

Volatiles in a peralkaline system: Abiogenic hydrocarbons and F–Cl–Br systematics in the naujaite of the Ilímaussaq intrusion, South Greenland[☆]

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Abstract

Agpaitic rocks comprise most of the exposed part of the 1.16 Ga old, 8×17 km large and about 1700 m thick Ilímaussaq intrusion in South Greenland. Within these, more than 600 m thick sequence of sodalite-rich “naujaites” (mainly sodalite+arfvedsonite+alkali feldspar+nepheline+eudialyte+aenigmatite) are interpreted as a sodalite flotation cumulate. Sodalites show two to three different zones in cathodoluminescence (CL) and at least two zones in thin sections. The CL zones can be related to chemical differences detectable by electron microprobe, whereas relations with optical zonations are less obvious. Compositional trends in sodalite reflect trends in the evolution of volatile contents in the melt. The sodalite at Ilímaussaq is almost free of Ca and closely corresponds to the pure Na–Cl sodalite endmember with about 7 wt.% of Cl; S contents reach up to 0.9 wt.%. Cl/Br ratios range from 500 to 1700. Raman spectroscopy shows that S is present as $[\text{SO}_4]^{2-}$ in sodalite, although sphalerite (ZnS) is a stable phase in naujaites. Peralkalinity and $f\text{O}_2$ conditions allow S^{2-} and $[\text{SO}_4]^{2-}$ to be present contemporaneously.

The whole naujaite sequence is divided into two parts, an upper part with low, homogeneous S contents and Cl/Br ratios in the sodalite cores, and a lower part with strongly variable and higher S contents and with Cl/Br ratios, which are decreasing downwards. The details of the S content and the Cl/Br ratio evolution show that sodalite strongly influences the halogen contents of the melt by scavenging Cl and Br.

The naujaites were formed from a highly reduced, halogen-rich magma in equilibrium with magmatic methane at about 800 °C, which, upon ascent, cooling and fractionation, exsolved an aqueous fluid phase. Both fluids were trapped in separate inclusions indicating their immiscibility.

Micrometer-sized aegirine crystals and primary hydrocarbon-bearing inclusions are abundant in the crystal cores. The inclusions were trapped at pressures up to 4 kbar, although the emplacement pressure of the intrusion is about 1 kbar. This indicates growth of the sodalite during melt ascent and a very effective mechanism of trace element scavenging during sodalite growth. Sodalite rims are devoid of aegirine or primary hydrocarbon inclusions and probably reflect the emplacement stage.

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1. Introduction

The Mesoproterozoic Ilímaussaq igneous complex is one of ten alkaline intrusive bodies in the Gardar igneous province, South Greenland. Since the first detailed description by Ussing (1912), numerous papers dealing with the Ilímaussaq complex have been published (e.g. Larsen and Sørensen, 1987; Rose-Hansen et al., 2001; Markl et al., 2001a,b; Marks and Markl, 2001). Thus, the petrography, petrology and geochemistry of the Ilímaussaq complex are relatively well known (e.g. Ferguson, 1964; Larsen and Sørensen, 1987; Bailey et al., 2001; Markl et al., 2001a, Marks et al., 2004b) and it can serve as a textbook example for the evolution of a peralkaline magma chamber.

Phase relationships, fluid evolution and element enrichment processes in the course of the crystallisation of silicate melts in general, and of agpaitic specifically, are strongly influenced by their volatile content and speciation (e.g. Lowenstern, 1994; Carroll and Webster, 1994; Metrich and Clocchiatti, 1996; Greenough et al., 1999; Moretti et al., 2003; Kravchuk et al., 2004). Therefore, understanding the type, stability relations and evolution of the fluid phases in igneous systems, and particularly of halogens (e.g. Marr et al., 1998; Webster and De Vivo, 2002; Schmitt et al., 2000; Carroll, 2005), is of prime importance. This, together with the fact that many Ilímaussaq rocks are strongly enriched in halogens (Bailey et al., 2001) and that methane and higher hydrocarbons of abiogenic origin occur in most of them (Petersilie and Sørensen, 1970; Konnerup-Madsen, 2001), makes the intrusion an ideal place to study the details of halogen partitioning and fluid evolution in peralkaline melts.

Hydrocarbon-bearing fluids are a typical feature of peralkaline and agpaitic rocks (Konnerup-Madsen, 2001; Potter and Konnerup-Madsen, 2003; Beeskov et al., 2006; Salvi and Williams-Jones, 2006; Ryabchikov and Kogarko, 2006), but their origin is still a matter of debate. An abiogenic origin is nowadays widely accepted (e.g. Konnerup-Madsen, 2001; Beeskov et al., 2006). Konnerup-Madsen and Rose-Hansen (1982) explained the hydrocarbons in the Ilímaussaq rocks by a late-magmatic reduction of a primary $\text{CO}_2\text{--H}_2\text{O}$ fluid. Another hypothesis invokes a Fischer–Tropsch-type reaction under post-magmatic conditions, for which again a CO_2 -rich fluid is needed (e.g. Salvi and Williams-Jones, 1997; Potter et al., 2004). Extended reviews of these models can be found in Potter and Konnerup-Madsen (2003) and Beeskov et al. (2006). A main point of criticism of both models is the requirement of a primary fluid containing CO_2 . Such a fluid is unlikely to have existed given the low $f\text{O}_2$

conditions recorded for the Ilímaussaq magmas (Markl et al., 2001a; Ryabchikov and Kogarko, 2006) and no fluid inclusion study at Ilímaussaq has ever reported high-temperature CO_2 fluid inclusions. Experimental and theoretical studies show that hydrocarbons form a stable fluid phase at high temperatures and high pressures when the oxygen fugacity is sufficiently low (Kenney et al., 2002). Indeed, they can form at $f\text{O}_2$ values close to the wüstite-magnetite buffer and $P\text{--}T$ conditions of the upper mantle from any carbonate species (Scott et al., 2004). Our data renew the model of the primary origin of the hydrocarbons in the Ilímaussaq rocks (Petersilie and Sørensen, 1970; Konnerup-Madsen and Rose-Hansen, 1982). We will show that the hydrocarbons are of primary magmatic origin and no CO_2 -rich fluid is needed to explain their occurrence.

2. Geology

Magmatism in the Gardar Province, South Greenland, is closely related to rifting between 1350 and 1140 Ma. Based on U–Pb chronology, two main periods of magmatic activity around 1280 Ma and between 1180 and 1140 Ma, respectively, can be separated (Upton et al., 2003). During these time spans, several alkaline to peralkaline plutonic complexes and a large number of dykes with variable compositions intruded the Ketilidian (1.7–1.8 Ga) granitic basement rocks (Julianehåb granite). The Ilímaussaq intrusion belongs to the second of these periods (Blaxland et al., 1976). Krumrei et al. (2006) dated the complex at 1161 ± 5 Ma using the Ar–Ar technique on amphiboles. It consists of alkaline to peralkaline, mostly agpaitic rocks. Controlled by early fault systems (Sørensen, 1966), the complex intruded at the contact between the Julianehåb granite and the late-Gardar Eriksfjord basalts and sandstones (Poulsen, 1964). The intrusion level was shallow and no metamorphic overprint at all has changed the mineralogy of the rocks (Upton et al., 2003).

Three pulses of magma intruded successively to 3–4 km depth (Larsen and Sørensen, 1987). The first one produced a silica-saturated to slightly under-saturated augite syenite, which is now found in parts of the intrusion as the outer shell and as xenoliths within the agpaitic rocks. Subsequently, a sheet of a peralkaline granite (called alkali granite in the literature on Ilímaussaq) intruded the augite syenite. According to Marks et al. (2004b), it represents a more evolved and crustally contaminated equivalent of the augite syenite that possibly assimilated from 10% to 15% of Archean lower crustal rocks. In a third stage, various nepheline syenites (pulaskite, foyaite, sodalite foyaite, naujaite, kakortokite and lujavrite) were formed mostly by low-

pressure in situ fractionation of a broadly phonolitic melt. They contain nepheline, eudialyte, sodalite, alkali feldspar, aegirine and arfvedsonite in various proportions as well as rare minerals like rinkite, aenigmatite, neptunite and others. These agpaïtes make up the major part of the complex (Fig. 1) and can be subdivided into a roof series (pulaskite, foyaite, sodalite foyaite and

naujaite, from the roof downwards), a bottom series (kakortokites), the most evolved rocks (lujavrites) in between and an unexposed part below the kakortokites. The current interpretation is that the roof and the bottom series are cumulates. The first formed by downward crystallisation and flotation of minerals less dense than the melt and the latter by gravitational separation after

