The Magmatic and Fluid Evolution of the Motzfeldt Intrusion in South Greenland: Insights into the Formation of Agpaitic and Miaskitic Rocks

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The 1.273 Ga Motzfeldt intrusive complex in the Gardar failed-rift Province in South Greenland formed from six successively intruding melt batches (SM1–SM6) interpreted to be derived from a common magma source at depth. Five units (SM1–SM5) crystallized an alkaline to peralkaline, miaskitic mineral assemblage of amphibole, clinopyroxene, feldspar, nepheline, Fe–Ti oxides, zircon, apatite, fluorite and rarely olivine. The last magmatic batch (SM6) is characterized by an agpaitic mineral assemblage of aegirine, nepheline, alkali-feldspar, eudialyte and rare fluorite or sodalite. Coexisting mafic minerals constrain the crystallization conditions of the miaskitic rocks to about 850–600 °C, whereas solidus temperatures below 500 °C are indicated by coexisting alkali feldspars in the agpaitic rocks. Oxygen fugacities during the orthomagmatic stage are below the FMQ (fayalite–magnetite–quartz) buffer (ΔFMQ ≈ 0–5 to –2–0) whereas late hema- toite provides evidence of a higher relative oxygen fugacity during late-stage alteration. The Nd and oxygen isotope compositions of amphiboles and pyroxenes are homogeneous throughout the complex and suggest a common, mantle-derived magma source for all six units which is comparable with other Gardar intrusions. The hydrogen isotopic composition of amphiboles (δD = 99 to –132‰) indicates low-temperature fluid–rock interaction with low fluid–rock ratios. Fluid inclusion studies indicate that H2O–NaCl fluids present during the magmatic stages in the miaskitic rocks had salinities of <10 wt % NaCl eq. Calcite crystals in fluid inclusions within these rocks suggest that CO2 or HCO3 was an important component of the original fluid phase. In contrast, the agpaitic unit is characterized by a CH4–H2O–NaCl fluid. The C–O–H isotopic compositions of the fluid inclusions in all units are consistent with mixing between a small volume of magmatic fluid and a large volume of meteoric water. The chemical evolution of the Motzfeldt complex is a type example of the connection of the transition from miaskitic to agpaitic mineral assemblages with redox-dependent fluid–solid equilibria. The transition from a relatively oxidized to a relatively reduced fluid is correlated with a change from a more reduced, Fe3+-bearing miaskite (taramite–arfvedsonite, zircon, SM1–SM5) to a more oxidized, Fe2+-bearing agpaitic assemblage (aegirine, eudialyte, SM6). We suggest that coupled fluid–solid redox equilibria involving Fe3+, Fe2+, CO2 and CH4 in this case were simply driven by temperature decrease and an overall increase in Na (± K) in the melt. This observation sheds light on the heavily debated miaskite–agpaitic transition. The combined temperature and compositional effect stabilized Fe3+, CH4 and enhanced the solubility of Zr (possibly as Na–Zr–Si–O complexes) in the latest stage melt (SM6) resulting in the crystallization of an agpaitic mineral assemblage. In terms of redox conditions during crystallization, the Motzfeldt rocks represent an intermediate case in the Gardar Province between more oxidized, CO2-dominat ed intrusions such as the syenite–carbonatite complex of Grønndal-Ika and CH4-dominated complexes such as the peralkaline granitic Puklen and the agpaitic Ilmaussaq complex.

KEY WORDS: agpaitic; methane; miaskite; nepheline syenite; redox reactions

INTRODUCTION

Agpaitic rocks are peralkaline nepheline syenites that are characterized by the occurrence of complex Na–Zr silicates such as eudialyte instead of the more common...
zircon and Fe–Ti oxides in miaskitic rocks (Sørensen, 1997). They represent some of the most highly differentiated magmatic rocks worldwide, sometimes exhibiting enrichments of high field strength elements (HFSE) such as Nb, Ta, U, Th, REE or Zr up to economic values (Sørensen, 1997). They occur as large intrusions (Ilúmaussaq: Larsen & Sørensen, 1987; Markl et al., 2001; Khibina and Lovozero: Kramm & Kogarko, 1994; Zaitsev et al., 1998), as smaller parts of intrusions (Motzfeldt and Qorøq: Jones, 1980, 1984; Coulson, 1997; Mont St. Hilaire: Horvath & Gauld, 1990; Tamazeght: Bouabdli et al., 1988; Marks et al., 2008) or as late-magmatic pegmatites (Crazy Mountains: Chakhmouradian & Mitchell, 2002; Oslo Rift: Brogger, 1890, Fitou: Vitrac-Michard et al., 1977; Gardiner Complex: Nielsen, 1994).

The petrogenesis of agpaitic rocks is not yet fully understood; however, they clearly originate from extensively differentiated, alkaline, mantle-derived mafic magmas (alkali basalts, nephelinites or benmoreites: Kramm & Kogarko, 1994; Sørensen, 1997). They show particularly long crystallization intervals down to temperatures <150 °C (Piotrowski & Edgar, 1970; Sood & Edgar, 1970; Kogarko, 1977, 1987; Kogarko et al., 1977; Larsen & Sørensen, 1987; Wolf, 1987) and can exhibit unusual melt immiscibility phenomena (Markl, 2001; 2002). The physico-chemical processes responsible for the formation of agpaitic mineral assemblages are not quantitatively understood and remain controversial. Markl et al. (2001) suggested and Krumrei et al. (2007) provided evidence for the existence of a very reduced, methanrich fluid phase at high, orthomagmatic temperatures. Both the high alkali content of the rocks and the low water activity (methane-forming reaction consumes water: \( \text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_4 + 2\text{O}_2 \)) would effectively prevent unmixing of a NaCl-rich hydrous fluid phase. Accordingly, Kogarko (1974), Kogarko & Romanchev (1983), Wallace et al. (1990) and Sørensen (1997) argued that HFSE and volatile elements are kept in the melt, which then gradually evolves towards silica-rich sodic aqueous solutions. Therefore, the melt would become highly enriched in alkalis and halogens compared with the differentiation products of similar parental magma compositions that exsolve a fluid phase at an earlier stage. This could be a prerequisite for the enrichment of HFSE complexes by halogens and for the formation of Na–HFSE–(halogen) minerals such as eudialyte.

Reduced conditions seem to be important for the evolution of strongly peralkaline and especially agpaitic rocks as evidenced by the studies of Konnerup-Madsen & Rose-Hansen (1982, 1984), Markl et al. (2001), Ryabchikov & Kogarko (2006), and Krumrei et al. (2007). In particular, the evolution and influence of a CH\(_4\)-bearing fluid phase seems to be of major significance (e.g. Markl et al., 2001; Nivin et al., 2001, 2002, 2005; Potter et al., 2004; Beeskow et al., 2006; Ryabchikov & Kogarko, 2006; Salvi & Williams-Jones, 2006; Krumrei et al., 2007). Several hypotheses for methane formation in peralkaline intrusive rocks have been suggested: (1) primary magmatic methane (e.g. Markl et al., 2001; Krumrei et al., 2007); (2) late-magmatic reduction of a CO\(_2\)-H\(_2\)O-rich primary fluid as a result of closed-system cooling (e.g. Peterslie & Sørensen, 1970; Konnerup-Madsen & Rose Hansen, 1982; Konnerup-Madsen, 2001; Ryabchikov & Kogarko, 2006); (3) late- to post-magmatic Fischer-Tropsch-type reactions (Salvi & Williams-Jones, 1997; Potter & Konnerup-Madsen, 2003; Potter et al., 2004).

In all these scenarios, the redox reaction
\[
\text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_4 + 2\text{O}_2
\]
plays a key role. Investigations of the redox conditions during the crystallization of peralkaline magmas are clearly crucial for understanding the details of the processes mentioned above.

In this respect, it is particularly useful to study the Motzfeldt intrusion in the Gardar Province of South Greenland, as its petrology is well known from the work of Jones (1980, 1984) and Jones & Larsen (1985) and it shows a transition from miaskitic to agpaitic rocks. We will show that the formation of agpaitic rocks in the Motzfeldt complex is a strong function of redox conditions.

### Regional Geology

The Gardar Province is a failed rift within which magmatic activity lasted from c. 1350 to 1120 Ma (Upton et al., 2003). It is characterized by 12 major intrusions (Fig. 1), which comprise carbonatites, gabbros, granites and nepheline syenites. Several intrusions including Ilúmaussaq, Motzfeldt and Qorøq contain agpaitic nepheline syenites with eudialyte and other complex Na–Zr–Ti silicates instead of miaskitic zircon and Fe–Ti oxides. Numerous dyke swarms presumably served as feeders for extensive regional volcanism evidenced by the basalts of the Eriksfjord Formation (Escher & Watt, 1970; Upton et al., 2003) which also includes quartzitic sandstones.

The 1.275 Ga Motzfeldt intrusion (Upton et al., 2003) forms part of the large Igaliko complex, which also includes the Qorøq and Igdlérfigsállik intrusions (Emeles & Harry, 1970, Fig. 1). It intruded the Julianeháb batholith of the 1.3 Ga Kétlidlian orogen (Garde et al., 2002) at a depth of c. 4–6 km (Jones, 1980). The Motzfeldt intrusion mainly comprises nepheline syenites in which a number of several hundred metre long rafts of Eriksfjord basalts are embedded (Fig. 1). The intrusion was first mapped by Emeles & Harry (1970), Jones (1980) provided a detailed petrological investigation of the intrusive units SM1–SM6, which he defined based on cross-cutting relationships in the field (Fig. 1). The whole-rock geochemistry and mineralogy of the main rock-forming minerals were studied in detail by Jones (1980, 1984), Jones & Peckett (1980), Jones & Larsen (1985), and Bradshaw (1988). The complex atored economic interest during the Syduran...
When considerable amounts of Nb were discovered, especially in the NE part of the intrusion in unit SM1. In this paper we use the SM1–SM6 nomenclature of Emeleus & Harry (1970) and Jones (1980) instead of the more complex one proposed by Tukiainen et al. (1984) as this is better suited for addressing the transition from micasitic to agpaitic rocks. Furthermore, it is easier to compare our data with the earlier data of Jones (1980, 1984), Jones & Peckett (1980) and Jones & Larsen (1985).
PETROGRAPHY

Samples from units SM1, SM2, SM4, SM5 and SM6 (Table 1) were studied. In general, these rocks are miaskitic to agpaitic (± nepheline) syenites, interpreted to have originated from different magma batches (Jones, 1980). Detailed petrographic descriptions have been given by Jones (1980, 1984) and we summarize here only the most important information necessary to support our line of argument.

Miaskitic units SM1–SM5

The miaskitic units SM1, SM2, SM4 and SM5 are very uniform in terms of their mineral assemblages, but they vary in modal composition and grain size. Rock-forming minerals are amphibole, clinopyroxene, feldspar, nepheline, Fe–Ti oxides and accessory zircon, apatite, aenigmatite and pyrochlore (Jones, 1984).

