BØGGILDITE

A NEW PHOSPHATE-FLUORIDE FROM IVIGTUT, SOUTH GREENLAND

BY

HANS PAULY

Abstract.

A new compound fluoride, phosphate-fluoride, was discovered by R. Bøgvap in 1950 in the boundary rock of the cryolite mass in the quarry in Ivigtut. South Greenland. He published a brief notice of the fact and had managed to give the mineral the name boggildite in honour of Professor em. O. B. Bøggild, when Bøgvad died in the summer of 1952 in the midst of his work in Ivigtut. The following description is made on the material found by Bøgvad. Further material has not been discovered, and there thus exists only a good 100 grams of the mineral. It is monoclinic, X-ray examinations showing that it is pseudorhombic, belonging to space group No. 14 P21/c It appears in columnar aggregates up to 12 mm long and some millimeters wide; it is salmon-coloured. Bøggildite is colourless under the microscope; α , β , γ are respectively 1.462, 1.466 and 1.469. 2 V lies between 78 and 80°. Axial dispersion can hardly be seen. The composition of the mineral corresponds to the formula Na₂Sr₂Al₂(PO₄)F₂. It may be grouped together with the mineral known from Ivigtut, jarlite.

PREFACE

During the years R. Bøgvad worked with the occurrence of cryolite in Ivigtut as geologist with Kryolitselskabet Øresund A/S, several new minerals appeared which he has described. Bøgvad had looked forward to the day when he could link name of his former teacher, Professor O. B. Bøggild, to a mineral from Ivigtut.

It was therefore with particular pleasure, in the spring of 1952, upon the occasion of Professor Bøggild's 80th birthday, that Bøgvad was able to present a sample of still a new mineral and obtain permission to give it the name of bøggildite.

We would like to take this opportunity to point out that the publication of the description of bøggildite most appropriately marks the 50th anniversary of the first sizable, comprehensive description of Greenland's minerals which Bøggild published in 1905: Mineralogia Groenlandica.

ARNE NOE-NYGAARD.

ACKNOWLEDGEMENT

It is the author's belief that it is in the spirit of Bøgvad to thank Professor O. B. Bøggild once more for the permission to attach his name to the new mineral.

To Professor Arne Noe-Nygaard, who has followed the work of examining the new mineral with great interest, the author owes sincere thanks for the opportunity of completing this investigation. At the same time, one cannot omit expressing a regret that it was not Bøgvad himself who carried it through, for surely with his great personal knowledge he could have contributed a good deal of valuable material to the investigation.

It is a pleasure for the author to thank Kryolitselskabet Øresund A/S for the permission to publish this work.

The author owes special thanks to A. H. NIELSEN both for his chemical analyses and determinations and, not least, for the interest and kindness Mr. NIELSEN has shown the author during the work and in discussing the various problems connected with it.

The author was also very grateful for receiving Aage Jensen's information on the conditions of the discovery. Finally, warm thanks are expressed to Stig Bak-Jensen for his willingness to undertake the universal stage measurements, the results of which are essential for the understanding of the optical properties of the mineral.

Mrs. Marguerit Jantzen has kindly undertaken the translation.

Mineralogical Department Kryolitselskabet Øresund A/S Copenhagen

HANS PAULY.

BØGGILDITE

In the summer of 1950, R. Bøgvad found in the cryolite deposit in Ivigtut "a new mineral for Ivigtut and perhaps a completely new fluoride" as he himself has noted in this diary. The preliminary examinations had already shown that a completely new mineral was under consideration, and this was confirmed by later examinations which revealed that this was a heretofore unknown phosphate-fluoride. In 1951 Bøgvad published a provisional notice on the discovery in which he reported the following:

"A new mineral has been discovered in the south wall of the cryolite mine near the boundary of the cryolite toward the surrounding greisen, in which it is enclosed, accompanied by siderite, fluorite, black cryolite, quartz, green mica, and sphalerite. The mineral is monoclinic (or triclinic), twinning lamellae occur, and some crystal faces are fairly well developed. H. = 4-5; G. = 3.66; colour is flesh red; optically +; axial angle rather large; $1.46 < \alpha, \beta$, and $\gamma < 1.47$. — According to a chemical analysis by A. H. Nielsen, the composition is: Na₂Sr₂Al₂(PO₄)F₉. A full description of the mineral will appear in the near future."

