Anker Weidick

TRONA AND THERMONATRITE FROM THE ILÍMAUSSAQ ALKALINE INTRUSION, SOUTH GREENLAND

Contribution to the mineralogy of Ilímaussaq, no. 17

HENNING SØRENSEN, ERIK S. LEONARDSEN AND OLE V. PETERSEN

SØRENSEN, H., LEONARDSEN, E. S. & PETERSEN, O. V.: Trona and Thermonatrite from the llímaussaq alkaline intrusion, South Greenland. Bull. geol. Soc. Denmark, vol. 20, pp. 1–19. Copenhagen, July 9th, 1970.

Powdery trona and thermonatrite have been found as crusts on the walls of cavities in ussingite in a drill core in the northern part of the Ilímaussaq intrusion. The ussingite forms the core in a thin vein intersecting naujaite enriched in villiaumite.

The optical and X-ray data of the two minerals are identical to those of trona and thermonatrite from saline deposits. The aggregates of sodium carbonate contain a few grains of ussingite, villiaumite, tugtupite, analcime, sodalite(?) and natrolite(?).

The sodium carbonates are considered to have been deposited at low temperature from strongly saline "brines" trapped in cavities in ussingite. The villiaumite was formed at higher temperatures and appears to be earlier than the ussingite.

The drill core in question, like all other villiaumite-bearing drill cores from llímaussaq, is covered by an efflorescense of sodium acetate trihydrate which also is associated with the sodium carbonates. This substance was clearly formed after the collecting of the drill core.

During a routine examination of drill cores from the Kvanefjeld plateau, situated near the north-west contact of the Ilímaussaq alkaline intrusion, one of the authors (H.S.) found a white micro-crystalline aggregate in drill core no. 6 at a depth of 109.74 m below the surface. The aggregate formed a partial covering to the roof of a small cavity in ussingite.

A closer examination of the aggregate showed it to be a mixture mainly of the minerals trona and thermonatrite with sodium acetate trihydrate. The same mixture, but with varying proportions of the constituents, has subsequently been identified at the bottom of the same cavity and in several very small cavities at depths between 109.8 m and 112.1 m in the same drill core.

SØRENSEN, LEONARDSEN, PETERSEN: Trona and Thermonatrite



Fig. 1. The cavity in the drill core no. 6, containing the trona and thermanatrite. \times 2.

Mineralogy

General description

The main cavity occurs in almost pure ussingite and measures approximately $3 \times 2 \times 2$ cm (fig. 1). The walls of the cavity are partly lined by crystals of ussingite, which are now the subject of a separate study.

The filling of the central part of the cavity is not preserved. This is the cause of a distinct separation between the irregular roof and the pan shaped floor of the cavity.

The very fine-grained aggregate covering the bottom of the cavity, which has a characteristic ripple-mark-like surface, and the white aggregate covering the irregular roof of the cavity are made up of a trona-thermonatrite-

sodium acetate trihydrate mixture (identical X-ray powder diagrams). Patches of partially dissolved villiaumite occur along the margins of the »pan«. The white aggregate on the roof is mixed with pink villiaumite and numerous small colourless grains of ussingite (but in amounts too small to give any lines on an X-ray powder diagram of the entire aggregate).

X-ray diffraction

X-ray powder diagrams of the total aggregate from the roof as well as of the part of this aggregate insoluble in water were prepared in a Guinier-Hägg camera. Silicon and quartz, respectively, were used as internal standards. In the calculation of the lattice constants the weighted means of α_1 and α_2 wave-lengths for copper radiation 1.5418 Å have been used.

In table 3 the observed d-values from the total aggregate are compared with the d-values of trona, thermonatrite and sodium acetate trihydrate recorded in cards nos 11-643, 8-448 and 14-753 respectively of the ASTM Powder Diffraction File, 1967. Although a few departures do occur it seems permissible to conclude that the major part of the aggregate is a mixture of these three substances.

The reciprocal lattice constants of both trona and thermonatrite have been calculated and adapted by means of 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 E. S. Leonardsen was used. The calculated $\sin^2\theta$ values are compared with the observed values for both minerals in table 3. The lattice constants determined from these sets of $\sin^2\theta$ values are given in table 1.

The few additional lines on the diagram have not been identified.

	Trona	Thermonatrite
2	from Ilin	maussaq
a ₀	20.423 ± 0.005 Å	10.728 ± 0.003 Å
b ₀	$3.495 \pm 0.001 \text{ Å}$	5.253 ± 0.002 Å
c ₀	10.336 ± 0.003 Å	$6.476~\pm~0.003$ Å
β	$106.42^{\circ} \pm 0.02^{\circ}$	
Vol	707.7 A ³	364.9 Å ³

Table 1

The part of the aggregate insoluble in water has been identified as ussingite by comparison of X-ray powder diagrams even if some discrepancies between the intensities of corresponding lines were noticed.

1*

Sodium acetate trihydrate also occurs as acicular, white to colourless, aggregates efflorescing abundantly on the parts of this and other drill cores from Ilímaussaq containing villiaumite. It was also identified on crystals of trona in a specimen labeled trona, German East Africa, (Min.Mus, coll. number 1963.399).

Optical properties

The optical examination was carried out on a powder preparation consisting almost exclusively of rectangular grains with high birefringence. All grains are length fast. These grains are considered to be single crystals of thermonatrite and trona and not cleavage pieces.