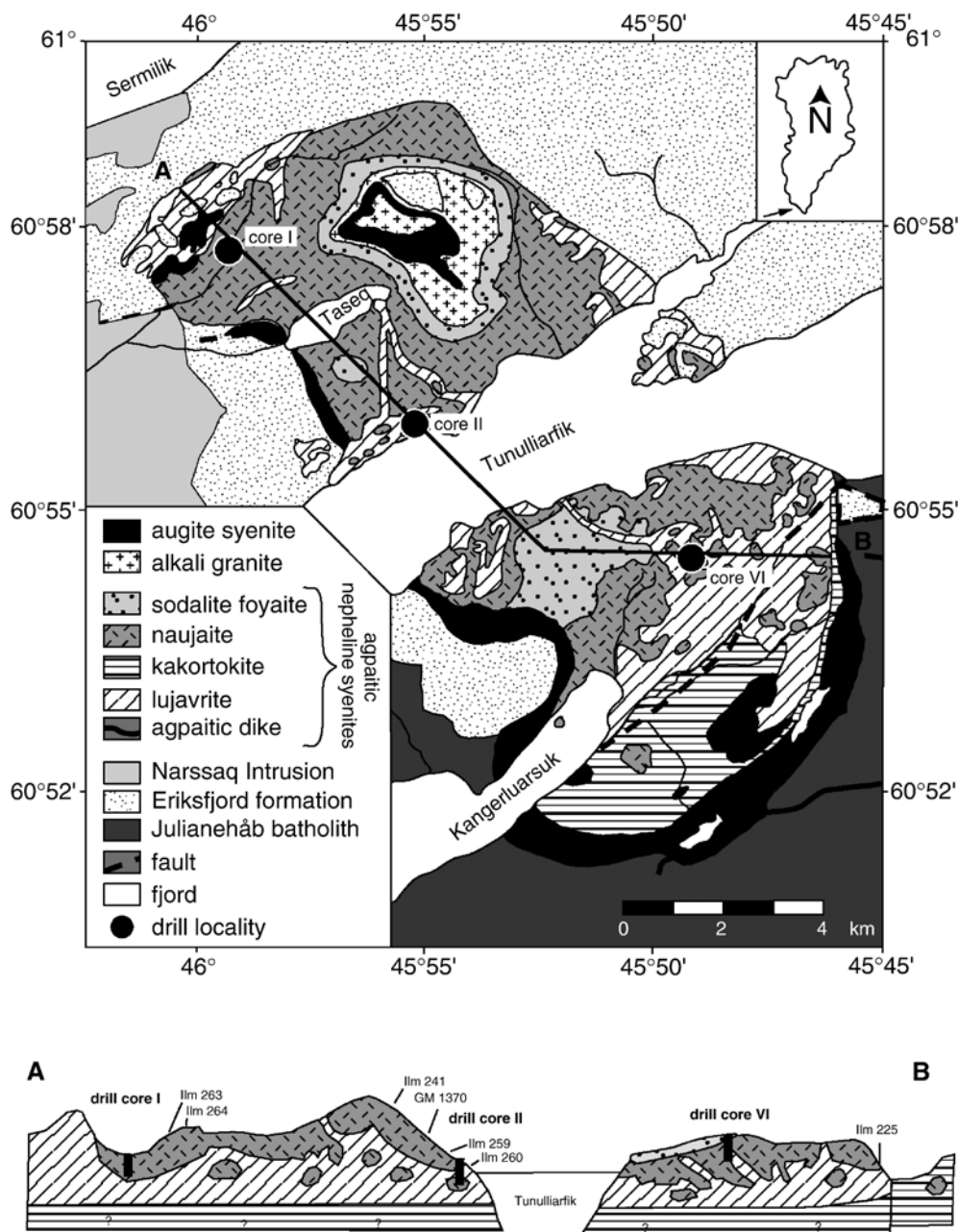


Fig. 1. Geological map of the Ilímaussaq intrusion with a schematic cross section (after Rose-Hansen and Sørensen, 2002). The drill locations are marked on the map and the sample locations of the surface samples are given in the cross-section.

the solidification of the roof series. The residual melts intruded the roof cumulates along fractures (Larsen and Sørensen, 1987). Recently, however, Sørensen et al. (2006) provided evidence for the idea that the bottom cumulate and the lujavrites were formed from a separate magma batch. Numerous pegmatites and late-magmatic to hydrothermal veins occur in all parts of the intrusion.

One of the agpaite syenites of the roof series, the naujaite, is a more than 600 m thick and slightly layered body that represents approximately 40% of the exposed volume of the complex (Rose-Hansen and Sørensen, 2002). Large naujaite xenoliths occur in the rocks below it (kakortokite and lujavrite). Therefore, Sørensen et al. (2006) argue for an originally even thicker naujaite horizon that was reduced to the present dimensions by piecemeal stopping. To explain the enormous amount of sodalite, the magma volume from which the sodalite crystallised must have been several times larger than today's volume of the complex. Bailey et al. (2001) and Bailey (2006) provide geochemical evidence for two naujaite generations formed from two slightly different magma compositions based on differences in the contents of B, Br, S and Be in the sodalites and two different Zr–U regression lines in whole rock analyses.

Several publications mainly dealing with the isotopic composition of the rocks show that the different magma batches, starting with the augite syenite and ending with the evolved nepheline syenites, originated from a single source (Nielsen and Steenfelt, 1979; Larsen and Sørensen, 1987; Stevenson et al., 1997; Marks et al., 2004b). The extreme fractionation trend found in the Ilímaussaq complex appears to be governed by low water activity, low SiO₂ activity and low oxygen

fugacity in the parental melt (Larsen, 1976, 1977, 1981; Markl et al., 2001a,b; Marks and Markl, 2001).

3. Petrography of the naujaite and fluid inclusions therein

The petrography of the Ilímaussaq rocks is reported in many publications (e.g. Ussing, 1912; Ferguson, 1964; Sørensen, 2001). The naujaite is a roof cumulate formed by flotation of minerals less dense than the melt, mainly sodalite. The sodalite crystals are euhedral and show areas with oriented inclusions of aegirine needles. Sodalites from the lower part of the naujaite sequence have aegirine-free rims or even lack aegirine inclusions at all. Large crystals of aegirine, arfvedsonite, eudialyte, and alkali feldspar enclose the sodalites poikilitically. Accessory minerals are fluorite, villiumite, sphalerite, apatite, aenigmatite and others.

The samples of this study mainly come from three naujaite-bearing drill cores (cores I, II and VI) described by Rose-Hansen and Sørensen (2002) (see also our Fig. 2). The drilling locations are marked in Fig. 1. These drill core samples were supplemented by samples collected from the surface. Together, they were arranged in a stratigraphic order using Fig. 13 in Rose-Hansen and Sørensen (2002). In this order, we present our results in the following Tables and Figures. We note that the stratigraphic position of the naujaite mass in drill cores II and VI may be unclear because these are most probably xenoliths. However, the density contrast between solid naujaite and the lujavrite melt is very small (Sørensen et al., 2006, and references therein). Therefore, the naujaite masses in drill cores II and VI are most probably not far below their original position.

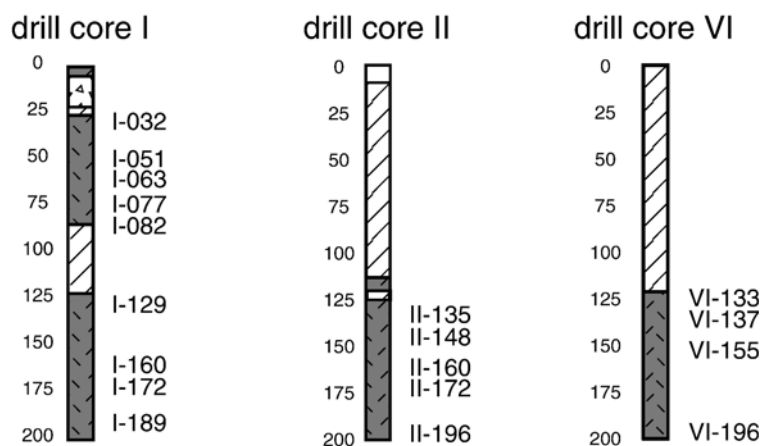


Fig. 2. Lithologies of the three naujaite-bearing drill cores and the samples taken from them. Modified after Rose-Hansen and Sørensen (2002), same lithologies as in Fig. 1. The numbers to the left of the cores refer to the depth (m) below the surface at the drilling location.

Under the cathodoluminescence microscope (CL), the sodalite grains show a strong zonation with up to three zones of light orange to brownish and purple colours (Fig. 3). The zonation starts with a purple zone in the core in the case of two-zone crystals (Fig. 3a) and with a light orange zone in the case of three zones changing to brownish colours towards the rim (Fig. 3b). In most samples, the euhedral crystals are overgrown by more or less irregular rims of a younger sodalite generation with brightly orange colours. Some grains are concentrically zoned (Fig. 3c), others seem to have old cores (Fig. 3d). These cores have darker orange luminescence colours than the overgrowths. There is no clear correlation between the aegirine content of the sodalites or the stratigraphic position of the sample in the naujaite sequence and the CL zonations.

Two types of fluid inclusions can be found in the sodalites; those dominated by hydrocarbons (HC) and those dominated by aqueous high-salinity fluids. The

aqueous inclusions are located only in those parts of the sodalites that are free of aegirine needles, whereas inclusions with hydrocarbons occur in both the aegirine-bearing and the aegirine-free parts (Fig. 4a). Aqueous inclusions are always of secondary origin. They are aligned along inclusion trails or they form clusters (Fig. 4b). Aqueous inclusions occur accumulated in those samples that were taken close to lujavrite. With increasing distance to lujavrite, the amount of aqueous inclusions decreases.

