Zoning in steenstrupine-(Ce) from the Ilímaussaq alkaline complex, South Greenland: a review and discussion

Alexander P. Khomyakov and Henning Sørensen

Most crystals of steenstrupine are metamict, but some are crystalline throughout or in thin marginal zones parallel to the crystal faces of metamict crystals. The anisotropic parts of the crystals have lower contents of U and Th than the interior isotropic parts. Some features, such as high contents of Na in the anisotropic steenstrupine, favour formation of the zonation as a result of crystallisation in a medium in which decreasing amounts of U and Th were available during the last stages of growth of the crystals. One reason for this could be the fixation of U and Th in interstitial pigmentary material. Another feature, the fact that steenstrupine adjacent to fractures penetrating the crystals from the surface is anisotropic, indicates that leaching and recrystallisation may also play a role in the transformation of parts of metamict steenstrupine into an anisotropic phase.

Keywords: agpaitite, Ilímaussaq, mineral zonation, nepheline syenites, steenstrupine

Steenstrupine-(Ce), with the formula Na_{14}Ce_{6}Mn_{2}Fe_{2}(Zr,Th)(Si_{6}O_{18})(PO_{4})_{2}3H_{2}O, is an important rock-forming mineral in the hyper-agpaitic lujavrites of the Ilímaussaq complex, South Greenland (Sørensen & Larsen 2001, this volume). It is the main radioactive mineral in the Kvanefjeld uranium deposit in the northern part of the complex. In the hyper-agpaitic lujavrites it takes the place of eudialyte, the main rare-element mineral in the agpaitic rocks of the complex: naujaite, kakortokite, and aegirine and arvedsonite lujavrites. Steenstrupine is also common in the hyper-agpaitic pegmatites and hydrothermal mineralisations and in the fenitised volcanic roof of the Kvanefjeld plateau (see Sørensen (1991) for a review of the literature on the occurrence of steenstrupine in the Ilímaussaq complex).

In the Lovozero complex of the Kola Peninsula, Russia, steenstrupine-(Ce) is common in the zeolite-rich cores of pegmatites and in hydrothermal veinlets composed of ussingite, natrolite, analcime, etc. (Khomyakov 1995; Semenov 1997).

Steenstrupine is a complex silico-phosphate mineral composed of more than 20 elements. It often occurs as well-developed trigonal crystals. Most grains are metamict and X-ray amorphous. There are, however, also non-metamict crystals which give distinct X-ray patterns. Makovicky & Karup-Møller (1981) and Moore & Shen (1983) described the crystal structure of steenstrupine based on the examination of an occurrence of crystalline steenstrupine.

The mineral is often altered, which is demonstrated by the great variation in the contents of Na_{2}O from more than 10 wt% to less than 1 wt%. In the crystal structure Na^+ is easily substituted by H^+ (Makovicky & Karup-Møller 1981; Moore & Shen 1983).

The aim of this paper is to describe and discuss the occurrence of anisotropic rims on metamict crystals of steenstrupine.

Zoned crystals of steenstrupine-(Ce)

Zoning in steenstrupine has been described by a number of authors.

Bøggild (in Bøggild & Winther 1899) distinguished three main morphological types of the mineral based on samples from pegmatites and veins. Types I and II are metamict and type III is non-metamict. The type...
III crystals may be anisotropic throughout, but some crystals have an isotropic or weakly anisotropic central part. All three types may have thin marginal zones which are often anisotropic. There may be a gradual decrease in the degree of metamictisation from centre to rim; more commonly there is a sharp transition to the thin anisotropic rims. In thin section the unaltered steenstrupine crystals are generally clear yellow in the central isotropic parts. The marginal parts are often dark brown and may be isotropic or anisotropic. The dark-coloured marginal parts may send tongues along fissures into the interior of the crystals. The part of the crystals adjacent to the tongues are generally anisotropic (Fig. 1). This means that the anisotropic zones penetrate into the interior of the crystals. These observations have been confirmed by the subsequent authors quoted below.

Buchwald & Sørensen (1961) described steenstrupine from lujavrites, pegmatites and hydrothermal veins coupled with an autoradiographic examination of the distribution of radioactive elements in the crystals. They especially noted the occurrence of several thin zones parallel to the crystal faces (Fig. 2). In some cases there is a gradual increase in anisotropy from centre to margin.