The refractive index $n\alpha'$ has been determined by suspending the material in KEL-F (n = 1.409) and petroleum (n = 1.431), the refractive index $n\gamma'$ by means of the λ -T variation method; optical glass was used as internal standard (Micheelsen, 1957). The determinations, which were carried out by R. Waagstein, gave the following indices of refraction for $\lambda = 589$ nm:

 $n\alpha' = 1.42 \pm 0.01$ $n\gamma' = 1.54 \pm 0.01$

When using the data for trona and thermonatrite given in table 2, the optical examination shows that the powder preparation consists of rectangular grains of trona and/or thermonatrite resting on {001} and elongated after b and a, respectively. Due to the small difference between the $n_{\alpha \text{ trona}}$ and $n_{\alpha \text{ thermonatrite}}$, the small difference between $n_{\gamma' \text{ trona}} \simeq n_{\gamma \text{ trona}}$ and $n_{\gamma \text{ thermonatrite}}$, and the practically identical axial figures of the two minerals (only very few axial figures were obtained), it was not possible to distinguish the two minerals optically.

	nα	nβ	nγ	$2V_{\alpha}$	Optical orientation	System and habit	Cleavage
Trona	1.412	1.492	1.540	720	$\begin{array}{l} \alpha = b \\ \gamma : c = 83^{\circ} \end{array}$	Mon. platy after {001} and/or elongated after [010]	{100} and {101}
Thermo- natrite	1.420	1.506	1.524	480	$\begin{array}{l} \alpha = a \\ \gamma = b \end{array}$	Orth. platy after {001} or {100}	{010}

Table 2

The sodium acetate trihydrate is optically negative, $2V_{\alpha}$ varying from large to about 60°. The birefringence is large – about that of trona; one direction of perfect cleavage yields obtuse optic axial figures; and $n_{\beta} \sim$ 1.48₍₁₎. These properties correspond closely to the optical properties of artificial sodium acetate trihydrate, Merck pro. ana.

The following minerals have been observed forming a few grains in the powder preparation: ussingite (anisotropic, medium birefringence, $n \sim 1.50$), villiaumite (isotropic, n = 1.328), tugtupite (uniaxial, $n \ge 1.49$), analcime ? (isotropic, $n \le 1.48$), sodalite ? (isotropic, $n \sim 1.483$), natrolite ? (anisotropic, low birefringence, $n \sim 1.483$) and an unidentified mineral (isotropic, $n \ge 1.333$).

Occurrence

The site of the vertical drill hole no. 6 is situated at an altitude of 623.5 m about 160 m north of the trial excavation in the central part of the Kvanefjeld plateau (see Sørensen et al., 1969). The uppermost 55 metres of the core consist of altered basalt from the roof of the intrusion. This rock is veined by lujavrite which contains xenoliths of naujaite. The lower-most part of the core is made up of naujaite veined by separate dykes of fine-grained and medium-grained lujavrite (Sørensen et al., 1969) and by thin veins of ussingite, sodalite, etc. Ussingite veins are present especially at depths between 103 and 114 m below the surface (fig. 2).

The naujaite and lujavrite of this core are rich in disseminated villiaumite (cf. Bondam & Ferguson, 1955).

In the part of the drill core rich in ussingite veins the naujaite is cut by dykes of fine-grained arfvedsonite lujavrite which are up to about 0.6 m wide and dip at about 45° . The naujaite appears to be enriched in ussingite adjacent to the lujavrite veins.

The ussingite veins are up to about 0.3 m wide and are steep to vertical. They follow a wavy course and it is therefore quite possible that all »veins« at depths between 109.55 and 112.20 m are portions of one and the same vein.

The ussingite veins have border zones made up of large anhedra of yellow sodalite and of fine-grained aggregates of arfvedsonite, steenstrupine, natrolite, etc. There may be small flakes of epistolite. The yellow sodalite appears to replace the adjacent naujaite and there is thus a gradation from vein to naujaite. The cores (central parts) of the veins are made up mainly of ussingite sometimes with crystals of chkalovite (up to a few cm across) in the outer parts and also containing sphalerite, epistolite, schizolite and Limica. DRILL HOLE NO. 6 KVANEFJELD

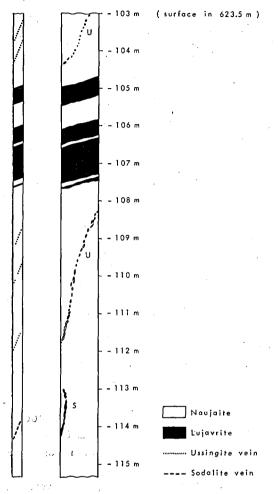


Fig. 2. Generalized section of the part of the drill core in which sodium carbonates have been found. Left side: features as observed on the drill core; right side: interpretation of observations.

At depths of 109.60 m and 110.10 m the uppermost part of the ussingite core of one vein (or two veins?) is rich in villiaumite while this mineral is absent in the lower part of the vein where small cavities in the ussingite contain white crusts of trona, etc. Apart from these occurrences of villiaumite this mineral has not been found in the ussingite veins of this drill hole. In the larger cavities there are pink aggregates of tugtupite in the marginal zones of the trona.

At depths between 114.15 and 114.85 m below the surface the naujaite contains an almost vertical vein, 1-2 cm thick, composed mainly of yellow sodalite with villiaumite along the margins. Sodalite is lacking in the uppermost part of the vein observed in the drill core. Arfvedsonite predominates in this part of the vein.

Petrography

The naujaite cut by the ussingite veins is very fresh having small green crystals of sodalite 0.1–0.8 cm across, enclosed in anhedra of microcline, aegirine, arfvedsonite and eudialyte. Nepheline and aenigmatite are scarce in the specimens examined. There is very little late or secondary analcime and natrolite, but granular aggregates of natrolite may occur along cracks in grains of sodalite and microcline.

