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AN OCCURRENCE OF VILLIAUMITE IN THE ILÍMAUSSAQ INTRUSION, SOUTH GREENLAND

BY

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WITH 1 PLATE

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Abstract.

Villiaumite was found in drill cores from the Ilímaussaq Intrusion, South Greenland.

The villiaumite is found in parageneses which have undergone alteration and in late stage, analcime-rich veins occurring in the per-alkaline rocks, lujavrite and naujaite. Villiaumite is the last formed mineral, crystallizing in a comparatively water-rich environment.

Chemical analysis: F = 44.81, Na = 54.23, insoluble 0.80.

Spectrographic data: 100 ppm Al; less than 100 ppm Si, Ca and Mg; 50 ppm Mn.

Villiaumite in this occurrence is cubic; a = 4.633 Å. R. I. = 1.325

INTRODUCTION

The Ilímaussaq Intrusion forms part of the alkaline province of South Greenland, and is situated near the settlement of Narssaq, at 61° north and 46° west.

The detailed petrology of the intrusion has been described by Ussing (1911), while Sørensen (1958) discussed and reviewed certain features of the general geology of the complex.

Villiaumite was found in core during a restricted drilling program in the northern part of the intrusion, namely in the Kvanefjeld area. These specimens contribute to the study of villiaumite found in the two agpaitic rock types, naujaite and lujavrite. The Kvanefjeld area has been described by Bondam (Bondam and Sørensen, 1958). The villiaumite occurrence has previously been mentioned in a note by Bondam (1960).

So far, villiaumite has been observed only in the agpaitic rock suite of the Ilímaussaq Intrusion, as the drilling has been confined to areas of these rock types. Due to the solubility of villiaumite, it has not been observed in the field, although numerous small vugs have been noted in the surface rocks.

This work was carried out under the auspices of the Grønlands Geologiske Undersøgelse using the laboratory facilities of the Mineralogisk Museum, Copenhagen and Kryolitselskabet "Øresund". The authors gratefully acknowledge the encouragement and assistance received from these institutions. Thanks are due to H. Sørensen for critically reviewing the manuscript.

Geological Setting of the Kvanefjeld in Relation to the Intrusion.

The earliest rock of the intrusion is an augite syenite of just saturated composition. The magma has intruded through the Julianehåb granite and the later Gardar continental series of basalts and sandstones (USSING, 1911, WEGMANN, 1938, SØRENSEN, 1958, HAMILTON, 1962, FERGUSON, 1962).

There has been chilling of the augite syenite magma against the roof and along the margins. The magma then proceeded along an undersaturated differentiation trend, forming horizontal saucer shaped bodies in the central part of the intrusion. This differentiation was interrupted by an injection of alkali-acid rocks into the higher part of the magma chamber, where reaction took place with the earlier undersaturated rocks to form hybrids. Thereafter undersaturated differentiation continued, giving rise to a series of per-alkaline, agpaitic rocks (FERGUSON 1962). It is thought that a considerable amount of volatiles helped the original augite syenite magma to achieve this super-undersaturated differentiation (FERGUSON, 1962, SØRENSEN, 1958).

Finally a residual liquid, rich in volatiles, was squeezed and injected into the overlying rocks during a final stage of slumping and brecciation, giving rise to the fissile lujavrites.

The Kvanefjeld area lies along the northern border of the intrusion where the former horizontal, saucer-shaped rock series have been upturned into a vertical position, exposing the breccia zone where the naujaite, augite syenite and Gardar volcanics are enclosed in lujavrite.

The final stage of the intrusion is marked by an alteration, presumably autohydrothermal, due to late stage fluid cencentrations. The action of this phase is widespread. In the Kvanefjeld area, it is accompanied by the development of pegmatitic veins and lens-shaped bodies.

Short Description of the Agpaitic Host Rocks.

Naujaite.

Naujaite is characterized by being made up of feldspar, aegirine, arfvedsonite and eudialyte of pegmatitic dimensions, while sodalite crystals are included in the above mentioned minerals.

