Conversion of nepheline to sodalite during subsolidus processes in alkaline rocks

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Abstract

Cathodoluminescence (CL) petrography of nepheline syenites of the Igaliko complex, Gardar province, South Greenland shows that sodalites possess embayed contacts against nepheline, and have formed by a process of metasomatic replacement. This texture is demonstrated clearly by CL, since sodalite luminesces bright orange and nepheline is poorly luminescent. The transformation from nepheline to sodalite results in a volume change which leads to a network of fractures in which deep-blue luminescent fluorite is precipitated. Fluorite is formed since the chlorination process involved in the transformation causes localised reductions of the salinity of the fluid and therefore a decrease in the solubility of fluorite. Sodalite–fluorite textures observed using CL allow sodalites of secondary origin in alkaline igneous rocks to be identified.

Nephelines and sodalites, when observed using scanning electron microscopy, possess small micropores. By analogy with recent work on alkali feldspars, pervasive alteration of nephelines may occur by fluid flow assisted by a permeable micropore network.

KEYWORDS: feldspathoids, cathodoluminescence, microporosity, Igaliko, Gardar, Greenland, alkaline rocks.

Introduction

NEPHELINE, sodalite and cancrinite are feldspathoids often found coexisting in undersaturated alkaline rocks. Textural evidence (e.g. Powell, 1976; Finch, 1990) often suggests that cancrinite can be formed by the reaction of carbon-dioxide-bearing fluids and nepheline *in the subsolidus*, and a replacive relationship is evident in thin section due to the marked birefringence differences between nepheline ($\delta = 0.005$) and cancrinite ($\delta = 0.025$) (Deer *et al.*, 1983). A similar secondary origin has been suggested for sodalite on the basis of experimental work (Barker, 1976; Sharp *et al.*, 1989), involving the chlorination of nepheline by brines. However, due to the small birefringence difference, and the commonly weakly anisotropic nature of sodalite, the textural relationship between nepheline and sodalite is difficult to see in thin section. The present study uses the different cathodoluminescence properties of sodalite and nepheline to study the relationship between, and interconversion of,

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nepheline and sodalite. In addition, since CL colours do not depend on the full thickness of the slide, the apparent gradational changes in the properties of oblique boundaries can be reduced.

In the present study, rocks of the Igaliko complex, Gardar province, South Greenland, which has been reviewed by Emeleus and Harry (1970), were examined. The Gardar is a mid-Proterozoic alkaline rift province (Emeleus and Upton, 1976; Upton and Emeleus, 1987) with a range of alkali basaltic to agpaitic intrusions. The Igaliko complex is the largest undersaturated complex in the province, comprising five centres, the Motzfeldt, North Qôroq, South Qôroq, Early Igdlerfigsalik and Late Igdlerfigsalik centres (Fig. 1). Rb–Sr isochrons for four of the centres suggest ages of 1310 Ma (Motzfeldt), 1290 (N. Qôroq), 1160 Ma (S. Qôroq) and 1143 Ma (L. Igdlerfigsalik) (Upton and Emeleus, 1987). No age data exist for the Early Igdlerfigsalik centre.

Cathodoluminescence

CL petrography has been carried out on samples from four of the five Igaliko centres:

Key   Centre

	M	MOTZFELDT
	N	NORTH QÔROQ
	S	SOUTH QÔROQ
	E	EARLY IGDLERFIGSALIK
	L	LATE IGDLERFIGSALIK

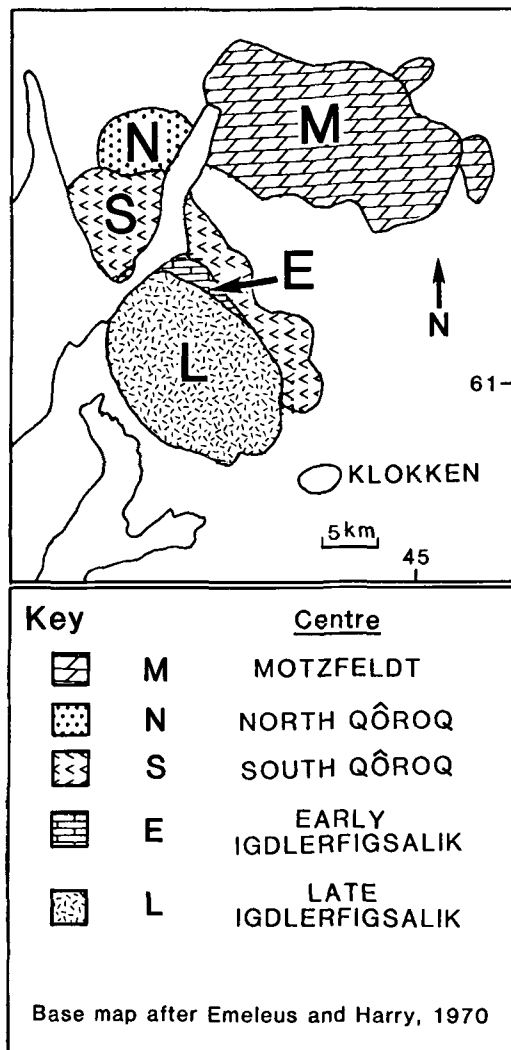Base map after Emeleus and Harry, 1970

FIG. 1. Simplified geology of the Igaliko complex. A more detailed map is given by Emeleus and Harry (1970) and exact sample locations in Finch (1990).

Motzfeldt, South Qôroq, Early and Late Igdlerfigsalik. The general disposition of the centres is given in Fig. 1 and exact sample locations are given by Finch (1990). Sodalite, where present, was observed to demonstrate bright yellow or orange luminescence, in contrast to the very poorly luminescent nature of nepheline. The system used in the present study was a Nuclide ELM2BX cold cathode luminoscope operating at 12 kV acceleration at 800 μA current.

The geological literature contains very little about CL of feldspathoids, and yellow–orange luminescent sodalites have not been reported from natural systems. However, the cathodoluminescence properties of sodalites have been studied by materials scientists. According to Schipper et al. (1972), yellow luminescence in sodalites arises from electron exchanges between Fe^{2+} and S^{2-} impurities. Zoning in yellow and orange luminescent carbonates has been related to variations in the relative amounts of Fe, Mn and Mg impurities (e.g. Marshall, 1988), and the development of shades of orange in sodalites may be due to an analogous mechanism.

Cathodoluminescence of nephelines was observed to be very faint indeed, and appeared to the eye as a very dull grey colour. Exposure of nepheline CL colours to 1000 ASA photographic film (exposure times around 3 minutes) demonstrated that the luminescence was a pale blue colour and in one case oscillatory zoning was seen. Blue luminescence has not previously been described from nephelines, although blue CL colours are common from the structurally similar alkali feldspars (e.g. Marshall, 1988; Finch and Walker, 1991). In this case the luminescence is explained in terms of E'-defects in the structure (Geake et al., 1977; Rae and Chambers, 1988).

CL- petrography of the Igaliko rocks

The contacts between nephelines and sodalites have been observed using CL in samples from the Igaliko complex. In many cases, the contacts are embayed, suggesting that sodalite is present as a result of replacement of nepheline (Plate 6a). This reaction can be represented by