The arfvedsonite is often partly replaced by schizolite and sodalite and the eudialyte is almost always partially replaced by lovozerite, schizolite, steenstrupine and perhaps villiaumite. The nepheline, when present, is partially replaced by sodalite and natrolite. Round grains of fluorite may be rimmed by schizolite.

Two types of sodalite may be distinguished in thin section. The primary poikilitically enclosed sodalite (green) is crowded with small microlites of arfvedsonite and aegrine (Ussing, 1898). These primary grains may be rimmed by sodalite without microlites and there are also areas of microlitefree sodalite (yellow) which appear to be of late origin.

Villiaumite occurs as anhedral grains which are mainly confined to grain boundaries, also those of sodalite enclosed in microcline, and to fractures and cleavages in aegirine and eudialyte. The interstitial villiaumite sends offshoots into adjacent sodalite and microcline.

The naujaite is intersected by veins dominated by either natrolite or sodalite or ussingite.

In thin sections of sample 111.50 irregular veinlets of granular natrolite penetrate the naujaite. These veins contain Li-mica, steenstrupine crystals, lovozerite, arfvedsonite and villiaumite. The villiaumite occupies interstitial areas. The naujaite adjacent to these veinlets is rich in yellow sodalite and the adjacent eudialyte is strongly replaced by lovozerite.

A sodalite-rich veinlet was studied in thin sections of nos 114.10, 114.15 and 114.36. It is dominated by anhedra of yellow sodalite and villiaumite which may be a few cm across. The contact zones are mainly composed of prisms of arfvedsonite and crystals of steenstrupine, both of which have grain sizes of 1 mm or less. Sodalite and schizolite also occur and there are veinlets of granular natrolite.

The sodalite zone contains corroded grains of chkalovite, small prismatic grains of arfvedsonite, small steenstrupine crystals, and schizolite. Villiaumite occurs as interstitial anhedra and as fine impregnations in zones of fracturing in the sodalite and may in these cases be associated with granular natrolite. The villiaumite may enclose crystals of steenstrupine, schizolite and lovozerite.

SØRENSEN, LEONARDSEN, PETERSEN: Trona and Thermonatrite

The sodalite is intersected by zones of fine-grained ussingite which may be associated with the granular natrolite. The adjacent sodalite is partially replaced by more coarse-grained ussingite. Villiaumite may occur in the marginal parts of the ussingite zones but is otherwise lacking in these places. The ussingite encloses needles of aegirine and arfvedsonite, steenstrupine crystals, lovozerite, corroded grains of sodalite and chkalovite, and small »blebs« of natrolite.

The naujaite adjacent to the ussingite veins, contains a good deal of ussingite, as seen in thin sections of nos 104.20, 106.05 and 108.84. Ussingite penetrates the naujaite along grain-boundaries and partially replaces sodalite and microcline. Sodalite crystals enclosed poikilitically in aegirine may also be substituted by ussingite and ussingite occurs along the cleavages of the aegirine. The ussingite encloses areas of villiaumite, especially in the marginal parts of the veins, but villiaumite is very scarce in the ussingite.

The naujaite adjacent to the ussingite veins may be enriched in small crystals of steenstrupine and small prisms of arfvedsonite and schizolite, and there is often a rim of yellow sodalite which appears to be partly replaced by the ussingite. The euclalyte of the naujaite is substituted by aggregates of lovozerite, katapleiite, Li-mica and steenstrupine.

The ussingite veins were studied in thin sections of nos 110.42 and 112.18. The border zones of these veins have small crystals of steenstrupine, arfvedsonite, schizolite, epistolite and aegirine in a matrix of yellow sodalite. There may be patches of microcline and large rounded grains of chkalovite (partially crushed). Ussingite penetrates this zone and contains corroded remnants of sodalite and microcline. There are also patches of granular natrolite in the border zones; this is associated with albite.

The cores of the veins are made up mainly of granular ussingite with grain sizes up to 0.5 cm or more. The grains display irregular extinction, bent cleavages and have sutured outlines. There are areas of fine-grained ussingite.

In the ussingite there are corroded grains of chkalovite (with partial rims of sodalite and analcime), schizolite, steenstrupine crystals, lovozerite, arfvedsonite, aegirine, corroded patches of sodalite and perhaps also of analcime.

The fine-grained lujavrite intersecting the naujaite was examined in nos 91.63, 91.75, 106.23 and 106.95. These lujavrites are rich in usingite and further contain nepheline, microcline, arfvedsonite, steenstrupine, aegirine, sodalite, natrolite, albite and naujakasite.

The ussingite replaces nepheline, microcline and albite. In patches analcime replaces nepheline and microcline. There are scattered grains of villiaumite.

Poikilitic grains of steenstrupine have lath-shaped inclusions of ussingite which are probably pseudomorphs after microcline.

The fillings of sodium carbonates in cavities in ussingite could not be studied in thin section.

Discussion

On the distribution of carbon compounds in Ilímaussaq

Only small amounts of carbon compounds have been noted so far in Ilímaussaq.

Veinlets and thin fracture fillings of calcite occur rarely in foyaite, pulaskite and aegirine veins intersecting naujaite. This calcite may be associated with fluorite and natrolite (E.I. Semenov, personal communication). Small grains of carbonate minerals have occasionally been observed in thin sections of the agpaitic rocks of the intrusion.

Cerussite has been noted as an alteration product of galena (E.I. Semenov, personal communication).

Bastnäsite has been found in quartz-aegirine veins in the alkali granite of the uppermost part of the intrusion (E.I. Semenov, personal communication) and is furthermore found in albite-aegirine-hematite veins in the country rocks of the intrusion (Hansen, 1968).