The sodalite content of the rock is usually 35 to 45 per cent. Sodalite-rich varieties with 60 to 70 per cent sodalite are known.

The normal feldspar is a perthite which can develop micro- and crypto phases.

The aegirine and arfvedsonite frequently undergo acmite replacement.

The eudialyte is normally clear; rare-earth mineral alteration can usually be observed.

The nepheline and sodalite often have subordinate replacement by analcime and natrolite.

Lujavrite.

The lujavrites are characterized by being medium- to fine-grained rocks which display a strong preferred orientation of the prismatic minerals, giving the rock a distinct fissility.

There are two main varieties of lujavrite in the Ilímaussaq intrusion, an arfvedsonite-rich black lujavrite and an aegirine-rich green lujavrite. The villiaumite was only located in the black lujavrite as drilling was carried out in an area poor in green lujavrite. It is not thought that villiaumite has a particular preference for the black rather than the green lujavrite.

In the normal black lujavrite, the arfvedsonite forms prisms of 1 to 2 mm long, together with minor aegirine needles.

Microcline and albite make up separate plates from 1 to 2 mm in width.

The feldspathoids, nepheline and sodalite, form rounded grains, 1 to 2 mm in diameter.

Eudialyte commonly occurs as hexagonal plates about 1 mm in diameter.

The Paragenesis of Villiaumite.

General.

So far, villiaumite has been observed only in parageneses which have undergone alteration, as well as in late stage, analcime-rich, pegmatite veins or pegmatitically developed, recrystallization centres of the Kvanefjeld occurrence.

In naujaite the villiaumite is inhomogeneously disseminated. The grains average 2 mm in diameter.

There does not appear to be much structural control, although there seems to be a tendency to concentrate in local areas while still remaining disseminated. Entirely barren areas are rare in a villiaumite-occurring zone. Villiaumite is absent, however, in most of the bore

holes. When it is present, it occurs in all agpaitic rock types, having a slight preference for the naujaite.

Vugs, filled by villiaumite, are not uncommon in the naujaite. These vugs are usually associated with the occurrence of ussingite. In only one case was a stringer of villiaumite noted, passing through the naujaite.

In lujavrite the disseminated villiaumite grains are generally smaller than in naujaite, averaging about 1 mm in diameter. Barren villiaumite areas are common within a continuous homogeneous lujavrite; there is an alternating villiaumite- and non-villiaumite sequence. Usually the villiaumite makes up 2 per cent of the mineral content of the lujavrite when it is present.

On one occasion a vug of about 3 cm diameter was present in lujavrite, filled with villiaumite of an intense deep carmine colour. The radioactive trace elements are concentrated in the lujavrites, this may explain why the colour of villiaumite in lujavrite is of a deeper red than in naujaite.

Spectacular amounts of villiaumite were observed in pegmatitic segregations in analcime-rich parts of the naujaite. A section from one drill hole (Kv. 6), at 110.0 m depth, shows the following interesting mineral association: villiaumite, ussingite and chkalovite as main constituents, together with small aegirine needles. Both villiaumite and chkalovite are included in ussingite. Ussingite occupies the greater part of the section: its colour is faint violet to light pink.

A number of cavities in the ussingite are filled with a fine-grained, white mineral which on x-ray examination turned out to be villiaumite. The white villiaumite is microscopically very different from the usual carmine-coloured villiaumite. As far as is known, this is the only occurrence of reprecipitated villiaumite found in nature.

In the above mentioned pegmatitic paragenesis the villiaumite attains a size of about 4 cm.

Microscopic.

Villiaumite in naujaite.

The feldspar is either albite-twinned, microcline perthite or cryptoperthite. Peculiar to some of the alkali feldspars is a narrow rim of untwinned albite. In most instances there has been partial analcime and occasional ussingite replacement of the feldspars.