Unit SM1 consists of <1 cm size grains, nepheline is absent and pyroxene is rare in the investigated samples. However, Jones (1980) described nepheline- and/or pyroxene-bearing varieties. Some samples contain primary magmatic fluorite (JS190, JS195, JS197; Schönenberger et al., 2008). SM2 (only one sample, 326012, provided by H. Emeleus) consists of large, turbid feldspar laths (Fig. 2a) with interstitial brownish amphibole. The samples from unit SM4 (JS36, JS97, JS171, JS172) are relatively fine-grained (grain size <0.5 cm). Amphibole is occasionally poikilitic (Fig. 2d). Rinkite occurs intergrown with Fe–Ti oxides (Fig. 2c). The minerals in SM5 (Table 1) are much coarser (<2 cm) than in the other units. Feldspar characteristic forms laths several centimetres long. Occasionally, colourless to slightly green clinopyroxene occurs as cores within brown amphibole (Fig. 2h). Rare sodalite forms interstitial grains.

Alteration phenomena include the common turbidity of feldspars and replacement of amphibole by green pyroxene especially in units SM1, SM2 and SM5. SM1 is the most altered unit. Secondary minerals such as biotite, fluorite, quartz, titanite, and hematite are common. Calcite and cancrinite occur mainly as alteration products of nepheline, but also of feldspars in all units. Furthermore, calcite was observed in thin veinlets cutting all other rock types. Secondary veins consist of fluorite and/or quartz (SM1), fluorite ± calcite, ± aegirine (SM4) and fluorite ± feldspar (SM5). The unusual occurrence of quartz may be attributed to the assimilation of rafts of the Eriksfjord formation, which contain large amounts of quartzitic sandstone.

Agpaitic unit SM6

The samples of unit SM6 (Table 1) are dominated by green, euhedral to hypidiomorphic clinopyroxene, large euhedral nepheline and feldspar laths together with interstitial nepheline, eudialyte and minor amounts of fluorite and sodalite (Fig. 3). Amphibole is rare (Jones, 1980, 1984) and does not occur at all in the studied samples. The nepheline syenitic rocks of unit SM6 are called ‘lujavrites’.

Table 1: Investigated samples indicating the type of analyses performed

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M, microprobe; sep, O, H and Sm/Nd isotopes from mineral separates; fl, fluid inclusion analysis; flis, fluid isotopes; IC, ion chromatography; CC, carbonate isotopes.
based on their textural similarity to rocks from the Kola peninsula, Russia, and the Ilímaussaq intrusion in the Gardar Province. Magmatic modal layering is common and three distinct varieties of rocks can be defined: white (feldspar-dominated), green (pyroxene- and nepheline-dominated) and black (pyroxene-dominated) lujavrite (see Jones, 1980, 1984). The eudialyte in these rocks is especially heavily altered to complex REE-bearing phases.

![Textures observed in the miaskitic units](https://academic.oup.com/petrology/article-abstract/49/9/1549/1497494/1553)

**Fig. 2.** Textures observed in the miaskitic units [back-scattered electron (BSE) images]. (a) Heterogeneously exsolved alkali feldspars in SM2 (32602). (b) Amphibole in unit SM1. It is altered to secondary amphibole with magnetite intergrowths. (c) Ilmenite and magnetite of SM1 [JS96] interpreted to have crystallized simultaneously. (d) Amphibole of SM4 [JS97] with inclusions of pyroxene and magnetite. (e) Magnetite and rinkite intergrown in unit SM4 [JS72]. (f) Finely exsolved magnetite of SM4 [JS71]. (g) Typical amphibole–feldspar association in SM4 [JS56]. (h) Complex pyroxene–amphibole texture from SM5 [JS108] where a core of primary pyroxene is rimmed by secondary amphibole.
Alteration products are cancrinite, zircon, calcite, pectolite and trace element (REE)-rich minerals such as catapleiite, zirfesite, pyrochlore and others (Jones, 1980; Jones & Larsen, 1985). Comparable alteration phenomena were investigated in detail in the nearby Qoroq intrusion (Coulson, 1997).

**ANALYTICAL METHODS**

All analyses were carried out at the Institut für Geowissenschaften, Universität Tübingen, Germany. A JEOL 8900 electron microprobe was used for analysing minerals for their major element contents. The beam current was 15 nA and acceleration voltage 15 kV. Counting time on the peak positions ranged between 16 s for major elements and 60 s for minor elements, and background counting times were half the peak time. A focused electron beam was used; however, Fe–Ti oxides, feldspar and nepheline were analyzed with a defocused beam (up to 20 μm beam diameter) to avoid alkali migration and/or to obtain average compositions. The overlap of F Kα and Fe Lβ peaks was corrected and an internal φpZ correction (Armstrong, 1991) was applied. Analytical uncertainties are below 1% (relative) for major elements, and up to around 5% (relative) for minor elements.

Details of the oxygen isotope analysis techniques for e. 10 mg handpicked pyroxene and amphibole mineral...
separates have been given by Marks et al. (2003), who followed the methods of Sharp (1990) and Rumble & Hoering (1994). The determination of the hydrogen isotopic composition of c. 50 mg amphibole mineral separates was performed according to the method of Vennemann & O’Neil (1993). Oxygen and hydrogen isotopic compositions were analyzed on a Finnigan MAT 252 mass spectrometer. The analytical precision of the oxygen isotope analyses of the standards (NBS-28 quartz; Valley et al., 1995) is ±0.1‰ and the precision of the in-house kaolinite standard for hydrogen isotopic analyses is ±2‰. All stable isotope analyses in this study are reported in permil (‰) in standard notation relative to VSMOW (oxygen and hydrogen) and VPDB (carbon).

Detailed description of the analyses of the Nd isotopic compositions of ~10 mg of hand-picked mineral separates have been given by Marks et al. (2003). After spiking with a 150Nd/144Nd Sm tracer, the samples were dissolved in HF at 180°C in poly-tetrafluoro-ethylene (PTFE) reaction bombs. Sm and Nd were separated in quartz columns using 1.7 ml Teflon powder coated with HDEHP (di-ethyl hexyl phosphate) for cation exchange. A Finnigan MAT 262 thermal ionization mass spectrometer was used. Analyses of the LaJolla standard yielded a 143Nd/144Nd ratio of 0.511824 ± 10 (±2σ error, n = 13). The blank of the total procedure (chemistry and loading) was <100 pg for Nd. The decay constant of Lagmair & Marti (1978) was used for 137Sm (6.54 × 10^{-12} a^{-1}). Present-day CHUR values of 0.9767 (45Sm/144Nd; Jacobson & Wasserburg, 1980) and 0.512638 (143Nd/144Nd; Goldstein et al., 1984) were applied to calculate εNd(t) values. Initial Nd isotope ratios were corrected for an age of 1.275 Ga (Upton et al., 2003; J. McCreat, unpublished data). The uncertainty in εNd(t) ratios is <0.5 based on analytical errors.

For fluid inclusion investigations, doubly polished, 100–300 µm thick wafers of nepheline, fluorite, feldspar and quartz were analyzed using a Leica DMLP microscope and a Linkam THMS 600 heating–cooling stage for fluid petrography and microthermometry. The heating–cooling stage was calibrated using synthetic CO₂ and H₂O standards. The accuracy of melting and homogenization temperatures is ±0.2 and ±2.0°C, respectively. Raman spectroscopy was performed using a Dilor Jobin Yvon Raman spectroscope. Fluid inclusions and the mineral matrix were analyzed using a blue argon laser (488 nm) for a wave number range between 600 and 4500 cm⁻¹. Counting times varied between 10 and 60 s.

The bulk chemistry of the fluid inclusions was determined using a Dionex ICS1000 ion chromatography system with a CS-12A cation column and an AS9-HC anion column. All samples were treated with concentrated (65%) HNO₃ at 60–70°C in a sand bath for 4 h and washed with triple deionized water for 7 days to prevent any contamination from the HNO₃ washing procedure. After having ground 2 g of each sample in an agate mortar, the salts were dissolved in 10 ml triple deionized water. For anions, 5 ml were injected. To the remaining 5 ml, 10 µl of 33% HNO₃ were added to ensure a pH value between 2 and 3 required for the cation column. The run time of the samples was 30 min. Analytical errors are in the range of 20% relative (Kohler et al., 2008).

Fluid inclusions in fluorite samples were analyzed for their C, H and O isotopic composition using the low-temperature crushing method described by Friedman (1953), Craig (1961) and Vennemann & O’Neil (1993). The samples were carefully hand-picked, dried and mechanically crushed. Fluorite, which was found to be finely intergrown with carbonate, was treated with concentrated HNO₃ prior to analysis to preclude any contamination effect on the fluid inclusion content. δD, δ18O and δ13C values of hydrocarbons, CO₂ and H₂O were measured on a Finnigan MAT-252 mass spectrometer. The analytical error is 0.3‰ for oxygen and carbon and better than 6‰ for hydrogen.

To analyze the isotopic composition of the calcite crystals trapped in fluid inclusions, one fluorite sample (JS809) was thoroughly washed with concentrated HCl to remove possible carbonate intergrowths. This sample was heated to 1000°C in the same analytical set-up as that used for the isotope analyses of the fluid inclusions to thermally decompose the calcite daughter crystals (e.g. Hollemann & Wiberg, 1995). The thermal decomposition of calcite proceeds according to the reaction CaCO₃ → CaO (solid) + CO₂ (gas, measured; Hollemann & Wiberg, 1995). Significant fractionation of oxygen isotopes can be ruled out at the high temperatures used (c. 1000°C; e.g. Zheng, 1999).

The oxygen and carbon isotopic composition of carbonates were analyzed according to the method described by Spolt & Vennemann (2003), using a ThermoFinnigan GasBench connected directly to a Finnigan MAT 252 mass spectrometer. Orthophosphoric acid (100%) was added to <500 mg of carbonate powder or several grams of whole-rock powder to release the CO₂ from the sample. To remove water vapour and interfering gases, the CO₂ vapour was led via a He stream and a gas chromatograph column. Subsequently the CO₂ was passed into the mass spectrometer. The standard analytical errors are 0.1‰ for δ18O and δ13C. As petrographic investigations showed that apart from carbonates, cancrinite may also be present in the samples, test measurements were performed to extract the CO₂ only from calcite and not from cancrinite. These measurements yielded excellent values for a reaction time of 85 min where >98 vol.% of calcite reacted whereas only minor amounts of CO₂ from cancrinite were detected (<2 vol.%).

RESULTS

Mineral chemistry

Electron microprobe analyses were carried out on minerals of units SM1, SM2, SM4, SM5 and SM6. Only a brief summary of the data is given here, as Jones (1980, 1984) has
already characterized the mineral chemistry of the intrusive phases in detail.

**Amphibole**

The composition of the amphiboles from units SM1–SM5 (Table 2) is mainly characterized by the exchange CaAl ↔ NaSi and ranges from Ca-dominated via Na–Ca to Na-dominated compositions including taraminite, katophorite, ferro-nyboite and arvedsonite (Leake, 1997). Fe\(^{3+}\) is mostly below 1 \(\text{a.p.f.u.}\). The fluorine content is around 1 wt % (SM1, SM2, SM4) but is up to 3·5 wt % (= 1·7 \(\text{a.p.f.u.}\)) in unit SM1. Amphiboles from SM5 exhibit larger variations obeying the Fe–Fe avoidance rule (e.g. Marks et al., 2003; Schonenberger et al., 2006).