Dahllite (staffellite) forms crusts on fractures in naujaite, etc. but is only present in small quantities (Bøggild, 1915).

Primary gas-liquid inclusions in nepheline from naujaite and in chkalovite and tugtupite from late veins are rich in CO_2 . The aqueous solutions of the inclusions in the chkalovite are highly saline with up to 40 weight per cent NaCl (Sobolev et al., 1970).

By evacuation of powders of naujaite at room temperature rather large quantities of hydrocarbon gases may be collected. These probably originate from secondary fluid inclusions. The naujaite and other rocks of the intrusion furthermore contain disseminated bitumens. The isotopic composition of the carbon of the gases favours a non-biogenic (mantle) derivation of the carbon (Petersilie & Sørensen, 1970).

The observations mentioned above indicate that carbon-bearing gases were present in the original gas phase of the agpaitic magma, but that the physico-chemical conditions during crystallization of the magma did not favour the formation of carbonates, etc. Carbonate ions appear further to have been available only in small quantities during the formation of the late veins. As pointed out by Sørensen (1962, pp. 188 and 212) this may be due to a concentration of CO₂ in the gas phase expelled early in the consolidation of the magma and to a fixation of carbonate ions as complex ions in the residual alkaline fluids. When these complex ions were made unstable at low temperatures, deposition of the rare elements took place and CO_2 was released and concentrated in the vapour phase if the pressure was sufficiently low. During this stage the crusts of calcite and dahllite may have been formed.

The powdery tugtupite associated with the sodium carbonates may have been deposited when beryllium-carbonate (-chlorine-fluorine?) complexes were made unstable (cf. Govorov & Stunzhas, 1963). In this connection should be pointed out that tugtupite is often found in vugs (Sørensen et al., in preparation).

Paragenesis of sodium carbonates

Trona and thermonatrite occur as crusts on the walls of cavities in ussingite. The ussingite forms the cores of thin veins intersecting naujaite. The naujaite is also cut by dykes of fine-grained lujavrite adjacent to which it is enriched in ussingite.

The ussingite veins are zoned with yellow sodalite, natrolite, villiaumite, arfvedsonite, etc. concentrated along the margins. Sodalite appears to have formed first together with chkalovite. Fine-grained natrolite associated with villiaumite occurs in fractures in the sodalite and in the adjacent naujaite. The ussingite appears to be later than these minerals and partially replaces the sodalite. The naujaite adjacent to the veins is also impregnated with ussingite along grain boundaries.

There is no indisputable evidence of natrolite replacing ussingite at this locality although this is commonly found in other veins in Ilímaussaq (Sørensen et al., in preparation).

The evidence presented above suggests that ussingite was formed by pneumatolytic or hydrothermal ussingitization of sodalite veins and naujaite.

On the origin of the sodium carbonates

At least three modes of formation may be considered:

1. Sodium carbonates have been demonstrated to be true magmatic minerals forming lavas and ash layers at, for instance, Oldoinyo Lengai, Tanzania (Dawson, 1962), which is a volcanic carbonatite complex. Melts of sodium carbonate may be formed by liquation as demonstrated experimentally by Koster van Groos & Wyllie (1965) in the system CaO – Na₂O – Al₂O₃ – SiO₂ – CO₂ – H₂O.

The occurrence of »globules« of sodium carbonates in ussingite is a natural equivalent of this system but according to the available evidence

ussingite was formed by pneumatolytic or hydrothermal processes and it is therefore unlikely that the sodium carbonates were formed from a melt.

2. Kogarko (1961 and 1962) has discussed the association of villiaumite and schairerite (Na₂SO₄.NaF) from the Lovozero intrusion, Kola Peninsula. These two minerals form mixed aggregates in the interstices between nepheline and feldspar in pegmatites. This association is considered to have been deposited at elevated temperatures due to the low solubility of sodium sulphates and sodium fluoride at temperatures close to the critical temperature of water. Schairerite and villiaumite are therefore, in contrast to NaCl, stable at high temperatures in the presence of water vapour. At lower temperatures the two minerals are unstable and are therefore dissolved. This explains the frequent occurrence of leaching cavities (elatolites) in Lovozero. Such cavities are also widespread in Ilímaussaq. The high temperature assemblage is consequently preserved only in places where it was sheltered from low temperature hydrothermal alteration.

Kogarko (1964) has also pointed out that in highly alkaline systems hydrous silicate melts may, according to experimental data, pass gradually into aqueous solutions without separation of a gas phase, even at relatively low pressure. This means that the volatile compounds remained in the solutions to give sodalite, villiaumite, etc. In Lovozero villiaumite became unstable during zeolitization and ussingitization, but it is stable together with analcime.

In Ilímaussaq villiaumite is associated with natrolite, but appears to be earlier than ussingite.

Sodium carbonate, like sodium sulphate, has a low solubility at high temperatures, but is easily soluble in water at low temperatures. The trona and thermonatrite might therefore have been formed by processes similar to those put forward by Kogarko for the Lovozero villiaumite. The wide distribution of villiaumite, the supposed scarcity of carbonates in Ilímaussaq and the occurrence of sodium carbonates in cavities in ussingite do not favour a genetic connection between villiaumite and sodium carbonates.

It may further be pointed out that according to Ikorskii (1967) villiaumite in the Khibina intrusion, Kola Peninsula, crystallized from solutions enriched in hydrocarbon gases at temperatures lower than 500° C, which also speaks against the primary association of villiaumite and sodium carbonates.