Based on their textures, HC-bearing inclusions are partly primary, partly secondary. The primary inclusions often exhibit negative crystal shapes (Fig. 4c). They are disseminated randomly in the sodalite cores between aegirine needles but are, in most cases, not attached to them. Secondary HC-bearing inclusions form trails (Fig. 4d). The lack of clear age relationships at intersections of hydrous with hydrocarbon inclusion trails suggests that the two types of trails were formed

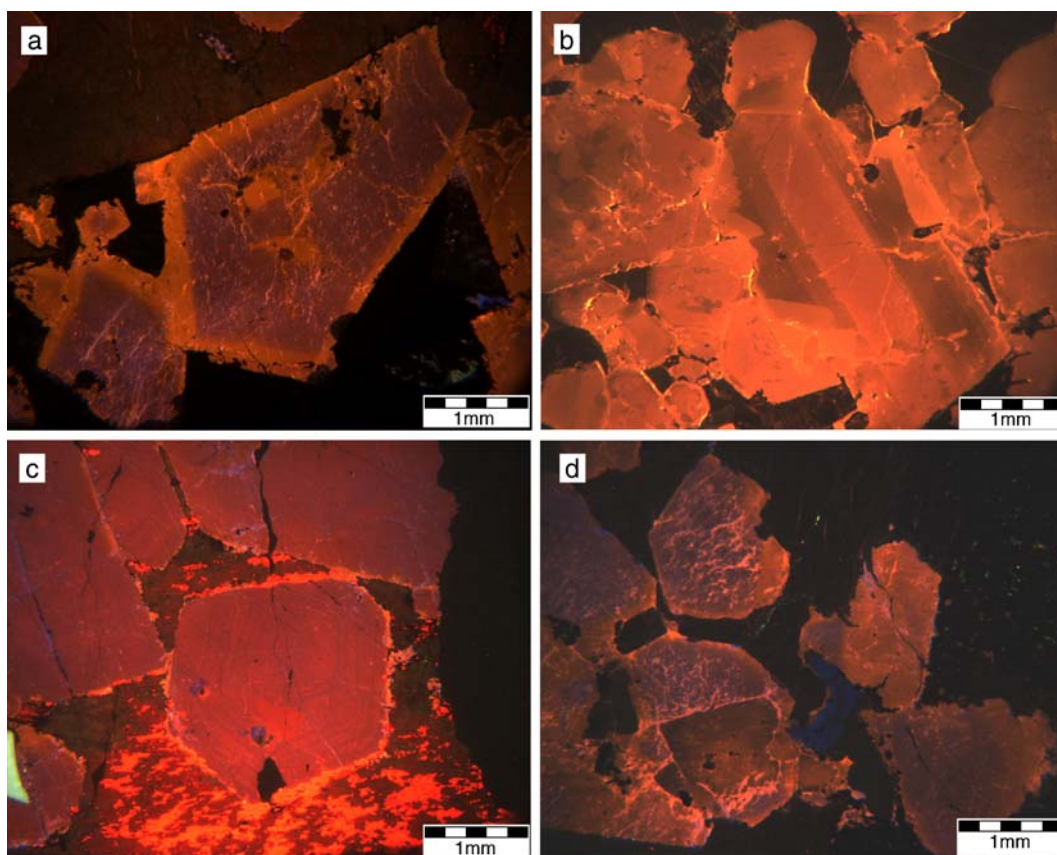


Fig. 3. CL-photomicrographs of sodalite. (a) Sodalite with two CL-zones. (b) Sodalite showing three CL-zones starting with light orange colours in the core, turning to a more brownish zone; the rims show light orange colours again. (c) Concentrically zoned sodalite with an oscillating zonation of narrow purple and reddish zones. (d) Sodalite crystals with two-zone zonation and additional dark-coloured old cores.

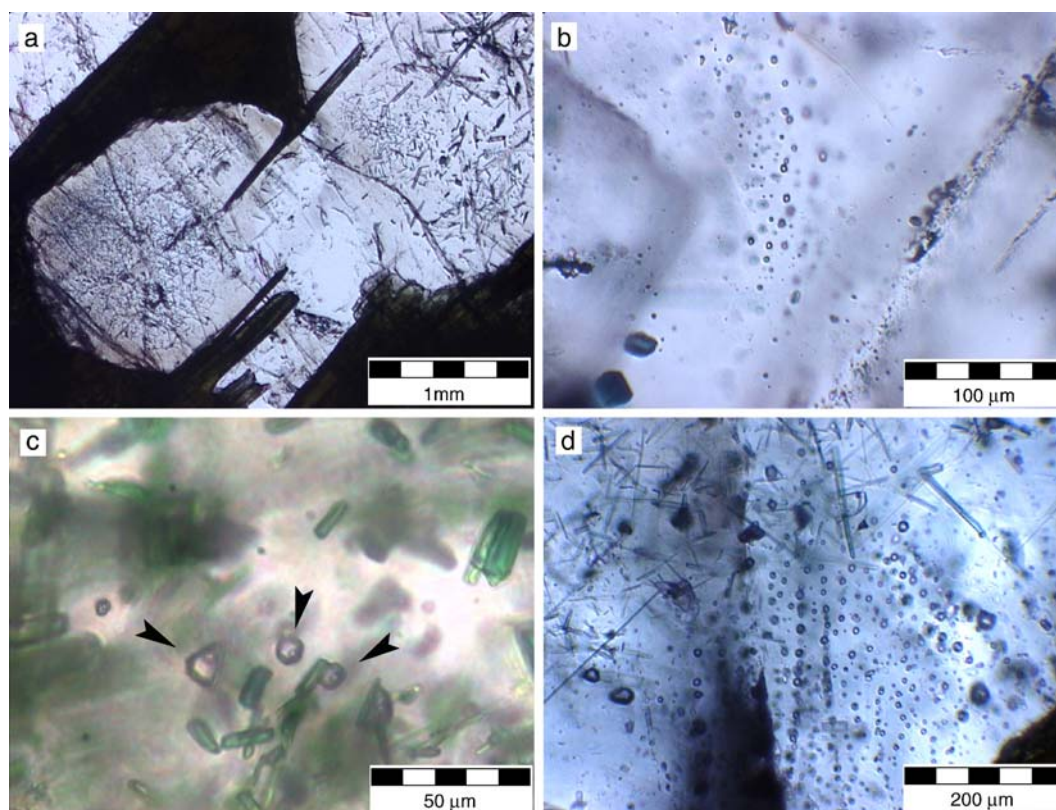


Fig. 4. Photomicrographs of sodalite. (a) Distribution of aegirine needles in sodalite showing areas with abundant and oriented aegirine needles in the cores and aegirine-free areas at the rims. (b) Trail of aqueous inclusions ($\sim 5 \mu\text{m}$ in diameter) in an aegirine-free part of sodalite. (c) Primary hydrocarbon-bearing inclusions marked by the black arrows between green aegirines. They are approximately $10 \mu\text{m}$ in diameter and show negative crystal shapes. They exhibit a gas bubble because they are pictured at -100°C before homogenisation (at -96.1°C). (d) Large trail of secondary hydrocarbon-bearing inclusions cutting through an aegirine-free part of sodalite. Note that the trail does not proceed into the aegirine-bearing part on top.

contemporaneously. Very rarely, [Konnerup-Madsen et al. \(1979\)](#) found inclusions in chkalovite from a hydrothermal vein and in nepheline from the naujaite that trapped both fluid types. This proves that both fluids existed from the magmatic naujaite phase to the hydrothermal phase of the intrusion.

4. Methods

4.1. Cathodoluminescence (CL)

For the CL analyses, we used a Technocyn 8200 Mk 4 Luminoscope fitted with an Alcatel Vacuum Pump at the Universität Tübingen. The chamber is mounted on a Zeiss Microscope of which the normal stage was replaced by the CL chamber. Acceleration voltage and beam current of the electron gun were set to 14.5 kV and $300 \mu\text{A}$, respectively. Pictures were taken with a digital camera (DVC 1310-FW) mounted on the third

ocular of the microscope. Typical exposure times were 3 to 6 s.

4.2. Electron microprobe

Major element compositions of sodalite were determined using a JEOL 8900 electron microprobe at the Institut für Geowissenschaften, Universität Tübingen, Germany. For calibration, both natural and synthetic standards were used. The beam current was 15 nA and the acceleration voltage was 15 kV . The counting time on the peak was 16 s for major elements, and $30\text{--}60 \text{ s}$ for minor elements. Background counting times were half of the peak counting times. To avoid Na migration under the electron beam, sodalite was analyzed using a defocused beam of $20 \mu\text{m}$ diameter. Data reduction was performed using the internal $\phi\rho Z$ procedures of JEOL ([Armstrong, 1991](#)). Mean values of sodalite composition are presented in [Table 1](#).