**Clinopyroxene**

The composition of the pyroxenes varies from diopside/hedenbergite-dominated pyroxenes via aegirine–augite to almost pure aegirine-endmember pyroxenes (Table 3, Fig. 4). The diopside/hedenbergite-rich pyroxenes mainly occur in SM4 and SM5 as cores that are overgrown by aegirine–augite. Jones (1980) also described such pyroxenes from units SM1 and SM2 (Fig. 4). Unit SM6 only crystallized almost pure aegirine. The jadeite content increases with increasing NaFe\(^{3+}\) content, but does not exceed 8 mol %. Zr\(O_2\) is up to 1·2 wt % in our samples, but has been reported to attain 6·96 wt % (Jones, 1980; Jones & Peckett, 1980).

**Fe–Ti oxides**

The Fe–Ti oxides from units SM1, SM4, SM5 and SM6 (Table 4) are titanomagnetites that are commonly heterogeneous exsolved to magnetite with lamellae of the hematite–ilmenite–pyrophanite solid solution series. In unit SM1, Ti, textures suggest that ilmenite (\(\text{Hm}_{77–85}\text{Hm}_{3–7}\text{Py}_{90–10}\)) and titanomagnetite (\(\text{Mt}_{65–74}\text{Us}_{44–36}\)) crystallized as (primarily) separate grains (Fig. 2). Finely exsolved titanomagnetite from SM4 (Fig. 2) shows reintegrated average compositions of \(\text{Mt}_{60–78}\text{Us}_{30–22}\). Reintegrated titanomagnetites from SM5 usually show compositions of \(\text{Mt}_{50–60}\text{Us}_{30–44}\) and a few compositions reach extreme values of \(\text{Mt}_{37}\text{Us}_{6}\). Magnetites occurring as alteration products of amphibole (e.g. sample JS180, SM5; but also in other samples from SM1 and SM4) commonly have a composition of \(\text{Mt}_{50–60}\text{Us}_{30–40}\). In SM6, no primary Fe–Ti oxide phase is present but almost pure hematite (\(\text{Hm}_{94–99}\text{Ilm}_{0–5}\text{Py}_{0–2}\)) occurs as an alteration product of aegirine.

**Feldspars**

Feldspars commonly exhibit coarse perthitic exsolution textures (Fig. 2, SM1–SM5). The composition of the reintegrated feldspar grains is: SM1 \(\text{Ab}_{32–75}\text{Or}_{27–54}\); SM2 \(\text{Ab}_{47–65}\text{Or}_{45–58}\); SM4 and SM5 \(\text{Ab}_{37–52}\text{Or}_{50–65}\). This corresponds to an increase in the Or component from SM1 to SM5. The anorthite content of the feldspars is always <\(\text{An}_1\). In SM6 two separate feldspars of almost end-member composition \(\text{Ab}_{60–70}\text{Or}_{30–40}\) and \(\text{Ab}_{30–50}\text{Or}_{50–60}\) crystallized, as noted by Jones (1980) and Jones & Larsen (1985).

**Nepheline**

Because of the strong alteration of nepheline within our samples from units SM1 and SM2, nepheline was analyzed in units SM4–SM6 only. Its composition ranges from \(\text{Na}_{74}\text{K}_{20}\text{Q}_{26}–\text{Na}_{76}\text{K}_{23}\text{Q}_{21}\) (Fig. 5). Jones (1980) and Jones & Larsen (1985) reported nepheline from other units with similar compositions.

**Isotopic composition of mineral separates**

The isotopic composition (O, H, Nd, Table 5) of amphibole was determined from SM1 (JS193, JS196), SM2 (32602), SM4 (JS171, JS172) and SM5 (JS108, JS181), and of pyroxenes from SM6 (JS70, JS114, JS159).

The \(\delta^{18}O\) values range from +4·2 to +5·3\(^{\circ}\%\) (VSMOW, Fig. 6). Samples from SM1 have the lowest values (+4·2 and +4·6\(^{\circ}\%\)). The \(\delta^D\) of amphibole varies between −98 and −132\(^{\circ}\%\) (VSMOW) with SM1 and SM2 having the lowest values of −120–180 (SM1), −127–6\(^{\circ}\%\) (SM1) and −132–3\(^{\circ}\%\) (SM2), respectively.

Initial \(t_{\text{Nd}}(t)\) values (\(t=1275\) Ga; Upton et al., 2003; J. McCread, personal communication, 2007) for the mineral separates range from +0·1 to +2·4. SM1 and SM2 have the lowest values whereas SM4 and SM5 have values similar to those for SM6 (+0·9 to +2·4, Fig. 6).

Carbon and oxygen isotope compositions of carbonates were analyzed for three whole-rocks from units SM5 and SM6 (JS159, JS164, JS181, Table 6) that contain finely disseminated calcite occurring as alteration products and/or in very small veinlets. \(\delta^{13}C\) values range from −2·4 to −3·2\(^{\circ}\%\) (VPDB). The oxygen isotopic compositions of these samples varies from +21·9 to +24·2\(^{\circ}\%\) (\(\delta^{18}O\), VSMOW).

Additionally, calcite from one calcite vein within SM4 (JS67, Table 6) yielded a \(\delta^{13}C\) value of −4·4\(^{\circ}\%\) (VPDB) and a \(\delta^{18}O\) value of +7·8\(^{\circ}\%\) (VSMOW). Calcite crystals from fluid inclusions analyzed in one sample (JS109, Table 6) have \(\delta^{13}C\) and \(\delta^{18}O\) values of −39\(^{\circ}\%\) and +81\(^{\circ}\%\), respectively.

**Fluid inclusion investigations**

**Petrography and microthermometry**

Fluid inclusions were analyzed from magmatic fluorites of SM1 (JS190, JS197) and SM6 (JS88, JS122; Schonenberger et al., 2008) and magmatic nepheline and feldspar of SM4 and SM5 (JS171, JS172, JS104, JS108, JS180, Fig. 8).

Hydrothermal fluorites were studied from units SM1, SM4 and SM5 (Table 1) and secondary hydrothermal quartz in unit SM1 (JS180, JS277). Four types of fluid inclusions can be distinguished: (1a) saline–aqueous two-phase (liquid–vapour; \(l\)–\(v\) ) inclusions; (1b) saline–aqueous three-phase inclusions (liquid–vapour–solid; \(l\)–\(v\)–\(s\)); (2) pure \(CO_2\) two-phase (liquid–vapour; \(l\)–\(v\) ) inclusions (only in sample JS34); (3) aqueous-\(CH_4\) one- or two-phase
inclusions. The last fluid inclusion type is unique to the agpaitic unit SM6 whereas the first three types [(1a), (1b) and (2)] occur only in the miaskitic units SM1–SM5. Inclusions of type (1) also contain trace amounts of CO₂.

Saline–aqueous two-phase inclusions

In primary magmatic fluorite of SM1 (Fig. 8a), they mainly occur along (pseudo)secondary trails, have an irregular to rounded shape and reach sizes up to 40 μm. They have salinities of <3.5 wt % NaCl eq. and filling ratios of 0.85–0.95. The fluid inclusions in magmatic nepheline (units SM4 and SM5) are rectangular and generally <20 μm in size. They show negative crystal shapes and occur as isolated inclusions or in groups but also in pseudo-secondary trails and have filling ratios between 0.80 and 0.95. The isolated fluid inclusions are interpreted to be of primary origin (Shepherd et al., 1985). Fluid inclusions from primary magmatic minerals from SM4 (JS71, JS72) typically have salinities <2–5 wt % NaCl eq., but some reach 6–7 wt % NaCl eq. In nephelines from samples of SM5 (JS104, JS108, JS180), most fluid inclusions (80%) vary in salinity between 4 and 6 wt % NaCl eq. Hydrothermally formed (secondary) fluorites of units SM1, SM4 and SM5 mainly contain trails of secondary fluid inclusions and only a few isolated ones. They are commonly of irregular shape, but also rounded to angular (Fig. 8b). The size of fluid inclusions varies from <5 μm to 100 μm (Fig. 8). Necking-down was occasionally observed but these fluid inclusions were not further analyzed.

<table>
<thead>
<tr>
<th>Unit</th>
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<th>SM2</th>
<th>SM4</th>
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Table 2: Representative microprobe analyses of Motzfeldt amphiboles

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<th>TiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>ZrO₂</th>
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<td>0.35</td>
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<td>0.12</td>
<td>0.12</td>
<td>0.30</td>
<td>0.03</td>
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<tr>
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<td>0.12</td>
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<td>SM5</td>
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<td>99.49</td>
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Formula based on 16 cations and 23 anions

Si: 6.90
Al: 1.03
Ti: 0.21
Fe³⁺: 0.05
Mg: 0.99
Fe: 3.12
Mn: 0.14
Ca: 1.16
Na: 1.56
K: 0.31
Zr: 0.02
Cl: 0.00
F: 0.49
Sum: 16.00
For comparison, dotted curve 1 is general trend of clinopyroxene evolution in the diopside–hedenbergite–aegirine triangle [data from this study and Jones (1980)]. Fig. 4. Evolution of pyroxene composition in the diopside–hedenbergite–aegirine triangle [data from this study and Jones (1980)]. For comparison, dotted curve 1 is general trend of clinopyroxene evolution in the diopside–hedenbergite–aegirine triangle [data from this study and Jones (1980)].

Filling ratios commonly range from 0.80 to 0.95, but are fairly constant within single trails.

Fluid inclusions in hydrothermal fluorite samples of SM1 are typically characterized by a salinity of <5 wt % NaCl eq. Sample JS16 has two types of fluid inclusion, one with high salinity (>15 wt % NaCl eq. and another with <10 wt % NaCl eq. Quartz sample JS10 is dominated by secondary fluid inclusions with salinities varying from 6 to 9 wt % NaCl eq. Fluid inclusions in quartz from JS277 were either too small for microthermometry or showed metastable melting. Therefore, a mean salinity of 8.6 wt % NaCl eq. was used for calculating the ion content (see crush–leach results below). In fluorite samples from SM4, fluid inclusions with low salinities <3 wt % NaCl eq. predominate. Higher salinity fluid inclusions (up to 23 wt % NaCl eq.) commonly show brownish ice colours. Hydrothermally formed fluorites from SM5 (JS110, JS175, JS109) show two types of salinities: <5 wt % NaCl eq. and in the range of 7–11 wt % NaCl eq.