3. Semenov (1964) and Vlasov et al. (1959) report the presence of crusts of thermonatrite on fractures in rocks from Khibina and Lovozero of the Kola Peninsula.

Dorfman et al. (1967) have described stalactites of opal and trona in exploration openings in villiaumite-bearing nepheline syenites in the Lovozero intrusion. This material is considered to be a precipitate from aqueous solutions migrating in rocks containing nepheline and villiaumite. Sodium bicarbonate may then be formed at the expense of sodium fluoride.

In Ilímaussaq sodium carbonates have been found so far only in villiaumite-bearing rocks. This may indicate that migrating late fluids have dissolved villiaumite during subsequent precipitation of sodium carbonates.

Trona and thermonatrite are important constituents of some types of continental saline deposits. The association of these two minerals and the lack of nahcolite in the ussingite veins may by comparison indicate deposition at low partial pressures of CO_2 , the lack of soda (natron) deposition at not too low temperatures. The high salinity of the solutions precludes a high temperature of formation (cf. for instance Eugster & Smith, 1965).

The soda carbonates of Ilímaussaq occur in an environment rich in villiaumite of earlier formation. In saline deposits such as Searles Lake, California (Smith & Haines, 1964), trona is associated with nahcolite, galeite and schairerite (both Na₂SO₄.Na(F,Cl)), sulphohalite ($2Na_2SO_4$. NaCl,NaF), analcime, borates, etc. This indicates that NaF does not occur independently at near-surface conditions.

Heinrich (1966, p. 126) suggests that saline sodium carbonate deposits may be genetically connected with magmatic (carbonatitic) activity, since the Green River saline beds of Wyoming contain a number of minerals which are characteristic for alkaline igneous rocks.

Conclusions

The combined evidence from gas-liquid inclusions in minerals and from the late deposition of soda carbonates indicate that the late aqueous fluids of the agpaitic magma of Ilímaussaq were of the NaCl-type of thermal water containing NaCl, KCl and HCO₃- (cf. White et al., 1963 CO₂ was present in the gas phase at high temperatures, while hydrocarbons prevailed at intermediate temperatures.

The residual saline solutions very probably contained carbonate and fluorine complexes of rare metals. When these complex ions became unstable, villiaumite was formed at high temperatures while hydrocarbons synthesized from CO_2 and H_2O dominated the gas phase. At still lower temperatures sodium carbonates crystallized from strongly saline »brines« trapped in cavities in ussingite together with small amounts of tugtupite.

Sodium acetate trihydrate

As mentioned above, carbon-bearing gases were present in the original gas phase of the agpaitic magma. A synthesis of hydrocarbons from CO_2 , CO and H₂O may have taken place during the last stages of consolidation (see

p. 12), but it seems difficult to believe that the sodium acetate trihydrate should have been formed hydrothermally during this phase. It is also hard to believe that the continuous formation of sodium acetate trihydrate at room temperature and 1 atm. which can be observed on the drill cores and on the museum specimen of trona is due to purely inorganic processes. We therefore tentatively propose that the sodium acetate trihydrate is of biochemical origin even if traces of sponges and bacteria are lacking.

Added in proof

M. D. Dorfman, G. O. Piloyan & F. M. Onokhin (On sodium carbonate with 10 water – soda – from the Khibina alkaline massif (in Russian), *Transact. Miner. Museum, Moscow* 19, 159–164, 1969) have described the occurence and genesis of soda in the deep galleries of the apatite mines of the Khibina intrusion. This soda is found in crystal cavities in ussingite veins and as cores in aegirine-feldspar veinlets. Both types of veins contain villiaumite. There are inclusions of corroded villiaumite, and crystals of natrolite and barytes in the soda. The soda quickly decays into thermonatrite when exposed to the atmosphere. As soda is a mineral formed at low temperature it is considered a result of chemical weathering under arctic conditions of rocks containing nepheline and villiaumite caused by solutions containing dissolved CO_2 .

It cannot be excluded that the thermonatrite of Ilímaussaq also is secondary after soda and thus a result of low-temperature reactions in villiaumitebearing rocks. It should be pointed out, however, that the fine-grained powdery aggregates of thermonatrite and trona have constantly been seen immediately after opening of cavities in the ussingite of the drill core. A low temperature hydrothermal deposition of trona and thermonatrite is therefore also possible.

Acknowledgements. The authors wish to thank cand. polyt. I. Sørensen and cand. polyt. N. Hansen for the chemical tests carried out on the material and cand. mag. A. Kjøller who examined the material in order to find remnants of organisms.

The authors also wish to thank Mrs. R. Larsen who drew the figure, Mr. P. Riel who prepared the photograph, Mrs. M. Grumløse who typed the tables and Mr. T. C. R. Pulvertaft who kindly corrected the English of the manuscript.

Thanks are also due to the Director of the Geological Survey of Greenland, K. Ellitsgaard-Rasmussen, for permission to publish this report.

Dansk sammendrag

Trona og thermonatrit er fundet i borekærne nr. 6 fra Kvanefjeldsplateauet, Ilímaussaq. De to mineraler danner hvide jordagtige, krystalline aggregater på væggene i hulrum i ussingit. Ussingiten udgør den centrale del af en tynd åre, som skærer naujait beriget på villiaumit. Aggregaterne indeholder få korn af ussingit, villiaumit, tugtupit, analcim, sodalit (?) og natrolit (?).

Såvel de optiske data som røntgen-data af de to mineraler er identiske med de tilsvarende data for trona og thermonatrit fra saline aflejringer.

