In the analcime there are corroded grains of nepheline, and pseudomorphs after eudialyte that are mainly composed of katapleiite. Natrolite occurs as very pigmented areas composed of thin, in part radiating needles.

Sorensenite occurs as bunches of parallel prisms which are set in a matrix of tugtupite (plate 8, fig. 1). The latter also penetrates the sorensenite along grain boundaries and irregular cracks and appears to replace that mineral. Sorensenite is not in direct contact with microcline or analcime.

Tugtupite penetrates into the adjacent microcline and encloses well developed crystals of that mineral (plate 8, fig. 1). Tugtupite has occasionally a thin zone of sodalite in contact with analcime; in other places the two minerals are in direct contact. The tugtupite contains lines of brown pigmentation (bertrandite?). In places there are small needles of natrolite (?) enclosed in the tugtupite.

Some of the veins of albitite contain chkalovite without rims of tugtupite. The albititic matrix of these veins is very heterogeneous as to grain size. The anhedra of chkalovite have lobed outlines and are altered into analcime and beryllite (and gelbertrandite?) along cracks. There may also be epididymite in these zones, but no tugtupite. The chkalovite (and its beryllite veinlets) is cut by veins of microcline (and subordinate albite). They contain scattered prisms of sorensenite and a little niobophyllite.

Semenov et al. (1965) have described zoned bodies from Kvanefjeld composed of marginal microcline, arfvedsonite and steenstrupine, and of cores of analcime, sodalite and natrolite. They also contain chkalovite, sorensenite, pyrochlore and sphalerite; beryllite occupies thin fractures in the chkalovite (Andersen, 1967). The sorensenite is enclosed in analcime and is partly replaced by beryllite (Andersen, op. cit.). Andersen has described an occurrence of epididymite and eudidymite enclosed in analcime. Bertrandite partly replaces these two beryllium minerals but not the sorensenite present in this sample.

5. The Taseq plateau

A number of occurrences of tugtupite has been found on the Taseq plateau and on the slope between this plateau and the Gletscherelv. A preliminary account of the results of a detailed study of this area of beryllium mineralization is in preparation (Engell, Hansen, Kunzendorf & Løvborg). Therefore only a brief review of the known associations of tugtupite in this region will be presented here.

The beryllium-bearing veins studied so far are confined to the naujaites of the uppermost part of the intrusion. The veins are especially numerous just above regions in which veins of lujavrite intersect the naujaites.

Four main types of veins have been distinguished so far:

- a) In naujaite and coarse-grained lujavrite there are zoned pegmatites containing marginal microcline, arfvedsonite and rare steenstrupine and sodalite and cores of ussingite, albite, nenadkevichite, neptunite, sphalerite and tugtupite (Semenov, Kazakova & Aleksandrova, 1967, p. 5).
- b) Veins rich in ussingite have marginal zones of aegirine, yellow sodalite and steenstrupine. The cores are composed of ussingite, analcime, natrolite, epistolite, gerassimovskite, chkalovite, microcline, Limica, sphalerite, galena, molybdenite, chalchothallite, niobophyllite and rare tugtupite (cf. Semenov, Sørensen, Bessmertnaja & Novorossova, 1967).

The ussingite of the core forms fine-grained aggregates with a grain size less than 0.1 mm. There are inclusions of aegirine needles, sodalite, Li-mica, steenstrupine and schizolite.

The large grains of chkalovite enclosed in the ussingite are partially crushed and intersected by zones of granulation which are partly occupied by aggregates of ussingite, aegirine, analcime, sphalerite, schizolite, epistolite, Li-mica and steenstrupine. Tetragonal natrolite (and analcime) occurs in cavities in the ussingite (plate 8, fig. 2). There are small crystals of chabazite (?) in the natrolite.

In a few samples pink tugtupite forms narrow rims between chkalovite and ussingite and also fills fractures in these two minerals. The

tugtupite contains inclusions of chkalovite, ussingite and epistolite. Larger areas of tugtupite are intimately associated with Li-mica. There may be marginal sodalite.

Ussingite veined by natrolite is in places partially replaced by albitite which is either granular or cleavelanditic. There are generally zones of natrolite between ussingite and albite, and the albite laths may be set at right angles to the patches of ussingite. In these cases tugtupite encloses not only ussingite veined by natrolite but also albite, and there are veinlets of tugtupite in the albitite.

- c) There are several varieties of albitite in this vein type. A few of these have been mentioned briefly by Semenov & Sørensen (1966). Some of the veins are coarse-grained, recalling those of Tugtup agtakôrfia and Kangerdluarssuk; others are extremely fine-grained, but having patches of more coarse-grained albite.
- i. In the fine-grained albitites the matrix is composed of interlocking grains of albite less than 0.02 mm across, and there are scattered grains of microcline, larger laths of albite and a good deal of fluorite. Accessories are Li-mica, neptunite, schizolite, pseudomorphs after epistolite (?), pyrochlore, igdloite, sphalerite, aegirine, arfvedsonite, allanite and biotite.

Tugtupite occurs as centimetre-sized anhedra, penetrating the matrix of albite and microcline, mainly along grain boundaries but also along cracks in the albite. There are inclusions of albite, microcline, schizolite, arfvedsonite and neptunite (plate 9, fig. 1).

Some of these veins have patches of analcime containing inclusions of albite and microcline. Tugtupite appears to be associated with the analcime and contains inclusions of that mineral.

ii. In albitites containing eudidymite and epididymite there are patches of strongly pigmented analcime and tugtupite (Semenov & Sørensen, 1966). These albitites have late genthelvite (Bollingberg & Petersen, 1967) and leucophane.

Analcime occupies areas of irregular shape and appears to branch into the adjacent albite-microcline along grain boundaries. There are small patches of tugtupite at the ends of the veinlets.

The eudidymite and epididymite are separated from the adjoining albite and are penetrated by veinlets of analcime, tugtupite and Li-mica. Tugtupite also penetrates the albitite. The analcime and tugtupite are both strongly pigmented, and as they both display a gritty type of twinning they are difficult to distinguish from each other.

iii. In a boulder of albitite there are crystals of chkalovite up to 5 cm across and streaks of pyrochlore, neptunite and igdloite set in a matrix of coarse-grained albite. There are tabular crystals of albite in cavities.

The crystals of chkalovite have spherulite beryllite on irregular cracks and are separated from the albite by rims composed of eudidymite and epididymite. The cracks containing beryllite are cut by these rims (plate 9, fig. 2).

Between the epididymite and albite there are zones composed of gelbertrandite (?), beryllite and niobophyllite.

