

Geochemistry of boron in the Ilímaussaq alkaline complex, South Greenland[☆]

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Abstract

The distribution of boron has been studied in rocks and minerals of the Ilímaussaq complex, South Greenland, using optical emission spectrometry. In the silica-undersaturated rocks of intrusive phases 1 and 3, average B contents increased from 5.6 ppm in augite syenite to a maximum of 8.9 ppm in sodalite-rich agpaitic nepheline syenite (naujaite roof cumulate) and then decreased to 5.4 ppm in the final lujavrites. Boron only behaved as an incompatible element during certain stages of the fractionation history. Starting at the naujaite stage, sodalite crystals (60–45 ppm B) were fractionated by flotation and were also trapped among the heavy cumulus phases of the bottom cumulates. This prevented the significant build-up of B in late derivatives as seen in other nepheline syenites. Nevertheless, in late pegmatites and veins associated with the agpaitic rocks, B was locally concentrated in certain Be minerals and metamict/reworked minerals. In the silica-oversaturated rocks of intrusive phase 2, average B contents increased from 8.6 ppm in quartz syenite to 13 ppm in alkali granite.

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1. Introduction

The aim of this study is to describe and interpret the geochemistry of boron in the Ilímaussaq alkaline complex of South Greenland. Boron geochemistry in igneous rocks, especially alkaline varieties, is poorly known (Anovitz and Grew, 1996) and is therefore reviewed in some detail.

Goldschmidt and Peters (1932) showed that B was more abundant in sedimentary than in igneous rocks.

Harder (1974) proposed average contents for basalt (5 ppm), granite (12 ppm) and salic volcanics (30 ppm), but no estimate could be proposed for alkaline rocks.

In basalts, B is an incompatible element with bulk partition coefficients <0.07 (Ryan, 1989; Bindeman et al., 1998; Brenan et al., 1998). It is moderately incompatible in silicic rocks being partitioned into micas and plagioclase (Harder, 1974; Leeman and Sisson, 1996).

Fresh mid-ocean ridge basalts contain around 0.3–1 ppm B (Ryan and Langmuir, 1993), while ocean island alkali basalts generally contain 2–4 ppm B rising to 3–6 ppm in trachyandesites and roughly 6–13 ppm in trachytes, phonolites and rhyolites (Ryan et al., 1996).

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The systematics of B in arc volcanics point to its release during devolatilization in subducting slabs, its metasomatism of the sub-arc mantle and subsequent incorporation into arc magmas up to ca. 30 ppm (Ryan and Langmuir, 1993; Clift et al., 2003).

Boron contents in granitic and rhyolitic rocks range widely. Up to several thousand ppm are reported from peraluminous S-type rhyolites, and equivalent tourmaline-bearing granites and pegmatites, and are attributed to inheritance from B-rich metapelitic sources, often combined with prolonged fractionation (Pichavant et al., 1987; Breaks and Moore, 1992; London et al., 1996). Aureoles rich in borate minerals around granites probably stem from B loss in exsolving fluids (London et al., 1996; Woodford et al., 2001).

Morgan and London (1989) found that tourmaline is unstable in peralkaline melts and anticipated that B solubility would increase with fractionation until saturation was reached in a vapour phase or a B-bearing mineral other than tourmaline, e.g. reedmergnerite or searlesite.

Trivalent boron with its small ionic radius of 11 pm (Shannon, 1976) has a high ionic potential (27) and forms complex ions such as BO_3^{3-} and BO_4^{5-} . Given the largely covalent character of boron in such ions, it is more appropriate to compare tetrahedral covalent radii for B (88 pm), C (77 pm), Be (106 pm), P (110 pm), Si (117 pm) and Al (126 pm) (Pauling, 1960).

The location of B in synthetic and natural melts has been studied by Pichavant et al. (1984), Morgan and London (1989), Gan et al. (1994) and Dingwell et al. (1996). In granitic melts, B probably occurs as randomly distributed BO_4 and BO_3 units. BO_4 units probably join up with SiO_4 and AlO_4 units in the aluminosilicate network whereas BO_3 units form six-member rings lying outside the network. Addition of P_2O_5 promotes formation of PO_4 units at the expense of BO_4 units, but this effect is absent in depolymerized peralkaline melts where a higher proportion of BO_4 units are stabilized both because less Al competes for alkali cations to establish its tetrahedral coordination and because the abundant silicate Q^3 species shield the BO_4 units by releasing nonbridging oxygens and polymerizing into Q^4 species. Tourmaline decomposes to sodic amphiboles in alkaline melts. Instead, an alkali borosilicate mineral such as reedmergnerite (NaBSi_3O_8) is expected to crystallize from a peralkaline melt, assuming that B contents fractionate to high enough levels, temperatures fall below ~ 600 °C and saturation in a vapour phase is avoided. Limited solid solution is reported between the NaAl- and NaB-feldspars albite and reedmergnerite indicating that substitution of B for Al is possible,

though this only seems to take place in peralkaline systems. Addition of B to hydrous granitic melts leads to formation of B-OH complexes. In water-oversaturated metaluminous and peraluminous granitic compositions, B preferentially partitions into the aqueous vapour phase but its behaviour in analogous peralkaline systems is inadequately known.