Tronaen og thermonatriten anses for at være afsat ved lav temperatur fra stærkt saltholdige opløsninger indesluttet i hulrum i ussingiten. Villiaumiten er dannet ved højere temperatur og synes at være tidligere end ussingiten.

Samtlige villiaumit-holdige borekærner fra Ilímaussaq er dækket af en udblomstring af natrium-acetat-tri-hydrat, som også er associeret med tronaen og thermonatriten. Natrium-acetaten er dannet efter at borekærnerne er optaget.

> H. Sørensen, Institut for Petrologi, Østervoldgade 5–7, DK-1350 København K, Danmark.

> E. S. Leonardsen, Institut for Mineralogi, Østervoldgade 5–7, DK-1350 København K, Danmark.

> O. V. Petersen, Mineralogisk Museum, Østervoldgade 5-7, DK-1350 København K, Danmark.

> > September 4th, 1969

References

Bøggild, O. B. 1915: Dahllit fra Kangerdluarsuk. Meddr Grønland. 51, 437-443.

- Bondam, J. & Ferguson, J. 1962: An occurrence of villiaumite in the Ilímaussaq intrusion, South Greenland. Meddr Grønland 172(2), 12 pp.
- Dorfman, M. D., Goroshchenko, Ya. G., Sikorskaya, E. K. & Dorfman, A. M. 1967: Reaction between nepheline and aqueous solutions of sodium fluoride and carbon dioxide, *Geochemistry International* 4, 669-670.
- Eugster, H. P. & Smith, G. I. 1965: Mineral equilibria in the Searles Lake evaporites, California. J. Petrol, 6, 473-522.
- Govorov, I. N. & Stunzhas, A. A. 1963: The manner of the transport of beryllium and zoning of its deposits in the course of alkaline metasomatism. *Appendix to Symp*sium Problems of Postmagmatic Ore Deposition. Praha, 145-149.
- Hansen, J. 1968: A study of radioactive veins containing rare-earth minerals in the area surrounding the Ilímaussaq alkaline instrusion in South Greenland. Meddr Grønland 181(8), 47 pp.
- Heinrich, E. W. 1966: The geology of carbonatites. 555 pp. Chicago: Rand McNally & Company.
- Ikorskii, S. V. 1967: Organic matter in minerals of igneous rocks. (In Russian.) Izd. »Nauka«, 120 pp.
- Kogarko, L. N. 1961: Conditions of formation of villiaumite in nepheline syenites (Lovozero massif). *Geochemistry* 1, 84–87.

Kogarko, L. N. 1962: Chlorine-free schairerite from the nepheline syenites of the Lovozero massif (Kola Peninsula). Dokl. Acad. Sci. USSR, 139, 839-841.

- Kogarko, L. N. 1964: Geochemistry of fluorine in alkalic rocks, as illustrated by the Lovozero massif. *Geochemistry* 1, 50-56.
- Koster van Groos, A. F. & Wyllie, P. J. 1966: Liquid immiscibility in the system Na₂O-A1₂O₃-SiO₂-CO₂ at pressures to 1 kilobar. *Amer. J. Sci.* 264, 234-255.
- Micheelsen, H. 1957: An immersion method for exact determinations of refractive indices. The glass method. *Meddr dansk geol. Foren.* 13(4), 177–191.
- Petersilie, I. A. & Sørensen, H. 1970: Hydrocarbon gases and bituminous substances in rocks from the Ilímaussaq alkaline intrusion, South Greenland. Lithos 3. 59-76.
- Semenov, E. I. 1965: Hydrated carbonates of sodium and calcium. Crystallography 9, 88-90.
- Smith, G. I. & Haines, D. V. 1964: Character and distribution of nonclastic minerals in the Searles Lake evaporite deposit, California. U. S. Geol. Surv. Bull. 1181-P, 58 pp.
- 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 instrusion, South Greenland, Meddr Grønland 181(11), 32 pp.
- Sørensen, H. 1962: On the occurrence of steenstrupine in the Ilímaussaq massif, Southwest Greenland. *Meddr Grønland* 167(1), 251 pp.
- Sørensen, H., Hansen, J. & Bondesen, E. 1969: Preliminary account of the geology of the Kvanefjeld area of the Ilímaussaq intrusion, South Greenland. Rapp. Grønlands geol. Unders. 18, 40 pp.
- Sørensen, H., Danø, M., & Petersen, O. V. (*in preparation*): Mineralogy and paragenesis of tugtupite from the Ilímaussaq alkaline intrusion, South Greenland.
- Ussing, N. V. 1898: Mineralogisk-petrografiske Undersøgelser af grønlandske Nefelinsyeniter og beslægtede Bjærgarter. Meddr Grønland 14, 220 pp.
- Vlasov, K. A., Kuzmenko, M. V. & Eskova, E. M. 1959: The Lovozero alkaline massif. (In Russian.) Izd. Akad. Nauk. S.S.S.R., 624 pp. (English translation: The Lovozero alkali massif, 1-627, 1966. Edinburgh: Oliver & Boyd.)
- White, D. E., Hem, J. D. & Waring, G. A. 1963: Chemical composition of subsurface water. U. S. Gcol. Surv. Prof. paper 440-F, 1-67.