There is no tugtupite or analcime in this sample.

d) Tugtupite has been found in analcime veins as marginal zones around, and as thin veinlets cutting crystals of chkalovite. This tugtupite is associated with Li-mica. Analcime veinlets (with border zones of tugtupite) cut the chkalovite, and there are inclusions of analcime in the tugtupite.

Accessories in these rocks are schizolite, aegirine, neptunite, ore, steenstrupine and pyrochlore. There may be patches composed of interlocking laths of microcline with subordinate albite. The tugtupite encloses these two minerals.

The tugtupite of Lovozero

Apart from Ilímaussaq only one more locality of tugtupite (beryllosodalite) has been discovered, namely the Lovozero intrusion of the Kola Peninsula (Semenov & Bykova, 1960).

The mineral is rather rare in Lovozero. It forms masses up to 0.3 cm across in zeolite. It is cryptocrystalline in thin section and forms masses displaying a weak aggregate polarisation.

Tugtupite is secondary after chkalovite, which is usually found in masses of usingite. The usingite is replaced by analcime, natrolite and chabazite. Associated minerals are murmanite (the Ti-rich member of the murmanite-epistolite mineral group, in which epistolite is a Nb-rich member), aegirine II, sphalerite, schizolite, neptunite, steenstrupine, gerassimovskite, etc. (Semenov, Organova & Kukharchik, 1961; Yakovlevskaja & Semenov, 1963). This shows clearly that the mode of occurrence of tugtupite (beryllosodalite) is practically identical in the two closely related agpaitic intrusions, Lovozero and Ilímaussaq.

Discussion

Tugtupite in the Ilímaussaq intrusion is confined to veins dominated by albite and/or analcime. As discussed by Sørensen (1962), the albiteanalcime veins occur in zones of fracturing and displacement in naujaite and syenite, which in many cases were first occupied by felt-like aegirine. Remnants of these fracture fillings are occasionally found in the albiteanalcime veins, for example those mentioned from Kangerdluarssuk and Kvanefjeld.

For these reasons it may be concluded that the albite-analcime veins were formed after the consolidation of the naujaite. The veins may be continuous with veins of lujavrite and only in exceptional cases intersect lujavrite. It has therefore been assumed that these veins have been formed from fluids squeezed out from the crystallizing lujavrite magma which is considered a residual magma enriched in volatiles and rare elements (Sørensen, 1962, p. 174). In accordance with this interpretation the lujavrites are generally fine-grained and strongly laminated with bent laths of feldspar; pegmatites are rare.

The tugtupite-bearing veins of Ilímaussaq are generally composed of typically pneumatolytic-hydrothermal minerals and only rarely are there zoned bodies of pegmatitic type. These pegmatites are especially associated with a medium- to coarse-grained lujavrite with "subdole-ritic" texture which injects the naujaites, syenites, fine-grained lujavrites and the lavas of the roof in the Kvanefjeld area (cf. Sørensen et al., 1969). As mentioned on p. 28 the cores of these pegmatites are composed mainly of analcime and natrolite and closely resemble the analcime veins found elsewhere in Ilímaussaq. This association of true pegmatites with a non-laminated, fairly coarse-grained lujavrite indicates that only when the volatiles were retained in the lujavrite magma could pegmatites be formed. In the case of consolidation of lujavrite magma during deformation, the fluids were expelled and formed veins composed of the minerals which in the case of quiet crystallization would have formed the cores and replacement bodies of pegmatites.

The predominance of albite-analcime veins over late pegmatites in Ilímaussaq is in striking contrast to the scarcity of such veins and the predominance of pegmatites in Lovozero (see Vlasov et al., 1959).

The beryllium-bearing veins in Lovozero are interpreted by Vlasov et al. as complex pegmatites associated with poikilitic sodalite syenites. These pegmatites are often zoned and have replacement bodies composed of one or several of the following minerals: albite and/or microcline, analcime, natrolite and ussingite. Ussingite is considered to be late and replaces sodalite, prismatic natrolite and microcline. Chkalovite occurs near the margins of ussingite-rich bodies and is furthermore associated with natrolite, sodalite, schizolite, neptunite, sphalerite, steenstrupine and murmanite. There are practically no inclusions in the chkalovite (Vlasov et al., 1959; Yakovlevskaja & Semenov, 1963). The chkalovite-ussingite pegmatites are often subject to an intense hydrothermal reworking resulting in natrolitization of sodalite and ussingite, while chkalovite is replaced by epididymite, tugtupite or sphaerobertrandite.

According to Vlasov et al. (1959) eudidymite-epididymite in Lovozero is associated with albite-rich replacement bodies and may occur in leaching cavities in albite or natrolite. The associated minerals are fluorite, albite, natrolite, neptunite and schizolite; beryllite, sphaerobertrandite and gelbertrandite are products of alteration. Genthelvite occurs in hybrid pegmatites and leucophane forms spherulites in natrolite druses.

Thus the beryllium minerals of Lovozero were formed at a late stage under hydrothermal conditions.

The beryllium-bearing veins in Ilímaussaq are composed mainly of the minerals characteristic of the beryllium-bearing replacement bodies in the pegmatites of Lovozero. One might then ask if the patches of microcline, sodalite, eudialyte and aegirine found in the beryllium veins could be remnants of otherwise completely replaced naujaite pegmatites. The fact that the veins are sometimes found in zones of deformation in naujaite, and that they are closely associated spatially with lujavrite, makes it most likely that they are related to the lujavrites rather than to the naujaites, as already suggested above. This view is supported by the local occurrence of bleached inclusions of lujavrite in some of the albite-analcime-ussingite veins.

Paragenesis

The tugtupite-bearing veins studied in Ilímaussaq display rather pronounced paragenetic relations.

Minerals such as microcline, sodalite, eudialyte-eucolite and aegirine are of early formation. One, several or all of them may be lacking in individual veins. Microcline may be associated with felt-like aegirine.

Minerals such as ussingite, chkalovite, lovozerite, epistolite and prismatic crystals of schizolite appear to be closely related in time. The ussingite replaces microcline and sodalite and may be intersected by veins of fine-grained natrolite. There may be beryllite on cracks in the chkalovite. As the veinlets of fine-grained natrolite and beryllite are cut by the albite, they were apparently formed earlier than this mineral.

Albite appears to occur in several generations. Early sugary-grained albite is succeeded by cleavelanditic albite (and flat crystals in cavities), which again in some veins appears to be embedded in a matrix of fine-grained albite rich in fluorite.

Associated with the albite are analcime, sphalerite, steenstrupine and acmite. The analcime may have been formed from volatile-enriched fluids enclosed in the albitites. Around the patches of analcime there may be concentrations of steenstrupine and sometimes also of yellow

sodalite and tugtupite. In some veins the cleavelanditic albite is intersected by veinlets of fine-grained natrolite.