Table 1

Mean values of sodalite chemistry analysed by EMP

		n	Al ₂ O ₃	Na ₂ O	K ₂ O	Cl	SiO ₂	CaO	SO ₃	FeO	total
Sodalite rim	Ilm241	10	31.17	24.16	0.01	6.72	37.25	0.01	0.49	0.22	100.02
	Ilm264	20	31.31	23.76	0.02	6.66	37.43	0.01	0.60	0.33	100.12
	GM1370	11	31.11	25.13	0.02	6.85	36.93	0.01	0.30	0.14	100.48
	I-032	2	31.68	24.77	0.01	6.75	37.08	0.01	0.56	0.03	100.87
	I-077	8	31.29	24.74	0.02	6.63	37.07	0.01	0.80	0.17	100.73
	Ilm260	8	31.27	25.01	0.03	6.71	37.04	0.01	0.54	0.22	100.82
	Ilm225	4	31.13	24.43	0.01	6.56	36.86	0.01	0.76	0.24	99.99
	I-143	2	31.46	24.93	0.01	6.82	37.04	0.01	0.49	b.d.	100.75
	I-160	12	31.13	23.19	0.05	6.44	37.13	0.01	1.00	0.16	99.10
	I-189	8	31.03	23.96	0.02	6.75	36.91	0.01	0.63	0.20	99.50
	II-142	6	31.30	24.28	0.01	6.77	37.32	0.01	0.37	0.28	100.34
	II-199	4	30.84	23.7	0.01	6.82	36.85	0.01	0.44	0.13	98.80
Sodalite core	Ilm241	10	31.15	23.99	0.01	6.93	37.20	0.01	0.15	0.06	99.51
	Ilm264	18	31.36	23.84	0.01	6.98	37.52	0.01	0.09	0.09	99.89
	GM1370	8	30.95	24.96	0.03	6.87	37.03	0.11	0.12	0.27	100.33
	I-003	1	31.45	25.11	0.02	6.85	37.05	b.d.	0.33	0.09	100.90
	I-032	2	31.60	24.89	0.01	6.82	36.95	0.01	0.32	0.08	100.66
	I-077	6	31.30	24.87	0.01	6.76	37.13	0.01	0.46	0.12	100.66
	Ilm260	10	31.35	24.73	0.02	6.93	37.50	0.02	0.16	0.11	100.82
	Ilm225	4	31.06	25.11	0.02	6.94	36.93	0.01	0.17	0.29	100.52
	I-160	10	31.16	23.95	0.02	6.50	36.93	0.01	0.88	0.16	99.61
	I-189	10	31.01	23.71	0.02	6.60	36.97	b.d.	0.88	0.13	99.32
	II-142	4	31.43	24.44	0.01	6.73	37.37	0.01	0.54	0.17	100.69
	II-199	8	31.00	24.08	0.02	6.16	36.74	0.01	1.73	0.13	99.86
Old cores	Ilm264	3	31.25	23.49	0.01	6.89	37.48	0.01	0.14	0.07	99.34
	GM1370	15	31.21	25.22	0.02	6.83	36.71	0.01	0.22	0.07	100.29
	I-003	5	31.21	25.37	0.01	6.69	36.80	0.01	0.71	0.08	100.87
	I-032	8	31.22	25.16	0.02	6.73	37.27	0.01	0.51	0.06	100.96
	I-077	2	31.37	24.52	0.02	6.38	37.20	0.01	1.18	0.05	100.73
	Ilm225	2	30.94	24.82	0.02	6.91	37.11	b.d.	0.17	0.32	100.28
	I-143	6	31.52	24.94	0.01	6.42	36.88	0.01	1.13	0.05	100.94
	I-160	2	31.22	23.13	0.02	6.12	36.72	0.01	1.76	0.12	99.09
	I-189	2	31.26	24.32	0.02	6.40	36.87	0.01	1.15	0.15	100.16

n=number of analyses; b.d.=below detection limit.

4.3. Neutron Activation Analysis (NAA)

For the determination of bromine, hand-picked sodalite mineral separates were used. 100 to 150 mg of each sample were weighed into small polyethylene containers with caps that were welded to the containers with a hot glass rod in order to make them water tight. A standard solution of 0.2 mg/ml was prepared by dissolving a weighed amount of KBr in distilled water in a volumetric flask. Aliquots of 50 µl of this solution were pipetted onto filter paper in the same polyethylene containers as used for the samples. Four of these flux monitors were irradiated together with each batch of 10 samples in the TRIGA research reactor of the Institut für Kernchemie, University of Mainz, for 4 h at a flux of 2×10^{12} neutrons*cm⁻² *s⁻¹. In addition, two aliquots of a standard clay (TONY) that was calibrated against several international geological reference materials (Kuleff and Pernicka, 2002) were also irradiated with the samples.

The major aim was the determination of the bromine concentration so that the measuring scheme was optimised for this purpose. Since the samples contain very high concentrations of sodium, which produces ²⁴Na with a half-life of 15.0 h and emits high-energy gamma rays causing a high background, the samples were allowed to decay for 2 weeks. Bromine was determined by measuring the 559 keV gamma signal of ⁸²Br which decays with a half life of 35.3 h using a hyperpure germanium detector with an energy resolution of 1.9 keV at 1.33 MeV. The longer than usual decay period reduced the sensitivity of the bromine determination somewhat, but was sufficient for the concentration range encountered in the samples. In addition to bromine, 22 other elements were analysed whose concentrations are reported in Table 2. The analytical errors given represent only counting errors comprising background and signal. They are given in percent of the concentration value.

Table 2

Trace element contents of sodalite analysed by NAA

	Ilm241±[%]		Ilm264± [%]		Ilm263±[%]		I-032±[%]		I-051±[%]		I-063±[%]		I-077±[%]		VI-155±[%]		Ilm259±[%]	
Sc	0.08	5.7	0.06	5.5	0.13	4.6	0.16	3.6	0.09	5.2	0.07	6.8	0.09	4.8	0.16	3.8	0.05	7.3
Cr	5.19	18	4.62	11	5.06	11	3.58	11	4.69	11	6.29	10	5.14	10	4.58	15	4.34	11
Co	0.31	15	0.13	25	0.09	54	0.07	34	0.07	41	0.13	32	0.07	38	0.38	9.6	0.09	30
Zn	189	5.2	84.5	5.1	92.2	5.7	48.9	5.5	59.1	6.2	55.6	6.1	63.6	5.5	177	4.7	151	4.8
Br	67.1	4.0	141	3.0	60.2	4.0	65.4	4.0	69.1	4.0	87.6	4.0	85.6	3.0	80.3	4.0	110	4.0
Rb	497	5.5	186	5.4	66.9	7.6	22.9	8.8	44.4	8.6	221	5.3	61.2	6.6	150	5.1	146	5.6
Zr	b.d.		341	41	b.d.		b.d.		b.d.		b.d.		40.9	57	155	30	b.d.	
Sb	0.28	29	0.15	45	0.10	43	0.15	43	0.12	50	0.11	41	b.d.		0.80	14	0.15	28
Cs	21.7	3.7	4.84	3.9	0.93	8.3	0.09	36	0.27	20	5.24	4.1	0.39	11	1.93	4.8	1.46	6.5
Ba	b.d.		b.d.		b.d.		98	lim	b.d.		b.d.		b.d.		b.d.		b.d.	
La	31.9	3.9	11.9	5.0	1.29	10	11.8	4.5	4.18	8.7	1.49	10	8.99	5.4	37.3	3.1	5.00	3.4
Ce	58.4	3.1	22.5	3.1	16.2	4.3	27.8	3.1	9.33	5.5	3.57	13	16.7	4.1	59.1	2.9	7.83	7.2
Nd	25.9	54	11.9	47	7.5	78	18.1	42	8.45	74	7.43	59	5.13	72	12.7	45	b.d.	
Sm	3.15	2.8	1.12	3.3	0.17	6.5	1.40	3.4	0.58	4.5	0.21	6.5	1.00	3.5	2.50	2.8	0.25	4.8
Eu	0.30	8.9	0.18	9.8	0.16	12	0.22	8.4	0.16	17	0.13	17	0.18	14	0.28	8.0	0.09	17
Tb	0.42	12	0.49	9.4	0.25	15	0.21	13.1	0.10	26	0.14	42	0.12	20	0.89	7.9	0.35	18
Yb	0.29	lim	0.32	7.1	b.d.		0.29	lim	0.37	36	b.d.		0.29	47	2.03	12	0.22	40
Lu	0.06	39	b.d.		0.07	lim	0.04	lim	0.06	52	b.d.		0.04	59	0.27	21	0.09	24
Hf	0.21	24	0.63	8.6	0.47	12	2.54	6.1	1.30	8.4	0.14	28	0.85	8.1	6.42	6.1	0.23	15
Ta	0.25	19	0.25	16	1.0	10	1.21	7.4	0.42	13	0.19	28	0.44	11	1.38	7.8	0.14	24
Th	6.36	3.0	12.1	2.7	5.2	3.2	1.35	3.5	1.45	3.9	0.79	6.8	1.48	4.2	24.6	2.7	7.23	2.8
U	0.66	53	2.17	29	0.54	48	0.75	51	b.d.		0.53	43	0.54	45	3.40	18	0.81	22