Table 3. \times -ray data of trona, thermonatrite and sodium acetate trihydrate see pp. 16-19

Sørensen, Leonardsen, Petersen: Trona and Thermonatrite

1						н Ц	O N A				н Н	E R M	O N A T	RITE		SODIU	SODIUM ACETATE TRI HYDRATE	SODIUM ACETATE UNIDENTIFIED TRI HYDRATE IMPURITY
1				ASTM	CM No. 11-643	-643	Pre	Present paper		ASTI	ASTM No. 8-448	448	ц Ц	Present paper	er	ASTM A	LSTM No. 14-753	
No.	No. Int.	$\sin^2 heta_{obs}$	d _{hklobs} Int. d	Int.	d _{hklobs}	(* 1 त्रम	१त्रेष	sin ² height calc final calcul- ation	Weight in the final calcul- ation	Int.	bkl obs	1 म्म	1¥H	hki hki sin ² 9calo final calcul stion calcul stion	Weight in the final calcul- ation	e Int.	dobs	dots
-	2	0.00613	9.85	99		200		0.00620	1.0									
2	.4	0.00916	8.05										_					8.05
e	-#	0.00989	7.75	_												60	7.8	
4	,n	0.01224	6.97							•	_	_				2	7.0	
ŝ	N	0.02013	5.43	_												ື ຄ	5.4	
Ŷ	ŝ	0.02058	5.37			-				20	5.35	200	200	0.02065	1.0			
2	ŝ	0.02147	5.26							22	5.24	010	010	0.02154	0.5	30	5.2	
80	. 2	0.02466	4.91	140	4.92	(0 0 2 4 0 0	4 0 0	0.02478	1.0									
										N	4.72	110						
۰.	4	0.02733	4.66		_							-				90	4:65	·
9	n	0.03481	4.13	ŝ	4.12	-402	-402	0.03514	0.5	٥	4.12	201	201	0.03482	0.5			
Ξ	4	0.03678	4.02									_						4.02
12	4	0.03726	3.99	20	4.00	202	202	0.03729	1.0						_			
13	4	0.03813	3.95									_		-		20	3.93	
14	e	0.04325	3.71									-				10	3.71	
15	n	0.04506	3.63															3.63
16	e	0.04701	3.56									_				80	3.57	
17	2	0.04908	3.48									_						3.48
38	3	0.05011	3.44	20	3.43	011	110	0.05020	1.0			_						
19	e	0.05391	3.32													20	3.30	
20		3 0.05571	3.27	_			600	0.05576	1.0									(3.27)

<u> </u>								• .																	
		3.11		(3.00)		2.916					2,690														2.390
	3.17				3.01		2.87			2.74			2.66						2.52		2.45			2.40	
	60				100		ñ			60			20		_				40		60			20	
									1.0	0.5	1.0	0.0	•	0.0							0.5	0.0			1.0
									0.07734	0.07823	0.08218	0.08263		0.08339							0.09677	0.09888			0.10415
•									202	0 1 2	3 1 1	400		112							4 0 1	212			4 1 0
									0 2	1 2		0 0		1 2		5 7 0		2 0			10	2			
									2.768 2	2.753 0	2.684 3	2.678 4	<u> </u>	2.667 1		2.622 0		2.550 1			2.475 4	2.448 2			2.386 4 1 0
									100	61	8	53		80	·••	00		3			8	22	*		5
1.0	0.0		0.0	1.0			0.0	1.0							1.0	•	1.0		0.5			0.0	1.0		
0.05797	0.05920		0.06279	0.06345			0.07382	0*02640	0783						0.08477		0.08909		0.09427			0.09913	0.10068		
111	-602		(3 1 0 (4 0 2	116-		,	110	-312		4 ' - -					-511		-2 0 4		-5 1 2			<pre>{ 8 0 0 -1 1 3</pre>	602		
(6 0 0			(3 1 0 (4 0 2					-312		-					-511		-2 0 4		{-5 1 2	-8 0 2		800	602		
3.21	-		3.08					2.79		2.70					2.659		2.587		2.510	2.485	<u> </u>	2.447	2.426	· · · ··	
60			80					ŝ		8					100		20		ñ	2		60	20		
3.20	3.17	3.11	3.08	3.06	3.01	2.916	2.838	2.789	2.774	2.757	2.690		2.669		2.647		2.582		2,511		2.476	2.446	2.431	2.418	2.390
0.05800	0.05918	0.06141	0.06274	0.06341	0.06583	0.06988	0.07379	0.07639	0.07725	0.07820	0.08210		0.08329**)	•	0.08483		0.08914		0.09426		0.09694	0.09936	0.10060	0.10161	3 0.10408
2	ñ	~ ~	6	2	ž	4	10	ĉ	6	2	ŝ		2		10		ŝ		2		5	2	4	4	
21	22	24	25	26	27	28	29	ŝ	5	32	33		34		35		36		37		38	39	9 1	11	42