Sørensen (1962) described the paragenesis of steenstrupine in the various rock types and paid special attention to the relationship between eudialyte and steenstrupine. Steenstrupine may form overgrowths on eudialyte in pegmatites, and poikilitic grains of steenstrupine in lujavrites and recrystallised naujaites contain inclusions of fresh and altered crystals of eudialyte and in some rocks also of lovozerite. The small steenstrupine crystals in the lujavrites are primary magmatic minerals, whereas the poikilitic grains are late magmatic and may be associated with ussingite and analcime replacing the primary nepheline and feldspars of the rocks. The metamict grains of steenstrupine are surrounded by radiating fractures in the adjacent minerals (Fig. 3).

Semenov (1969) presented new chemical analyses of steenstrupine and described an altered variety, hydrosteenstrupine, poor in Na₂O, SiO₂ and P₂O₅ and enriched in REE₂O₃, Fe₂O₃, CaO and water.

Wollenberg (1971) undertook a fission track examination of steenstrupine crystals and determined the distribution of U and Th in zoned crystals of this mineral. He found that U is evenly distributed in the crystals, whereas Th is distributed in an irregular way with the highest contents in the centres of the grains.

Makovicky et al. (1980) examined a number of occurrences of steenstrupine, with emphasis on the radioactive lujavrites in the northern part of the Kvanefjeld plateau, by autoradiography, fission track studies and electron microprobe analyses. They determined the distribution of U and Th in zoned crystals of steenstrupine and also examined the behaviour of U and Th during alteration of the steenstrupine.
Makovicky & Karup-Møller (1981) described a crystalline steenstrupine from a vein and noted that partial metamictisation decreases from the centres through the finely zoned parts and surface replacement portions to the distinctly anisotropic rims of the crystals. The centres have a lower birefringence than the marginal zones.

We have examined zoned crystals of steenstrupine from drill core 50, 149.7 to 150.6 m below the surface. These crystals occur in hydrothermal veins in arfvedsonite lujavrite. According to gamma-spectrometric analyses of the drill core, the veins have 350 ppm U and 2000 ppm Th (Nyegaard et al. 1977). The steenstrupine crystals measure a few millimetres across. The interior parts of some crystals are turbid (Fig. 2), other crystals have clear, sometimes darker-coloured isotropic centres (Fig. 4), but there are also crystals which are anisotropic throughout but with very low birefringence. There are thin marginal anisotropic zones parallel to crystal faces. The anisotropic zones are often clear, but sometimes dark coloured in their exterior parts (Fig. 2). In a number of cases, zoned crystals of steenstrupine have nucleated on grains of aegirine (Figs 2, 4, 5). In these cases there is no zonation in contact with aegirine, whereas crystal faces and marginal zonation are found in contact with felsic minerals, primarily analcime, natrolite, ussingite and villiaumite. There is no zonation against primary grains of sodalite (Fig. 3).
Chemical composition of the zoned steenstrupine

The zoned grains of steenstrupine from drill core 50 have been analysed by electron microprobe. Crystal fragments were hand picked from crushed rocks and were analysed by G.N. Nechelyustov with a Superprobe-733 microanalyser. Standards were: chkalovite (Na, Si), microcline (K), diopside (Ca), strontium-apatite (Sr), BaSO4 (Ba), rhodonite (Mn), almandine (Fe), LaPO4 (La), CePO4 (Ce, P), PrPO4 (Pr), NdPO4 (Nd), SmPO4 (Sm), YPO4 (Y), ThO2 (Th), Li2NbO4 (Nb) and anatase (Ti). The results are presented in Table 1. The centres have 3.95–4.13 wt% ThO2, the rims 0.42–1.40 wt% ThO2 and from centre to rim there is an increase in Nb2O5, MnO, SrO, Na2O (in one sample), REE2O3 and P2O5, and a decrease in TiO2, FeO, CaO and Y2O3. U has not been analysed. From centre to rim there are sharp increases in the ratios Mn/Fe, La/Nd, REE/Th and Nb/Ti (Table 1). The anisotropic rims have distinctly lower contents of Th than the interior parts of the crystals.

Buchwald & Sørensen (1961) presented partial chemical analyses of some crystals of steenstrupine. The contents of U and Th vary from 0.21 wt% U and 1.66 wt% Th in the anisotropic type III crystals to 0.78 wt% U and 5.65 wt% Th in metamict vein steenstrupine. The autoradiographic examination showed that the metamict centres of steenstrupine crystals have α-track densities of 5000–13 600 α/cm2/hour, the anisotropic rims 1000–7000 α/cm2/hour. The altered grains of steenstrupine may have more than 35 000 α/cm2/hour.

Semenov (1969) reported 0.39 wt% U3O8 and 2.42 wt% ThO2 in steenstrupine from a vein, and up to 3.86 wt% ThO2 in altered steenstrupine (no data for U).