Eutectic melting temperatures (T_{euc}) generally range from ~40 to ~28°C. The low T_{euc} around ~40°C and the

**Table 3: Representative microprobe analyses of Motzfeldt clinopyroxenes**

<table>
<thead>
<tr>
<th>JS:</th>
<th>1</th>
<th>326012</th>
<th>97</th>
<th>171</th>
<th>171</th>
<th>172</th>
<th>108</th>
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<th>180</th>
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<tbody>
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<td>SM4</td>
<td>SM4</td>
<td>SM4</td>
<td>SM5</td>
<td>SM5</td>
<td>SM5</td>
<td>SM5</td>
<td>SM6</td>
</tr>
<tr>
<td>SiO₂ (wt %)</td>
<td>52.77</td>
<td>49.01</td>
<td>49.41</td>
<td>49.50</td>
<td>50.90</td>
<td>48.69</td>
<td>50.06</td>
<td>50.75</td>
<td>52.98</td>
<td>52.10</td>
<td>51.80</td>
</tr>
<tr>
<td>TiO₂ (wt %)</td>
<td>2.69</td>
<td>0.30</td>
<td>0.75</td>
<td>0.23</td>
<td>0.22</td>
<td>0.32</td>
<td>0.38</td>
<td>0.56</td>
<td>1.29</td>
<td>0.35</td>
<td>0.37</td>
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<tr>
<td>Al₂O₃ (wt %)</td>
<td>0.80</td>
<td>0.87</td>
<td>2.06</td>
<td>0.86</td>
<td>0.90</td>
<td>0.86</td>
<td>0.77</td>
<td>1.18</td>
<td>1.79</td>
<td>0.95</td>
<td>1.10</td>
</tr>
<tr>
<td>FeO (wt %)</td>
<td>27.58</td>
<td>25.20</td>
<td>17.94</td>
<td>24.47</td>
<td>24.76</td>
<td>24.91</td>
<td>23.03</td>
<td>13.55</td>
<td>27.08</td>
<td>28.56</td>
<td>28.27</td>
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<td>MnO (wt %)</td>
<td>0.02</td>
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<td>0.93</td>
<td>1.41</td>
<td>0.95</td>
<td>1.42</td>
<td>1.52</td>
<td>0.94</td>
<td>0.50</td>
<td>0.29</td>
<td>0.38</td>
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<tr>
<td>MgO (wt %)</td>
<td>0.04</td>
<td>1.11</td>
<td>6.88</td>
<td>1.76</td>
<td>1.89</td>
<td>1.65</td>
<td>2.74</td>
<td>9.91</td>
<td>0.27</td>
<td>0.10</td>
<td>0.12</td>
</tr>
<tr>
<td>Zr (ppm)</td>
<td>0.16</td>
<td>0.31</td>
<td>0.09</td>
<td>0.37</td>
<td>0.41</td>
<td>0.31</td>
<td>0.88</td>
<td>0.12</td>
<td>0.15</td>
<td>0.72</td>
<td>0.42</td>
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<tr>
<td>ZrO₂ (wt %)</td>
<td>0.60</td>
<td>18.17</td>
<td>22.17</td>
<td>15.56</td>
<td>9.87</td>
<td>18.10</td>
<td>16.62</td>
<td>22.49</td>
<td>0.67</td>
<td>1.79</td>
<td>2.22</td>
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<tr>
<td>Na₂O (wt %)</td>
<td>10.14</td>
<td>2.82</td>
<td>0.71</td>
<td>4.68</td>
<td>8.26</td>
<td>3.22</td>
<td>3.69</td>
<td>0.95</td>
<td>13.44</td>
<td>12.79</td>
<td>12.58</td>
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<tr>
<td>Total (wt %)</td>
<td>97.91</td>
<td>99.65</td>
<td>100.84</td>
<td>98.84</td>
<td>98.16</td>
<td>99.38</td>
<td>99.69</td>
<td>100.45</td>
<td>98.17</td>
<td>97.64</td>
<td>97.26</td>
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</table>

Formula based on 6 oxygens and 4 cations:

- Si: 1.99
- Al: 0.04
- Ti: 0.08
- Cr: 0.00
- Fe²⁺: 0.05
- Mg: 0.00
- Fe: 0.02
- Mn: 0.00
- Zr: 0.00
- Ca: 0.00
- Na: 1.02
- Sum: 4.00

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brownish ice colour of the higher salinity fluid inclusions indicate that salts other than NaCl are present in the fluid (e.g. CaCl₂, FeCl₃, MgCl₂ etc., see below; Shepherd et al., 1985; Davis et al., 1989; Borovikov et al., 2001). In addition, trace amounts of CO₂ and CH₄ were detected during isotope analyses.

All fluid inclusions homogenize to the liquid usually between 110 and 230°C. The dominant low-salinity fluid inclusions scatter over the whole temperature range independent of sample or unit. However, the higher salinity fluid inclusions (>10 wt % NaCl eq.) tend to have lower homogenization temperatures and may be interpreted as a later fluid phase present at lower temperatures, but still related to the same magmatic event (as later tectonic, metamorphic or magmatic events in the area are unknown; Upton & Emeleus, 1987).

(b) Saline–aqueous three-phase inclusions. In contrast to the two-phase inclusions described above, three-phase fluid inclusions additionally contain a solid phase (calcite; determined by Raman spectroscopic analyses; Fig. 8c–f). In general, they have a similar shape and size to the two-phase inclusions. The three-phase fluid inclusions occur not only as primary inclusions in nepheline (SM4, SM5), but also along secondary trails in hydrothermal fluorite. In these trails, the phase proportions of calcite–fluid–vapour are fairly constant (Fig. 8). In a few of the ‘fluid’ inclusions (sample JS109), the calcite minerals are very large and the inclusions contain up to 65 wt % calcite (recalculated using the densities of calcite and fluid). These ‘fluid’ inclusions may be better referred to as carbonate melt inclusions. In general, the fluid inclusions containing calcite show a melting behaviour very similar to fluid inclusions of type (la). However, the calcite predominantly occurs in inclusions with low salinities (Table 7). During heating experiments up to 450°C (at which temperature most inclusions decrepitated), the calcite never dissolved.

(2) Pure CO₂ fluid inclusions. Apart from types (la) and (lb), one fluorite sample (JS34) contains rounded to elongated (<50 μm) fluid inclusions of pure CO₂. These inclusions occur either in groups or within secondary trails together with aqueous fluid inclusions. Their melting temperatures range from −56.8 to −57.9°C and they homogenize to the vapour at temperatures between +28 and +34°C.

(3) Aqueous–CH₄ fluid inclusions. Magmatic fluorite from the agpaitic unit SM6 (JS88 and JS122) contains one- or two-phase (CH₄-bearing) fluid inclusions (Fig. 8g and h). They occur either along (pseudo-)secondary trails or (rarely) as isolated groups in which case they may be interpreted to be of primary origin. The fluid inclusions generally have a rounded to irregular shape and are up to 40 μm in size. They range from pure methane with homogenization temperatures between −75 and −93°C to mixed aqueous-methane inclusions. The aqueous–methane proportions vary considerably as methane clathrate does not always form during the heating–freezing experiments. The final ice melting temperatures of the inclusions scatter between −14 and −2°C and are not constant within
single trails. Methane clathrate melts between +3 and +21°C. No higher hydrocarbons or any other components were detected by Raman spectroscopy.

Ion chromatographic analyses

Ion chromatographic analyses of fluid inclusions were performed on fluorites and one quartz sample from SM1, SM4 and SM5. For samples finely intergrown with feldspar, no cation contents are reported, because of contamination effects during the analysis and preparation procedure.

The absolute ion concentration was calculated using the average salinity of the sample (Table 8). The calculations were performed using a Cl-factor, which was calculated according to the following equation:

\[
\text{Cl} = \left( \frac{\text{atom weight Cl}}{\text{atom weight NaCl}} \right) \times \frac{10000 \times \text{salinity (wt % NaCl eq.)}}{10000}.
\]

Chlorine content is up to 10 wt %, and Cl is by far the most abundant anion in the analyzed samples. Nitrate content is below 5000 ppm but is up to 1.4 and 2.0 wt % in samples JS109 and JS152, respectively. The significance of these values and the nitrogen species originally present in the fluid before sample preparation is not clear and we do not suggest that the fluid contained magmatic nitrate. The sulphate concentration is very low (<170 ppm). Bromine content is up to 620 ppm and averages around 400 ppm. The Cl/Br (weight) ratio is between 88 and 124 with two values at 268 and 356 (close to the value for modern seawater).

The dominant cation is Na, with values up to 10.7 wt %. The second most abundant cation is K with values up to 9000 ppm, but usually below 4000 ppm. Mg content ranges from 34 to 4558 ppm, averaging around 900 ppm. Ba content is very low with values <200 ppm; Sr is mostly masked by overlapping Ca but has contents <130 ppm in the two analyzed samples.

The anion–cation charge balance is always >1 because Ca and F were not quantified during the analyses because of their abundance in the host mineral (fluorite). However, a fluorine-free charge balance allows calculation of the minimum amount of Ca in the fluid. This estimation indicates that Ca is the second most abundant cation, with contents ranging from 0.2 to 2.5 wt % and with a mean Na/Ca ratio of 4.5 (except JS6). This is in agreement with the one analyzed quartz sample (JS277, Table 8), which gave an anion–cation ratio of 1.06 and a Na/Ca ratio of 4.0.

Isotopic composition of the fluid inclusions in fluorite

The δD of the inclusion water varies between −40.7 and −135.6‰ (VSMOW, Table 9, Fig. 10). δ18O values range from −8.7 to −20.9‰ (VSMOW). The δ13C and δ18O of inclusion CO2 ranges from −2.5 to −17.4‰ (VPDB) and from +26.7 to +42.7‰ (VSMOW), respectively (Fig. 7). The δ13C of inclusion methane could be determined in all samples and ranges from −27.2 to −30.9‰ (VPDB, Fig. 11). The hydrogen isotopic composition of methane could not be determined in all of the samples, as the recovered amount of hydrogen was too small to be analyzed in some cases. However, where analysis was possible, δD_methane values of −174 to −195‰ (VSMOW) were obtained, which are within the range of values measured in samples from other nepheline syenitic intrusions (e.g. Potter & Konnerup-Madsen, 2003; Graser et al., in press).
Table 5: Nd, O and H isotopic compositions of mineral separates

<table>
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<tr>
<th>Sample</th>
<th>Unit</th>
<th>Mineral</th>
<th>Sm (ppm)</th>
<th>Nd (ppm)</th>
<th>$^{142}$Sm/$^{144}$Nd</th>
<th>$^{142}$Nd/$^{144}$Nd</th>
<th>εNd(i)</th>
<th>$T_{DM}$ (Ga)</th>
<th>$\delta^{18}$O</th>
<th>$\delta^D$</th>
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<tbody>
<tr>
<td>JS195</td>
<td>SM1</td>
<td>Am</td>
<td>48.52</td>
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<td>1.77</td>
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<td>0.511877 ± 8</td>
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<td>1.73</td>
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<td>0.511793 ± 9</td>
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<td>n.a.</td>
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εNd(i) was corrected to the time of emplacement at about 1.275 Ga (Upton et al., 2003); $\delta^{18}$O and $\delta^D$ in % (VSMOW). n.a., not analyzed; $T_{DM}$ (Ga), Nd model ages relative to the depleted mantle (Liew & Hofman, 1997).

Table 6: $\delta^{13}$C and $\delta^{18}$O isotopic composition of Motzfeldt samples (in % VPDB and VSMOW)

<table>
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<tr>
<th>Sample</th>
<th>Unit</th>
<th>Type</th>
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<th>$\delta^{18}$O</th>
</tr>
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<td>cryst.</td>
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<td>8.1</td>
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<td>wr</td>
<td>-3.2</td>
<td>24.2</td>
</tr>
<tr>
<td>JS159</td>
<td>SM6</td>
<td>wr</td>
<td>-2.1</td>
<td>21.9</td>
</tr>
<tr>
<td>JS164</td>
<td>SM6</td>
<td>wr</td>
<td>-2.1</td>
<td>21.9</td>
</tr>
</tbody>
</table>

DISCUSSION

Estimation of crystallization temperatures and oxygen fugacity of the Motzfeldt rocks

Both nepheline and feldspar compositions can provide an estimate of the crystallization temperatures of the Motzfeldt rocks. Hamilton (1961; Fig. 5) calibrated the nepheline compositions so that they could be used as a temperature indicator. Based on the maximum values recorded (= crystallization temperatures), the nephelines of the Motzfeldt units SM4, SM5 and SM6 gave temperatures of ~1000°C, ~850°C and ~800°C, respectively, which are in good agreement with the data of Jones (1980) and Jones & Larsen (1985).