Arfvedsonite is usually in excess of aegirine. The latter is frequently found either homoaxially intergrown or as fragment inclusions, in the arfvedsonite. Homoaxial acmite replacement of the arfvedsonite has taken place. In extreme cases of alteration there are anhedra of neptunite, ussingite, white mica and schizolite, in association with the

acmite. In other cases the arfvedsonite has undergone heavy kataphoric-hornblende replacement.

The included sodalites are crowded with microlites of arfvedsonite and aegirine, which tend to concentrate towards the core. Usually there is a rim of analcime between the sodalite and the host mineral.

In all villiaumite specimens examined, the eudialyte was partly altered. The initial stages of this alteration is marked by a changing of colour of the normally clear eudialyte to a pale yellow. By complete alteration the eudialyte may be replaced by steenstrupine and possibly, in a few cases, by lovozerite.

The steenstrupine in these instances is marked by concentric zoning in brown colours, as viewed in plane polarized light. The zoning is less noticeable under crossed nicols. Two variations usually arise, the core of the mineral grains can be isotropic with a narrow birefringent rim or else the whole crystal is replaced by a slightly birefringent micro-granular aggregate. These crystals contain abundant aegirine microlites.

The naujaite containing villiaumite is always high in analcime. On all cases this mineral has totally replaced nepheline, which is conspicuously absent. Alkali feldspar and sodalite have been replaced to some extent by analcime.

Minor ussingite is usually present, either as large irregular anhedra showing a complicated multiple twinning or as fine granules frequently occurring in veins and fractures. These two varieties can be intimately mixed.

Ussingite can replace most of the minerals in the rock. In extreme cases of ussingite-replacement, flakes of it are included in the amphiboles and pyroxenes.

Villiaumite usually forms irregular anhedra 1 to 3 mm in diameter. It has a patchy colouring in varying shades of pale carmine-red. In some cases the villiaumite can display a very slight birefringence along the margin, otherwise it is normally isotropic. Small needles of aegirine and arfvedsonite or flakes of ussingite project into the villiaumite. Small, rounded, colourless, birefringent grains of analcime are also included locally. The villiaumite has a marked cubic cleavage, as shown in fig. 2.

In all the naujaite occurrences, villiaumite was either enclosed in sodalite, analcime or ussingite. In most of the cases, villiaumite penetrates into the surrounding minerals along cleavage and fracture directions. (see fig. 1).

Villiaumite in lujavrite.

The arfvedsonite has a slightly higher homoaxial acmite breakdown than usual, otherwise it is similar to the normal development in black lujavrite.

The microcline and albite laths have undergone minor analcime replacement.

Nepheline cores are present with a fringe of natrolite followed by a rim of analcime.

The sodalite has analcime replacement along the rim.

The eudialyte has been totally replaced by steenstrupine having a distinct concentric brown zoning in plane polarized light. Two types of pseudomorphs occur, those with an isotropic core and anisotropic rim and those that are made up of a birefringent microgranular aggregate.

The villiaumite has a patchy colouring, being shades of a pale carmine-red. There is sometimes a slight birefringence along the margin otherwise it is completely isotropic. Minor arfvedsonite prisms project into the villiaumite. Small rounded inclusions of sodalite are present.

The villiaumite is confined to areas in the lujavrite that were apparently occupied by either nepheline or sodalite, as can be inferred from the relationship of the arfvedsonite needles.

Usually, irregular shaped villiaumite anhedra are surrounded by sodalite, with veinlets of the former projecting into the surrounding minerals.

Discussion on Villiaumite Occurrences.

Villiaumite is only known from two other localities, both agpaitic nepheline syenite intrusions.

The mineral was first named and described by LACROIX (1911) from Iles de Los, Guinée, where villiaumite is found as a disseminated accessory in a eucolite—sodalite—arfvedsonite-nepheline syenite, particularly well developed on the island of Rouma. In following publications he made further studies of the Rouma rocks (LACROIX, 1924).