Unfortunately, Bøgvan did not live to give the promised description of the mineral, he died suddenly of a heart attack while working in the region of Ivigtut in August, 1952.

It appears from Bøgvad's diaries that the mineral was found the 2nd of June, 1950, in some samples which were collected on the 31st of May, 1950. Aage Jensen, who was with Bøgvad when he collected these samples, states that Bøgvad, who had found the reddish mineral in some larger blocks of greisen rock lying in a pile of material blasted down from the south wall of the mine, had noticed it as being something out of the ordinary. Bøgvad cut out all that could be seen, and when the character of the new mineral had been ascertained, the pile was thoroughly searched and those places to which this material had been taken from the mine earlier in the year, were examined further. A portion of samples with reddish minerals in them were collected, but all of them proved to be composed of known minerals which were discoloured by iron oxide.

8 HANS PAULY.

The collection Bøgvad made on the 31st of May resulted in three pieces, weighing 200, 300 and, 500 grams, in which the greatest amount of the new mineral is found. Besides this, there were quite a few small pieces which contained varying amounts of the mineral. The total amount of bøggildite in this material is believed to be a little over 100 grams.

We are still on the lookout for the new mineral, both in Ivigtut and in the plant in Copenhagen where the products of the mine are worked over and where there is an opportunity to go through the waste in a comparatively thorough way. Further material has not been found, and the following description is therefore based solely on those samples found by Bøgvad.

Description of the hand specimens.

As mentioned above, the material was found in loose blocks in the "granite"-pile at the southern wall of the quarry. That means that it comes from those rocks which surround the cryolite and which are removed before the latter is broken. The mineral has not been observed in situ. Bøgvad places it in the greisen (the rock which surrounds the cryolite) and adjacent to the former's boundary to the cryolite itself. This is quite natural when one takes into consideration the character of the hand specimens. They cannot possibly come from the cryolite mass itself, and, on the other hand, the mineral's composition is such that it no doubt belongs to the greisen rock, though to special parts of it which are actually found most frequently in the vicinity of the boundary of the cryolite mass.

The hand specimens consist of greenish-yellow rocks with some dark to black minerals in them, and they are, if not dominated by, at least strongly characterised by the contrasting salmon colour of the bøggildite.

The greenish-yellow colour arises from a fine-grained mica which since olden times has been called "ivigtite". As a rule, it is so fine-grained that only under the microscope can one discover the individual "scales". It can be so coarse-grained, though, that the scales can be up to a millimeter in diameter. Chemically it is a K-mica, and it should probably be termed as sericite.

It is believed to be characteristic of the new mineral that it is always found in a matrix of this mica, in which it appears together with a few other minerals. The description of the specimens, therefore, naturally falls into two sections: a description of the mineral outside the matrix, and a description of the matrix itself and its components.

In one hand specimen, a xenolite-like mass is found, partly surrounded by the matrix, constisting of fluorite and mica (ivigite) together

with some quartz. It is a rather compact mass constisting of grains of millimeter size. It is believed that this rock corresponds to certain altered rocks which are found here and there in the boundary of the cryolite mass. It contains a little pyrite and sphalerite as well as albite, which appears as thin crusts or as crevice fillings.

The second specimen contains, besides the matrix, a small quantity of massive, milky quartz appearing as irregular patches in the matrix. Bøggildite is not found in these parts of the specimen.

The largest of the hand specimens differs somewhat from the other two in that the greenish matrix is found in a larger mass of quartz-sphalerite in a "pegmatitic" development, penetrated, i. a., by fluorite in finegrained form. The quartz-sphalerite mass consists of equal-sized lumps, several centimeters in size, of massive, milky quartz and sphalerite The sphalerite contains chalcopyrite in numerous tiny droplets, and thereby takes on a greenish-gray sheen, which is quite characteristic. The sulphide is partly idiomorphic against the surrounding masses.