The fission-track study carried out by Wollenberg (1971) gave the following results: metamict centres of crystals have 0.42–0.72 wt% U and 3.3 wt% Th, while the rims have 0.20–0.27 wt% U and 1.39 wt% Th. The anisotropic type III steenstrupine contains 0.05–0.37 wt% U.

Hansen (1977) reported U and Th contents in steenstrupine in the ranges 0.1–1.4 wt% U and 0.2–7.4 wt% Th. For the anisotropic type III steenstrupine he found 0.13 wt% U and 0.73 wt% Th. His electron microprobe studies revealed that there is a great variation in the chemical composition of steenstrupine, even between grains in the same thin section, especially in the contents of Na, Ca, Fe and Mn.

Makovicky et al. (1980) presented a wealth of information about the chemical composition of steenstrupine from lujavrite with special emphasis on the alteration of the mineral. The fission track studies revealed up to 1 wt% U3O8 in the altered centres and

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Fig. 3. Steenstrupine crystal in sodalite (so) and analcime (an), with radiating fractures. The crystal is clear, but with a slightly turbid isotropic interior. The marginal anisotropic zone shows zonation parallel to the crystal faces. The marginal zone has a few fractures perpendicular to the crystal faces. The steenstrupine crystal is situated between two large crystals of sodalite (lower left and upper right) against which there are no crystal faces. Crystal faces and zonation are only developed in contact with analcime. a: plane polarised light, b: crossed polarised light. Kvanefjeld, drill core 53 at 145.20 m; scale bar 0.6 mm.
0.2–0.5 wt% $\text{U}_3\text{O}_8$ in the light-coloured parts of the crystals. The microprobe analyses showed a variation in the Th content from 0.27 to 5.69 wt% Th, with some zoned crystals from 3.11–3.74 wt% Th in the centres to 1.03–2.05 wt% Th in the rims.

Makovicky & Karup-Møller (1981) reported an average content of 0.46 wt% U in zoned partly anisotropic vein steenstrupine crystals. According to the fission-track data of Makovicky et al. (1980), the centres have 0.6–0.8 wt% $\text{U}_3\text{O}_8$, the marginal parts 0.3–0.4 wt% $\text{U}_3\text{O}_8$. The microprobe analyses reported by Makovicky & Karup-Møller (1981) have been recalculated from element to oxide form and are presented in Table 1. ThO$_2$ varies from 5.04 to 1.83 wt% from centre to rim; Y$_2$O$_3$ also decreases from centre to rim, whereas there is an increase in ZrO$_2$, MnO, Na$_2$O and P$_2$O$_5$ from centre to rim. The contents of the other elements are similar in centre and rim.

The information available on the chemical composition of zoned steenstrupine crystals from pegmatites and veins consistently shows a marked difference in the contents of U and Th in the central, often metamict parts of the crystals and the thin, often anisotropic rims. In addition the rims are enriched in Na, Mn, P, Zr, Nb and in some examples also REE, and impoverished in Y.
Discussion

The well-developed crystal forms of the metamict grains of steenstrupine and the surrounding radiating fractures in the adjacent minerals, an indication of volume increase during metamictisation, show that steenstrupine was originally crystalline. It may therefore be assumed that the crystal structure allows only a limited content of U and Th without breaking down into the metamict state in accordance with the fact that crystalline anisotropic steenstrupine shows the lowest measured contents of U and Th. The anisotropic type III steenstrupine has the highest contents of Na\textsubscript{2}O of all analysed steenstrupine grains, 11.23 wt\% (Bøggild & Winther 1899), 14.2 wt\% (Hansen 1977), which indicates that secondary leaching must have been very weak. It should be remembered that Na\textsuperscript{+} is easily substituted by H\textsuperscript{+} during alteration of the crystals (Makovicky & Karup-Møller 1981). Crystals with higher contents of U and Th have been transformed into the metamict state and in many cases altered into aggregates of secondary minerals as described by Buchwald & Sørensen (1961), Sørensen (1962), Semenov (1969) and Makovicky et al. (1980). In the strongly altered grains, U and Th are retained in thorite, thorite and unidentified pigmentary material, which have the highest recorded contents of U and Th.

Buchwald & Sørensen (1961) considered two explanations for these phenomena: either the anisotropic rims are primary, formed in a medium poor in U and Th, or alternatively, the anisotropic rims have been formed by secondary processes.