GERASIMOVSKII (1941) published data on the second occurrence in poikilitic sodalite syenite from the Lovozero complex on the Kola Peninsula. Later it was found in a wide range of different peralkalic rocks, though it is particularly well developed in poikilitic sodalite syenite. Other alkaline rocks in which villiaumite occurs are juvite, lujavrite, malinite, urtite and ijolite-urtite (VLASOV et al., 1959).

The third known occurrence in the Ilímaussaq intrusion is found in similar sodalite-rich rocks.

Villiaumite seems therefore rather specifically tied to the peralkaline parageneses.

Opinions have been divergent as to the water content of the volatiles. LACROIX (1924) discussing the genesis of villiaumite on the base of the paragenesis of the Rouma nepheline syenites, mentions

water as an important mineralizing agent. It was emphasized, though, by GERASIMOVSKII (1941) that villiaumite could only be formed in parageneses in which water has been of minor importance as a mineralizing agent due to the solubility of villiaumite in water at elevated temperatures.

Bearing in mind that hydrofluoric acid is a weak acid in a water bearing environment at hydrothermal temperatures, not readily attacking the silicate phase or entering crystal structures, it seems, judged by the descriptions of the respective parageneses, that LACROIX's assumption is correct.

The mineral assemblage of the Kvanefjeld occurrence is very similar to that of the Rouma occurrence, containing minerals which are comparatively rich in water, like analcime and ussingite. Moreover it is clear that villiaumite is the last formed mineral. This means that hydrofluoric acid present in the volatile phase reacts in the final stage of rock formation. The chemical environment, with a surplus of sodium, makes villiaumite one of the few possible late-stage fluorine minerals to be formed in water-containing systems.

Chemical Analyses of Villiaumite.

The chemical analysis was carried out on material with a purity of 99.2 per cent. It was accomplished at the laboratories of Kryolitselskabet "Øresund" by Mrs. E. L. MORTENSEN.

The following analytical methods were used: F has been precipitated as PbClF and calculated on the base of the Cl-content of the precipitate.

Na has been determined as a sulphate.

Table 1. Chemical data on villiaumite.

Loc. Anal.	Rouma PISANI	Lovozero K. SOKOVA	Kvanefjeld E. L. MORTENSEN
F	44.2	45.28	44.81
Na	53.4	53.83	54.23
Cl	n.d.	n.d.	–
K	tr	0.32	–
Mg	tr	–	n.d.
Ca	1.2	–	–
ZrO_2	1.5	–	n.d.
insoluble	–	0.84	0.80
sum	100.3	100.12	99.84

Table 2. The Na/F ratio.

Rouma	Lovozero	Kvanefjeld	sodium fluoride
1.208	1.189	1.210	1.211

The chemical composition of the Kvanefjeld villiaumite is given in table 1 together with that of the two other known natural occurrences, Rouma (Iles de Los) and Lovozero (Kola Peninsula).

In order to gain comparable data on the three different villiaumite analyses the Na/F ratio has been computed and listed in table 2, together with the same ratio for sodium fluoride.

Spectrographic Data.

Several spectrographic analyses were run on the Kvanefjeld villiaumite. This work was carried out by Mr. IB SØRENSEN, Mineralogical Museum, Copenhagen.

The normal runs showed a persistent and varying content of Al, Si, Mg and Ca due to minute inclusions of other minerals in the villiaumite.

A carefully selected sample, without any visible impurities, contained about 100 ppm Al, 100 ppm Ca and less than 100 ppm Si and Mg.

Recrystallized villiaumite showed amounts of less than 100 ppm Si and Ca.

Mn is found in an amount of about 50 ppm, Sr and Ba were below the limit of detection.

Data on the Lovozero villiaumite also show low Ca and low Mg. The higher figures for Al and Si are certainly due to mineral impurities. Fe, Ti, Ni and Co were not determined in the Kvanefjeld villiaumite, as these elements usually give unreliable figures.

Structural Data.

The structure of villiaumite has been investigated by BARTH and LUNDE (1927) on material from Iles de Los.