The tugtupite is often associated with analcime and may penetrate not only into albite and analcime but also into the large grains of chkalovite and their crack fillings of beryllite. Li-mica, epistolite (+ gerassimovskite and nenadkevichite) and sometimes niobophyllite and monazite (or rhabdophanite) may be associated with the tugtupite. Tugtupite often forms veinlets in the albitites.

Later than the tugtupite are crusts and cavity fillings of tetragonal natrolite and chabazite (?) and the lamellar aggregates of pyrochlore, neptunite and igdloite (which may, however, be pseudomorphs after epistolite).

The fine-grained albite may also be of late formation; it is associated with fibrous aggregates of schizolite and katapleiite.

It should be emphasized that all stages of the evolution mentioned above are rarely present in one and the same vein.

In the pure ussingite-chkalovite veins tugtupite is generally lacking or is present in very insignificant amounts. In a few specimens chkalovite occurs in albititic veins without any trace of tugtupite. These veins are poor in analcime. This chkalovite may have beryllite on cracks and marginal epididymite and eudidymite which again may be partially replaced by bertrandite (Andersen, 1967) or gelbertrandite (?).

In the albitites containing epididymite-eudidymite (Semenov & Sørensen, 1966) there is no chkalovite. Tugtupite and Li-mica are associated with analcime, and there is late genthelvite and leucophane.

Finally it should be mentioned that in drill hole no. 22 on the Kvanefjeld plateau tugtupite and analcime appear to be late members of an association containing eudialyte, microcline, albite, nepheline, aegirine, sorensenite and other minerals.

Thus, while chkalovite is an early mineral in the veins, epididymite-eudidymite associated with albite are later and tugtupite with analcime later still. In accordance with this, tugtupite appears to be formed at least partly at the expense of chkalovite, sorensenite and perhaps epididymite-eudidymite.

The reason why there are several stages of formation of albite and natrolite and why beryllite appears to be an early product of alteration of chkalovite may be that there are several intrusive phases of lujavrite so that hot fluids have been squeezed into fractures in naujaite at intervals and from different lujavritic sources.

Preliminary examinations of fluid inclusions in some minerals from Ilímaussaq (Sobolev et al., 1970) have given the following temperatures of homogenization of primary liquid-gas inclusions:

sorensenite 400–420°C, tugtupite 440–460°C, chkalovite 860–980°C.

These temperatures have not been corrected for pressure of formation. The significance of the high temperature of homogenization of chkalovite will be discussed in a later paper. The temperatures of homogenization of sorensenite and tugtupite are within the range of temperatures estimated by Sørensen (1962).

Thus tugtupite appears to have been formed hydrothermally more or less at the same time as analcime and Li-mica. Like these two minerals it often forms crystals lining cavities in albitite, and in places it appears to have filled cavities lined by crystals of albite and microcline. It is very likely that the beryllium content of the fluids involved in the formation of these minerals is partly derived by leaching of the agpaitic rocks adjacent to the fractures through which the fluids percolated, and partly a primary component of the residual magmatic fluids. The agpaitic rocks of Ilímaussaq are, according to Gerasimovskii (1968), exceptionally rich in beryllium and lithium, with average contents of these two metals of 30 ppm and 310 ppm respectively. In Lovozero the average contents are 8.7 ppm Be and 55 ppm Li; the average values found in granites are 6.5 ppm Be and 40 ppm Li.

Chkalovite and sorensenite appear to have been deposited directly from the alkaline fluids; epididymite-eudidymite are partly primary, partly formed at the expense of chkalovite. Beryllite is mainly secondary, as is

Table 6. Chemical analyses of chkalovite, tugtupite, beryllite and eudidymite from the Ilimaussaq intrusion (weight percent)

	Chkalovite	Tugtupite (beryllium) sodalite)	Beryllite	Eudidymite
SiO_2	57.78 12.56	51.58 5.40	31.0 38.0	72.53 10.39
Al_2O_3 Fe_2O_3	- tr.	11.15 tr.	0.2	0.65 0.16
MgO	0.16	0.20	~	_
CaO	29.20	25.52		$0.60 \\ 11.91$
$K_2O \dots H_2O^+ \dots$	0.09	0.12	- 22.7	0.20
H_2O^-	0.02	0.03	6.8	3.11
S	0.17 0.14	0.33 7.28		_
Total	100.12	101.61	98.7	100.55
Analyst	ME MOURITZEN	ME MOURITZEN	I. Sørensen	M. E. KAZAKOVA
Reference	Sørensen (1962)	Sørensen (1962)	Andersen (1967)	Semenov & Sørensen (1966)

tugtupite which is formed at the expense of chkalovite or sorensenite, although in some cases (as when occurring in crystal cavities) tugtupite and beryllite also appear to be precipitated directly from the fluids involved.

As seen in table 6 the formation of beryllite at the expense of chkalovite represents a very strong leaching of SiO₂ and Na₂O so that the alteration product is strongly enriched in beryllium and water. The removal of SiO₂ and the precipitation of beryllium indicate an alkaline environment:

$$\begin{array}{ccc} 3~\mathrm{Na_2BeSi_2O_6} + 4~\mathrm{OH^-} \rightleftarrows ~\mathrm{Be_3SiO_4(OH)_2.H_2O} + 6~\mathrm{Na^+} + 5~\mathrm{SiO_3^{--}} \\ \mathrm{mol~volume} & 231~\mathrm{cm^3} & 77~\mathrm{cm^3} \\ \mathrm{chkalovite} & \mathrm{beryllite} \end{array}$$

As demonstrated by Andersen (1967) the association of beryllite and sorensenite may be interpreted as a result of a forceful injection of Be-rich solutions into a consolidated rock. This is because beryllite occurs on fractures in sorensenite which appears to be chemically unaltered. However, the beryllite in chkalovite described by Andersen (1967) is clearly a product of alteration of the chkalovite. Beryllite may therefore partly have been formed as an alteration product of chkalovite, and partly as a precipitate from residual solutions in cavities when beryllium complexes are made unstable (Beus, 1966).

A possible scheme for the transformation of chkalovite into tugtupite may be written:

This process takes place under such alkaline conditions that some beryllium is removed in the form of beryllate ions. There is no evidence of redeposition of the released beryllium.

The difference in mol volume may explain the observation that grains of chkalovite subjected to replacement by tugtupite are often shattered (chkalovite: $V_0 = 3058 \ {\rm \AA}^3$, Z = 24; tugtupite: $V_0 = 658 \ {\rm Å}^3$, Z = 1).

An indication of the alkaline conditions prevailing during the formation of tugtupite is the association of tugtupite and analcime.