	Ilm260±[%]		VI-196±[%]		Ilm225±[%]		I-160±[%]		I-172±[%]		II-148±[%]		II-172±[%]		II-196±[%]	
Sc	0.09	4.7	0.35	3.2	0.10	4.5	0.06	6.0	0.32	3.0	0.07	6.2	2.11	2.6	0.07	5.6
Cr	4.60	10	5.13	15	4.17	11	5.45	9.2	4.16	11	4.81	15	7.82	11	4.86	10
Co	0.10	35	0.16	27	0.08	38	0.10	27	0.22	20	0.17	24	0.07	77	0.10	29
Zn	218	4.6	203	4.7	55.6	5.4	86.4	5.6	37.6	6.9	166	4.6	94.7	5.7	87.5	4.8
Br	100	4.0	134	3.0	40.6	5.0	40.1	5.0	47.3	4.0	67.5	4.0	95.2	4.0	54.7	4.0
Rb	50.4	6.8	140	5.8	424	4.8	8.76	19	20.1	11	21.5	13	31	14	33.8	8.9
Zr	b.d.		b.d.		b.d.		b.d.		124	27	b.d.		3588	50	b.d.	
Sb	0.20	37	0.34	27.1	0.21	34	0.17	43	0.15	10	0.23	24	0.29	31	0.12	43
Cs	0.55	8.7	5.02	4.0	0.98	6.5	0.70	9.4	1.43	5.3	5.46	3.9	1.21	9.4	3.34	4.0
Ba	b.d.		120		b.d.		b.d.		b.d.		b.d.		152	32	b.d.	
La	25.8	3.5	17.6	4.0	15.7	3.7	127	3.3	52.6	3.2	2.44	9.6	179	2.9	6.77	4.8
Ce	50.4	2.9	40.3	3.2	23.4	3.5	211	2.8	108	2.8	4.73	7.4	371	2.7	10.7	4.5
Nd	29.7	36	24.8	43	7.50	49	67.5	41	51.5	41	b.d.		159	45	7.63	88
Sm	3.15	2.7	2.47	2.9	1.15	3.1	3.47	2.8	6.63	2.6	0.15	14	21.9	2.6	1.03	2.3
Eu	0.42	6.9	0.31	8.4	0.21	9.0	0.30	8.1	0.75	5.8	0.10	18	2.53	4.7	0.14	11
Tb	0.61	8.8	0.59	9.8	0.35	11	0.26	14	0.64	9.5	0.05	56	2.79	7.0	0.12	19
Yb	0.34	7.1	0.36	lim	1.06	16	0.32	7.7	1.96	14	0.09	73	21.1	9.9	0.25	57
Lu	0.13	34	0.13	39	0.14	27	0.05	11	0.24	21	0.03	9.2	2.55	11	0.07	46
Hf	1.30	6.8	0.86	8.4	2.40	6.5	0.36	12	4.85	6.6	0.11	43	74.1	6.0	0.76	9.4
Ta	0.61	10	3.19	6.8	0.61	10	0.27	24	2.86	8.2	0.08	44	17.9	6.2	0.22	23
Th	9.28	2.7	12.8	2.7	8.10	2.8	5.56	3.0	2.10	3.3	0.90	5.3	7.20	3.1	1.78	3.5
U	1.48	27	2.47	22	1.76	22	1.51	36	4.95	34	b.d.		10.5	20	0.90	33

b.d.=below detection limit; lim=very large error because of element content close to detection limit.

4.4. Fluid inclusion studies

The microthermometric measurements were carried out at the Universität Tübingen fluid inclusion laboratory. Microthermometric determinations were made on doubly polished wafers (about 500 µm thick), using a Leica microscope equipped with a Linkam THM600/S

heating–freezing stage. Accuracy of the measurements was ensured by calibration against the melting point of pure CO₂ (−56.6 °C), pure H₂O (0.0 °C) and the critical total homogenisation temperature of pure H₂O (374.1 °C) in synthetic fluid inclusion standards. The reproducibility of melting temperatures is 0.1–0.2 °C, of homogenisation temperatures around 2–3 °C. Apparent

salinities in the aqueous inclusions are expressed as weight percent (wt.%) NaCl equivalent, calculated using data from Bodnar (1993) based on the final ice melting temperature for two-phase inclusions.

4.5. Raman spectroscopy

The composition of the fluid inclusions was determined qualitatively by a confocal laser Raman

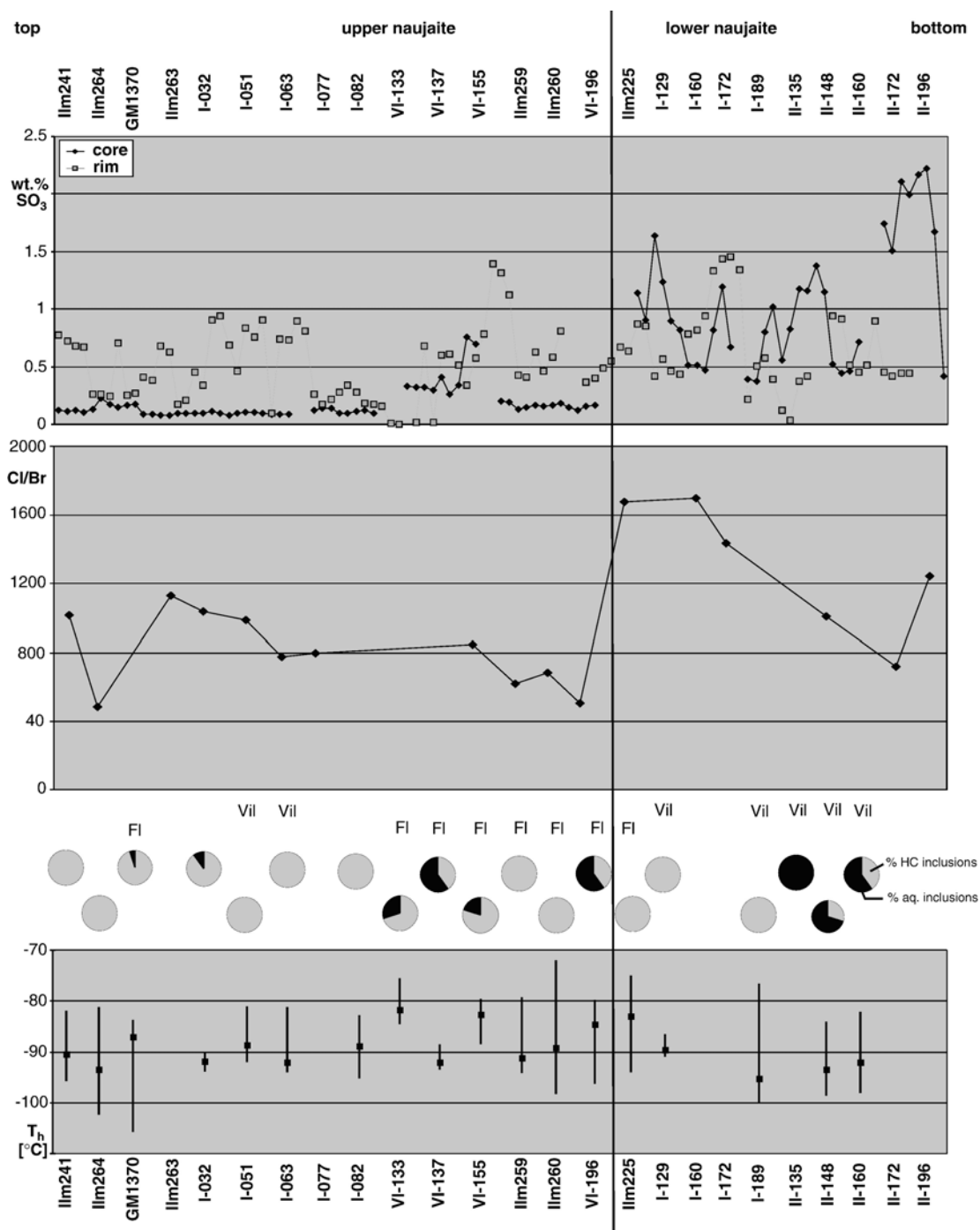


Fig. 5. Stratigraphic arrangement of S analyses in sodalite cores and rims, Cl/Br ratios, the fluoride mineral found in the samples, the fluid inclusion inventory of the samples and the homogenisation temperatures of the primary hydrocarbon-bearing inclusions. Note that the fluid inclusion data and the type of fluoride mineral are not correlated to the systematics in the sodalite mineral chemistry.

microprobe Dilor LABRAM 2 equipped with a Peltier cooled CCD detector at the Universität Tübingen. We used an Argon laser with a wavelength of 514.5 nm. The system was calibrated against silicon and diamond standards. Since sodalite has a strong fluorescence, only qualitative analyses were possible. Especially wavenumbers above 3500 cm^{-1} are totally obscured by this fluorescence.

5. Sodalite mineral chemistry

Selected microprobe analyses of sodalite from various stratigraphic levels are presented in Table 1. The sample spots and profiles were selected according to the CL-zonations to investigate the relation between major and minor element compositions and these zonations. In general, the sodalites from the naujaite contain only very minor amounts of Ca and K. From the top of the naujaite downwards, the SO_3 content in the sodalite cores with relatively dark CL colours remains stable at $\sim 0.15\text{ wt.}\%$ for approximately two thirds of the sequence. Then, it increases strongly with depth to values above $2\text{ wt.}\%$ (Fig. 5). Cl in the cores shows an inverse behaviour. The brighter luminescing rims exhibit a wide scatter in SO_3 along the entire profile. Based on the data summarised by Ostroumov et al. (2002), which show that the wavenumber of 990 cm^{-1} is indicative for the sulphate ion (see Table 1 therein), our Raman measurements

show clearly that the sulphur species in the sodalites is $[\text{SO}_4]^{2-}$ (Fig. 6). This frequency appears in all our Raman spectra, while frequencies indicative for other sulphur species are absent.