LACROIX (1924) had stated that the mineral is tetragonal. BARTH and LUNDE found that the structure was nearly identical with that of sodium fluoride which had been determined some years earlier to be cubic. They further discuss the anomalous behaviour of villiaumite under the polarizing microscope, and reach the conclusion that the

structure of villiaumite is pseudo-cubic, estimating the c/a ratio as 1.005 from measurements of the width of the powder pattern lines.

As to the cause of the deviation from the cubic lattice, BARTH and LUNDE decide that radioactive radiation, combined with mechanical deformation, possibly explains the anomalous behaviour of villiaumite compared to chemically prepared sodium fluoride. Radiating sodium fluoride during 40 hours caused a faint red colouring: mechanical deformation, though gave no anomalous reactions on sodium fluorine.

GERASIMOVSKII (1941) published structural data of the Lovozero villiaumite without comment. Powder diagrams, prepared by E. P. MERCHERIKOVA, were used. The reflections were compared with those of sodium fluoride: judged from the tabled data, the Lovozero villiaumite is cubic.

The structure of the Kvanefjeld villiaumite has been determined by Mrs. M. DANØ, Mineralogical Museum, Copenhagen, on the Philips diffractometer, using Cu K-alpha radiation with a current of 20 mA at 36 kV.

The mineral is cubic. There is a tendency of a broadening of the peaks which means that it is slightly anomalous. A flattening of the peaks may be expected when the lattice is distorted by hard radiation.

The structural data are given in table 3.

Table 3. Structural data of villiaumite from Kvanefjeld.

hkl	d
200	2.317
220	1.638
220	1.638
222	1.338
400	1.158
420	1.036
422	0.9457

a: 4.633 Å

Refractive Index.

The crystals of villiaumite were too small to allow refractive index determinations by goniometer. Normal immersion methods combining sodium light and halofluorcarbon liquids were used. The colour variation of the villiaumite does not appear to correspond to a refractive index change.

R. I. = 1.325 (accuracy 0.001).

BIBLIOGRAPHY

BARTH, T. and LUNDE, G., 1927: Über das Mineral Villiaumit. Centr.bl. f. Min. etc. 1927 A, 57—66.

BONDAM, J. and SØRENSEN, H., 1958: Uraniferous nepheline syenites and related rocks in the Ilímaussaq Area, Julianehaab District, Southwest Greenland. Proc. 2nd UN Int. Conf. on the Peaceful Uses of Atomic Energy. *2*, 555—559.

BONDAM, J., 1960: Uranundersøgelser på Kvanefjeldet ved Narssaq. (foredragsreferat) Medd. Dansk Geol. Foren. Bd. 14, 3.

FERGUSON, J., 1962: Possible mode of emplacement of Ilímaussaq Intrusion. Medd. Dansk Geol. Foren. Bd. 15.

GERASIMOVSKII, V., 1941: O villiomite iz Lovozerskii tundr. Doklady Akademii Nauk SSSR *32* (7).

HAMILTON, E., 1962: Petrochemistry of the northern half of the Ilímaussaq Intrusion. Medd. om Grønland (in press).

LACROIX, A., 1911: Les syénites néphéliniques de l'archipel de Los et leurs minéraux. Nouv. Arch. du Mus. *3*, 5. ser.

— 1924: Nouvelles observations sur les syénites néphéliniques des iles de Los (Guinée). C. R. Acad. des Sc. *178*, 1109—1114.

SØRENSEN, H., 1958: The Ilímaussaq batholith. A review and discussion. Medd. om Grønland. Bd. *162*, 3.

USSING, N. V., 1911: Geology of the country around Julianehaab, Greenland. Medd. om Grønland Bd. 38.

VLASOV, K. A., KUZMENKO, M. V. and ESKOVA, E. M., 1959: Lovozero Alkaline Massif. Akademii Nauk SSSR.

WEGMANN, C. E., 1938: Geological investigations in Southern Greenland. Part I: On the structural divisions of Southern Greenland. Medd. om Grønland Bd. 113, Nr. 2.