Sodium-fluorine complexes of beryllium, which are stable in near neutral solution, may also participate in the transportation of the dissolved beryllium and may have been operative in the formation of epididymite-eudidymite, which are generally associated with albite and fluorite and thus may have been formed from weakly acid solutions. In Khibina and Lovozero the albite-epididymite-bearing veins may also contain quartz (Vlasov et al., 1959; Beus, 1966).

In conclusion, it appears that tugtupite has been formed from alkaline aqueous fluids at temperatures around 400°C and at a fairly high volatile pressure since S and Cl take part in the crystallization of the mineral, and since the replaced anhedra of chkalovite often are shattered.

The sequence beryllite-epididymite-tugtupite may indicate that the solutions at the stages during which these minerals were formed were respectively alkaline – neutral (or acid) – strongly alkaline. This may reflect an advancing wave of hydrothermal solutions, as discussed by Korzhinsky in a number of papers (for instance Korzhinsky, 1959). The writers favour, however, the view that there have been several injections of hydrothermal fluids into vein systems. Residual fluids were squeezed out from successive injections of lujavrite magma at different stages of crystallization. As they have travelled different distances through the rocks, it is reasonable to assume that the various residual fluid phases have differed from one another with respect to chemical composition, temperature and vapour pressure.

References

- Andersen, E. Krogh, Danø, M. & Petersen, O. V. 1969: A tetragonal natrolite. Meddr Grønland 181 10, 19 pp.
- Andersen, S. 1967: On beryllite and bertrandite from the Ilímaussaq alkaline intrusion, South Greenland. *Meddr Grønland* 181 4.II, 11-27.
- Beus, A. A. 1966: Geochemistry of beryllium and genetic types of beryllium deposits. San Francisco and London. W. H. Freeman and Company, 389 pp.
- Bollingberg, H. & Petersen, O. V. 1967: Genthelvite from the Ilimaussaq alkaline intrusion, South Greenland. *Meddr Grønland* 181 4.1, 1-9.
- Danø, M. 1966: The crystal structure of tugtupite a new mineral, Na₈Al₂Be₂Si₈O₂₄(Cl,S)₂. Acta crystallogr. 20, 812-816.
- Danø, M. & Sørensen, H. 1959: An examination of some rare minerals from the nepheline syenites of South West Greenland. *Meddr Grønland* 162 5, 35 pp.
- Engell, J., Hansen, J., Kunzendorf, H. & Løvborg, L. (in prep.): Beryllium mineralization in the Ilimaussaq intrusion, South Greenland. *Rapp. Grønlands geol. Unders.* 33.
- Gerasimovskii, V. I. 1968: Geochemistry of agpaitic nepheline syenites. Rep. 23rd int. geol. Congr. Czechoslovakia, 6, 259-265.
- Korzhinsky, D. S. 1959: The advancing wave of acidic components in ascending solutions and hydrothermal acid base differentiation. *Geochim. cosmochim. Acta* 17, 17-20.
- MICHEELSEN, H. 1957: An immersion method for exact determinations of refractive indices. Bull. geol. Soc. Denmark 13, 177-191.
- Povarennykh, A. S., Platonov, A. N., Tarashchan, A. N. & Belichenko, V. P. (in press): The colour and luminescence of tugtupite (beryllosodalite) from Ilimaussaq, South Greenland. *Meddr Gronland*. 181, 14.

- Semenov, E. I. & Bykova, A. V. 1960: [Beryllosodalite]. Dokl. Akad. Nauk. SSSR 133, 1191-1193. (In Russian).
- Semenov, E. I., Gerasimovsky, V. I., Maksimova, N. V., Andersen, S. & Petersen, O. V. 1965: Sorensenite, a new sodium-beryllium-tin-silicate from the Ilímaussaq intrusion, South Greenland. *Meddr. Grønland* 181 1, 19 pp.
- Semenov, E. I., Kazakova, M. E. & Aleksandrova, R. A. 1967: The Lovozero minerals nenadkevichite, gerassimovskite and tundrite from Ilimaussaq, South Greenland. *Meddr Grønland* 181 5.I, 1–11.
- Semenov, E. I., Organova, N. I. & Kukharchik, M. V. 1961: New data on minerals of the lomonosovite-murmanite group. Soviet Phys. Crystallogr. 6, 746-751.
- Semenov, E. I. & Sørensen, H. 1966: Eudidymite and epididymite from the Ilimaussaq alkaline intrusion, South Greenland. *Meddr Gronland* 181 2, 22 pp.
- Semenov, E. I., Sørensen, H., Bessmertnaja, M. S. & Novorossova, L. E. 1967: Chalcothallite a new sulphide of copper and thallium from the Ilimaussaq alkaline intrusion, South Greenland. *Meddr Grønland* 181 5.II, 13–26.
- Sobolev, V. S., Bazarova, T. Y., Shugurova, N. A., Bazarov, L. Sh., Dolgov, Yu. A. & Sørensen, H. 1970: A preliminary examination of fluid inclusions in nepheline, sorensenite, tugtupite and chkalovite from the Ilímaussaq alkaline intrusion, South Greenland. *Meddr Grønland* 181 11, 32 pp.
- Sørensen, H. 1960: Beryllium minerals in a pegmatite in the nepheline syenites of Ilimaussaq, South West Greenland. Rep. 21st int. geol. Congr., Norden 17, 31-35.
- Sørensen, H. 1962: On the occurrence of steenstrupine in the Ilimaussaq massif, Southwest Greenland. *Meddr Grønland* 1671, 251 pp.
- Sørensen, H. 1963: Beryllium minerals in a pegmatite in the nepheline syenites of Ilímaussaq, South West Greenland. Rep. 21st int. geol. Congr. Norden 27, Contributions to discussions, 157-159.
- Sørensen, H., Hansen, J. & Bondesen, E. 1969: Preliminary account of the geology of the Kvanefjeld area of the Ilimaussaq intrusion, South Greenland. *Rapp. Grønlands geol. Unders.* 18, 40 pp.
- VLASOV, K. A., KUZMENKO, M. V. & ESKOVA, E. M. 1959: [The Lovozero alkali massif]. Akad. Nauk. SSSR, 624 pp. (In Russian). English translation: Edinburgh; Oliver & Boyd, 627 pp., 1966.
- YAKOVLEVSKAJA, T. A. & SEMENOV, E. I. 1963: [New data on chkalovite]. Trudy miner. Muz. 14, 265-267. (In Russian).