There are a few strictly idiomorphic crystals, in the quartz mass itself, of a completely black sphalerite, marmatite, which strongly differs from the sphalerite first mentioned in that, *i. a.*, it does not contain any chalcopyrite droplets. The crystals are several millimeters in size.

The sample also contains smaller amounts of pyrite, mainly in the fluorite mass; galena, molybdenite and a zircon known from the greisen in Ivigtut, which is brownish-gray and pyramidally developed, are also observed.

The greenish-yellow matrix and the minerals appearing in it are the same in all three samples. Pyrite crystals of millimeter size are evenly distributed in the matrix; they are all developed as pyritohedra (210). Sphalerite occurs in crystals which are several millimeters in size. Chalcopyrite is not found in this sphalerite, and it differs from both of the above-mentioned types of the mineral in being fairly light brownish-yellow. Thus, three different types of this mineral are found in these hand specimens. An iron analysis of the light sphalerite revealed 1.34 % Fe corresponding to 2.1 % FeS. The very black sphalerite probably contains 10 % Fe if one is permitted to compare it with other known dark varieties of the mineral from Ivigtut, on the basis of the colour.

The light sphalerite, as stated above, is nicely crystallised in the green mica. If it borders on quartz, which here appears in partly idiomorphic form, the sulphide takes on the crystal faces of the quartz. The characteristic form of sphalerite is also relinquished in the presence of bøggildite. It is even seen as lamellae alternating with the twinning lamellae of bøggildite.

The quartz described above is as clear as glass in opposition to the quartz outside the matrix. Where it borders the bøggildite, just as in the case of the sphalerite, one can see the surfaces of the bøggildite imprinted in the quartz.

A few small crystals of zircon, developed with practically the pyramid faces only, are seen in the matrix. Their colour is a pronounced gray as opposed to the ordinary zircon known in greisen which is brownish. If one can judge from the colour, it is probable that it is only a matter of small crystals of a type of zircon which has proved to be characteristic for the matrix in all of the bøggildite samples. It appears most often in black lumps of a more or less regular form. In cross-section it is sometimes roughly rectangular. A polished surface of this zircon shows a variation in colours from almost white in the central part to nearly black in the outer sections.

This type of zircon has not previously been noticed in material from Ivigtut. A spectrographic examination of the mineral was undertaken by K. Ellitsgaard-Rasmussen, Mag. scient., of the Mineralogical Museum, University of Copenhagen.¹) Besides the elements: Zr, Fe, Si, Ca, Al, Mn, were found Dy, Tm, Yb. The following elements were not found: Er, Gd, Ho, La, Ne, Pr, Sm. The most interesting thing was that Yb seemed to be present in not insignificant amounts, perhaps on the order of $0.x^{\circ}/_{\circ}$.

The following partial analysis of the mineral was carried out by A. H. Nielsen in the Chemical Laboratory of Kryolitselskabet Øresund A/S (The Øresund Cryolite Company, Ltd.).

Zircon from Bøggildite Matrix

SiO_2
ZrO ₂
$Fe_2O_3^2$)
$TiO_2 \dots 0.36$
CaOnone
MgO none
MnO 0.72 —
Loss on ignition
Al ₂ O ₃ is present

It seems to be the rule that an intermediate layer of "ivigite" is always found between the zircon and the bøggildite. The sulphides, on the other hand, are seen to be in direct contact with the zircon, which

 $^{^{1}}$) The author wishes to take this opportunity to express his appreciation for this work.

²⁾ Determined as total iron.

also applies to the quartz. The light sphalerite often appears as veins cutting through the zircon.

Galena is found in rather small quantities together with quartz and the light sphalerite in contact with bøggildite, and a slight amount of albite can be seen together with the new mineral. This is probably the same kind of albite which occurs in one of the hand specimens as fissure fillings.