Jones (1990) assumed that the feldspars from SM1 to SM5 crystallized at hypersolvus conditions and constrained the minimum temperature of formation of these feldspars to the range 650–800°C. These temperatures are
Fig. 7. Isotopic composition of CO₂ from fluid inclusions, calcite from veins, altered samples and calcite crystals from fluid inclusions compared with reference data from other Gardar rocks or fluids (Igaliko region: Pearce & Leng, 1996; Coulson et al., 2003; Ivigtut complex: Köhler et al., 2000; Grønneblade-Ika intrusion: Halama et al., 1993).

slightly lower than the temperature estimates based on nepheline and may reflect solids rather than liquidus temperatures. The crystallization of two separate feldspars (albite and orthoclase, Fig. 3) in the agpaitic unit SM6 suggests lower crystallization temperatures below the feldspar solvus (e.g. McDowell, 1986; Brown & Parsons, 1989). The very pure endmember compositions indicate temperatures as low as 500 °C.

For the miaskitic units, coexisting olivine, clinopyroxene and Fe-Ti oxides can be used to constrain crystallization temperatures, oxygen fugacities and silica activities using two different approaches. Temperature and oxygen fugacities can be obtained for samples containing the coexisting Fe-Ti oxide minerals magnetite and ilmenite provided that they crystallized in equilibrium as assumed for samples JS195–JS197 in SM1 (Fig. 2). Calculations according to Andersen & Lindsley (1985) using the spreadsheet of Lepage (2003) gave temperatures of 640–690 °C at fO₂ values below the FMQ buffer (ΔFMQ = 0-13). However, two-oxide thermometry is strictly valid only for quenched (volcanic) rocks, as Fe, Ti and Mg may re-equilibrate at subsolidus conditions. Therefore, the calculated temperatures and oxygen fugacities have to be interpreted with care. However, the results give an approximate indication of the T-fO₂ conditions that prevailed during the evolution of the Motzfeldt complex.

To at least partially overcome the problem of fast (subsolidus) re-equilibration of the coexisting Fe-Ti oxides, the QUILF approach was used (for the theoretical background, see Frost & Lindsley, 1992; Lindsley & Frost, 1992; Andersen et al., 1993). The QUILF method (software package by Andersen et al., 1993) uses olivine–pyroxene–Fe-Ti oxide equilibria to calculate T-fO₂ conditions. The temperature is calculated based on Fe, Mg and Ca exchange between clinopyroxene and olivine. Oxygen fugacities and silica activities are calculated using equilibria between Fe-Mg silicates and Fe-Ti oxides. Marks & Markl (2001) gave details of the approach for application to syenitic rocks.

Because of the lack of fresh olivine in our samples (it is rare and altered to iddingsite), we used the olivine and pyroxene compositional data of Jones (1980, 1984). This is justified, as Jones’ pyroxene analyses are identical to those in our study (Fig. 4). Hence, we combined his analyses with the Fe-Ti oxide analyses, as these were not analyzed by Jones. Obviously, in doing this, we assume that our Fe-Ti oxide compositions of samples JS181, JS180 and JS108 (from SM5) were in equilibrium with olivine and pyroxene with similar compositions to those reported by Jones (1980, 1984); pyroxene core compositions with high diopside content.

With respect to the uncertainty as to whether the minerals really crystallized in equilibrium, the results have to be regarded as rough estimates of T and fO₂ only. Calculations yielded temperatures from c. 600 to 800 °C at fO₂ conditions below the FMQ buffer (ΔFMQ = −0.5 to −2) at qSiO₂ between 0.3 and 0.5. These calculations are in good agreement with the data obtained by two-oxide thermometry and temperature constraints based on nepheline and feldspar compositions. The temperatures have to be regarded as solidus temperatures (e.g. Marks & Markl, 2001). The calculated T-fO₂ conditions of the miaskitic rocks lie in a region where a CO₂-fluid is stable and only slightly above the CH₄-stability field (Huijzena, 2001, 2005; see discussion below).

Because of the lack of suitable mineral assemblages, the oxygen fugacity for SM6 could not be estimated. However, the high Fe³⁺/Fe⁰ total ratio (Fig. 12, Jones, 1980) and the occurrence of aegerine instead of titanomagnetite and Fe²⁺-rich amphibole may indicate a higher oxidation state than in the earlier pulses (which does not necessarily mean a higher fO₂ because of the strong temperature dependence of the fO₂-buffer reactions). The late-magmatic alteration to hematite clearly indicates fO₂ conditions above the hematite–magnetite buffer.

Isotopic constraints derived from mineral separates

The initial εNd values (corrected for an age of 1.275 Ga; Upton et al., 2003) are relatively homogeneous, varying by only ±2.3 εNd units. The similarity to the Ilimaussaq (Marks et al., 2004) and Grønneblade-Ika intrusions (Halama et al., 2005), the basalts of the Eriksfjord formation (Halama et al., 2003) and Igaliko–Quassiaruk lamprophyres and carbonatites (Coulson et al., 2003, Fig. 6) suggests that these intrusions or rocks formed from similar mantle sources. The Nd model ages of 1.5–1.8 Ga relative
Fig. 8. Typical fluid inclusions (FI). (a) Secondary and pseudo-secondary fluid inclusions [FI type (1a)] from JS197 (SM1). (b) Secondary fluid inclusions [FI type (1a)] in SM4 (JS68). (c) Fluid inclusion (FI) with large calcite crystal [FI type (1b)] from SM1 (JS6). (d) Secondary fluid inclusions with calcite crystals [FI type (1b)] in primary magmatic fluorite from SM1 (JS16). (e) Primary fluid inclusion (in the centre of photograph) with large calcite crystal [FI type (1b)] in JS172 (nepheline, SM4). (f) Secondary fluid inclusion with calcite crystals [FI type (1b)] in nepheline (JS60, SM5). (g) Irregular, pure methane fluid inclusions [FI type (3)] in JS60 (SM6). (h) Irregular, pure methane fluid inclusions [FI type (3)] in JS172 (SM6), visible bubble because photograph was taken at ~110°C in close association with H₂O-rich fluid inclusion.
Table 7: Microthermometric data for Motzfeldt fluid inclusions

<table>
<thead>
<tr>
<th>JS</th>
<th>Unit</th>
<th>Mineral Type</th>
<th>n</th>
<th>T(me) (°C)</th>
<th>T(m) H₂O (°C)</th>
<th>T(h) H₂O (°C)</th>
<th>Salinity (wt % NaCl eq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>SM1</td>
<td>fl-sec (1a) l-v</td>
<td>9</td>
<td>-25 to -48</td>
<td>-1.7 to -14.2</td>
<td>107-284</td>
<td>2.9-18.0</td>
</tr>
<tr>
<td>9</td>
<td>SM1</td>
<td>fl-sec (1a) l-v</td>
<td>7</td>
<td>-28 to -32</td>
<td>-0.6 to -5.8</td>
<td>106-245</td>
<td>1.1-19.0</td>
</tr>
<tr>
<td>9</td>
<td>SM1</td>
<td>fl-sec (1b) l-v-s</td>
<td>2</td>
<td>-2.3 to -7.2</td>
<td>-3.9-10.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>SM1</td>
<td>qtz-sec (1a) l-v</td>
<td>34</td>
<td>-20 to -40</td>
<td>-3.8 to -14.1</td>
<td>99-264</td>
<td>6.2-17.9</td>
</tr>
<tr>
<td>16</td>
<td>SM1</td>
<td>fl-sec (1a) l-v</td>
<td>34</td>
<td>-35 to -75</td>
<td>-0.8 to -24.1</td>
<td>111-288</td>
<td>1.4-25.0</td>
</tr>
<tr>
<td>16</td>
<td>SM1</td>
<td>fl-sec (1b) l-v-s</td>
<td>20</td>
<td>-30 to -35</td>
<td>-0.7 to -21.7</td>
<td>94-310</td>
<td>1.2-23.5</td>
</tr>
</tbody>
</table>

n, number of fluid inclusions analyzed; T(me), eutectic melting; T(m) H₂O, final melting of ice; T(h) H₂O, total homogenization temperature to the liquid. Fluids analyzed in: fl-sec, hydrothermal fluorite; qtz-sec, hydrothermal quartz; fl-prim, primary magmatic fluorite; fsp-prim, primary magmatic feldspar; ne-prim, primary magmatic nepheline. Fluid type: l-v, liquid-vapour two-phase inclusions; l-v-s, liquid-vapour-solid three-phase inclusions; CO₂, pure CO₂-bearing fluid inclusions; aq. CH₄, mixed aqueous-CH₄-bearing inclusions; pure CH₄, pure CH₄ inclusions. T(m) clathrate, measured CH₄-clathrate (CH₄ x 5-75 H₂O) melting temperatures in mixed aqueous-CH₄-bearing fluid inclusions in JS88 and JS122.
to the depleted mantle (Liew & Hofmann, 1987) are most probably related to the Ketilidian orogeny at this time (Garde et al., 2002), and fall into the range of other model ages for rocks from the Gardar Province (e.g. Marks et al., 2004). Hence, we are dealing with a large magmatic province that is fed from a similar source over a large spatial and temporal interval.

Similar to the Nd isotopic values, the $\delta^{18}\text{O}$ values of the minerals define a narrow range (between +4.2 and +5.3‰) and suggest an isotopically rather homogeneous melt throughout the various units. The $\delta^{18}\text{O}$ of a nepheline-syenitic melt in equilibrium with the analyzed minerals can be constrained using the approach of Zheng (1993a, 1993b) and Zhao & Zheng (2003) as shown by Halama et al. (2005). Assuming an equilibration temperature of 800°C, the fractionation between amphibole (hornblende) and melt is $\approx 1/3$, and aegerine–melt fractionation is $\approx 0.3\%$. Thus the original melt would have a $\delta^{18}\text{O}$ between 5-2 and 6-9‰. These values are not only typical mantle values (e.g. Kyser, 1986; Eiler, 2001; Marks et al., 2004), but also $\delta^{18}\text{O}$ values characteristic of other syenitic intrusions (e.g. Taylor & Sheppard, 1986; Harris, 1995; Dallai et al., 2003; Marks et al., 2004). The two samples from SMI show slightly lower $\delta^{18}\text{O}$ amphibole values of +4.2 and +4.6‰. Such lower values are usually attributed to interaction with low-$\delta^{18}\text{O}$ meteoric fluids (compare O isotopic composition of the fluid inclusions of this study; Marks et al., 2003). The locally intense alteration, the turbidity of feldspars and the occurrence of hydrothermal alteration minerals (e.g. hematite, fluorite, calcite, etc.), especially in unit SMI, support such an interpretation.

The $\delta^D$ values are lower than ‘normal’ magmatic values, which are usually between −50 and −80‰ (see Hoefs, 1997). The most likely process to explain the unusual hydrogen isotopic composition may be post-magmatic interaction with a meteoric fluid, as the hydrogen isotopic composition reacts very easily to the infiltration of an H$_2$O-rich fluid phase. This is due to its low concentration in minerals compared with oxygen (e.g. Taylor, 1974, 1977). Using the mineral–water fractionation factors for arfvedsonite (at 400°C; Graham et al., 1984) and for hornblende (at 450–800°C; Suzuki & Epstein, 1976), a coexisting fluid would have a $\delta^D$ of c. −60 to −110‰. These values are in good agreement with our isotope analyses of water content of fluid inclusions, which ranges from −40 to −135‰ ($\delta^D$, VSMOW). If indeed the hydrogen isotopic composition reflects late- to post-magmatic alteration by a meteoric fluid phase, the fluid–rock ratio that caused this shift must have been low, because otherwise it should also be visible in the O isotope compositions.