Bromine exhibits a stratigraphic behaviour similar to that of sulphur. It increases from the uppermost naujaite downwards, from 60 ppm to $\sim 140\text{ ppm}$, then dropping to values below the initial and increasing again. Cl/Br values range from 500 to 1700 (Fig. 5). The upper naujaite exhibits homogeneous and slightly decreasing Cl/Br ratios whereas the lower naujaite starts with high Cl/Br values that decrease downwards.

Most of the sodalites show zonations in their Fe content; the rims have higher contents than the cores (Fig. 7). Some crystals show a more complex zonation with a maximum in the core, then a decrease outwards and a final increase at the rim. Bailey (2006) found that sodalite from the early naujaite (refers to our upper naujaite) contains more B, Br, S and Be than sodalite from the later naujaite (our lower). Two different Zr–U regression lines reported in Fig. 6 in Bailey et al. (2001) support this separation of the naujaite into two types.

Trace elements were determined using the Neutron Activation Analysis (NAA) of hand-picked sodalite concentrates. In general, the mantle-normalised trace element patterns exhibit strong depletion of elements like Sc, Cr and Co (Fig. 8). HFS elements are weakly and LIL elements are strongly enriched. Because of the aegirine

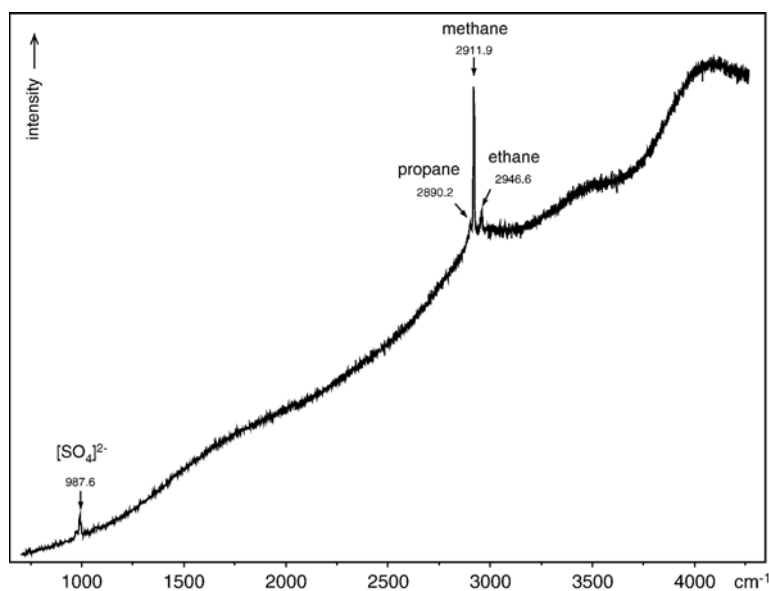


Fig. 6. Raman spectrum of HC-bearing inclusions from the inclusion trail in Fig. 4d showing the wavenumbers typical of methane, ethane and propane and the sulphate frequency of the host sodalite. The strong increase of the background with increasing wavenumbers is due to the strong fluorescence of sodalite.

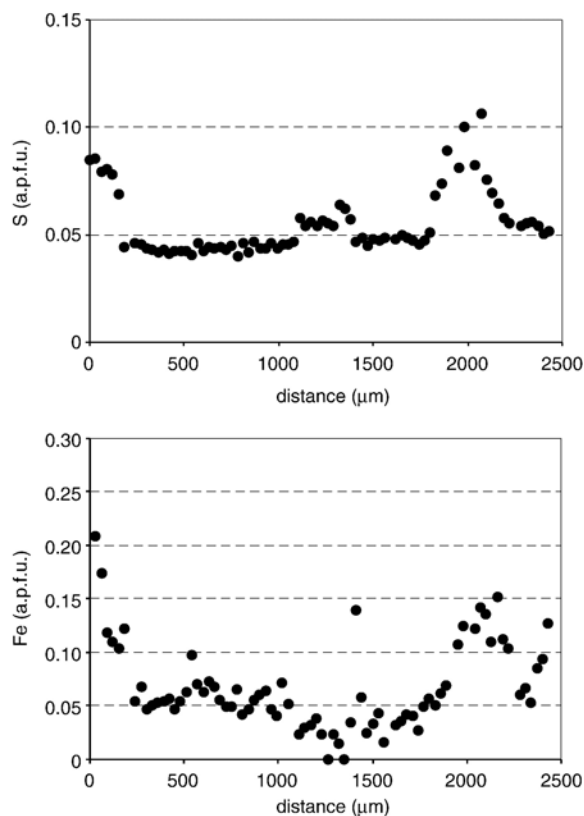


Fig. 7. Diagrams showing zonation of sodalite (from sample I-032) in S and Fe content. Both elements exhibit a similar behaviour with more homogeneous values in the core and increasing values towards the outer rim.

needles enclosed in most sodalites, the resulting values are mixtures of sodalite and aegirine. In order to evaluate this problem, we compared the analyses to those from later formed large aegirine crystals occurring interstitially in the naujaite (see analyses in Marks et al., 2004a). Trace elements hosted by the sodalite are Rb, Cs and Ba in concentrations up to 500, 22 and 150 ppm, respectively. No stratigraphic trends for these elements are observed. Although some REE are missing in our analyses, it is clear that aegirine is responsible for the measured contents of the REE. The normalised REE patterns are very similar to those from the large arfvedsonite and aegirine crystals enclosing the sodalites (Marks et al., 2004a). Other elements that reflect the influence of the aegirine needles are Zr, Hf, Fe, Sc and Zn.

6. Fluid inclusions in sodalite

The gas content and the composition of the gas trapped in fluid inclusions were summarised by Potter and Konnerup-Madsen (2003). The naujaite contains by far the highest gas contents of the Ilímaussaq rocks ($\sim 60 \text{ cm}^3/\text{kg}$). The gas consists mainly of methane, but other components such as ethane, propane and higher hydrocarbons as well as minor amounts of hydrogen and nitrogen were also found. CO and CO₂ are only present in traces. Konnerup-Madsen et al. (1979) reported very similar bulk values for sodalite from the naujaite, which proves that sodalite is the host of most of the gases.

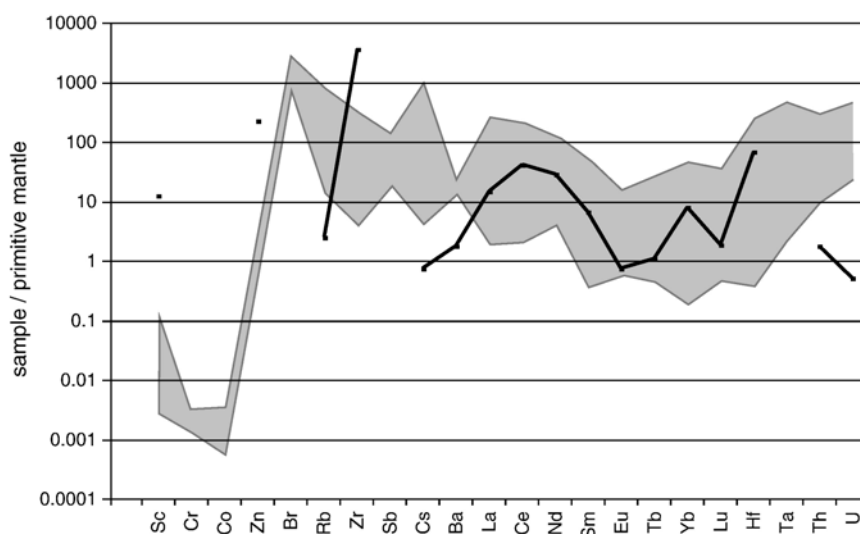


Fig. 8. Trace element pattern of sodalite (shaded area) compared with large interstitial aegirine from the naujaite (black line and dots, data from Marks et al., 2004a). The high variability of most elements is due to different amounts of aegirine needles enclosed in the sodalites. See text for further discussion.

Primary hydrocarbon-bearing inclusions homogenise at temperatures between -106°C and -85°C into the liquid phase. Based on Raman analyses, they contain only methane. Hydrocarbon-bearing inclusions in trails are a mixture of different HC species with methane being the dominant one. Their homogenisation temperatures are higher and exhibit a wide scatter between -85°C and -10°C due to variable proportions of higher hydrocarbons. The composition of the secondary HC-bearing inclusions changes with the stratigraphic position of the samples. In the upper parts, the proportion of higher hydrocarbons like ethane and propane is higher. In the lower parts, the fluid is almost pure CH_4 . Due to the strong fluorescence of sodalite during Raman analyses, it was not possible to quantify these observations. However, based on Fig. 7A in Konnerup-Madsen et al. (1979), the homogenisation temperatures can be used for an estimation of the HC composition. For the highest measured temperature indicating the highest content of higher hydrocarbons, a methane content from 50% to 60% is derived. This is in fairly good agreement with the values summarised by Potter and Konnerup-Madsen (2003) given the fact that we compare a single inclusion with sodalite bulk values.