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PLATES

- Fig. 1. No. 77450,3: Tugtupite. Kvanefjeld: Pseudocubic penetration triplet in tugtupite. The twin planes are $\{101\}$. The microphotograph has been taken with crossed nicols, $\lambda = 491$ nm and with addition of a phase difference of app. 440 nm to make the (001) section nearly black but the (100) and the (010) sections different. $\times 19$.
- Fig. 2. No. 21059. Tugtup agtakôrfia. 23.8×, + nic.: Shattered grain of chkalovite. The single fragments show undulatory extinction and are separated by zones of crushing made up of aggregates of chkalovite with some tugtupite. Note lines of fluid inclusions (healed fractures) in the chkalovite.
- (H. Micheelsen phot.).

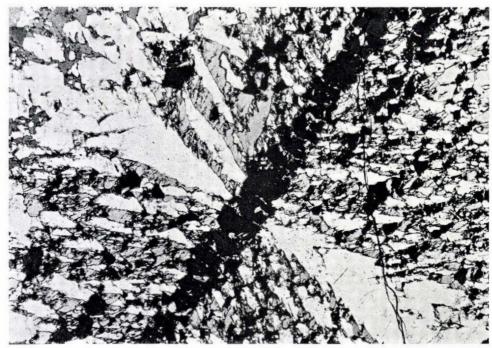


Fig. 1

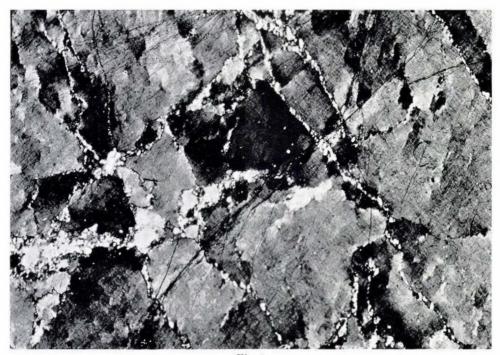


Fig. 2

- Fig. 1. No. 21059,2. Tugtup agtakôrfia. 23.8×, +nic: Anhedron of chkalovite (upper half) veined by fine-grained tugtupite with inclusions of chkalovite branching out from larger and more coarse-grained aggregate of tugtupite. Note the twinning of the tugtupite.
- Fig. 2. No. 3 a. Tugtup agtakôrfia. $23.8\times$, +nic: Stellar aggregates and single crystals of microcline enclosed in tugtupite. The tugtupite is enclosed in albite and contains corroded inclusions of the latter. All minerals are cut by thin veinlets of tetragonal natrolite.

(H. Micheelsen phot.).



Fig. 1



Fig. 2

- Fig. 1. No. 77231. Head of Kangerdluarssuk. 23.8×, +nic: Border zone of fine-grained aegirine (top) and zone of sodalite (bottom). Between these zones there is a fine-grained aggregate of albite and microcline which also occupies cleavage fractures in the sodalite.
- Fig. 2. No. 66134. Head of Kangerdluarssuk. $23.8 \times$, + nic: Fine-grained albitite with amoboid-shaped areas of analcime having cores of sodalite. There are small needles of aegirine in the albitite.

(H. MICHEELSEN phot.).

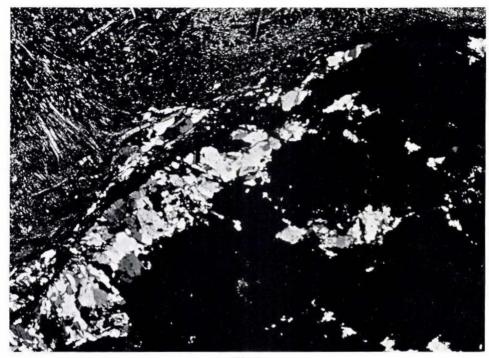


Fig. 1

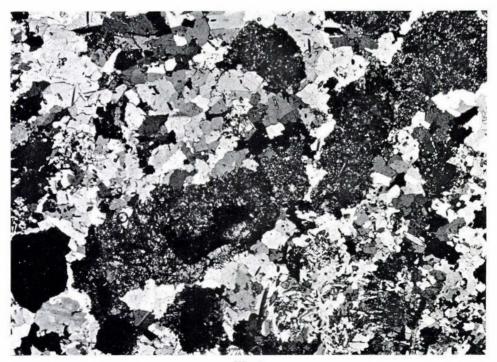


Fig. 2

- Fig. 1. No. 66135 c. Head of Kangerdluarssuk. 23.8×, + nic. Interfingering of cleavelanditic albite (right) with fine-grained albitite (left). The latter has elongated areas of analcime (black).
- Fig. 2. No. 66133 a. Head of Kangerdluarssuk. $23.8\times$, + nic. Border of tugtupite veinlet (bottom) having flakes of Li-mica in contact with albitite.
- (H. MICHEELSEN phot.).



Fig. 1

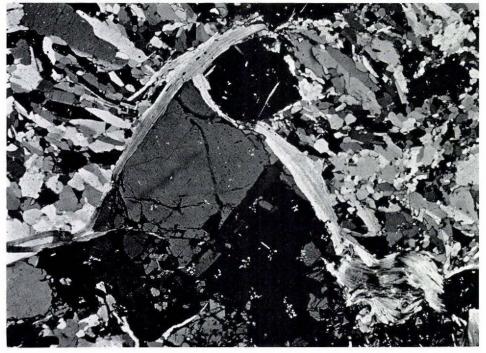


Fig. 2

- Fig. 1. No. B.2. Head of Kangerdluarssuk. $23.8\times$, + nic. "Foliaceous" albite cut by veinlets of fine-grained natrolite.
- Fig. 2. No. 64901 b. Head of Kangerdluarssuk. 23.8×, + nic. Albite (bottom) with interstitial ussingite veined by fine-grained natrolite. Upper left corner: larger mass of ussingite veined by fine-grained natrolite. Upper right corner: twinned tugtupite with inclusions of albite and ussingite and with a partial rim of sodalite (black).
- (H. Micheelsen phot.).

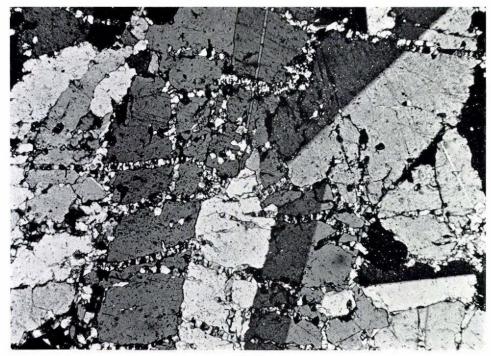


Fig. 1



Fig. 2

- Fig. 1. No. 77227 a. Head of Kangerdluarssuk. 23.8×, + nic. Patches of ussingite veined by natrolite (centre top) separated by zone of sodalite and flakes of Li-mica from tugtupite which is the most abundant mineral on the photo.
- Fig. 2. No. 64750,1 Kvanefjeld. $23.8\times$, + nic. Mass of tugtupite (bottom) into which crystals of albite protrude.
- (H. MICHEELSEN phot.).