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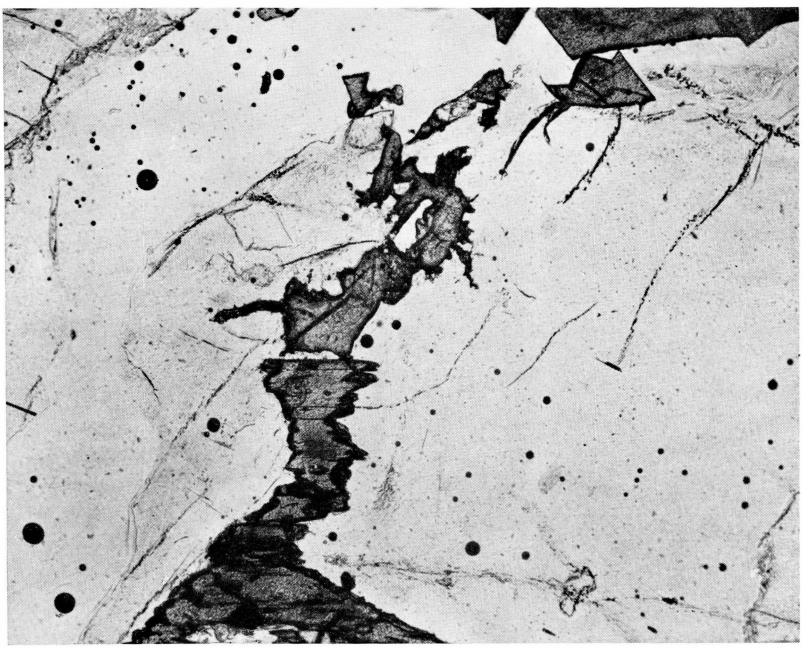

Fig. 1. Villiaumite (grey) enclosed in ussingite (white) and penetrating along fractures. Aegirine showing cleavage is present in the lower half of the photograph. Plane polarized light × 26. (photo CHR. HALKIER).

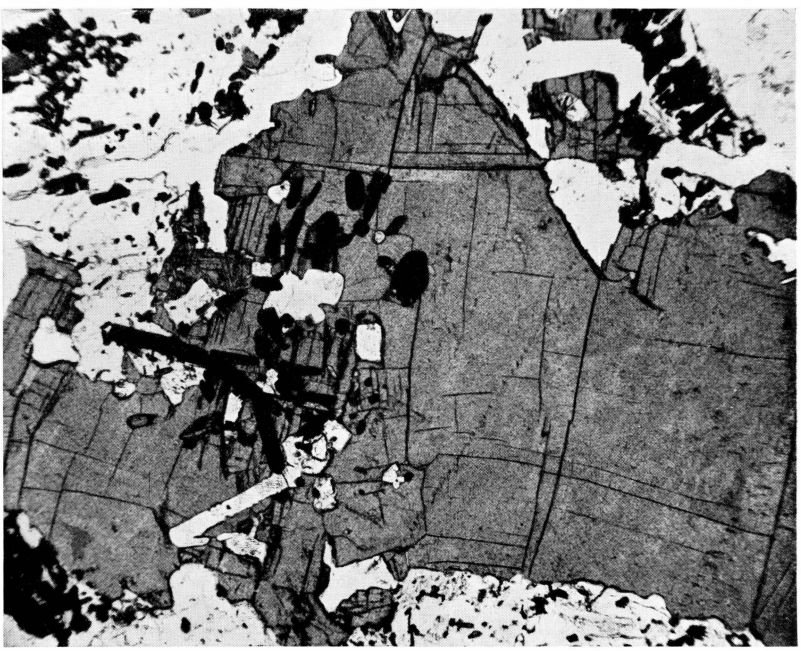

Fig. 2. Large anhedra of villiaumite (grey) showing cubic cleavage. Arfvedsonite prisms (black) are poikilitically included. The white areas are now occupied by natrolite pseudomorphs, probably after feldspar. Plane polarized light × 26. (photo CHR. HALKIER).