$$6NaAlSiO_4 + 2NaCl° = Na_8Al_6Si_6O_{24}Cl_2,$$

nepheline   from the fluid   sodalite
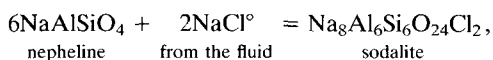
ignoring the presence of a potassic component in the nepheline, which is presumably exchanged for sodium in the fluid during the reaction. The transformation results in an increase in the equivalent unit cell volume ($6NaAlSiO_4$ = 547 $Å^3$, Buerger et al., 1954; $Na_8Al_6Si_6O_{24}Cl_2$ = 701 $Å^3$, Hassan and Grundy, 1984), and it is observed that where chlorination has been pervasive in the Late Igdlerfigsalik rocks, sodalites are fractured with a secondary deep-blue luminescing mineral infilling interstices (Plate 6b). The transformation must be accompanied by some dissolution of the nepheline to accommodate the volume increase. In some cases (e.g. Plate 6c), the modal amount of this mineral in the sodalite becomes considerable. The deep-blue luminescence of this mineral fades with exposure to the electron beam. Two possibilities were considered for the identity of the deep-blue luminescent mineral: first, it is

known that some sodalite varieties can luminesce a deep-blue colour, and that luminescence fades with longer exposure (Hassib *et al.*, 1977). However, a similar luminescence has been observed in fluorite (Marshall, 1988). Larger grains of the deep-blue mineral were observed adjacent to the vein-network texture, and electron-probe analysis confirmed these to be fluorite. The cause of the deep-blue luminescence in both sodalite and fluorite is due to the same effect, namely the presence of F-centres in the lattice (i.e. electrons in the positions of Cl and F respectively), and it has been further shown by Blake *et al.* (1988) that exposure to the electron beam is capable of both creating and destroying such defects. Hence it cannot be ruled out by CL that the larger grains are fluorite whereas the mineral in the vein-network is a variety of sodalite with identical luminescence properties.

The veined sodalite texture was also examined under backscattered SEM imagery. If the blue luminescence was due to defects in sodalite, then the veins would be invisible under backscattered SEM, since the change in the relative molecular-mass caused by a defect would be effectively nil. However, if the veins were composed of fluorite, then the veining would be visible, since fluorite and sodalite have different relative molecular masses. Mean relative molecular masses for sodalite and fluorite are 11.106 and 14.647 respectively, which correspond (Lloyd, 1987) to Z values of 0.1367 and 0.177. This Z difference is well within the resolution of the backscatter detector used. A view of a veined sodalite under backscattered SEM is presented in Fig. 2. In this figure, the vein network is visible as trains of solitary grains (F) in the sodalite, associated with micropores (M, see later). Hence the identity of the blue luminescent mineral was confirmed as fluorite.

According to the experimental work of Richardson and Holland (1979), the solubility of fluorite increases with increasing salinity in hydrothermal brines. Local reductions in the salinity of the fluid, caused by the chlorination of nepheline, would reduce the solubility of fluorite in the system and cause its precipitation around and within the fractured sodalite. Hence veining of sodalite by fluorite can be taken to indicate that the sodalite is formed in the subsolidus by chlorination of nepheline. This allows a sodalite to be identified as secondary, even when the original nepheline is no longer present. All of the units of the igneous centres studied here showed sodalite-fluorite textures of this type, and hence it is concluded that the vast majority of the sodalite present in this complex is secondary in origin.
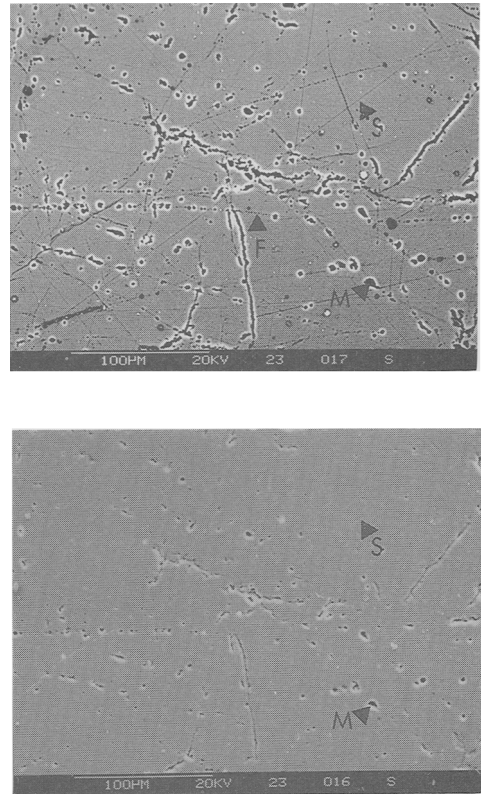