Fluid inclusions in the sodalites filled with a two-phase aqueous solution are exclusively of secondary origin. Ice melting temperatures are around -20°C , which corresponds to a salinity of ~ 22 wt.% NaCl-equiv. The inclusions homogenise over a broad range of temperatures between 50 and 250°C into the liquid phase.

7. Discussion

7.1. Evolution of the fluid phase

According to the work of Sharp et al. (1989), sodalite crystallisation starts at high temperatures between 800 and 1000°C , provided the activity of NaCl in the melt is sufficiently high. For the onset of sodalite crystallisation in a naujaite sample from Ilímaussaq, Piotrowsi and Edgar (1970) experimentally determined temperatures of 1190°C at 1 bar and 900°C at 1 kbar water pressure, respectively. In their experiments, sodalite is the first phase on the liquidus. The water activity in the melt during sodalite crystallisation was low (Markl et al., 2001a) and fluid inclusions indicate that no aqueous fluid was present during the main period of sodalite formation. If an aqueous fluid phase were expelled from the melt at this stage, NaCl would strongly partition into it (Kilinc and Burnham, 1972) and, hence, become unavailable for sodalite crystallisation. The formation of

sodalites from a water-deficient melt is also supported by our fluid inclusion data, which do not show high-temperature aqueous inclusions. Therefore, the primary HC inclusions are interpreted to have formed at a temperature between 800 and 1000°C .

Several experiments performed at high temperatures and pressures showed that CH_4 fluids are typical for melts with low oxygen fugacities (e.g. Holloway and Jakobsson, 1986; Scott et al., 2004). Methane and higher hydrocarbons will form spontaneously at mantle P – T -conditions and oxygen fugacities close to the magnetite–wüstite buffer. During ascent to pressures below ~ 25 kbar, hydrocarbons other than methane become unstable relative to methane (Kenney et al., 2002). Consequently, the primary HC-bearing inclusions in the sodalites contain only methane.

Some HC-bearing inclusions containing only methane reflect trapping pressures of 3–4 kbar (Fig. 9). This is much deeper than the emplacement level of the intrusion at about 1 kbar. HC-bearing inclusions showing this feature are located exclusively in sodalite parts with aegirine needles. Hence, the aegirine-bearing parts of the sodalites crystallised at considerably higher P – T conditions than the aegirine-free parts, presumably in a deeper magma chamber or during the ascent of the magma, whereas the rims formed during or after the final emplacement. The position of the ν_1 vibration of methane in our Raman spectra also argues for entrapment at higher

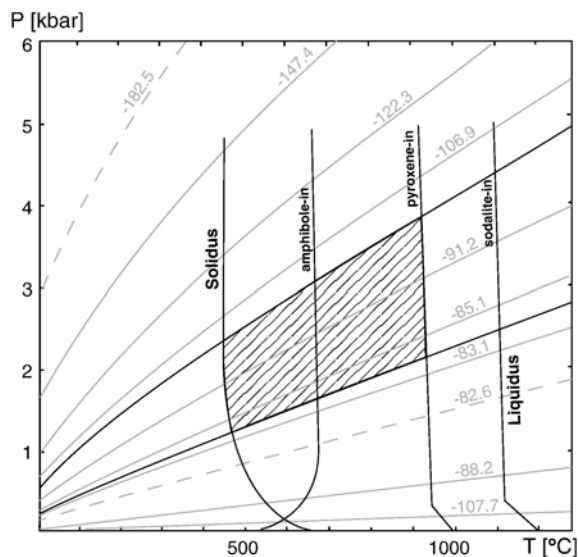


Fig. 9. P – T diagram with isotherms of homogenisation temperatures of pure methane inclusions (from van den Kerkhof, 1988) and experimentally determined phase relations of the naujaite (from Konnerup-Madsen and Rose-Hansen, 1982). The hatched box expresses the field of formation of the primary hydrocarbon-bearing fluid inclusions in P – T space.

pressures. At atmospheric pressure, this vibration is located at 2917 cm^{-1} ; higher pressures shift the frequency to lower values (Burke, 2001 and references therein). We observed values as low as 2908 cm^{-1} indicating pressures from 3 to 4 kbar, which is in excellent agreement with the entrapment pressure derived from the homogenisation temperatures. The enormous amount of sodalite present in the naujaite argues for crystallisation from a magma chamber much thicker than today's exposed vertical thickness of the intrusion, i.e. 1700 m (Sørensen, 2001; Sørensen et al., 2006). Our data provide evidence for sodalite crystallisation in a deep magma chamber and in an ascending magma.

In general, the solubilities of fluid phases such as H_2O , CO and CO_2 in melts are significantly lower at low $f\text{O}_2$ than under more oxidising conditions (Kadik et al., 2004). Methane in its molecular form is almost insoluble in melts. The equilibration of a CH_4 fluid with a silicate melt is associated with the formation of OH^- and to a lesser extent H_2O . Carbon is present as amorphous or atomic C, but may form Si–C bonds in the melt, which effectively depolymerise the silicate network (Taylor and Green, 1987; Kadik et al., 2004). Water is much more soluble in melts than hydrocarbons. The water activity in the first melt batch was very low (i.e. <0.2) but increased with further fractionation to values between 0.4 and 0.8 in the earlier rocks of the agpaite magma batch, i.e. pulaskite, foyaite, sodalite foyaite and naujaite (Markl et al., 2001a). During sodalite crystallisation, CH_4 was the dominant fluid phase whereas water remained dissolved in the melt. The water activity increased during fractionation of sodalite and reached the point where an aqueous fluid was expelled from the melt. This aqueous fluid and the still existing hydrocarbon fluid were trapped contemporaneously in the sodalites. Separate inclusion trails lead to the conclusion of their immiscibility. The exsolution of the aqueous fluid may have terminated the formation of sodalite because Cl would strongly partition into such a fluid (Kilinc and Burnham, 1972). Indeed, the salinities of the aqueous inclusions in the Ilímaussaq rocks are moderate to high (up to 60 wt.% NaCl equivalent, Konnerup-Madsen, 2003). Unfortunately, we have no information about the amount of fluid exsolved and we have, therefore, no direct evidence whether the fluid mass was sufficient to remove enough Cl from the melt to stop sodalite crystallization, but we believe our hypothesis to be a geologically realistic one.

The formation of the aqueous fluid inclusions may have been also related to the lujavrite formation, because the amount of aqueous inclusions increases with decreasing distance to lujavrite (Fig. 5, see the samples from drill

core II and VI). This model is not in contradiction to the findings of Marks et al. (2004b), who explained the very low δD values of amphiboles by the equilibration with a hydrous fluid that was generated by oxidation of a primary hydrocarbon-bearing fluid, because this equilibration happened at temperatures as low as 350°C .

The generation of the trapped hydrocarbons by late-to post-magmatic Fischer–Tropsch (FT) type reactions is unlikely for several reasons (see also Beeskov et al., 2006). Some of the inclusions are unequivocally identified to be of primary origin based on their textures (Fig. 4c), and they record entrapment pressures higher than the pressure corresponding to the final emplacement level. This means that these inclusions were enclosed well above temperatures and pressures favourable for a FT type reaction (Anderson, 1984). Although sulphur is known to poison the catalysts that are needed for the FT reaction (Madon and Taylor, 1981), we found abundant HC-bearing inclusions in those sodalites from the lower part of the stratigraphy that contain elevated amounts of S. Furthermore, we did not detect any CO_2 in the inclusions in sodalite, which would be a prerequisite for an FT-type reaction. Bulk analyses show that this species is only present as tiny traces (see Potter and Konnerup-Madsen, 2003).

Ryabchikov and Kogarko (2006) calculated the stable C–H–O fluid phase in agpaite rocks at $f\text{O}_2$ -conditions applicable to Ilímaussaq ($\Delta\text{FMQ}=-3$). Their results show that methane is in addition to H_2O the most dominant gas species over a broad range of temperatures in the system C–H–O. Furthermore, their calculated gas composition is in perfect agreement with the sodalite bulk analyses (Potter and Konnerup-Madsen, 2003).

The arguments presented above render the generation of the hydrocarbons by a FT-type reaction unlikely. Konnerup-Madsen (2001) calculated a $\delta^{13}\text{C}$ value of $-4.5 \pm 1.5\%$ PDB for bulk hydrocarbon gases from the Ilímaussaq rocks; this is in excellent agreement with mantle values (Kyser, 1986). The higher hydrocarbons we found in secondary inclusions may have been formed by polymerisation of primary methane. This would also explain the occurrence of H_2 in sodalite bulk analyses (Konnerup-Madsen et al., 1979). According to Des Marais et al. (1981), higher hydrocarbons generated in this way have lower $\delta^{13}\text{C}$ values than the methane, which has been demonstrated for the higher hydrocarbons in Ilímaussaq (Konnerup-Madsen, 2001).