Fig. 1



Fig. 2

- Fig. 1. No. 64750,2. Kvanefjeld. $23.8\times$, + nic. Analcime (top) and chkalovite (bottom). There is a thin zone of tugtupite between these two minerals (centre). Most of the black areas of the tugtupite rim are due to holes in the thin section.
- Fig. 2. No. 77450,3. Kvanefjeld. $23.8\times$, + nic. Chkalovite penetrated by tugtupite which contains small needles of aegirine.
- (H. MICHEELSEN phot.).

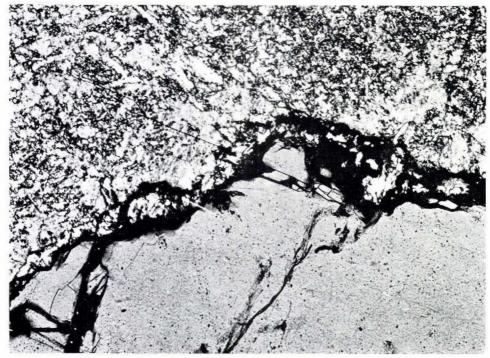


Fig. 1

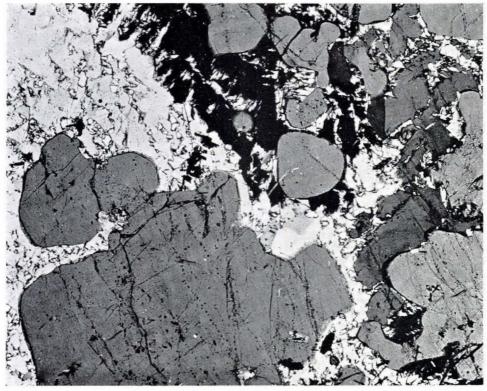


Fig. 2

- Fig. 1. Drill core 22-63.92. Kvanefjeld. $23.8\times$, + nic. Group of sorensenite crystals (centre) enclosed in tugtupite which displays coarse twinning (top) and fine twinning (bottom). There are partially corroded crystals of microcline in the tugtupite.
- Fig. 2. No. 77252 a. The Taseq slope. $23.8 \times$, +nic. Corroded and partially crushed crystals of chkalovite cut by granulated zone of chkalovite with subordinate tugtupite. Bottom left: fine-grained matrix of ussingite with aggregates of tetragonal natrolite needles.

(H. MICHEELSEN phot.).

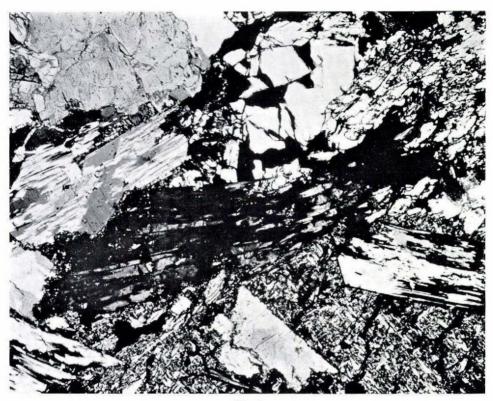


Fig. 1



Fig. 2

- Fig. 1. No. S.1. The Taseq slope. $23.8\times$, + nic. Tugtupite (lower half) in fine-grained albitite (upper half). Note corroded crystals of microcline, albite and Li-mica in the tugtupite.
- Fig. 2. No. X.2. The Taseq slope. $23.8\times$ + nic. Chkalovite intersected by thin veinlets of beryllite (black on the photograph). Top: rim of epididymite cutting the beryllite veinlets and replacing the chkalovite.
- (H. MICHEELSEN phot.).



Fig. 1



Fig. 2

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KOMMISSIONEN FOR VIDENSKABELIGE UNDERSØGELSER I GRØNLAND

BD. 181 · NR. 14

GRØNLANDS GEOLOGISKE UNDERSØGELSE BULLETIN NO. 95 II

THE COLOUR AND LUMINESCENCE OF TUGTUPITE (BERYLLOSODALITE) FROM ILÍMAUSSAQ, SOUTH GREENLAND

CONTRIBUTION TO THE MINERALOGY OF ILIMAUSSAQ, No. 21

BY

A. S. POVARENNYKH, A. N. PLATONOV, A. N. TARASHCHAN AND V. P. BELICHENKO

WITH 2 FIGURES AND 3 TABLES IN THE TEXT

С РУССКИМ РЕЗЮМЕ

KØBENHAVN C. A. REITZELS FORLAG

> BIANCO LUNOS BOGTRYKKERI A/S 1971

Abstract

Tugtupite, Na_4 [BeAlSi₄O₁₂] Cl, is a mineral with bright pink colour and yelloworange UV-luminescence. The visible region of the spectral absorption curves and the luminescence spectrum of tugtupite from the Ilimaussaq alkaline massif (South Greenland) were studied. Calculated and experimental values of vibrational frequencies of different molecular ions were compared, and it was established that the luminescence of tugtupite is caused by S_2^- molecular ions occupying the position of Cl ions in the crystal structure. These ions are also the cause of the colour of tugtupite, probably in combination with other, thermically less stable, radiation centres.

РЕЗЮМЕ

Тугтупит Na_4 [BeAlSi₄O₁₂] Cl — минерал, имеющий ярко-розовую окраску и желто-оранжевую УФ-люминесценцию. Были изучены кривые спектрального поглощения в видимой области и кривая спектра люминесценции образцов тугтупита из пегматитов щелочного массива Илимауссак (Южная Гренландия).

На основе сравнения рассчитанных и экспериментальных величин колебательных частот различных молекулярных ионов было установлено, что причиной люминесценции тугтупита являются молекулярные ионы S_2^- , расположенные в его структуре на местах ионов Cl. Они же обусловливают окраску тугтупита, хотя в отношении последней не исключается роль и других, термически менее устойчивых, радиационных центров.

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Introduction

The mineral tugtupite (beryllosodalite) has been found in the Ilímaussaq (South Greenland) and Lovozero (Kola Peninsula) alkaline intrusions (Sørensen, 1960; Sørensen, Danø & Petersen, in press; Semenov & Bykova, 1960).

It belongs to the beryllo-alumino-tectosilicates and is isotypical with the sodalite group minerals. It is tetragonal, pseudocubic. Density -2.30; hardness $-5^{1}/_{2}$. Cleavage bipyramidal distinct. The mineral is uniaxial (or nearly so) positive, $n_{0} = 1.496$ and $n_{e} = 1.502$ (Danø, 1966).