At trace-element levels, it is difficult to establish B substitution mechanisms in minerals (Harder, 1974; Grew, 1996). BO_4 tetrahedra, rather than BO_3 triangles, probably substitute at trace levels for SiO_4 and AlO_4 tetrahedra in common silicates. However, the increased abundance of B in residual magmas may lead to the formation of independent minerals containing BO_4 groups as in reedmergnerite or BO_3 groups as in tourmaline. Substitution of B in various Be minerals and silicophosphates also occurs. In volatile-rich environments, rare occurrences of $\text{B}(\text{OH})_4^{1-}$ ions (kalborsite) and BF_4^{1-} ions (avogadrite) should be noted. When aqueous fluids escaping from granitic melts have high enough pH to stabilize tourmaline, Smith and Yardley (1996) argue that B is mainly present as boric acid, $\text{B}(\text{OH})_3$, leading to trigonal coordination in hydrothermal tourmalines.

2. Previous studies on nepheline syenites and phonolites

The boron contents and mineralogy of nepheline syenites and phonolites are compiled in Table 1 (see Anovitz and Grew, 1996 for the structure and chemistry of minerals). Whole-rock B analyses are only occasionally presented but it appears they increase from a background level of 5–10 ppm to a few values >100 ppm. Boron typically concentrates in the more evolved rocks of a magma series and in derivative pegmatites. Higher B values, along with B minerals, are found in rocks thought to be contaminated by B-rich marine sediments, e.g. pegmatites from Langesunds Fjord, Norway (Ofteidal, 1964). The highest contents occur in K-rich magmas like those in the Italian volcanic province where source regions for melting probably include B-rich sediments (Taddeucci, 1968; Tonarini et al., 2004). Within this province, besides the rare B minerals of volcanic ejecta in the Sabatini area (Della Ventura et al., 1992), B minerals have been found in fumaroles, boric acid lagoons and drill tubing (Scherillo, 1940; Anovitz and Grew, 1996).

Boron appears to be present in most rock-forming minerals of nepheline syenites and phonolites. In addition, a distinctive suite of borosilicates and borates is reported from pegmatites, both at the magmatic stage

Table 1
Boron contents and minerals in nepheline syenites and phonolites

Locality	Rock type and mineral B contents (ppm), B minerals	Reference
Worldwide	Nepheline syenite (6–95), median (15)	1
Worldwide	Phonolite (5–156), median (16)	1
Worldwide	Nepheline syenite (8.5)	2
Bohemia	Phonolite (5)	2
Germany	Phonolite (4.3)	2
Lovozero	Nepheline syenites—phase I (6), phase II (15), phase III (18); late zones of hyperagpaite pegmatites—searlesite, reedmergnerite, leucosphenite, M65 (NaBSiO ₄)	3, 4, 5
	Contact zone—?topaz	6
Khibina	Nepheline syenites, hyperagpaite—kalborsite, leucosphenite	5
	Peralkaline metasomatites—kalborsite, leucosphenite	7
Ilímaussaq	Augite syenite (3.5), granite (30), naujaite (17), kakortokite (17), aegirine lujavrite (5), arfvedsonite lujavrite (4)	8
	Rock-forming minerals—sodalite (13), eudialyte (6), polyolithionite (4), analcime (2), K-feldspar, arfvedsonite (< 1)	8
	Pegmatite—stillwellite-(Ce)	9
Srednetatarskii	Foyaite (ca. 3), foyaite pegmatite (ca. 60)	10
	Pegmatite—britholite (3100), melanocerite (10,000)	10
	Contact aureole—dravite	10
Kuznetsky		
Alatau	Nepheline syenite—thorian melanocerite-(Ce)	11
Tyezhsar	Nepheline syenite (10–30), pegmatites (50–60)	12
	Syenites—tourmaline	12
	Plagioclase, nepheline (30), biotite, aegirine—augite, hastingsite (10)	12
	Albitized pegmatite—caryocerite (1000)	12
Magnet Cove	Nepheline syenite pegmatite (40)	13
Mont Saint-Hilaire	Nepheline syenites—cavities and seams in xenoliths; late crusts in altered pegmatite—leucosphenite, datolite, dravite, poudretteite, stillwellite-(Ce), tadjhikite-(Ce); cavities in sodalite syenite xenoliths—searlesite, UK53 (NaBSiO ₄), UK53a, UK53b; Si and Be minerals from silicate cavities—UK48 (Ca–Y silicate), UK48a (Ca–Ce silicate)	14, 15 16, 17 18, 19
Langesunds Fjord	Nepheline syenite (8.5); rock-forming minerals—feldspar (7), hornblende+apatite+oxides (7)	
	Nepheline syenite pegmatites, magmatic stage—homilite, nordenskiöldine, melanocerite-(Ce), tritomite-(Ce), stillwellite-(Ce), tadjhikite; Be minerals—leucophanite (ca. 100), meliphanite (ca. 1500), gadolinite-(Ce) (1700); other minerals—eudialyte—eucolite (9–74), catapleiite (50), cancrinite, ferro-edenitic hornblende (3), lepidomelane (1.5); metamict minerals—thorite (600), REE minerals (up to 1500); nepheline syenite pegmatites; hydrothermal stage—hamborgite, datolite, berborite; Be minerals—bromellite (4300); unknown stage—cappelenite-(Y), stillwellite-like mineral (UK-3)	2 20, 21 22, 23 24, 25, 26, 27
Kilimanjaro	Phonolites—anorthoclase phenocrysts (35)	28
Sabatini	Volcanic ejecta of feldspathoidal sanidine syenite, vugs—peprossiite-(Ce), stillwellite-(Ce), hellandite, vicanite-(Ce)	29 30, 31
Point of Rocks	Phonolite sill, vugs—searlesite	32