7.2. Sodalite mineral chemistry and melt evolution

The stratigraphic variations of the sulphur content of the sodalite cores are interpreted to reflect Cl depletion

during fractionation of sodalite. Different Cl/S ratios in sodalite are hence interpreted to directly reflect different Cl/S ratios in the melt. The brightly luminescing rims reflect local variations in the Cl/S ratios in the residual melt pockets between the sodalite grains floating and solidifying at the roof of the magma chamber. As long as there is enough Cl available in the melt, the incorporation of sulphur in sodalite is minor. When the Cl content decreases with further fractionation, sulphur becomes an important substituent.

Although sphalerite is a common mineral in the naujaite, the Raman measurements indicate the sulphur to be present as $[\text{SO}_4]^{2-}$ in the sodalites. Incorporation of more reduced sulphur species is known only from Ca-bearing members of the sodalite group, i.e. haüyne and lazurite (Ostroumov et al., 2002; Di Muro et al., 2004). Obviously, the incorporation of sulphur in sodalite as S_2^- or S_3^- is related to the Ca component. Despite the low oxygen fugacity in the agpaite melt batch (Markl et al., 2001a; Marks and Markl, 2001), S is present as sulphate since sodalite from the naujaite is almost Ca-free. Additionally, the high alkali contents in the melt stabilise the coexistence of sulphate with sulphide at relatively low oxygen fugacities around the FMQ buffer (Baker and Rutherford, 1996). This effect is caused by the formation of Na_2SO_4 groups in the melt even at more reduced conditions (Tsujimura et al., 2004), although

the underlying mechanism of this observation are still unclear. Since the initial $f\text{O}_2$ of the agpaite magma is too low for this sulphate-stabilising effect of the high alkali content in the melt (i.e. $\Delta\text{FMQ} \sim -3$), the sulphur content in the sodalite cores from the upper naujaite is relatively low. In contrast, sodalite cores from the lower naujaite and the later formed sodalite rims with bright CL colours contains much more sulphur and hence is interpreted to have formed at higher $f\text{O}_2$ conditions. This increase in $f\text{O}_2$ with fractionation of the agpaite magma was also documented by Markl et al. (2001a).

Bailey et al. (2001) and Bailey (2006) introduced the idea of a two-stage formation history of the naujaite. Our data support this idea. The sulphur content and the bromine content of the sodalites exhibit changes in the lower part of the naujaite sequence. Bailey (2006) explained the geochemical differences in the naujaite by a layered magma chamber with an extended thickness of several kilometres. Our results are in agreement with this interpretation, but indicate formation of the two types of naujaite from slightly different melt compositions at depth, because the differences in the sodalite core composition are not related to different fluid inclusion populations. We found primary fluid inclusions recording a higher entrapment pressure in both naujaite parts but the composition of sodalites from the two parts is slightly different. It is not unreasonable to assume slightly

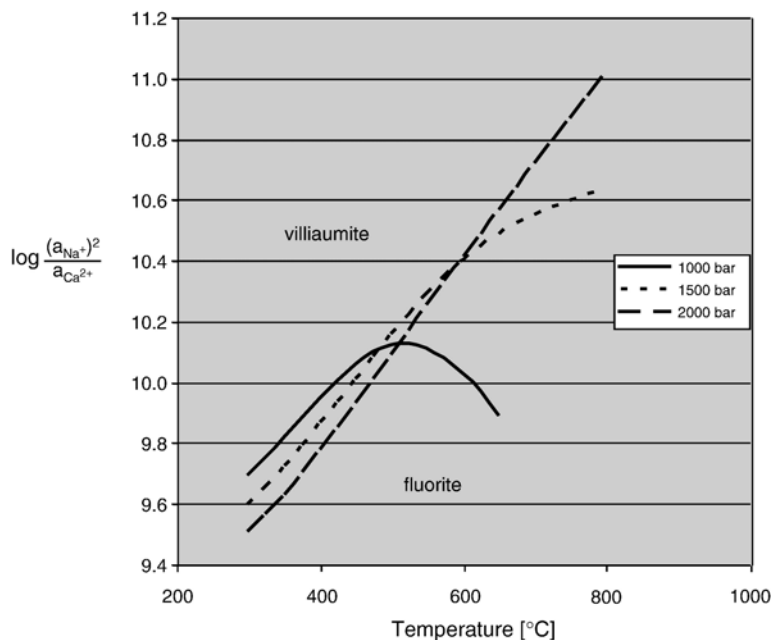


Fig. 10. Diagram of $\log((a_{\text{Na}^+})^2 / a_{\text{Ca}^{2+}})$ versus temperature at various pressures for the reaction $2 \text{NaF} + \text{Ca}^{2+} \rightarrow \text{CaF}_2 + 2 \text{Na}^+$ calculated with the HCh software (Shvarov and Bastrakov, 1999) and the UNITERM database. Thermodynamic data of fluorite and villiaumite are from Robie and Hemingway (1995) and that of Ca^{2+} and Na^+ from Shock et al. (1997).

different melt compositions in a slowly crystallising magma chamber of such a thickness.

Fluorine is enriched in the agpaite melt during prolonged fractionation and reached its maximum in the kakortokite stage. In the lujavrites, the F content is still high but somewhat lower than in the kakortokites. Due to the low Ca contents and the abundance of Na in the melt, villiaumite (NaF) appears in some parts of the naujaite. Nonetheless, fluorite was found in other parts of the sequence (Fig. 5). Both minerals were not observed together in the same sample. The occurrence of fluorite despite the very low Ca contents in the naujaite melt records the extreme F enrichment in the late melt stages. The variations in $\text{Na}^+/\text{Ca}^{2+}$ activity (Fig. 10) may be related to the influx of Ca-bearing fluids (Graser et al., in preparation) or to local phenomena dependent on variable crystallisation conditions. In contrast to Cl, Br and I, which are exhausted by the extensive formation of sodalite, the F content of the melt remains high or increases. This process finally leads to the formation of a late-stage villiaumite-rich lujavrite and abundant fluorite in some late-stage veins and hydrothermal alteration zones. Hence, the naujaite stage fractionates Cl, Br and I from F.

It is interesting to note, that the bottom cumulates (kakortokites), which crystallised after the solidification of the naujaite, contain high amounts of F (up to 2.1 wt.%; Bailey et al., 2001) mainly present as fluorite. Additionally, the contents of Ca and Mg in amphiboles and pyroxenes are significantly higher (Marks et al., 2004a) suggesting the kakortokite formation from a more primitive, replenished melt. Mixing of these two melts, the F-rich residual melt of the roof series (including the naujaite) and the later batch with higher Ca-contents (the kakortokite magma) would lead to the precipitation of abundant fluorite. This mixing probably took place at depth because there is a time gap between both stages. This idea is in agreement with the results of Sørensen et al. (2006) that the roof cumulates and the kakortokite–lujavrite series represent two different melt batches.

8. Summary

The naujaite, a sodalite flotation cumulate from the agpaite Ilimaussaq complex, offers a unique possibility to understand the evolution of the volatile phase during the crystallisation of a large peralkaline magma chamber. The sodalite composition and the fluid inclusion population yield information on the halogen budget of the melt and the composition of the coexisting fluid phase. Two types of fluid inclusions can be found in the

sodalite crystals from the naujaite, secondary aqueous inclusions and hydrocarbon-bearing inclusions of both primary and secondary origin. For their entrapment, we prefer a two-stage model in the development of the fluid phase due to the contrasting solubilities of water and hydrocarbons in the melt. From the beginning of sodalite crystallisation, a hydrocarbon fluid clearly was in equilibrium with the melt. The initial water activity was very low but increased with further fractionation. At this stage, sodalite began to crystallise at depths of 10–12 km trapping tiny aegirine needles and the primary hydrocarbon fluid. The NaCl activity in the melt decreased with further fractionation of sodalite from 0.4 to values well below 0.1 (Markl et al., 2001a), while the water activity increased and finally reached the point where an aqueous fluid was expelled from the melt. Because NaCl strongly partitions into the aqueous fluid, the copious formation of sodalite ended with the exsolution of this fluid. Therefore, the aqueous fluid was trapped only as secondary inclusions in sodalite. According to Konnerup-Madsen (2001), the two coexisting fluids are immiscible, and we confirm that in most cases they appear as separate fluid inclusions in the sodalites. Due to the exhaustion of Cl in the melt by the sodalite crystallisation itself and possibly by the exsolution of a NaCl-rich aqueous fluid, sodalite occurs only in smaller quantities in the later formed kakortokites and lujavrites. The high-salinity aqueous fluid trapped in secondary trails in the sodalites seems to be related to the lujavrite because the amount of aqueous inclusions decreases with increasing distance of the sample from the lujavrite. We are therefore convinced that hydrocarbons were the stable fluid phase during crystallisation of all Ilimaussaq rocks, while water-rich fluids may have occurred additionally in the lujavrite and later hydrothermal and pegmatitic stage only.

The sodalite composition reflects the changes in the melt composition during ascent and sodalite fractionation. Except for fluorine, the halogens are effectively scavenged from the melt by the crystallising sodalite. The remaining melt enriched in F was mixed with a following magma batch containing higher amounts of Ca, which resulted in the precipitation of fluorite and the exhaustion of Ca. Later on, the F content of the melt built up again leading to the formation of villiaumite in the latest-formed lujavrites.

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