Gmelinite and herschelite from the Ilímaussaq intrusion in South Greenland

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SUMMARY. Hypogene alteration of ussingite from the southern part of the Ilimaussaq intrusion in South Greenland has resulted in the formation of three associations: gmelinite-apophyllite, gmeliniteherschelite-earthy-natrolite, and earthy natrolite alone. Ussingite reacted with late magmatic fluids, producing the secondary minerals either by *in situ* replacement of the ussingite or in cavities, which may be up to 3 cm across.

IN 1972 a 25 cm large angular ussingite block (specimen GGU 150113) was found in the southern part of the Ilímaussaq intrusion in South Greenland. It was located near the edge of the naujaite plateau just north-east of the head of the Kangerdluarssuk fjord. Small amounts of aegirine, steenstrupine, and sphalerite have crystallized penecontemporaneously with the ussingite. The following minerals, present in small amounts, have developed during hypogene alteration of the ussingite: gmelinite, herschelite, apophyllite, and 'earthy natrolite'. They occur in or near cavities up to 3 cm across (fig. 1). Gmelinite and herschelite have not previously been found in Greenland.

Mineral descriptions

Gmelinite is mainly granular, transparent, and colourless, and has a grain size ranging from 0.01 to 0.2 mm (fig. 2). There are also idiomorphic crystals defined by a hexagonal prism terminated by a basal pinacoid (fig. 3). The maximum length of these crystals is one mm.

An emission spectral analysis of gmelinite from the cavity shown in fig. I gave 0.5 % Ca. The analysed material occurs as a crust developed upon partly altered ussingite (figs. 2 and 3). Microprobe analyses on very fine-grained gmelinite intergrown with herschelite in thin section 150113 D from areas of extensively altered ussingite gave $0.7\pm0.2 \%$ Ca (17 grains analysed).

A Guinier powder pattern (film 2020) completed on a portion of the material used for the emission spectral analysis gave: $a = 13.737 \pm 0.003$ Å and $c = 10.061 \pm 0.004$ Å.

Herschelite is granular, transparent, and colourless, and has an average grain size of 0.15 mm (fig. 4). Growth lines, marking a hexagonal prism of the mineral, are always present. Microprobe analyses on the mineral in thin section 150113 D gave 1.4 ± 0.4 % Ca (15 grains analysed). An emission spectral analysis on a mixture of herschelite and gmelinite gave 2.7 ± 1.0 % Ca. From Guinier powder pattern no. 2708

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FIGS. I to 4: FIG. I (top left). Cavity in ussingite block. Note the irregular shape of the gmelinite layer with numerous small circular druses. The surface of each of these is covered by radiating gmelinite crystals. FIG. 2 (top right). Anhedral ussingite grains have been partly altered to very fine-grained gmelinite, which forms irregularly shaped, patchy areas. A crust of granular gmelinite has crystallized upon the ussingite crystals. Upon this crust idiomorphic gmelinite crystals project into the empty space of the cavity (upper part of the photograph). A few flakes of apophyllite (at arrows) lie within the gmelinite layer (Thin section. Nicols crossed). FIG. 3 (bottom left). Gmelinite crystals enclosing a relatively large flake of apophyllite. (Electron microscope photograph). FIG. 4 (bottom right). Irregularly shaped aggregate of herschelite (dark) and veinlets of very fine-grained gmelinite in ussingite (Thin section. Nicols crossed).

the following cell dimensions were calculated: $a = 13.807 \pm 0.006$ Å and $c = 14.995 \pm 0.019$ Å.

Apophyllite is transparent, pink in colour, and occurs as irregularly shaped flakes with an average size of 0.5 mm (figs. 2 and 3). It displays in thin section anomalous bluish-green interference colours of first order under crossed nicols. The material available was not sufficient for analysis but its identity was confirmed by Guinier powder pattern no. 1982.

Earthy natrolite is extremely fine-grained and occurs in dense yellow brown to bluish-green pebble-shaped aggregates up to 0.5 cm in size. An emission spectral analysis gave 1.7 ± 1.0 % Ca.

GMELINITE AND HERSCHELITE FROM ILÍMAUSSAQ

Ussingite is granular, pale pink in colour and varies in grain size from 2 to more than 10 mm. Towards cavities it develops crystal faces. Microprobe examinations have shown that the mineral contains no detectable amount of calcium.

Aegirine, steenstrupine, and sphalerite are present in very small amounts and have not been studied in any detail as no relations exist between them and the ussingite alteration minerals. Aegirine crystals may reach a size of several cm and that of steenstrupine about one cm. Sphalerite is dark brown in colour and occurs in aggregates up to a few cm in size.