FIG. 2. Backscattered (top) and secondary electron (bottom) images of fluorite veining in sodalite. On the backscattered image (top), the black areas correspond to either scratches on the slide (S), micropores in the sodalite (M) or discrete fluorite grains (F). The micropores and scratches are distinguished from the fluorite grains since the former are also visible on the secondary electron image. The association of fluorite with the micropores in trains indicates that the micropore system acted as a conduit to metasomatic fluids. The sample is GGU 58230 (South Qôroq centre).

This suggestion is often supported by the preservation of embayed contacts against original nephelines.

Microporosity and the mechanism of alteration

Recent work on alkali feldspars (Worden *et al.*, 1990; Walker, 1990; Finch and Walker, 1991) has shown that hydrothermal alteration of alkali feldspars occurs not only by passage of fluids along grain boundaries, but also by fluid flow assisted by a permeable micropore network within the alkali feldspars themselves. The exact

temperature at which the micropore network forms is not known, but in the feldspar in the Klokken intrusion must be below c. 450 °C (Worden et al., 1990). The presence of turbidity in nephelines and sodalites, directly analogous to that observed in alkali feldspars, suggests that feldspathoids too may possess micropores. In the case of alkali feldspars, it has been suggested (Worden et al., 1990) that primary microporosity results from the exsolution of water from the feldspar structure, hence pristine alkali feldspars should contain greater amounts of water than altered ones. Non-turbid nephelines have also been shown to contain up to 0.5% water (Beran and Rossman, 1989), a far greater amount than is observed in most analyses of nepheline, and by analogy with the structurally similar alkali feldspars, it is possible that alteration of nepheline is so pervasive because of water exsolution and the development of micropore networks.

Backscattered and secondary electron SEM imaging of nephelines and altered sodalites from the Igaliko complex have confirmed the presence of numerous micropores in both nepheline and sodalite, and furthermore, the levels of microporosity observed were relatively high. Backscattered SEM studies of sodalite–fluorite veining textures (see above) have shown that the grains of fluorite which comprise the veins are associated with lines of micropores (Fig. 2). Since the fluorite is known to be secondary, and given the role of fluid flow through micropore systems in alteration of alkali feldspars (Finch and Walker, 1991), it is reasonable to suggest that the fluorite has been precipitated from a fluid passing along the micropore network. This indicates that microporosity is also important in the conversion of nepheline to sodalite.

Conclusions

Nepheline can be converted to sodalite by metasomatic fluids in the subsolidus. The transformation is accompanied by the precipitation of fluorite in veins and fractures within the sodalite. Fluorite is formed due to local reductions in salinity during the transformation of nepheline to sodalite. These three phases can be viewed readily using cathodoluminescence petrography due to clear differences in CL colours.

Micropores are present in nepheline and sodalite and are spatially associated with secondary fluorite grains in sodalites. This indicates that the micropores in feldspathoids assist in fluid flow during metasomatism, a process analogous to that described from alkali feldspars.