ASTM No. 11-643 Freent paper 2.373 ASTM No. 11-643 Preeent paper 2.373 Ankloba hkl,ba hkl* 2.373 40 2.259 -5 1 3 0.11565 2.256 -5 1 3 (-5 1 3 0.11565 2.241 2.259 -5 1 3 0.11574 2.219 2.2186 -5 1 2 0.11574 2.219 2.186 {-7 1 2 2.04 0.11674 2.2147 20 2.149 5 1 2 5 1 2 0.12863 2.2147 20 2.149 5 1 2 5 1 2 0.12863 2.2147 20 2.149 5 1 2 5 1 2 0.12863 2.2147 20 2.149 5 1 2 5 1 2 0.12863 2.147 20 2.149 5 1 2 5 1 2 0.12863 2.147 20 2.149 5 1 2 0.12863 2.147 20 2.149 5 1 2 0.12863 2.147 20 2.149 5 1 2 0.12863 2.147 20 2.149 5 1 2 0.12863 2.147 20 2.119 0.12863 0.12863 2.058 40 2.040 2.040 0.14	eL		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1				H H	TRONA	1			T H I	ERMO	N A T	RITE		SODIU TRI I	CODIUM ACETATE TRI HYDRATE	SODIUM ACETATE UNIDENTIFIED TRI HYDRATE IMPURITY
sin ² 0.0ba dhkl 0.0ba Int. dhkl 0.0ba 0.10551 2.373 40 2.259 0.11680 2.256 40 2.259 0.11680 2.219 5 2.183 0.11680 2.219 5 2.186 0.12473 2.219 5 2.186 0.12249 2.2130 2.214 5 0.12891 2.120 2.149 5 0.12891 2.120 20 2.149 0.12891 2.120 20 2.149 0.12891 2.120 20 2.149 0.12891 2.120 20 2.149 0.12891 2.120 20 2.149 0.14038 2.056 2.040 0.040 0.14038 2.002 0.14452 2.028 40 2.032 0.14452 2.003 0.14450 2.032 0.14450 0.14450 0.2032					AST	i 🛫	-643	Pre	sent paper		ASTM	ASTM No. 8-448	148	Å	Present paper	4	ASTM N	ASTM No. 14-753	, , , , , , , , , , , , , , , , , , ,
7 0.10551 2.373 40 2.259 7 0.11680 2.256 40 2.259 5 0.11680 2.241 5 5.186 6 0.11839 2.241 5 5.186 7 0.12249 2.219 5 2.186 9 0.12249 2.203 5 2.149 4 0.12249 2.219 5 2.149 4 0.12253 2.183 5 2.149 4 0.13228 2.183 20 2.149 5 0.12473 2.183 20 2.149 4 0.12528 2.183 20 2.149 5 0.14038 2.183 20 2.040 7 0.14279 2.040 40 2.040 7 0.14452 2.012 2.012 2.040 6 0.14608 2.0012 2.032 2.032	No.	Ë.	, sin ² 0obs	d ^h klobs	Int.	d _h kt _{obs}		1 भूम	sin ² 0calc			Int. ^d hklobs	१भूम	1भूम	dhklobs hkl hkl sin ² 9 calc final calculation			dobe	Int. dobs dobs
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	-4		0.10551	2.373							62	2.372	121	1 2 1	0.10551				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$											2	2.356	202					_	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$																	0	2.33	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					40		-513	(-513	0.11585)								_		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	47 			2.256				0	0.11674	0.0							10	2.26	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	4			2,241							20	2.238	111	4 1 1	0.11832	1.0			
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	4		0.12070	2.219										-					2.219
5 2.136 5 2.132 4 0.12473 2.183 5 2.136 4 0.12891 2.147 20 2.149 5 5 5 4 0.12228 2.147 20 2.149 5 5 2 5 0.13228 2.120 20 2.119 3	4			2.203				_						-			60	2.21	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$, ,			_											
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	34			2.183							15	2.181	3 1 2	312	0.12469	1.0			
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	4			2.147	20		-		0.12883	1.0									
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	<u>بر</u>		0.13228	2.120	20		÷	-	0.13255	0.5							20	2.13	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$											Ÿ	2.114	320						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				2.064	20				0.14001	0.0	17	2.065	4 0 2	402	0.13929	0.0	20	2.07	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	<u>م</u> ر			2.058				-804	0.14055	0.0							60	2.03	
7 0.14452 2.028 40 2.032 {-7 1 3 -10 0 2 5 0.14679 2.012 4 0.14688 2.003	5			- 2.040	40			-1 1 2-}	0.14266 0.14268	0.0								<u>.</u>	
7 0.14452 2.028 40 2.032 {-7 1 3 -10 0 2 5 0.14679 2.012 40 2.032 1 0 0 2 4 0.14608 2.003											-	2.036	022						
5 0.14679 4 0.14808	2		7 0.14452	2,028	40		{ -7 1 3 -10 0 2		0.14450	1.0									
4 0.14808	ñ			2.012							26	2.010	321	321	0.14681	1.0			
-	ň		4 0.14808	2.003							20	20 2.004 1 2	8	122	0.14803	0.1			

18

•

Sørensen, Leonardsen, Petersen: Trona and Thermonatrite

																								. <u> </u>		
				•																						
		1.98		1.93				1.87			1.81		1.78							1.72						
		15		15				20			ŝ		ŝ							20						
			_													•				··					0.5	0.0
																									0.21524	0.21888
																									520	123
	510		113		412	222	5 1 1		420	213		600	_	322	030		313	130	601		(512)	- c	•	_		
	1.985		1.961		1.920	1.905	1.898		.1.875	1.869		1.787		1.770	1.750		1.741	1.7262	1.7220		1.6926	1.6802		_		
	4		n		2	5	4		e.	2	_	7		Ś	4		~	2	-		n	. 9	, ,	_		
0.0		0.0									_		0.5			1.0				0.0			0		0.5	0.0
0.14915 0.14932 0.14933		0.15383						0.16718					0.18779			0.19570		_		0.20064	0.20093		0.21029	0.21117	0.21524	0.21851 0.21865 0.21878
4 0 7 6 1 2 7 1 2 7 1 2		114						-9.1.2					-315			911				0 2 1	0		~	-6 0 6 -6 0 6	617	-+
					_								_													
1.996		1.965						1.886						-								• .				•
30		30						20												:						
1.994		1.964						1.886					1.778			1.742				1.720				1,680	1,662	1.648
0.14941		0.15411						0.16714					0.18789			0.19581				0.20079				0.21060	0.21523	0.21884
-4		ŝ						n n					<u>م</u>	<u>.</u>		ŝ								4	ν Ţ	
57		58						60					61			62				Ŀ9	}		;	64	65	66