![Fig. 9. Histogram of wt % NaCl eq. (calculated after Bodnar, 1993) of all investigated fluid inclusions in the miaskitic units [fluid inclusion types (a) and (b)].](https://academic.oup.com/petrology/article-abstract/49/9/1549/1497494)

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**Table 8: Results of ion chromatography analyses of fluid inclusion content**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unit</th>
<th>min.</th>
<th>sal.</th>
<th>F$^-$</th>
<th>Cl$^-$ (a)</th>
<th>Br$^-$</th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>Cl/Br</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Li$^+$</th>
<th>Mg$^{2+}$</th>
<th>Sr$^{2+}$</th>
<th>Ba$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>a/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>JS6</td>
<td>SM1</td>
<td>fl</td>
<td>5-7</td>
<td>n.a.</td>
<td>34472</td>
<td>278</td>
<td>666</td>
<td>49</td>
<td>124</td>
<td>45670</td>
<td>1454</td>
<td>26</td>
<td>80</td>
<td>b.d.</td>
<td>58</td>
<td>n.a.</td>
<td>2096</td>
<td>1.15</td>
</tr>
<tr>
<td>JS9</td>
<td>SM1</td>
<td>fl</td>
<td>5-3</td>
<td>n.a.</td>
<td>31761</td>
<td>258</td>
<td>3313</td>
<td>156</td>
<td>123</td>
<td>27839</td>
<td>1998</td>
<td>6</td>
<td>209</td>
<td>b.d.</td>
<td>59</td>
<td>n.a.</td>
<td>7824</td>
<td>1.86</td>
</tr>
<tr>
<td>JS16</td>
<td>SM1</td>
<td>fl</td>
<td>11-2</td>
<td>n.a.</td>
<td>67704</td>
<td>190</td>
<td>2884</td>
<td>165</td>
<td>356</td>
<td>56724</td>
<td>3015</td>
<td>38</td>
<td>1115</td>
<td>128</td>
<td>194</td>
<td>n.a.</td>
<td>13350</td>
<td>1.69</td>
</tr>
<tr>
<td>JS277</td>
<td>SM1</td>
<td>qtz</td>
<td>8-6</td>
<td>n.a.</td>
<td>1353</td>
<td>51887</td>
<td>590</td>
<td>770</td>
<td>65</td>
<td>40473</td>
<td>1478</td>
<td>84</td>
<td>1003</td>
<td>57</td>
<td>22</td>
<td>10106</td>
<td>—</td>
<td>1.06</td>
</tr>
<tr>
<td>JS152</td>
<td>SM4</td>
<td>fl</td>
<td>14-7</td>
<td>n.a.</td>
<td>88513</td>
<td>489</td>
<td>19832</td>
<td>18</td>
<td>181</td>
<td>107341</td>
<td>4046</td>
<td>18</td>
<td>4568</td>
<td>b.d.</td>
<td>125</td>
<td>n.a.</td>
<td>18803</td>
<td>1.53</td>
</tr>
<tr>
<td>JS168</td>
<td>SM4</td>
<td>fl</td>
<td>1-9</td>
<td>n.a.</td>
<td>11497</td>
<td>107</td>
<td>151</td>
<td>5</td>
<td>108</td>
<td>9570</td>
<td>398</td>
<td>1</td>
<td>34</td>
<td>b.d.</td>
<td>34</td>
<td>b.d.</td>
<td>2401</td>
<td>1.80</td>
</tr>
<tr>
<td>JS225</td>
<td>SM4</td>
<td>fl</td>
<td>16-3</td>
<td>n.a.</td>
<td>98590</td>
<td>828</td>
<td>635</td>
<td>13</td>
<td>119</td>
<td>67182</td>
<td>3260</td>
<td>13</td>
<td>289</td>
<td>b.d.</td>
<td>45</td>
<td>n.a.</td>
<td>23758</td>
<td>2.12</td>
</tr>
<tr>
<td>JS274</td>
<td>SM4</td>
<td>fl</td>
<td>7-9</td>
<td>n.a.</td>
<td>47469</td>
<td>475</td>
<td>3722</td>
<td>31</td>
<td>100</td>
<td>44008</td>
<td>8667</td>
<td>b.d.</td>
<td>1317</td>
<td>b.d.</td>
<td>6798</td>
<td>n.a.</td>
<td>11336</td>
<td>n.a.</td>
</tr>
<tr>
<td>JS109</td>
<td>SM5</td>
<td>fl</td>
<td>3-5</td>
<td>n.a.</td>
<td>31751</td>
<td>311</td>
<td>11029</td>
<td>135</td>
<td>102</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>JS175</td>
<td>SM5</td>
<td>fl</td>
<td>3-2</td>
<td>n.a.</td>
<td>19469</td>
<td>73</td>
<td>4713</td>
<td>b.d.</td>
<td>268</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

*a*Average salinity of all analyzed samples.

*b*Calculated Ca$^{2+}$ content assuming balanced uncharged fluid, a/c = 1.

All values in ppm except for sal., Cl/Br and a/c ratios. min., host mineral of fluid inclusions; sal., average salinity of fluid inclusions of the sample in wt % NaCl eq.; Cl$^-$ (a), calculated chlorine content; a/c, calculated anion–cation balance (molar), n.a., not analyzed; b.d., below detection limit.
Table 9: Isotopic composition of fluid inclusions ($H_2O$, $CO_2$, $CH_4$)

<table>
<thead>
<tr>
<th>Unit</th>
<th>SM1</th>
<th>SM4</th>
<th>JS12</th>
<th>JS15</th>
<th>JS122</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta D_{H2O}$</td>
<td>−95.8</td>
<td>−156</td>
<td>−189</td>
<td>−152</td>
<td>−174</td>
</tr>
<tr>
<td>$\delta^{18}O_{H2O}$</td>
<td>−9.66</td>
<td>−5.88</td>
<td>−6.33</td>
<td>−7.00</td>
<td>−5.88</td>
</tr>
<tr>
<td>$\delta^{13}C_{CH4}$</td>
<td>−27.21</td>
<td>−30.80</td>
<td>−27.80</td>
<td>−28.15</td>
<td>−28.90</td>
</tr>
<tr>
<td>$\delta^{13}C_{CO2}$</td>
<td>n.a.</td>
<td>−3.46</td>
<td>n.a.</td>
<td>−4.20</td>
<td>n.a.</td>
</tr>
<tr>
<td>$\delta^{18}O_{CO2}$</td>
<td>−5.49</td>
<td>−6.38</td>
<td>−4.50</td>
<td>−5.05</td>
<td>−6.00</td>
</tr>
<tr>
<td>$T_{eq. H2O-CO2}$</td>
<td>10.0</td>
<td>28.50</td>
<td>12.5</td>
<td>42.10</td>
<td>17.0</td>
</tr>
<tr>
<td>$T_{eq. CO2-CH4}$</td>
<td>342.5</td>
<td>311.0</td>
<td>260.5</td>
<td>311.0</td>
<td>250.0</td>
</tr>
<tr>
<td>$\Delta_{H2O-CO2}$</td>
<td>55.36</td>
<td>50.25</td>
<td>38.06</td>
<td>55.25</td>
<td>45.37</td>
</tr>
</tbody>
</table>

All values in %o VSMOW (for D and O isotopes) and in %o VPDB (for C isotopes); $T_{eq. H2O-CO2}$ and $T_{eq. CO2-CH4}$ are equilibration temperatures between O and C, respectively (in °C); $\Delta_{H2O-CO2}$ is fractionation water-CO$_2$ ($\delta^{18}O$).

Fig. 10. Isotopic composition of fluid inclusion water. The good agreement with data from the Iivgut complex fluids (Kohler et al. 2008) and Canadian Shield brines (Frape & Fritz, 1982; Frape et al., 1994; Bottomley et al., 1994) should be noted. Reference data for magmatic, metamorphic, and meteoric waters from Sheppard (1986).

Other processes that could also cause depleted $\delta D$ values include extreme degassing of magmatic fluids, assimilation of organic-rich sediments and oxidation of magmatic methane (see Marks et al., 2004). However, no signs of extreme degassing of magmatic fluids, such as the presence of a large contact aureole around the intrusion, are observed and no organic-rich sediments have been described anywhere in the vicinity of the Motzfeldt intrusion or in the Gardar Province as a whole (Marks et al., 2004). Our fluid inclusion study suggests that CO$_2$ and not CH$_4$ was the dominant carbon species in the fluid during most of the differentiation history of the Motzfeldt magmas (see below).

Fig. 11. $\delta^{13}C$ (CH$_4$) vs $\delta^{13}C$ (CO$_2$). Equilibration temperatures according to Richet et al. (1997). Reference data for Iivgut and Ilimmuaaq from Kohler et al. (2008) and Graser et al. (in press), respectively.

The isotopic composition of the calcite from a calcite–fluorite vein lies within the mantle box of Taylor et al. (1977; see also Kyser et al., 1982; Des Marais & Moore, 1984; Deines, 1989; Clarke et al., 1993; Keller & Hoefs, 1995; $\delta^{18}O$ 7-8‰; $\delta^{13}C$ –4-4‰). The values are in accordance with analyses by Pearce & Leng (1996), Pearce et al. (1997), Goodenough (1997), Coulson et al. (2003), Taubald et al. (2004) and Halama et al. (2005) from various carbonate or carbonatite localities in the Gardar Province, suggesting a common mantle source of the carbonates.

Three whole-rock powders (JS15 and JS164 from SM6; JS16 from SM5) containing considerable amounts of calcite veinlets and/or calcite as an alteration product of feldspar and carbonates (e.g. Fig. 3) were also analyzed for their C and O isotopic composition. The $\delta^{18}O$ values range from +21.9 to +24.2‰ and $\delta^{13}C$ from –24 to –3.2‰ (Fig. 7). Similar values...
FORMATION OF AGPAITIC ROCKS

Fig. 12. $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ vs $(\text{Na} + \text{K})/\text{Ca}$ for whole-rock data from Jones (1980). The increase in $(\text{Na} + \text{K})/\text{Ca}$ equals a fractionation increase. As shown by several workers, the arrow may indicate a temperature decrease (see text for further discussion).

for samples from SM1 and SM4 were obtained by J. McCreaeth (personal communication, 2007). The results are comparable with those obtained by Pearce & Leng (1996) and Coulson et al. (2003) from the area around the Motzfeldt intrusion (i.e. Igalko region). The $\delta^{13}$C values lie near those reported for mantle rocks (Taylor et al., 1967; Keller & Hoefs, 1995) and therefore possibly suggest mantle derivation. The oxygen isotope values are considerably enriched in $^{18}$O with regard to mantle rocks and are more typical of secondary and/or low-temperature alteration of calcite (Deines, 1989; Demény et al., 1998). The slight enrichment of $\delta^{18}$O and variably enriched $\delta^{13}$C might be explained by the model of Deines (1989), who stated that $\delta^{18}$O increases with fractionation and with a decreasing carbonate:silicate ratio (see also Worley et al., 1995). Furthermore, Tichomirowa et al. (2006) assumed that increasing $\delta^{18}$O values could be explained by interaction with water-rich fluids, which is the most likely explanation for the observed heavy oxygen isotopic composition (see below). Hence, only the C isotope signature would probably preserve the mantle record during hydrous alteration if the C concentration of the infiltrating fluid is low. Kühler et al. (2008) used a similar explanation for the observed change in $\delta^{18}$O at constant $\delta^{13}$C of $\text{CO}_2$ for fluid inclusions from another Gardar intrusion, the Ivigtut complex (see discussion of fluid inclusion results).