1: Author's compilation, 2: Harder (1959), 3: Gerasimovsky et al. (1966), 4: Khomyakov and Rogachev (1991), 5: Khomyakov (1995), 6: Pekov (2000), 7: Kost'ilyeva-Labuntsova et al. (1978), 8: Gerasimovsky (1969), 9: Karup-Møller (1975), 10: Sveshnikova et al. (1976), 11: Andreeva (1968), 12: Meliksetyan (1971), 13: Erickson and Blade (1963), 14: Chao and Watkinson (1972), 15: Grice et al. (1987), 16: Mandarino and Anderson (1989), 17: Horváth and Gault (1990), 18: Chao et al. (1990), 19: Wight and Chao (1995), 20: Andersen et al. (1996), 21: Oftedal (1964), 22: Segalstad and Larsen (1978), 23: Goldschmidt and Peters (1932), 24: Bollingberg et al. (1983), 25: Giuseppetti et al. (1990), 26: Larsen et al. (1987), 27: Neumann (1985), 28: Stern (1969), 29: Della Ventura et al. (1992), 30: Della Ventura et al. (1993), 31: Maras et al. (1995), 32: DeMark (1984).

and especially in fluid-mobile settings such as vugs, fissures, late crusts, associated contact aureoles and metasomatized xenoliths. Boron notably substitutes for Si and Be in a number of pegmatite minerals. There are also irregularly high levels of B in REE and Th–U minerals. At Langesunds Fjord, REE-rich borosilicates may have formed by chemical changes taking place during metamictization of a crystalline precursor, probably a B-, REE-rich apatite group mineral (Larsen, 1996).

3. Geology of the Ilímaussaq complex

The Ilímaussaq complex is one of the youngest members of the mid-Proterozoic Gardar continental rift zone province of South Greenland. The complex was intruded into calc-alkaline granitoids of the Ketilidian orogen (Garde et al., 2002) and into the overlying sandstones and lavas of the Gardar supracrustals.

The Ilímaussaq complex was emplaced in three main phases (Larsen and Sørensen, 1987). Phase 1 is

composed of a mildly alkaline augite syenite. Phase 2 consists of quartz syenite and alkali granite and represents a major break in the magmatic evolution of the complex. Phase 3 rocks are thought to be derived from the same magma series as phase 1, a series held in deep magma chambers beneath the complex (Larsen and Sørensen, 1987). Phase 3 starts with slightly peralkaline Si-undersaturated rocks, which evolve into the agpaite nepheline syenites of the complex. These nepheline syenites consist of a series of roof cumulates and a series of floor cumulates which are overlain by intervening lujavrites. The roof rocks crystallized downwards, forming the succession pulaskite, foyaite, sodalite foyaite and naujaite. The naujaite is an agpaite sodalite syenite, which contains up to 75 vol.% sodalite and is at least 600 m thick.

The exposed kakortokite floor cumulates are ~200 m thick and show macrorhythmic layering with rhythmic units numbered from -11 to +17 (Bohse et al., 1971). Each three-layer unit starts with a black arfvedsonite-rich layer, which is overlain by a red eudialyte-rich layer and then a thicker white layer rich in alkali feldspar. Sodalite is a cumulus phase in the lowermost part of the kakortokites (Sørensen and Larsen, 1987). These kakortokites are followed by transitional layered kakortokites composed of three-layered units labelled upwards from F to A.

The overlying lujavrite series is at least 500 m thick; its lowermost part is dominated by aegirine-rich varieties with local eudialyte-rich layers, while the upper part is composed of arfvedsonite-rich varieties.

Small intrusions of medium- to coarse-grained (M-C) lujavrite intrude the arfvedsonite lujavrites but are thought to represent a more primitive stage of the lujavrite magmas (Andersen et al., 1981).

Pegmatites and veins, often with exotic mineralogy, are associated with the main rock types at Ilímaussaq. A number of minerals, notably Be minerals (Engell et al., 1971; Markl, 2001), were taken from these agpaite derivatives for B analysis.

A few examples of dykes representing Ilímaussaq liquids (Bailey et al., 2001) and four microsyenites studied by Rose-Hansen and Sørensen (2001) were also analysed.

4. Analytical methods

Boron was determined by optical emission spectrometry (OES/DC arc; large Hilger Quartz spectrograph). Rock and mineral powders were weighed out to 10 mg on a microbalance to an accuracy of 0.001 mg. Carbon powder and Pd as internal standard were added

to the material in a single-crystal sapphire mortar. Kodak SA-1 plates were used and the measurement of line intensities was made on a Jarrel Ash microphotometer. Standards were produced by mixing trace elements into a mineral and synthetic base. Silicate reference materials such as G-2 were also used. Relative standard deviation during analysis was less than 10% and the detection limit was 3 ppm. 6 ppm B was found in the standard STM-1, which is close to the recommended value of 6.4 ppm (Govindaraju, 1994). Unfortunately, B data could not be obtained during routine analysis of eudialyte because of interfering lines. Previous results on Ilímaussaq rocks and minerals were also based on OES methods (Gerasimovskiy, 1969). Accuracy was around ± 30 –40% and may explain why these results are roughly 20% higher than values presented here.

Analyses of major elements and most trace elements were obtained by XRF; U was analyzed by delayed neutron counting, Be by AAS and F by photometry.