As is characteristic of all mineral species of the feldspathoid group, tugtupite has a distinct coloration and luminiscence. It is bright crimson and has an orange luminescence. The nature of these optical properties is investigated in this paper.

Chemical composition and structure

With respect to chemistry tugtupite differs from sodalite in that two atoms of Al are substituted by Be and Si, giving the following formula: Na₄ (BeAlSi₄O₁₂) Cl. Danø (1966) has shown that the Be and Al atoms are ordered in the framework, BeO₄ and AlO₄ tetrahedrons being located on fourfold axes, which decreases the mineral symmetry from cubic, as in sodalite (Pauling, 1930), to tetragonal (pseudocubic) with the parameters a = 8.583 and c = 8.817 (Danø, 1966).

Each of the four oxygen atoms in the $\mathrm{BeO_4}$ and $\mathrm{AlO_4}$ tetrahedrons is linked only with Si atoms (common for two tetrahedrons), and therefore these tetrahedrons are of regular form. One third of the $\mathrm{SiO_4}$ tetrahedrons in the tugtupite structure are entirely bound to analogous tetrahedrons, and the other two thirds have apices in common with two $\mathrm{SiO_4}$ tetrahedrons and with $\mathrm{AlO_4}$ and $\mathrm{BeO_4}$ tetrahedrons, which results in a rather strong distortion (Si-O = 1.566–1.646).

The Na atoms are in the framework cavities in fourfold coordination and are surrounded by three atoms of O and one atom af Cl. The Cl atoms are surrounded by four Na atoms. Each of the oxygen atoms bound to Be is unsaturated with respect to valency and has a half excess charge, which, taking into account a resonance displacement of electron

1,40

100,16

A. V. BYKOVA (1960)

 $-O = Cl_2 \dots \dots$

 $-0 = S \dots \dots$

Analyst.....

Weight percent Tugtupite from Bervllosodalite from Ilímaussag Lovozero 51,58 50,45 $SiO_2.....$ Al₂O₃..... 11.15 12,56 Not determ. 0.043 Fe,O, Traces Not determ. 5.40 5.30 0,20 Not determ. CaO...... Not determ. 0,50 25,52 23,26 K.O..... 0,12 0,40 H₂O..... 0,03 1.51 S 0,33 Not determ. 101,61 101,56

1,64

0,16

99,81

M. MOURITZEN (1960)

Table 1. Chemical analyses of tugtupite (beryllosodalite).

clouds enables two of four O atoms to have one localized electron for short periods. For the O atoms surrounding Al such electron localization is possible for only one in four.

In the normal stoichiometrical composition excess negative charges in the $\mathrm{BeO_4}$ and $\mathrm{AlO_4}$ tetrahedrons ($^1/_4$ Cl + $^1/_4$ O_{Al} + $^1/_2$ O_{Be}) are strictly compensated by the positive Na⁺ charges. However, in displacing or removing the weakly bonded Na and Cl atoms from their positions in the structure, favourable conditions are created for localization of electrons that can be easily excited.

Heterovalent isomorphic substitution of atoms is an essential generator of defects in feldspathoid framework structures. The most common example of this is the substitution of Cl by S atoms, as in S-sodalite known as hackmanite (Vorobieva, 1946). As can be seen from the chemical analysis (table 1), the content of sulphur in tugtupite is considerable. But it is difficult to say a priori whether it is represented in the structure by simple ions S^{-2} or by molecular ions such as S_2^{-2} or S_2^{-2} (Schulmann & Kirk, 1964). In both cases the location of S atoms in the positions of the Cl atoms results in the appearance of local disturbances of the valency balance. This may manifest itself either in the presence of negative vacancies or in the appearance of excess negative charges on the sulphur ions.

The colour of tugtupite

The optical absorption spectra of tugtupite were measured by means of the spectrophotometer "SF-4A" with a special device for examination of powdered samples.

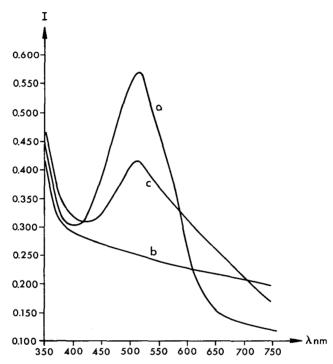


Fig. 1. The spectral absorption curves of tugtupite in the region 350-700 nm: a: naturally coloured sample; b: decoulourized by heating at 450° C; c: irradiated with X-rays.

The bright pink (crimson) colour of tugtupite is conditioned by a wide band of light absorption in the visible region within the range 440–600 nm with the maximum at 510 nm (fig. 1, curve a). The optical density of the sample is considerably lower in the red region (600–750 nm) of the spectrum than at shorter wave lengths (350–600 nm).

The sample was completely decolourized and became white after heating to 450° C. The optical density of the heated sample was preserved in the ultraviolet region, but decreased gradually with increasing wave length in the visible region of the spectrum (fig. 1, curve b).

A sample decolourized by heating was exposed to X-rays (tube "BSV-2", Mo-radiation, 40 kV, 10 mA). After irradiation for 2 hours the sample acquired a pink colour. The absorption band within the range

450-600 nm (with the maximum at 510 nm), which is analogous to that of the naturally coloured sample, was partially restored, though it did not reach its original intensity (fig. 1, curve c). When the dose of irradiation was increased, the colour was intensified. The artificial colour of tugtupite obtained by irradiation is unstable and disappears completely after exposure to day light for 2-3 hours. This indicates that the colour centres obtained in this way are unstable. A similar phenomenon can also be observed on naturally coloured S-containing sodalite (hackmanite) from pegmatites of the alkaline rocks of the Kola Peninsula (Borgström, 1901; Vorobieva, 1946).

The luminescence of tugtupite

When investigating samples of tugtupite in ultraviolet light a bright yellow-orange luminescence was observed. The spectrum (fig. 2) was recorded on a special spectrophotometer which made it possible to register

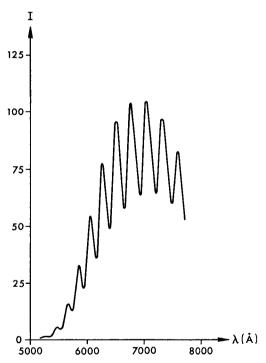


Fig. 2. The luminescence spectrum of tugtupite ($T = 77^{\circ}$ K).

luminescence within the range 300-800 nm. Luminescence was produced by the line at 365 nm of the mercury spectrum; the spectra were photographed at the temperature of liquid nitrogen (77° K). The luminescence of the samples did not disappear even after heating to 900° C, and

the spectrum of the heated samples is similar to that of the non-heated ones.