Bøggildite.

Physical Properties.

Bøggildite itself is well crystallised and appears as columnar aggregates in the matrix. The individual crystals in these aggregates can be up to 12 mm long. The mineral apparently consists of elongated prismatic crystals with a nearly square-shaped cross-section. The faces are striated lengthwise in a way that is somewhat similar to the striation in plagioclase. If crystalfaces other than those described here as prismatic are observed, they always prove to be imprints of other crystals. So in spite of its comparatively free position in the fine-grained mica, it has obviously been impossible for the bøggildite to form free crystals where the terminal faces were also developed.

Definite signs of cleavage have not been observed; but in crushed material of the mineral it is occasionally possible to find individual grains which are completely regular parallelepipeds. This, together with the microscopic examination of the material, seems to indicate a possibility for at least two directions of cleavage (which constitute the prismatic form in the fragment). They cannot be particularly prominent, however.

The surfaces of the fracture, which are rather even, reveal a greasy luster; the crystal faces vitreous.

The hardness is between 4 and 5. Parallel with the longitudinal direction, the hardness seems to be close to that of fluorite, while at right angles to this direction it is a little greater, though distinctly less than the hardness of apatite.

BØGVAD has determined the specific gravity to be at 3.66. This determination was made on the analysis material itself with the help of a pycnometer. The amount of material used was 5 grams. The standard error in this determination is probably 1 to 2 percent.

The mineral is salmon-coloured as seen in potashfeldspar or certain calcite varieties, for example. As it is surrounded by the greenish-yellow "ivigitie", the hand specimens are really rather attractive in appearance, see Plate I, fig. 4.

Under the microscope the mineral is colourless, though in thicker grains slightly reddish; it shows no pleochroism. In most grains there are many different kinds of inclusions: vacuoles, both with and without libellae, as well as inclusions of solid material. The latter can often be elongated bodies, a few μ long; as a rule, they are oriented according to definite directions in the bøggildite. This also applies frequently to the other kinds of inclusions.

In powdered preparations, no definite shapes which can with certainty be interpreted as a sign of cleavage can be seen on the grains. Thus, the position of the directions of the extinctions can be given mainly in relation to the above-mentioned oriented inclusions. Parallel extinctions in connection with symmetrical interference figures are seen here as well as asymmetrical extinctions.

Asymmetrical interference figures, in close proximity to the acute bisectrix, occur with remarkable frequency, and the interference figures in the vicinity of the obtuse bisectrix is seen too frequent and uniform for these orientations to be due to pure coincidence. On this basis, it could therefore be assumed that there must be two different directions of cleavage in the mineral: both rather slight, but the one that corresponds to a section near the acute bisectrix is more pronounced than the other. Whether or not there exist further directions of cleavage cannot be determined from the microscopic study.

As a rule, some grains can be seen in the preparations which consist of several lamellae where the boundaries of the individual lamellae are fairly straight. If there are several lamellae in a grain, they are always seen together in pairs, as the optical orientation is the same for "every other" lamella. One obtains the above-mentioned interference figures, in the vicinity of the acute bisectrix for such lamellae also. It is these twinning lamellae which give the faces of the crystals their striated appearance.

All in all, the optical conditions must be taken as a sign of the fact that the mineral crystallises in the monoclinic system. X-ray examinations show that bøggildite crystallises monoclinically pseudorhombically. These X-ray examinations were carried out on small fragments of the material having the above-mentioned regular parallelepipedic shape. The longitudinal direction of these fragments, which according to the optical examination can be seen to be the same as the longitudinal direction of the crystals, is called the a-axis.