5. Boron geochemistry at Ilímaussaq

5.1. Overview

Boron contents in Ilímaussaq rocks, along with contents of major elements and of trace elements relevant to the evolution of B, are presented in Table 2. No single differentiation parameter can be applied throughout the magmatic evolution at Ilímaussaq and various parameters have been used at various stages (Fig. 1).

Average B contents in the phases 1 and 3, Si-undersaturated rocks increase from augite syenite (5.6 ppm) and pulaskite/foyaite (5.6 ppm) to sodalite foyaite (8.4 ppm) and naujaite (8.9 ppm), but then decrease through bulk kakortokite (7.9 ppm) to lujavrite (5.4 ppm). In contrast, rising levels are found in phase 2 quartz syenite (8.6 ppm) and alkali granite (13.0 ppm).

The bulk content of B in the agpaite nepheline syenites is 7.7 ppm, which can be rounded to 8 ppm, somewhat lower than the value of 10 ppm proposed by Gerasimovskiy (1969).

Contents of B in dykes representing Ilímaussaq liquids (Bailey et al., 2001) probably rise from about 4 ppm in the initial augite syenite to 7 ppm at the onset of the agpaite stage and then fall to 5 ppm in the later lujavrite liquids.

5.2. Silica-undersaturated series

In the phase 1 augite syenites, B contents roughly increase from 4 to 8 ppm along with rising levels of the

Table 2

Average analyses of major and key trace elements in Ilímaussaq rock types

	Phase 1		Phase 2		Phase 3									
	Fine augite syenite	Coarse augite syenite	Quartz syenite	Alkali granite	Pulaskite	Foyaite	Sodalite foyaite	Naujaite	Black kakortokite	Red kakortokite	White kakortokite	Aegirine lujavrite	Arfvedsonite lujavrite	Medium- to coarse-grained lujavrite
No.	6	5	5	8	11	5	9	13	11	5	11	10	8	3
SiO ₂ (wt.%)	55.82	56.14	63.59	72.01	60.34	58.50	49.98	46.32	48.60	52.22	52.57	54.09	52.63	53.68
TiO ₂	2.29	1.64	0.32	0.28	0.19	0.32	0.30	0.40	0.44	0.35	0.20	0.18	0.20	0.37
Al ₂ O ₃	14.94	16.15	14.53	10.52	16.53	16.16	17.96	20.20	8.47	10.93	15.76	15.93	13.71	13.22
Fe ₂ O ₃	2.03	1.47	3.03	2.65	3.38	3.07	4.77	3.39	8.26	5.61	5.82	8.29	4.55	3.48
FeO	8.82	7.64	4.07	3.18	2.42	4.38	4.57	4.11	14.84	5.72	4.36	0.92	7.36	8.23
MnO	0.24	0.22	0.18	0.14	0.18	0.21	0.25	0.19	0.47	0.40	0.26	0.22	0.55	0.61
MgO	1.01	1.35	0.15	0.14	0.14	0.16	0.13	0.13	0.48	0.28	0.21	0.11	0.12	0.16
CaO	3.47	3.88	0.96	0.40	1.53	2.02	1.83	1.89	2.48	3.58	1.92	0.69	0.34	0.25
Na ₂ O	5.53	5.16	5.41	4.88	8.19	7.56	11.55	14.63	8.67	10.43	9.55	11.52	10.18	7.91
K ₂ O	4.25	4.83	6.60	4.52	4.94	5.31	3.76	3.48	2.51	3.02	4.69	2.95	3.47	5.40
P ₂ O ₅	0.74	0.52	0.02	0.02	0.05	0.05	0.05	0.03	0.02	0.04	0.03	0.03	0.44	0.47
H ₂ O ⁺	0.47	0.46	0.34	0.30	1.06	1.26	2.80	1.51	2.28	2.50	2.25	2.69	4.05	3.36
H ₂ O ⁻	0.20	0.16	0.16	0.15	0.20	0.21	0.26	0.22	0.19	0.20	0.22	0.19	0.24	0.12
CO ₂	0.07	0.07	0.07	0.07	0.12	0.07	0.08	0.08	0.06	0.06	0.07	0.06	0.06	0.07
Others	0.25	0.38	0.85	0.93	0.56	0.67	1.80	3.82	2.11	4.48	2.30	1.73	1.88	2.24
	100.13	100.07	100.28	100.19	100.03	99.95	100.09	100.40	99.88	99.82	100.21	99.60	99.78	99.57
-O	0.07	0.11	0.14	0.16	0.11	0.10	0.30	0.79	0.44	0.34	0.33	0.04	0.13	0.11
	100.06	99.96	100.14	100.03	99.92	99.85	99.79	99.61	99.44	99.48	99.88	99.56	99.65	99.46
Al	0.92	0.85	1.10	1.23	1.14	1.12	1.28	1.38	2.00	1.87	1.32	1.39	1.49	1.43
Rb (ppm)	69	97	438	481	323	301	395	332	193	314	525	662	685	1280
La	71	74	252	325	223	236	540	409	393	1330	555	1410	3300	2830
Th	4.1	5.7	53	79	38	26	54	33	15	46	43	55	89	466
U	1.3	1.7	16	27	9.4	7.5	15	9.6	6.0	21	17	58	178	490
Zr	288	431	1950	2035	2230	1870	3200	3610	5830	20100	7610	7250	4130	724
Nb	55	92	312	291	327	250	546	580	495	1890	779	648	445	484
Be	3.5	3.2	28	22	16	14	31	21	15	28	26	32	46	104
F	990	1340	3310	3850	2270	2170	3090	4740	10200	6160	7070	502	1310	1140
Cl	185	500	190	185	230	150	6900	25100	520	3010	1070	440	550	300
Br	n.d.	1.0	0.8	0.4	0.9	0.3	17	57	0.9	1.7	1.1	0.2	n.d.	n.d.
I	n.d.	n.d.	0.4	0.4	n.d.	n.d.	0.6	0.5	n.d.	n.d.	0.5	n.d.	0.7	1.8
S	520	825	40	37	105	70	265	485	35	240	220	340	850	1100
B (average)	5.4	5.8	8.6	13	6.1	4.7	8.4	8.9	9.4	6.6	7.9	6.3	5.0	5.7
B (range)	3–9	5–8	5–13	9–15	4–8	4–5	4–18	4–32	3–20	3–12	5–11	4–10	3–9	4–8
B (no.)	5	4	5	8	8	4	10	10	7	5	9	8	10	3