The luminescence spectrum of tugtupite presents a wide band consisting of 11 narrow equispaced bands, the spectral positions of which are given in table 3.

Table 2. Vibrational frequencies of the molecular ions of oxygen and sulphur

Molecular ions of oxygen	$\Delta v_{ m av}$, cm ⁻¹	Author		ılar ions ulphur	$\Delta v_{ m av}$, cm ⁻¹	Author
O ₂ +	1876	Herzberg, 1950	S_2^0		726	Herzberg,
O_2^0	1580	Herzberg, 1950	S_2^-	in KCl	587	Rolfe et al. 1961
O_2^-	1260 ± 70	SCHULMANN & KIRK, 1964	S_2^-	in KBr	580	Rolfe et al. 1961
O ₂ in NaCl	975	SCHULMANN & KIRK, 1964	S_2^-	in Na ₂ SO	O₄ 567	Rolfe et al., 1961
O ₂ in KCl	980	SCHULMANN & KIRK, 1964	S_2^-	in CaSO,	600	Data of
O ₂ in KBr	962	Schulmann & Kirk, 1964	S_2^-	in BaSO	4 620	authors

Similar spectra are typical for absorption and radiation of various molecular ions, for instance the diatomic molecules H_2 , F_2 , O_2 , S_2 (Herzberg, 1950). Molecules, as well as atoms, have discrete energy levels – electronic, vibrational and rotational – the energetic positions of which are different in the spectra. In the ultraviolet and visible regions electronic bands are usually observed associated with transitions between different states of electron shells of molecules. A definite set of vibrational nuclear energy levels corresponding to each state of the electron shells and radiation (or absorption) of the molecule will be presented by an electron-vibrational spectrum; vibrational processes complicate the structure of the electronic band.

Discussion

On the basis of what has been said, one can draw the conclusion that the luminescence spectrum of tugtupite is of electron-vibrational nature and due to the presence of molecular ions in the crystal structure. The distances (Δv) between the narrow bands of the spectrum correspond to the distances between the vibrational sublevels of the basic state of molecular ions (Herzberg, 1950; Rolfe, Lipsett & King, 1961).

The luminescence centres can be unequivocally identified by the EPR method, but in our case this method is not suitable because of the cryptocrystalline nature of the object under study. Nevertheless, on the basis of the known experimental data (Pringsheim, 1949; Schulmann & Kirk, 1964), one may conclude that molecular ions of oxygen and sulphur can be the luminescence centres in tugtupite.

Each of such ions is characterized by a definite average vibrational frequency ($\Delta v_{\rm av}$) depending mainly on the electronic structure of the ion and, to a lesser extent, on the crystal field of the compound in which this ion is present. Average vibrational frequencies of molecular ions of oxygen and sulphur are presented in table 2.

Table 3.	Frequency	characteristic o	of the	luminescence	spectrum o	f tugtupite
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Number of band	v, cm-1	Δv , cm ⁻¹	I (°/°)
1	18868	620	1,4
$2\ldots\ldots$	18248	580	5,2
3	17668	574	15,2
4	17094	565	30,4
5	16529	529	51,9
6	16000	592	74,3
7	15408	593	91,0
8	14815	570	99,0
9	14245	547	100,0
10	13698	506	92,4
11	13192		79,0

 $\Delta v_{\rm av} = 568$ cm⁻¹ (see table 3) of tugtupite calculated from the luminescence spectrum coincides with the value of Δv for the molecular ion of S_2^- . The luminescence of the studied samples may therefore be associated with this ion. Radiational transitions in the ion S_2^- take place from one of the vibrational sublevels of the excited state to the vibrational sublevels of the basic state $2_{\pi_{s/s}}$.

The temperature stability of the tugtupite luminescence should be noted. This gives reason to suppose that the molecular ion S_2^- is almost as stable in the tugtupite structure as ionic S in lazurite. The difference here seems to be purely quantitative. In the latter mineral atoms of S predominate. Their action is thus more concentrated and, consequently, the position is more stable, which is particularly expressed in the fact that its colour cannot be wiped out at the highest temperatures (Vorobbieva, 1946).

It is obvious that the crimson colour of tugtupite is due not only to the molecular ions S_2^- , which are the cause of its luminescence, but also to still other, thermically less stable, radiation centres, for example $(SO_4)_2^-$, as is established for ussingite (Povarennykh, Platonov & Belichenko, 1970).

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References

- Borgström, L. 1901: Mineralogiska notiser. 4. Hackmanit ett nytt mineral i sodalitgruppen Geol. För. Stockh. Förh. 23, 563-566.
- Danø, M. 1966: The crystal structure of tugtupite a new mineral Na₈Al₂Be₂Si₈O₂₄ (Cl, S)₂. Acta crystallogr. **20**, 812–816.
- Herzberg, G. 1950: Molecular spectra and molecular structure (2nd ed.) Vol. 1. Spectra of diatomic molecules. 658 pp. Princeton, New Jersey: van Nostrand.
- Pauling, L. 1930: The structure of sodalite and helvite. Z. Kristallogr. Kristallgeom. 74, 213-225.
- POVARENNYKH, A. S., PLATONOV, A. N. & BELICHENKO, V. P. 1970: On the colour of ussingite from the Ilimaussaq (South Greenland) and Lovozero (Kola Peninsula) alkaline intrusions. *Meddr dansk geol. Foren.* 20, 20–26.
- Pringsheim, P. 1949: Fluorescence and phosphorescence. 794 pp. New York: Interscience Publishers, Inc.
- ROLFE, J., LIPSETT, F. R. & KING, W. J. 1961: Optical absorption and fluorescence of oxygen in alkali halide crystals. *Phys. Rev.* 123, no. 2, 447-454.
- Schulmann, J. H. & Kirk, R. D. 1964: Luminescent sulfur centers in alkali halides and other inorganic solids. *Solid St. Communs* 2, 105-108 (Suppl. Jl Phys. and Chem. of Solids).
- SEMENOV, E. I. & BYKOVA, A. V. 1960: [Beryllosodalite]. Dokl. Akad. Nauk SSSR 133, 1191-1193 (In Russian).
- Sørensen, H. 1960: Beryllium minerals in a pegmatite in the nepheline syenites of Ilimaussaq, South-West Greenland. Rep. 21st Int. geol. Congr. Norden 17, 31-35.
- Sørensen, H., Danø, M. & Petersen, O. V. (in press): On the mineralogy and paragenesis of tugtupite from the Ilímaussaq alkaline intrusion, South Greenland. *Meddr Grønland* 181¹³.
- VOROBIEVA, O. A. 1946: [Thermocoloration of hackmanite from Luyavrurt]. [D. S. Belyankin jubilee vol., Acad. Sci. USSR], 122-129. (In Russian).

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