Anisotropic rims as primary crystallisation products

A decrease in the contents of U and Th in the media in which the crystals grew could be a result of the
onset of crystallisation of other minerals rich in U and Th. Such minerals are, however, not associated with the steenstrupine. Steenstrupine itself may have such a high capacity to extract U and Th from melts and hydrothermal solutions that the supply of these elements was exhausted during the late stages of crystallisation. The studies of Hansen (1977) and Bailey et al. (1983), however, demonstrate that a considerable part of the U and Th in the agpaitic rocks of the Ilímaussaq complex is easily leached out. Therefore, it cannot be bound in silicate minerals but was most probably retained in the residual liquids and subsequently deposited as intercumulus pigmentary material (or in some examples retained in the alteration products of steenstrupine formed by means of reaction between the crystals and late interstitial liquids). These mechanisms may explain why decreasing contents of U and Th were available for the latest stages of growth of the steenstrupine crystals.

Steenstrupine in pegmatites and hydrothermal veins frequently nucleates on aegirine as demonstrated in Figs 2, 4 and 5. In these examples there is no zonation in contact with aegirine, whereas crystal faces and marginal rims are developed against analcime, natrolite, ussingite and villiaumite, but not against earlier-formed sodalite. The zonation abuts against aegirine (Figs 2, 4). These observations strongly support the view that the zonation is a growth phenomenon coupled with a general increase in alkalinity of the residual melts and fluids, resulting in an enrichment in Na, Mn, Nb, REE and P in the marginal zones of the crystals (Table 1).

The formation of zonation may thus have taken place before the metamictisation of the inner parts of the crystals.

It is possible that the physical conditions changed so that U and Th were taken up in a fluid phase and removed from the melt. U-Th mineralisations in the fenitised volcanic rocks of the roof of the complex are indications of fluid transport of U and Th into the country rocks (Sørensen et al. 1974). The possibility that a high oxygen fugacity was the cause of the mobilisation of U as (UO₂)₂⁺ is not likely since the vapour phase of the agpaitic melts was rich in hydrocarbons (Petersilie & Sørensen 1970; Konnerup-Madsen 2001, this volume).

Anisotropic rims formed by secondary processes

Alternatively, the anisotropic marginal zones may have been formed by secondary processes. This could be due to an early leaching of U and Th from the marginal parts of the crystals before metamictisation or to leaching of U and Th from metamict crystals of steen-
strupine combined with recrystallisation of the thin rim of the leached crystals. Makovicky & Karup-Møller (1981) emphasise the importance of exchange of Na⁺ and H⁺ in the crystal structure of steenstrupine and mention the possibility that the crystal structure of leached steenstrupine may have the ability to accept substantial amounts of Na⁺ back into the structure. One may however doubt that such processes would result in a repetition of perfectly parallel marginal zones; some aggregate structure would be more likely (Makovicky & Karup-Møller 1981, p. 302). Leaching is a more straightforward explanation of the presence of anisotropic steenstrupine adjacent to fractures penetrating from the crystal surface into the crystals (Fig. 1) and of the presence of anisotropic steenstrupine in the marginal parts of the crystals with the densest systems of fractures (Fig. 6). But the fact that the anisotropic rims have higher contents of Na than the metamict centres of the crystals contradicts leaching as the main cause of formation of the anisotropic rims. It should also be remembered that anisotropic marginal zones occur in crystals which are practically free from fractures.

Makovicky et al. (1980, p. 25) observed zoning only in partly to fully altered grains and did not observe zoning in metamict grains and extremely altered grains. They presumed that primary compositional zoning becomes visible only after the process of alteration and only develops in the compositionally suitable grain portions. In the material studied by us, anisotropic
zoning is found in metamict grains which in thin section have clear, unaltered centres.

It is of interest to note that steenstrupine crystals with zonation similar to that described here have so far not been found in the Lovozero complex. This may be caused by a lower degree of alkalinity in Lovozero, as indicated by the absence of rock-forming naujakasite (cf. Khomyakov et al. 2001, this volume; Sørensen & Larsen 2001, this volume). Most steenstrupine at Lovozero appears to have crystallised during later stages than at Ilímaussaq, that is at declining alkalinity. Under these conditions the activity of Na was insufficient for the recrystallisation of metamict steenstrupine.

Conclusions

The fact that the marginal zones of the steenstrupine crystals are thin and perfectly parallel and enriched in Na is most easily understood as a growth phenomenon and is less likely to be the result of leaching and recrystallisation. The lobes of anisotropic steenstrupine that penetrate from the crystal surfaces along fractures into the interior of the crystals are, however, best understood as a leaching phenomenon. Such examples have, however, not been included in the present examination of zoned steenstrupine crystals.

The type of marginal zonation of steenstrupine crystals studied in this paper can best be explained as a result of primary growth of the crystals in a medium relatively depleted in U and Th and enriched in Na and REE.

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