Others—S, Cl, F and other traces as oxides; Al—agpaitic index, (Na₂O+K₂O)/Al₂O₃ (mol); n.d.—not detected (Br<0.2 ppm, I<0.4 ppm); analysts: J.C. Bailey, R. Gwozdz, R. Fuge, B. Damgaard, H.J. Bollingberg and Rock Geochemistry Laboratory of the Denmark and Greenland Geological Survey.

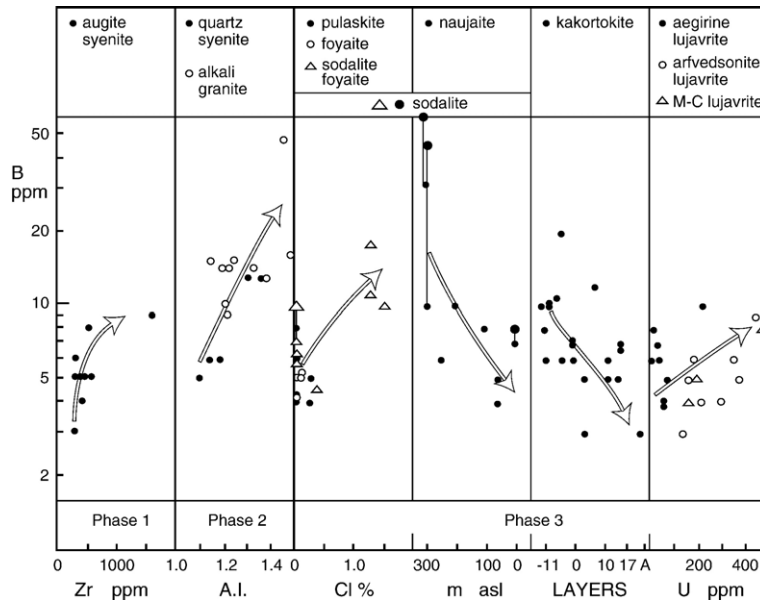


Fig. 1. Evolutionary trends of boron in rocks of phases 1–3, Ilímaussaq complex. Two B analyses in alkali granite (20, 60 ppm) from Gerasimovskiy (1969) were reduced by 20% (Section 4.1) and also plotted. Sodalites are indicated by larger symbols and tie lines to host rock. Preferred differentiation parameters change at different stages in the complex: Zr (ppm), AI—agpaite index $(\text{Na}+\text{K})/\text{Al}$ (mol), Cl (wt.%), metres above sea level, numbered layers in kakortokite, U (ppm) (see text).

agpaite index and incompatible elements such as Zr (Fig. 1). Further differentiation, in the early phase 3 rocks—pulaskite, foyaite and sodalite foyaite—leads to B contents rising along with Cl from ~ 6 and 800 ppm, respectively, to ~ 11 and 15,000 ppm, respectively. This reflects the increasing proportion of intercumulus sodalite in the more evolved samples. Sodalite, from a sodalite foyaite sample with only 7 ppm B, contains 10 ppm B (Table 3).

With the appearance of cumulus sodalite in the naujaite, B became sharply concentrated in the sodalite. The two earliest sampled naujaite (154345, 154346) at 300 m above sea level (Fig. 1) contain 32 and 10 ppm B with 60 and 45 ppm in their respective sodalites (Table 3). In the first sample, a separated mixture of microcline + nepheline contains 8 ppm B, while in the second sample microcline and nepheline both contain 9 ppm B. A late naujaite (154330) from sea level shows a return to

background levels of 7 ppm B with only 8 ppm in the sodalite.

High contents of B in the earliest cumulus sodalite are paralleled by high contents of Br, S and Be. Furthermore, as the B content decreases in the later cumulus sodalite, this is again matched by falling contents of the same three elements (Table 3).

In the kakortokites, layers -11 to -4 contain significant amounts of sodalite and average 10 ppm B. Layers 0 to $+17$ only occasionally have small amounts of sodalite and average ~ 6 ppm B. Black kakortokite A from the transitional layered kakortokites is free of sodalite and only contains 3 ppm B. Against this overall decrease in B contents (Fig. 1), variations in the amount of cumulus sodalite within a single kakortokite unit exercise a second-order control. Thus, within layer -9 , a red kakortokite with around 5 vol.% sodalite contains 6 ppm B, whereas the white layer with around 10 vol.% sodalite contains 10 ppm B. In general, there is no obvious concentration of sodalite in black, red or white kakortokite layers, and B contents are similar in the three types of layers (Table 2).