Discussion of fluid inclusion results

The fluid inclusions present in primary minerals of the miaskitic units SM1, SM4 and SM5 are of both primary and secondary origin. Their salinities are commonly <5 wt % NaCl eq. The few higher salinity fluid inclusions possibly represent a different (low-temperature) fluid generation.

Regarding the commonly observed calcite crystals in the low-salinity fluid inclusions, we may ask whether these minerals are ‘true’ daughter minerals or if they are just accidentally trapped solid crystals. The fact that in certain secondary fluid inclusion trails, each fluid inclusion contains a calcite crystal in constant phase proportions (Fig. 8) suggests that these are indeed daughter minerals. They crystallized after entrapment from a fluid originally undersaturated in calcite. However, accidental trapping cannot be completely ruled out for samples in which only few inclusions contain calcite.

The fact that both two-phase (liquid–vapour) and three-phase (liquid–vapour–solid) fluid inclusions occur in the miaskitic rocks provides evidence that during their evolution the fluid was characterized by $\text{H}_2\text{O}$ and NaCl with variable amounts of $\text{CO}_2$ (or $\text{HCO}_3^-$). Unfortunately, the sample material did not allow us to decipher the exact relative chronologies of entrapment of the two types of fluid inclusions, because of the lack of adequate cross-cutting relationships.

In contrast to the $\text{H}_2\text{O}$–NaCl–$\text{CO}_2$ fluid in the miaskitic rocks, fluid inclusions in magmatic fluorite from the agpaitic rocks (SM6) are characterized by $\text{H}_2\text{O}$–NaCl–$\text{CH}_4$ without any calcite. The close association of pure methane, mixed $\text{H}_2\text{O}$–NaCl–$\text{CH}_4$ and (almost) pure $\text{H}_2\text{O}$–NaCl inclusions suggests that they formed from a heterogeneous, but definitely reduced fluid displaying immiscibility.

Based on stratigraphic reconstructions, pressure conditions during emplacement of the Motzfeldt intrusion were probably between 1 and 2 kbar as suggested by Jones (1980). Similar conditions were obtained for the Ilmaussaq intrusion (Konnerup-Madsen & Rose-Hansen, 1984). Accordingly, a pressure correction of 50–100°C has to be applied to the homogenization temperatures of the fluid inclusions. The homogenization temperatures range from 78 to 343°C (Table 7) with the majority lying between 100 and 200°C. Accordingly, formation temperatures between 150 and 300°C can be assumed (Bakker, 2003; not applicable to fluid inclusions from SM6 as they are assumed to be trapped from a heterogeneous fluid). No inclusions could be calculated for inclusions containing calcite, as no total homogenization temperature could be determined. Not even partial dissolution of the calcite crystals was observed and it is unclear to us whether the dissolution of the crystals was inhibited kinetically or because the formation temperatures were much higher than the decrepitation ones.

The results of our crush–leach analyses support our microthermometric results indicating that the fluid is, in addition to $\text{H}_2\text{O}$, dominated by Na, Cl and minor amounts of Ca. Other ions are only of minor importance. The Cl/Br ratios (by weight) of our samples mostly lie between 95 and 120. The high Cl/Br ratio in sample JS6 may be attributed either to a mixture of a high- and a low-salinity fluid and/or to another fluid generation (higher proportion of higher salinity fluid inclusions in this sample). The predominant low Cl/Br ratios are comparable with those of
other peralkaline Gardar intrusions (Kohler et al., 2008; Graser et al., in press). This similarity across the Gardar Province may suggest a common halogen source, which is in agreement with the Nd isotope-based assumption of a common mantle source of the magmas in general and a common evolution process of the fluid phase. The Cl/Br values of about 100 suggest that unmixing or exsolution of a fluid phase preferentially partitions Br into the fluid relative to the melt and early crystallizing minerals, as suggested by the experiments of Bureau et al. (2000) and Bureau & Métrich (2003).

**Isotopic composition of inclusion \( H_2O \)**

In terms of H and O isotopic composition, the water within the inclusions closely follows the present-day meteoric water line (MWL, Craig, 1961) and falls within the published data array for the Ivigtut complex (Köhler et al., 2008) and Canadian Shield brines (Fritz; Frap & Fritz, 1982; Frap et al., 1984; Bottomley et al., 1994). However, the isotopic composition of the inclusion water is slightly shifted to the left of the MWL. This may be attributed either to equilibration with \( CO_2 \) (Richet et al., 1977; Cartwright et al., 2000; Köhler et al., 2008) or to low-temperature isotopic equilibration with the host-rocks at low water/rock ratios (Fritz & Fritz, 1982; Kelly et al., 1986; Sheppard, 1989). A mixing process with a fluid of unknown origin cannot explain the displacement of the data to the left of the MWL as all known ‘reservoirs’ lie to the right of the MWL (e.g. magmatic or metamorphic waters, Hoefs, 1997). We prefer the second explanation, as the volume of \( CO_2 \) in the fluid inclusions is negligible compared with the dominant water–salt mixture (up to 95 mol %). Furthermore, the available fractionation factors between amphibole and water (Suzuki & Epstein, 1976; Graham et al., 1984) suggest that the hydrogen isotopic composition of the inclusion water (\( \delta D = 40 \text{ to } -100 \% \)) could represent equilibrium values. The low oxygen isotopic values (\( \delta^{18}O = -5 \text{ to } -25 \% \)) of the inclusion water, however, are not in equilibrium with the analyzed oxygen isotope compositions of the mineral separates (\( \delta^{18}O = +4 \text{ to } +3 \% \)). This again points to interaction of a low proportion of meteoric water with the rocks (low fluid–rock ratio; see above, discussion of isotopic composition of mineral separates).

**Isotopic composition of inclusion \( CO_2 \)**

In all analyzed samples (except for JS122, SM6), trace amounts of \( CO_2 \) were detected during the isotope analyses. The \( \delta^{13}C \) values of \( CO_2 \) define two groups (Fig. 7), which may be explained in the following way. \( \delta^{13}C \) values between \(-2 \text{ and } -6 \% \) (VDPB) resemble primary magmatic and/or mantle values (Taylor et al., 1967; Keller & Hoefs, 1995). The second group is defined by lower \( \delta^{13}C \) values ranging from \(-10 \text{ to } -17 \% \). These lower values are commonly explained by contamination with organic-rich material, which is, however, unknown in the Gardar Province (e.g. Marks et al., 2004). Calcite crystals in the fluid inclusions were observed in (almost) all studied samples irrespective of carbon isotopic composition. Therefore, there seems to be no influence from these crystals on the isotopic composition. However, the fluorite samples with low \( \delta^{13}C \) values are very finely intergrown with carbonates. The fractionation of carbon between calcite and \( CO_2(aq) \) based on the fractionation factors of Ohmoto & Goldhaber (1997) is \( 8 \% \) at low temperatures (20–50°C). Such a fractionation could account for the difference in carbon isotopes between the two groups (even regarding the fact that calcite intergrowths were removed by treating the samples with acid prior to analysis). However, the geological significance of this process remains enigmatic.

The very similar range of \( \delta^{18}O \) values of \(-4 \text{ to } -14 \% \) obtained for lamprophyres, phonolites and carbonatites from the Motzfeldt (Igaliko) region (Fig. 7; Pearce & Leng, 1996) points to a common carbon isotopic source and evolution in the whole region and in different rock types, inviting speculation about \( CO_2 \) metasomatism in the mantle source region.

The \( \delta^{18}O \) value of inclusion \( CO_2 \) ranges from +26–7 to +42–7% (VSMOW). The inclusion \( CO_2 \) is considerably enriched in \( ^{18}O \) and is much higher than normal carbonatitic mantle values (Fig. 7; e.g. Taylor et al., 1967; Halama et al., 2005). We follow the argumentation of Köhler et al. (2008), who pointed out the similarity in isotopic composition to \( CO_2 \) vesicles in mid-ocean ridge basalt (MORB) (Pineau & Javoy, 1983). They explained these high values by low-temperature isotopic exchange with oxygen from the inclusion water. Using the fractionation factors of Friedman & O’Neill (1977), the fractionation of oxygen between \( CO_2 \) and \( H_2O(aq) \) is around 40% at low temperatures (10–100°C). This is in accordance with the work of Richet et al. (1977), who reported a fractionation of 41.2 to 44.1‰ which may even be increased by the presence of dissolved salts in the fluid inclusions (Pineau & Javoy, 1983). The fractionation for the samples from the Motzfeldt intrusion ranges between 38.1 and 53.4‰, with a mean of 46.3‰ comparable with the data of Richet et al. (1977) and Köhler et al. (2008).

**Isotopic composition of inclusion \( CH_4 \)**

The carbon isotopic composition of \( CH_4 \) in the inclusions is fairly constant (\( \delta^{13}C = -27 \text{ to } -31 \% \) VPDB). Even the isotopic composition of \( CH_4 \) from fluorite in the agpaitic unit is within the range of the samples from the miaskitic rocks. Calculating the C isotopic equilibration temperatures between methane and \( CO_2 \) using the fractionation factors of Richet et al. (1977) results in values of 300–350°C (only \( \delta^{13}C \) values of \( CO_2 \) from samples in which the \( CO_2 \) has a mantle-like carbon isotopic composition were used; see above). These temperatures are only slightly higher than those deduced from the pressure-corrected fluid inclusion temperatures.

As no sign of organic material is found within the Gardar Province, the low \( \delta^{13}C \) values of \( CH_4 \) in the
FORMATION OF AGPAITIC ROCKS

in the relevant T–fO2 range (oxygen fugacity given as ΔFMQ). Different modelled curves represent x(CH4) in the fluid for different temperatures and carbon activities at 1 kbar calculated according to Huizenga (2001, 2005). At a constant relative oxygen fugacity (i.e. constant ΔFMQ), the x(CH4) increases with decreasing temperature. (b) Same as (a) but with x(CO2)/[x(CH4) + x(CO2) + x(H2O)] vs oxygen fugacity given as ΔQFM. At constant relative oxygen fugacity (i.e. constant ΔFMQ), the x(CO2) decreases with decreasing temperature. The change in fluid composition from an H2O–HCO3–CO2 to a CH4–H2O–NaCl–CaCl2(?) fluid can be explained by combining the T–fO2 data detailed above with theoretical calculations by Huizenga (2001, 2005), who used fugacity coefficients from Shi & Saxena (1992). Figure 13 shows that a CO2–H2O-dominated fluid at high temperatures generally evolves to a fluid dominated by CH4–H2O at lower temperatures at constant relative oxygen fugacities (expressed as ΔQFM in Fig. 13; see Konnerup-Madsen, 2001; Ryabchikov & Kogarko, 2006; Fig. 14) if fO2 is buffered by a mineral assemblage such as olivine–spinel–clinopyroxene–feldspar, in which clinopyroxene and feldspar buffer fO2 because of Ca-tschermakite- or jadeite-involving equilibria. This is in accordance with calculations using thermodynamic data from Robie & Hemingway (1995) assuming ideal gas behaviour, a C:H ratio of 0.5 and a pressure of

of amphibole, which commonly has a rather low Fe3+ content (Fe3+/Fe2+ <0.4 in Ilmaaussaq, Marks et al., 2007; see also Leake, 1997). Crystallization of aegirine would be a direct consequence of a change in oxidation state.