By means of the universal stage, α , β and γ were measured in relation to the longitudinal direction of the grains—the a-axis. About 20 measurements produced the result whereby γ could be assumed to be at right angles to the longitudinal direction. At the same time, the normal to the twinning plane was also measured, whereby it seemed to appear that the twinning plane should be (001). Not all of the grains were equally suitable for measuring, as the shape was often too irregular, and the deviation of these measurements was about \pm 8°. A grain was

subsequently selected whose form was indisputably good, a completely regular parallelepiped, and by means of measurements taken on this grain, the following angles were obtained:

13

$$\left.\begin{array}{l}
\alpha \wedge \mathbf{a} = 36^{\circ} \\
\beta \wedge \mathbf{a} = 54^{\circ} \\
\gamma \wedge \mathbf{a} = 90^{\circ}
\end{array}\right\} \quad \underline{\div} \ 1^{\circ}$$

It must be reasonable to assume from these results that γ coincides with the monocline b-axis and that the axial plane makes an angle of 36° with the a-axis. The average result for the angles of α , β and γ with the normal to the twinning plane for the previous measurements, combined with this last measurement (where a twinning plane could not be measured) still gives the result that the twinning plane must be assumed to be (001). The deviation is within a few degrees.

The refractive indices were determined by the immersion method, and mixtures of terpentine and petroleum, whose indices are suitable in this case, were used:

$$\left. egin{array}{l} lpha &= 1.462 \\ eta &= 1.466 \\ \gamma &= 1.469 \\ \gamma - lpha &= 0.007 \\ + 2 \ V &= 78^{\circ} - 80^{\circ} \end{array}
ight.$$

Axial dispersion weak

Chemical analysis.

The chemical analysis of bøggildite was carried out by A. H. Nielsen of the Chemical Laboratory, Kryolitselskabet Øresund A/S, who has previously published the results (A. H. Nielsen 1954). Before the chemical analysis took place, Bøgvad sent material for spectral analysis to Centrallaboratoriet, Boliden Gruvaktiebolag, Rönnskärsverken, where it was carried out by Allan Danielsson.

Spectral Analysis of Bøggildite. Analyst Allan Danielsson.

	7								
Ag		Cr		Mn	(+)	Sn		Sr	++
Al	++	Cu	(+)	Mo	()	Ta	_	Cs	ł —
As		Fe	(+)	Na	++	Te		Rb	
Au	-	Ga	_	Nb	l - i	Th			
Ba	+	Ge		Ni	-	Ti			
Be	-	Hg		P	++	Tl	_	٠	
Bi	_	Ir		Pb	(+)-+	V	()		
Ca	(+)	K	()	Pt		W	_		
Cd		Li	'	Sb		Zn	_		
Co		Mg	(+)	Si	(+)-+	Zr	[— [

[—] not detectable; (—) not detectable with certainty; (+) trace element less than $0.05 \, \%_0$; ++ 5 - 50 $\%_0$; +++ more than 50 $\%_0$; Cs and Rb: sensitivity is not so great; 0.01 $\%_0$ ought to be detectable, though.

The spectral analysis does not require much comment. Its most interesting aspect is the information it offers about the elements which are not present in the mineral.

Bøgvad has characterised the material for the chemical analyses in the following way: "The material for analysis contains only an extremely slight trace of quartz and "ivigtite". Traces of supposed sphalerite in particles of approximately μ size are found. Aside from this, it is very pure.

Analysis of bøggildite. Analyst A. H. Nielsen.

	Weight 0/0	Ion quotient		
Al	10.04	0.372		
A 1	10,04	0.812	0.373	2.01
Fe	0.06	0.001	3,3,13	
Sr	31.89	0.364		
Ва	0.35	0.003		
			0.379	2.04
Mg	0.18	0.007		
Ca	0.20	0,005		
Mn	tr.	_		
Zn	none	_		
Na	8.60	0.374		
	-	ĺ	0.378	2.03
К	0.15	0.004		
Li	tr.	_		
PO ₄	17.63	0.186	0.186	1.00
F	31.70	1.668	1.668	8.97
C1	none			
Ce	none			
H ₂ O±	none	<u> </u>		
Total	100.80			

Formula: Na₂Sr₂Al₂(PO₄)F₉.

Molecular weight calculated from the analysis 543.3.

Discussion.