The overlying varieties of aegirine lujavrite show only small variations in B contents close to 6 ppm. The early varieties of arfvedsonite lujavrites show low contents around 4 ppm B, but there is a tendency for increasing B contents up to 9 ppm in late P–REE–U-rich varieties.

Table 3
Analyses of key elements in sodalite from sodalite foyaite and naujaite

Rock type	Sample number	Cl (wt.%)	Br (ppm)	S (ppm)	Be (ppm)	B (ppm)
Sodalite foyaite	154351	1.5	89	270	23	10
Early naujaite	154356	7.1	282	1080	53	45
Early naujaite	154345	7.4	360	1180	34	60
Late naujaite	154330	5.6	135	650	15	8

Analysts: Haldis Johanne Bollingberg, J.C. Bailey.

The final intrusions of M-C lujavrite on Kvanefjeld are thought to represent a more primitive stage of the lujavrites (Section 3) and contain only 4–8 ppm B.

Naujakasite lujavrite contains 5 ppm B, similar to contents in nearby arfvedsonite lujavrites. The core and rim of an immiscible spheroidal body in arfvedsonite lujavrite (Sørensen et al., 2003) both contain 3 ppm B, significantly lower than the host rock with 6 ppm B.

Four microsyenites collected from Kvanefjeld and Narsaq Elv, and which appear to have lost their volatiles and residual elements during emplacement in fractures (Rose-Hansen and Sørensen, 2001), contain 3–6 ppm B, i.e. contents similar to those in the other Ilímaussaq rock types.

Analyses of Ilímaussaq minerals presented by Gerasimovsky (1969) revealed 13 ppm B in sodalite, but neither the rock type nor locality was specified. Lower contents were reported for other rock-forming minerals (Table 1).

5.3. Late and low-temperature rocks

In pegmatites, 3 ppm B was found in rinkite from a naujaite pegmatite. In an M-C lujavrite pegmatite, steenstrupine contains ~5 ppm B. A blue sodalite from a late pegmatite in schlieren lujavrite contains only ~3 ppm B, whereas a yellow sodalite from a cross-cutting steenstrupine pegmatite contains 55 ppm B. Semenov (1969) found a metamict brown Ce–Be silicate with 0.115% B in a foyaite (?) pegmatite. Boulders of an arfvedsonite–microcline–albite–natrolite pegmatite in till overlying kakortokites contain radiating crystalline aggregates of the REE borosilicate stillwellite. The stillwellite occurs in the core of the pegmatite, both in an albite–microcline association and in later-formed pure natrolite (Karup-Møller, 1975).

Within metasomatically reworked areas of earlier agpaite rocks, as well as late veins or hydrothermal zones of pegmatites, a considerable number of Be minerals has been reported. Their B contents vary widely: genthelvite (1600 ppm), helvite (76 ppm), epididymite (18 ppm), leucophanite (15 ppm), chkalovite (11 ppm), sorensenite (10 ppm) and tugtupite (8 ppm). The presence of B in eudidymite from albitite veins was detected by OES (Semenov and Sørensen, 1966). Leifite from an albitite vein contains 200 ppm B and appears to have been reworked: the excess Na in the mineral may be accommodated in positions where water molecules were previously located (Petersen et al., 1994).

In veins, a green sodalite from a neptunite-bearing vein contains 15 ppm B. Semenov (1969) reported

155 ppm B in a yellow variety of sodalite (similar to hackmannite) from a vein and 30 ppm B was found in a yellow sodalite from a geode in naujaite. Among other vein minerals, our analyses reveal B in ussingite (8 ppm) and natrolite (3 ppm) but not apatite (<3 ppm).

In veins from the Taseq area, Sørensen et al. (1974) reported a metamict steenstrupine with 0.23% B. In contrast, a crystalline steenstrupine from a vein at Tunulliarfik, despite gains and losses of H₂O and Na, only contained 63 ppm B and Makovicky and Karup-Møller (1981) concluded that B plays practically no role in the composition of steenstrupine.

5.4. Silica-oversaturated series

In the phase 2 silica-oversaturated rocks, B contents increase from 5 to 13 ppm in quartz syenite along with levels of SiO₂ and agpaite index, and merge into typical values for the alkali granite (9–15 ppm) (Fig. 1). A number of the alkali granite samples have suffered post-magmatic alteration but still maintain B contents of 13–15 ppm. In the more peralkaline varieties of the granite analyzed by Gerasimovsky (1969), B contents of 20–60 ppm were reported (Fig. 1).

The location of B in a B-rich sample of peralkaline granite–154379 with 14 ppm B–has been checked. Arfvedsonite (5 ppm) and aenigmatite (3 ppm) contribute little to the whole-rock value. Leucosphenite Na₄BaTi₂B₂Si₁₀O₃₀ was looked for but not found. Leucosphenite was previously reported as an accessory phase in alkali granite by Hamilton (1964), but was excluded from the latest list of Ilímaussaq minerals (Petersen, 2001).

6. Discussion

6.1. Source magma for Ilímaussaq complex

At Ilímaussaq, the B content of the early augite syenite and its chilled margin is around 5 ppm and corresponds closely to intermediate alkaline rocks (3–6 ppm) from intraoceanic settings far removed from continental crustal contamination (Ryan et al., 1996). The exposed and inferred crustal section around Ilímaussaq (Garde et al., 2002) lacks marine sediments or S-type granites and is an unlikely source for B contamination. Low B contents of the earliest phase 1 rocks therefore suggest that the immediate parent magma for phases 1 and 3 of the complex was ultimately mantle-derived and avoided subsequent B contamination (cf. Marks et al., 2004).