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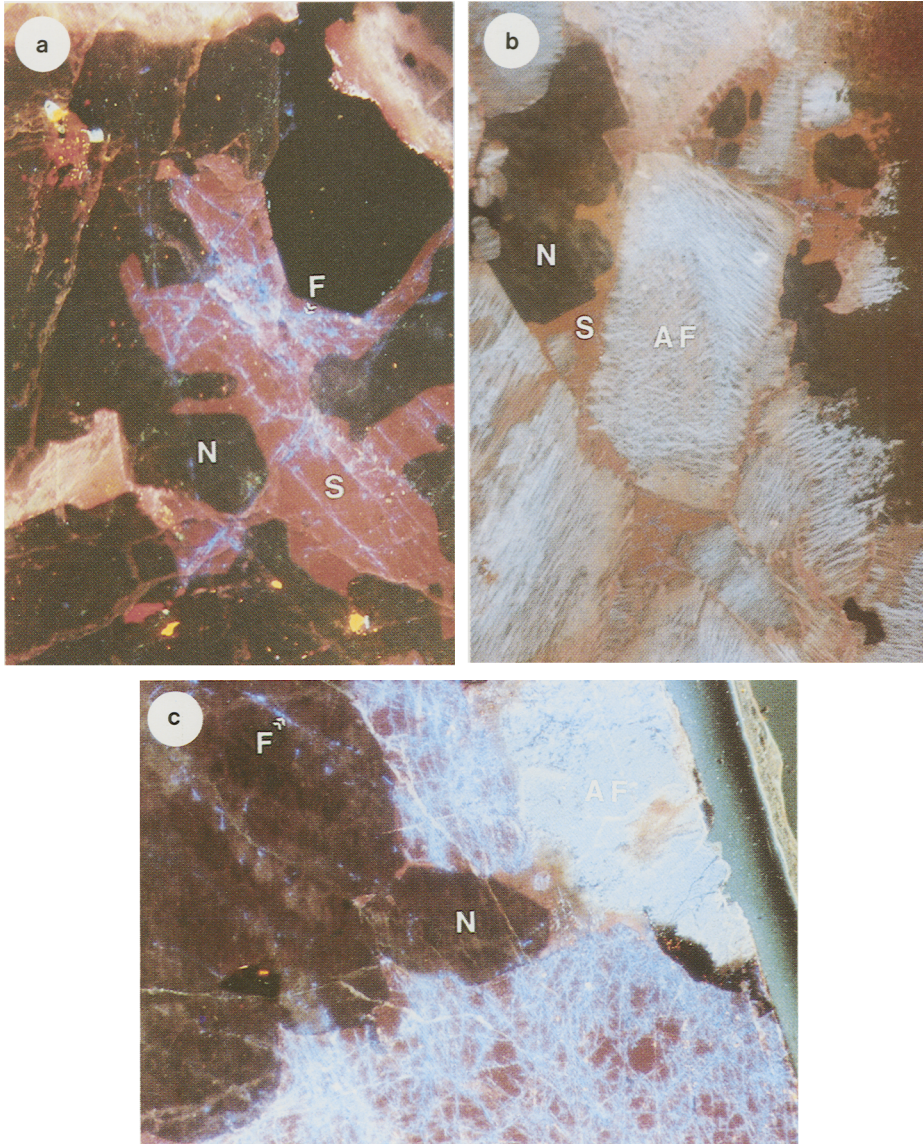Plate 6   A. A. FINCH

PLATE 6. (*a*) Contact between nepheline and sodalite, viewed under CL. The orange sodalite (labelled S) can be seen to possess embayed contacts against poorly luminescent nepheline (N). Fluorite veins (F) are also present. Longest side 4 mm. Sample Number GGU 43973 from the Early Igdlerfigsalik centre. (*b*) Interstitial original nepheline (labelled N), being replaced *in situ* by sodalite (S), viewed under CL. Sodalite luminesces orange and nepheline is poorly luminescent; alkali feldspar primocrysts (AF) are luminescing blue and pink. The sodalite may be seen to be veined by deep-blue luminescing fluorite to the right of the picture, and has embayed contacts against the nepheline. Longest side 4 mm. Sample number QT14 from the Late Igdlerfigsalik centre. (*c*) Sodalite–fluorite texture from South Qôroq. The original nepheline can be seen to the left (dull luminescence, marked N). Notice how the veins of fluorite (F) are beginning to extend into the nepheline. Longest side 4 mm. Sample number GGU 58230.