Mode of occurrence

The ussingite block is composed of more than 98 % ussingite enclosing the other primary minerals, aegirine, steenstrupine, and sphalerite. These occur in random distribution and orientation.

Cavities with a maximum size of three cm are present. Some of these are coated with earthy natrolite. They are partly filled with less than one cm large, 'pebble'-shaped aggregates composed of extremely fine-grained, light brown earthy natrolite.

Other cavities are characterized by the presence of gmelinite (fig. 1). The walls of these cavities are defined by subhedral usingite crystals upon which a layer of gmelinite has crystallized (fig. 2). The gmelinite forming this layer is granular except for a thin cover of idiomorphic gmelinite crystals, which project into the empty space of the cavities (figs. 2 and 3). Apophyllite is present in insignificant amounts and occurs either enclosed between gmelinite grains (fig. 2) or loosely attached upon the top of the hexagonal gmelinite crystals (fig. 3).

In one cavity the gmelinite layer is porous and many of the pores are filled with bluish-green earthy natrolite. Earthy natrolite also covers the gmelinite layers as a crust up to a few mm in thickness. Apophyllite and idiomorphic gmelinite are not present in this cavity.

The ussingite adjacent to the cavities has been partly altered to gmelinite and herschelite. Apophyllite and earthy natrolite are not present here. The gmelinite is very fine-grained and forms irregularly shaped aggregates within ussingite grains (fig. 2) or it is developed along veinlets cutting randomly across these (fig. 4). With increasing degree of alteration remnants of ussingite lie enclosed in areas of gmelinite. Rarely all the ussingite has been replaced. Numerous cavities, up to a few mm large, occur within these extensively altered areas and are considered to have formed by leaching, when the secondary minerals crystallized.

Herschelite occurs in irregularly shaped and well-defined aggregates within ussingite grains showing only slight gmelinite alteration (fig. 4). Similar aggregates also lie enclosed in aggregates of the very fine-grained gmelinite. A heterogeneous mixture of the two secondary minerals is a common feature.

General mode of occurrence of the minerals identified

Ussingite was first described by Bøggild (1913) from the Ilímaussaq intrusion, where it occurs as a common late stage hydrothermal vein mineral. So far it has been

S. KARUP-MØLLER

found only within this intrusion and in the Lovozero massif in the USSR, where it also represents a late-formed mineral.

It has not yet been possible to synthesize ussingite. The stability of naturally formed ussingite in water at above solidus temperatures (around $450 \,^{\circ}$ C) has been studied by Platt and Rose-Hansen (1975). Due to kinetics subsolidus reactions have not been examined.

Natrolite, albite, or both have formed as secondary minerals after usingite at several localities within the Ilímaussaq intrusion (Sørensen *et al.*, 1971). Natrolite and analcime have crystallized as usingite alteration minerals at the Lovozero massif (Yakovlevskaja and Semenov, 1963; Semenov *et al.*, 1961).

Cavities in ussingite from the northern part of the Ilímaussaq intrusion were found to contain small amounts of trona and thermonatrite (Sørensen *et al.*, 1970). These minerals are considered to have precipitated from fluids entrapped in the cavities. Alteration of the ussingite adjacent to the cavities could not be proven to have taken place.

Gmelinite is known only from a few localities. Within the Antrim basalts in Ireland it occurs in abundance near a pronounced fault zone for a distance of at least 24 miles (Walker, 1961a, b). It is speculated that intruding seawater along the fault zone was mixed with meteoric waters and chlorine contents caused the formation of the gmelinite.

Gmelinite has been synthesized in the system Na₂O, Li₂O, Al₂O₃, SiO₂, H₂O at temperatures below 95 °C (Pereyron *et al.*, 1971).

According to Semenov (1972) gmelinite has been found within the Lovozero nepheline syenites complex as an epithermal alteration product after usingite in naujaite pegmatites. The mineral also occurs as prisms possibly pseudomorphic after another silicate in chkalovite. Gmelinite has also been found together with other zeolites in pegmatites.

Herschelite, first described by Lévy (1825), is rare, and was long considered a sodiumrich variety of chabazite, but Mason (1962), while confirming that the two minerals are isostructural, produced evidence of a miscibility gap in the series.

Comparison of the cell dimensions of Ilímaussaq herschelite with those cited by Gude and Sheppard (1966) for herschelite and chabazite suggest that the two cannot be distinguished by these properties.