6.2. Boron evolution at Ilímaussaq

Boron is generally regarded as an incompatible element, which concentrates in residual magmas (Section 1). This agrees with the increasing contents of B reported from the Lovozero intrusion (Gerasimovsky et al., 1966) and for the silica-oversaturated (phase 2) rocks at Ilímaussaq. Short fractionation sequences within the long evolution of the silica-undersaturated rocks at Ilímaussaq also show trends towards enhanced levels of B (Fig. 1).

In contrast, at a relatively early agpaitic stage, B contents decrease from the early to late naujaite (roof cumulates) and from the earliest exposed to final kakortokites (floor cumulates). This declining trend for B can be attributed to its enhanced partitioning into sodalite, which becomes a liquidus phase in the naujaite and is still a significant liquidus phase in kakortokite layers –11 to –4.

In the immediately preceding rocks—the sodalite foyaites—sodalite was an intercumulus phase ranging up to 20 vol.%. The intercumulus sodalite crystallized from a trapped melt with only moderate levels of B since earlier crystallizing phases such as nepheline and potash feldspar had probably already removed significant amounts of B before the sodalite crystallized. Boron and Cl contents built up in the later, more evolved sodalite foyaites and Cl contents rose to a level where sodalite became a liquidus phase. At this moment, myriads of sodalite primocrysts were concentrated in the early naujaite and scavenged large amounts of B along with Cl, Br, Be, S and to a lesser extent I (Tables 2 and 3). A high sodalite/melt partition coefficient can thus be inferred for these elements.

Because of its low density, sodalite forms a flotation cumulate (Ussing, 1912). According to Sharp et al. (1989), at 927 °C, the density of sodalite is estimated at 2.21 g/cm³ compared to naujaite melt densities of 2.65 and 2.47 g/cm³ at 0.00 and 2.52 wt.% water.

Data presented here suggest that the floated sodalites from later, deeper naujaite have lower contents of B and associated elements. Sodalite chemistry may thus have the potential to act as a stratigraphic indicator within the naujaite.

The decrease in B and associated elements in the later sodalites could be linked to two controls. Firstly, since sodalite almost certainly has a high partition coefficient for B and associated elements, it will scavenge large amounts of these elements from the coexisting magma. The enormous amounts of sodalite in the naujaite imply crystallization from an extensive magma chamber, presumably many kilometres thick. This is consistent

with the occurrence of fluid inclusions in the sodalites of naujaite indicating pressures of 1.5 to 3.5 kb (Markl et al., 2001). Such profound scavenging should rapidly deplete the coexisting magma in its contents of B and associated elements so that later sodalites have progressively lower contents.

Secondly, the two Zr–U regression lines recognized within rocks of the roof series (Bailey et al., 2001) suggest that early and late naujaite crystallized from slightly different magmas. These two magmas were both capable of forming naujaite with the same rock-forming minerals but appear to record a clear distinction in U contents. This may reflect a layered magma chamber (cf. Bailey, 1995) and, on this basis, the observed changes in sodalite chemistry may also reflect the chemistry of a layered magma chamber.

In floor cumulates, sodalite is again a liquidus phase, in this case trapped and retained among the mass of heavy cumulus phases despite its low density. The kakortokites record the end of sodalite as a cumulus phase and this can be attributed to the virtual exhaustion of Cl in the coexisting magma.

6.3. Substitution of boron and associated elements in sodalite

The structure and chemistry of sodalite explain its highly specific suite of trace elements. The cavities of the sodalite structure are occupied by chloride ions tetrahedrally coordinated by sodium ions. Sodalites where Cl is replaced by larger halides have been synthesized and effective radii have been estimated at Cl 178 pm, Br 193 pm and I 214–217 pm (Taylor and Henderson, 1978). In Ilímaussaq, presumably in response to the low oxygen fugacity, the bulk of sulphur in sodalite occurs as sulphide (Gerasimovsky, 1969; author's unpublished data) rather than sulphate. In this case, the S²⁻ ion (156 pm) also replaces the Cl⁻ ion. Enhanced partitioning of Be ions into sodalite should give few structural problems since substitution of BeSi for AlAl accompanies structural transitions from sodalite to tugtupite and helvite (Hassan and Grundy, 1991).

At trace-element levels, B could enter the sodalite structure in several ways. The B³⁺ ion (88 pm) could enter the aluminosilicate framework, replacing the Al³⁺ (126 pm) or Si⁴⁺ (117 pm) ions though these substitutions are not favoured by the relatively large size differences or the valency difference for Si. Borate sodalites have been synthesized in which the framework of the complex borate ion (B₁₂O₂₄)¹²⁻ is isotypic with the naturally occurring aluminosilicate framework ion

($\text{Al}_6\text{Si}_6\text{O}_{24}$)⁶⁻ (Smith et al., 1961; Hassan and Grundy, 1984), but cations other than Na^+ are required to balance charges. Synthesis of sodium hydroxyborate enclathrated sodalite, $\text{Na}_{7.5}(\text{AlSiO}_4)_6(\text{B}(\text{OH})_4)_{1.5} \cdot 2\text{H}_2\text{O}$, indicates that B atoms can occur within the cage-like cavities of sodalite (Buhl et al., 1994). This substitution mechanism has the advantage that the complex $\text{B}(\text{OH})_4^-$ ion can be charge balanced by Na^+ alone, and it may partly explain why careful analyses of natural sodalite usually record structural water (Taylor, 1967) and why B contents are higher in sodalite than in other aluminosilicate minerals at Ilímaussaq (nepheline, feldspar and analcime).