As shown by the analysis, a halogenide compound of a hitherto unknown type is present. The phosphate tavistockite may be stoichiometrically written as $CaCa_2Al_2(PO_4)_2(OH)_6$; it could hardly be dismissed completely that there might be certain similarities between this mineral and bøggildite. A small sample which E. A. Jobbins, Ph. D., was so kind to send from the collections of the British Museum, has been subjected to an optical and X-ray examination, but there does not seem to be any resemblance between this mineral and bøggildite. A qualitative test for fluorine showed that there is a little fluorine in tavistockite.

Among the phosphates, there do not seem to be any that are analogous to bøggildite aside from the fact that every normal phosphate can be rewritten in such a way that it corresponds stoichiometrically to bøggildite.

Among the fluorides which can be compared to the new mineral, we are at present familiar only with the mineral jarlite. It contains, except for the phosphate radical, the same elements as those in bøggildite. Since there appeared to be certain discrepancies between the chemical data on jarlite and the physical, particularly the roentgenographical, the mineral has been subjected to another chemical analysis, after which a new formula has been suggested, as published by Bøgvad in his short notice which was partially quoted in the beginning of this paper (Bøgvad 1951). This formula is:

NaSr₂Al₂(F,OH)₁₁

The amount of alkali in jarlite, however, is so negligible that it is completely impossible to obtain stoichiometrical conformity between the two minerals. It is possible that by penetrating more deeply into the problems connected with the mineral jarlite, we will be able to arrive at an understanding of the relationship between the two minerals. Until then, one must be content with establishing jarlite as the mineral most closely related to bøggildite.

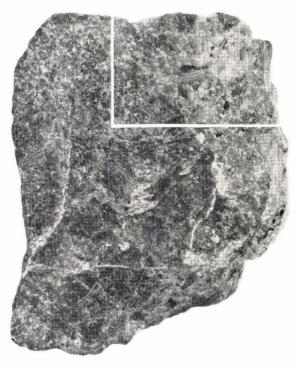
The occurrence of the two minerals is completely different. Jarlite belongs, so to speak, within the cryolite mass, while boggildite can definitely be placed in the boundary rock. This difference of environment and the resulting difference in the chemical composition probably provides part of the explanation of the origin of bøggildite. In this connection, it would be of interest to attempt to establish more accurately the temperature of formation. It should be possible to do this on the basis of the conditions implied by the close connection between light sphalerite and bøggildite. They certainly belong to the same formation, and the method advanced by Kullerud (Kullerud 1953) for temperature determination, with the help of the iron content of sphalerite, might very well provide information of interest. The amount of iron found in the light sphalerite as 2.1 % FeS, however, indicates temperatures under 138° C., which does not seem to be reasonable in connection with the paragenesis mentioned. It is a question of whether, in spite of the presence of pyrite in direct contact with the sphalerite, conditions have existed for the establishment of the iron equilibrium in ZnS, a factor required for the applicability of the method.

REFERENCES

- O. B. Bøggild: The Mineralogy of Greenland. Medd. o. Grønland, Bd. 149, Nr. 3, 1953. Copenhagen.
- RICHARD BØGVAD: New Minerals from Ivigtut, Southwest Greenland. Medd. o. Grønland, Bd. 92, Nr. 8, 1933. Copenhagen.
- Mineralogical observations on the Cryolite deposit at Ivigtut, Greenland. Medd. fra Dansk Geol. Forening, Bd. 12, 1951. Copenhagen.
- Dana: System of Mineralogy. 7. ed. Vol. II, New York 1951.
- Gunnar Kullerud: The FeS—ZnS System, a Geological Thermometer. Norsk Geol. Tidsskrift, Bd. 32, h. 2—4, 1953, Bergen.
- A. H. NIELSEN: Chemical Analysis of a New Mineral, Bøggildite, from Ivigtut, Greenland. Acta Chemica Scandinavica, 8, (1954) 136. Helsinki.



Bøggildite in the greenish-yellow matrix. 4:1.



Hand specimen with Bøggildite. The square indicates the area shown in colours above. Nat. size.