Chabazite is known from only one locality within the Ilímaussaq intrusion. According to Bøggild (1953) the mineral was found by Streenstrup in 1876. It occurs in a small, erratic sodalite syenite boulder as 1-2 mm large crystals in narrow fractures. Its identity has recently been confirmed by X-ray diffraction (Guinier film no. 2056), but the composition has not been checked.

Chabazite occurs as a late formed mineral at numerous localities within the Lovozero intrusion (Semenov, 1972). The presence of herschelite has not been reported.

Earthy natrolite is a very common mineral and occurs in abundance at numerous localities within the Ilímaussaq and Lovozero intrusions. It always represents a late-formed mineral.

Apophyllite is a relatively rare mineral both at the Ilímaussaq and at the Lovozero intrusions.

870

GMELINITE AND HERSCHELITE FROM ILÍMAUSSAQ

Origin of the secondary minerals

When the ussingite boulder was broken apart the cavities with the secondary minerals were seen to lie completely isolated in dense and homogeneous ussingite. Towards these cavities ussingite has developed crystal faces which suggests that the cavities were formed at the same time as the ussingite and not later from leaching processes. The formation of the secondary minerals is considered to be the result of reaction between ussingite and late or post magmatic mineral fluids in the cavities. Two modes of formation may be considered:

The fluids in the cavities were isolated from those which percolated the fracture systems at the time when the ussingite was formed. Later, a reaction between the ussingite and the entrapped and stagnant fluids resulted in the formation of the secondary minerals.

The fluids in the cavities were not stagnant. Late or post magmatic solutions may have migrated along fine fractures and mineral grain boundaries. Elements were then both added and removed from the fluids in the cavities while these fluids reacted with the ussingite.

The first alternative is supported by the fact that alteration of the ussingite has taken place only near the cavities and not along grain boundaries or 'invisible' fractures.

The second alternative is favoured by the presence of small amounts of calcium, which has not been detected in the ussingite but only in the secondary minerals. Analyses of ussingite by Bøggild (1913) and by Engell (1968) showed no calcium. The calcium in the secondary minerals is therefore assumed to be derived from the fluids present at the time when reaction between the fluids and the ussingite took place. The degree of alteration observed suggests that these fluids, if entrapped and isolated in the cavities, contained several percent of calcium.

Fluids in late vein minerals (nepheline, sørensenite, tugtupite, and chkalovite) contain NaCl (up to an estimated 44 %) and KCl, but CaCl₂ has not been observed and is either absent or present only in very small amounts (Sobolev et al., 1970). The average content of calcium in the agpaitic nepheline syenites of the Ilímaussaq massif is a mere 0.75 % (Gerasimovsky, 1969). A few of the more common Ilímaussaq minerals contain small but distinct amounts of calcium. According to Gerasimovsky (1969) eudialyte may contain from 6.90 to 11.0 %, arfvedsonite from 0.55 to 2.92 %, and aegirine from 1.10 to 1.93 %. However, distinct calcium minerals (calcite, fluorite, apatite, pectolite-schizolite, and a few others) occur only in very small amounts in late mineral veins. According to Sørensen et al. (1970) and Engell (1968) eudialyte and arfvedsonite have crystallized in the margins of ussingite-bearing mineral veins at several localities. They also found small amounts of relatively large, partly decomposed pectolite-schizolite crystals enclosed in ussingite. An appreciable content of calcium in the ussingite-forming mineral solutions therefore cannot be excluded. However, the sodium to calcium ratio must in any case have been high (11.5 in the nepheline syenites, Gerasimovsky, 1969), causing the crystallization of herschelite instead of the much more common chabazite.

Thin fractures with calcite have been observed to cut ussingite, but they are

S. KARUP-MØLLER

considered post-magmatic in origin and may not have crystallized from fluids derived from the agpaitic nepheline syenites.

Conditions favouring the formation of gmelinite

Natrolite occurs as the most common usingite alteration mineral in both the Ilímaussaq and the Lovozero intrusions. Formation of the rare gmelinite may have required unusual conditions of formation. As mentioned above, Walker (1961b) speculates that formation of gmelinite from the Antrim basalts was caused by chlorine contained in the mineralizing solutions.

Relatively large amounts of chlorine were present in the agpaitic nepheline syenites of the Ilímaussaq intrusion. The naujaites, for instance, contain an average of 2.48 % (Gerasimovsky, 1969). Chlorine has been found in large quantities in fluids entrapped in late-formed vein minerals (Sobolev *et al.*, 1970). Therefore, nucleation of gmelinite may possibly have been promoted by a critical amount of chlorine dissolved in the fluids in the cavities.

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872

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