6.4. Substitution of B in Be and P minerals

Boron is often concentrated in Be minerals, as predicted on the basis of their similar covalent radii and tendency to form complex ions. Among Be minerals analyzed here, B contents increase as Na contents of minerals fall—from 8 to 11 ppm in the most widespread Be minerals (chkalovite, tugtupite and sorensenite) through Na-poor epididymite (18 ppm) to the Na-free minerals helvite (76 ppm) and genthelvite (1600 ppm). Genthelvite from small cavities in albitites can be assigned to a low-temperature hydrothermal stage (Bollingberg and Petersen, 1967). Boron has a similar covalent radius to phosphorus but was undetected in a hydrothermal apatite.

6.5. Boron in fluid-open systems

The mobility of B in fluid-open systems (see Sections 1 and 2) has been monitored at Ilímaussaq. In general, rock types with clearly visible secondary alteration (alkali granite) or with gains and losses of interstitial zeolites (arfvedsonite lujavrite) show no related change in their B contents. Stillwellite from a pegmatite appears to crystallize as radiating aggregates during the late pegmatitic and succeeding hydrothermal stage. Common vein minerals—analcime, natrolite, tugtupite and ussingite—contain low or background levels of B indicating that B is not concentrated en masse at the hydrothermal stage. However, some Be minerals from post-magmatic veins or altered materials contain relatively high levels of B pointing to local B-rich fluids, and the same can be inferred from varied B contents in sodalites from veins (15–155 ppm). Metamict or reworked minerals (steenstrupine, brown Ce–Be silicate and leifite) appear to have absorbed B during late-stage processes such as ion-exchange, which led to gains and losses of H_2O and Na (cf. Andersen et al., 1996).

Boron dominantly exhibits a closed-system behaviour during magmatic processes at Ilímaussaq and remained undisturbed during post-magmatic alteration. Immobility of B was presumably promoted by the apatitic state of the melt, and by the relatively low B contents of the magmas which meant that rock-forming minerals could readily incorporate all the available B. Even during the transition from the late pegmatitic to succeeding hydrothermal stage of a kakortokite pegmatite, stillwellite crystallized in the same form. Only in some highly localized hydrothermal environments do erratic B contents in certain minerals point to gains and losses of B in a fluid medium.

6.6. Boron minerals in peralkaline systems

The paucity of B minerals at Ilímaussaq contrasts with their relative abundance in the intrusions at Lovozero, Khibina, Mont Saint-Hilaire and Langesunds Fjord (Table 1). This is probably explained by the low content of B in the starting magma at Ilímaussaq, the extraction of considerable B by sodalite during fractionation and the absence of contamination from B-rich sediments in wall rocks.

Predictions on the stability of Na borosilicates such as reedmergnerite rather than tourmaline in peralkaline melts (Morgan and London, 1989) have been sustained by advancing mineralogical studies (Table 1). Growing numbers of Ca-REE borosilicates also deserve emphasis; their high levels of bivalent and trivalent cations allow additional ways of ordering complex borate groups into mineral structures. B-rich feldspars have been predicted in peralkaline environments but not found. This partly reflects the fact that B contents >500 ppm have yet to be reported from alkaline silica-undersaturated rocks. Interstitial melts with increasing B contents probably develop in many nepheline syenite pegmatites and, depending on the timing of saturation of volatiles (mainly water), they will crystallize B phases or B-rich minerals at a late magmatic stage or during post-magmatic activity (vugs, veins, metasomatites in or around pegmatites). Hyperapatitic melts are thought to form during a continuous transition from magmatic to hydrothermal states (Khomyakov, 1995) and also lead to formation of B minerals (Lovozero, Khibina and Mont Saint-Hilaire). Preferential partitioning of B into an aqueous vapour phase is well established in experiments on metaluminous and peraluminous granitic compositions. Similar experiments need to be performed on peralkaline compositions. Observations in nature suggest that losses of volatiles and mobile elements such as B become less significant as peralkalinity increases. The

fixation of B along with Cl, Br and S into liquidus sodalite at an early agpaitic stage in the Ilímaussaq complex is one manifestation of this behaviour.

7. Summary and conclusions

- (1) The average content of B in agpaitic nepheline syenites at Ilímaussaq is 8 ppm, falling in the lower range of B in global nepheline syenites.
- (2) The low B content of the initial augite syenite magma and subsequent differentiates is consistent with the ultimate derivation of the Ilímaussaq parent magma from a mantle source, and rules out contamination by pelitic rocks.
- (3) Two processes controlled the distribution of B during differentiation of the silica-undersaturated series of intrusive phases 1 and 3. Firstly, B behaved as an incompatible element during short fractionation sequences. Secondly, decreasing contents reflect extraction of large amounts of B at the early agpaitic stage by floating sodalite and by sodalite trapped among heavy cumulus phases in the floor cumulates.
- (4) Locally in pegmatites and veins, B was concentrated in certain Be and metamict/reworked minerals. The REE borosilicate stillwellite was reported from a single pegmatite (Karup-Møller, 1975).
- (5) The silica-undersaturated magma series at Ilímaussaq largely behaved as a closed-system for volatiles and mobile elements such as B. Some veins and metasomatically reworked areas, however, locally record gains and losses of B.
- (6) The silica-oversaturated rocks of intrusive phase 2 show rising B levels from quartz syenite to alkali granite.

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