(2) A change of the melt’s alkali (Na)/iron ratio: arfvedsonite has an alkali (Na)/Fe ratio of 0–6, whereas aegirine has a ratio of 1; increasing alkalis relative to iron could drive a melt towards aegirine crystallization irrespective of redox conditions. Although nominally unrelated to redox conditions, crystallization of Fe–Ti oxides would effectively increase this ratio. Their crystallization, however, is again highly redox-dependent.

(3) The formation of a water-deficient fluid resulting from the methane-producing reaction

\[ \text{CO}_2 + 2 \text{H}_2\text{O} = \text{CH}_4 + 2 \text{O}_2. \]

Apart from consuming water and possibly inhibiting the formation of ‘water-rich’ amphibole, this reaction could be responsible for an increase of ‘free’ oxygen, which in turn could further oxidize the iron in the melt.

(4) The formation of eudialyte may be mainly related to the increased solubility of Zr (and possibly other HFSE; e.g. Kogarko, 1974; Watson, 1979; Watson & Harrison, 1983; Farges et al., 1991; Hanchar & Watson, 2003) in peralkaline melts because a high alkali/Al ratio inhibits crystallization of zircon or baddeleyite (Nicholls & Carmichael, 1969; Hoskin & Schaltegger, 2003). Finally and very importantly, the early exsolution of a hydrous fluid phase is inhibited as a result of the high alkalinity and low water activity. This retains Na, halogens and consequently also Zr and other HFSE in the melt (Kogarko, 1974; Treuil et al., 1979; Taylor et al., 1981). Therefore, the formation of eudialyte can be assumed to be a consequence of the high concentration of alkalis, the long crystallization interval and the inhibited exsolution of a fluid phase associated with the reduced conditions.

Change in fluid composition

The change in fluid composition from an H2O–HCO3–NaCl–CaCl2 to a CH4–H2O–NaCl–CaCl2 (?) fluid can be explained by combining the T–fO2 data detailed above with theoretical calculations by Huizenga (2001, 2005), who used fugacity coefficients from Shi & Saxena (1992). Figure 13 shows that a CO2–H2O-dominated fluid at high temperatures generally evolves to a fluid dominated by CH4–H2O at lower temperatures at constant relative oxygen fugacities (expressed as ΔQFM in Fig. 13; see Konnerup-Madsen, 2001; Ryabchikov & Kogarko, 2006; Fig. 14) if fO2 is buffered by a mineral assemblage such as olivine–spinel–clinopyroxene–feldspar, in which clinopyroxene and feldspar buffer fO2 because of Ca-tschermakite- or jadeite-involving equilibria. This is in accordance with calculations using thermodynamic data from Robie & Hemingway (1995) assuming ideal gas behaviour, a C:H ratio of 0.5 and a pressure of

The transition from miaskitic to agpaitic rocks

The transition from the miaskitic units SM1–SM5 to the agpaitic SM6 can be observed in the change in mineralogy, fluid composition, whole-rock alkali content and Fe3+/Fe2+. These changes should be related to a common process.

Mineralogical change

The change from miaskitic to agpaitic mineral assemblages (zircon and titanite to eudialyte) and from (Fe2+-rich) amphibole- to (Fe3+-rich) aegirine-dominated mafic minerals in very late-stage magmatic rocks may be related to several partly interrelated causes, as follows.

(1) Change in oxidation state: a dominance of Fe3+ over Fe2+ in the melt would effectively inhibit the crystallization
1 kbar with variable \(\frac{f(CH_4)}{f(CO_2)}\) ratios (Halama et al., 2005; Fig. 14). Additionally, the H/O ratio of the fluid may also be important for equilibrium (1), as a high H/O ratio favours hydrocarbons and a low H/O ratio favours carbon dioxide (e.g. Huizenga, 2001, 2005). Figure 14 shows that the calculated \(T-fO_2\) conditions for the mafic rocks from the Motzfeldt intrusion lie within the CO\(_2\) stability field, just slightly above the transition curve relating a CO\(_2\)-H\(_2\)O fluid with a CH\(_4\)-H\(_2\)O fluid. The evolution to lower temperatures at a constant relative oxygen fugacity may explain the observed change of the composition to a CH\(_4\)-dominated fluid in the agpaitic rocks. Obviously, only a slight decrease in oxygen fugacity caused by, for example, the increase in the melt’s alkali content, may also influence the carbon speciation in the fluid (see discussion below).

Fischer-Tropsch (F-T) type reactions (e.g. Salvi & Williams-Jones, 1997, 2006) are not believed to be important, as no sign of higher hydrocarbons and/or H\(_2\) was found in the fluid inclusions, nor are the CH\(_4\)-bearing fluid inclusions associated with the breakdown of hydrous minerals which would be necessary to trigger F-T-type reactions (e.g. Nivin et al., 2005; Salvi & Williams-Jones, 2006). A mixing process involving meteoric and magmatic water, which may be important for the formation of methane as suggested by Potter et al. (1999) and Nivin et al. (2005), is questionable for the Motzfeldt intrusion as no CH\(_4\)-bearing fluid inclusions were found in samples from the mafic rocks. The trace amounts of methane found during isotope analyses in the fluid inclusions may be more easily explained by the proposed respeciation model (Konnerup-Madsen et al., 1985; Ryabchikov & Kogarko, 2006).

The change in mineralogy (from Fe\(^{2+}\)- to Fe\(^{3+}\)-bearing mafic minerals) is closely linked to the change in fluid composition (from CO\(_2\) to CH\(_4\)), but it is very important to note that these changes work in different directions: whereas the first requires oxidation, the second requires reduction.

The whole-rock compositional change from Fe\(^{2+}\)- to Fe\(^{3+}\)-dominated linked to alkali content and C-O-H speciation. Generally, the speciation of a C-O-H fluid as well as the oxidation state of Fe is closely linked to the oxidation state.
of the magma (Bezos & Humler, 2005). Assuming fractional crystallization in a system closed with respect to oxygen (Byers et al., 1984), the Fe$_{3+}$/Fe$_{2+}$ ratio commonly increases (Bezos & Humler, 2005). As it is difficult to envisage how a magmatic system can be closed to oxygen diffusion, Bezos & Humler (2005) suggested that the Fe$_{3+}$/Fe$_{2+}$ ratio of a basaltic melt increases as a result of the highly compatible behaviour of Fe$^{3+}$ in olivine and the strong incompatibility of Fe$^{3+}$ in olivine and plagioclase. Although we are obviously not dealing with an olivine-fractionating system, the preferred uptake of Fe$^{3+}$ by, for example, amphibole, ulvospinel-rich titanomagnetite or ilmenite would explain the increasing Fe$_{3+}$/Fe$_{2+}$ in the Motzfeldt melt.

In magmatic systems, ferric and ferrous iron are related by the following equilibrium (e.g. Rüssell & Wiedenroth, 2004):

$$4 \text{Fe}^{3+} + 2 \text{O}^2- \leftrightarrow 4 \text{Fe}^{2+} + \text{O}_2. \quad (2)$$

It has been shown by a number of workers (Kress & Carmichael, 1988; Lange & Carmichael, 1989; Gerlach et al., 1998, 1999; Rüssell & Wiedenroth, 2004) that equilibrium (2) is shifted to the left with decreasing temperature and increasing Na and K content of the melt (e.g. Kress & Carmichael, 1999; Rüssell & Wiedenroth, 2004), which fits with the observations at Motzfeldt (Fig. 12; Jones, 1980). Accordingly, the peralkalinity of a melt and the degree of oxidation of iron (i.e. the stability of Fe$^{2+}$ vs Fe$^{3+}$) are strongly related (Sack et al., 1981; Kilinc et al., 1983; Kress & Carmichael, 1989, 1991; Lange & Carmichael, 1989; Gerlach et al., 1999; Rüssell & Wiedenroth, 2004). Using the empirical equation of Kress & Carmichael (1991) to calculate the oxygen fugacity in silicate liquids, an increase of the highly compatible behaviour of Fe$^{3+}$ in olivine and the strong incompatibility of Fe$^{3+}$ in olivine and plagioclase. Alternatively, we are obviously not dealing with an olivine-fractionating system, the preferred uptake of Fe$^{3+}$ by, for example, amphibole, ulvospinel-rich titanomagnetite or ilmenite would explain the increasing Fe$_{3+}$/Fe$_{2+}$ in the Motzfeldt melt.

Late-stage alteration phenomena involving peralkaline fluids

In general, late- to post-magmatic metasomatism involving a Na-rich fluid at higher relative oxidation state is typical of peralkaline magmatic complexes (Salvi & Williams-Jones, 1990; Nivin et al., 2001, 2002, 2003; Marks et al., 2003, 2004; Potter et al., 2004; Halama et al., 2005; Beeskow et al., 2006; Schonenberger et al., 2006; Fig. 14). For Motzfeldt, Jones & Larsen (1985) suggested that there was a continuous evolution from a low-$T$, peralkaline, volatile-rich melt that formed the agpaitic rocks (SM6) to a hydrothermal solution containing excess sodium (e.g. Tuttle & Bowen, 1958; Khomyakov, 1995). This fluid would be an efficient agent for metasomatism, especially in the roof zone of the intrusion (Jones & Larsen, 1985). The action of such a fluid is evidenced, especially in SM1, by the presence of secondary aegirine–augite or aegirine and the common occurrence of late-stage calcite or cancrinite, which records a Na- and HCO$_3$-bearing fluid. Jones & Larsen (1985) assumed that these alteration fluids had trace element characteristics similar to those of the lujavritic melts and therefore enriched the altered synclines with some trace elements up to sub-economic values.

In the agpaitic rocks, fluid metasomatism led to destabilization of the agpaitic assemblage (eudialyte, aegirine, CH$_4$) and sodalite was replaced by analcime and nepheline by sodalite + analcime, comparable with the reactions described by Markl et al. (2001) for the Ilmaussaq intrusion. The alteration of eudialyte resembles the textures described from the nearby North Qoroq intrusion (Coulson, 1997), stabilizing miaskitic minerals such as zircon, allanite–Ce), natrolite, hematite and calcite (Fig. 3). Mitchell & Lifervich (2006) suggested that this alteration of a primary magmatic agpaitic to a miaskitic assemblage may be explained by changing pH (see Khomyakov, 1995; Markl & Baumgartner, 2002).

SUMMARY AND CONCLUSIONS

Magmatic and fluid evolution of the Motzfeldt intrusion

The chemical evolution of the various magmatic units of the Motzfeldt intrusion suggests one continuous crystallization sequence. Fe$^{2+}$-rich miaskitic mineral assemblages are followed by a late-stage Fe$^{3+}$-rich agpaitic mineral assemblage. Based on the Nd and O isotopic composition of mineral separates, both the miaskitic and the agpaitic rocks in the Motzfeldt intrusion appear to have been derived from the same magma source and show minimal signs of crustal contamination. Hence, their different mineralogical and geochemical evolution must be explained in terms of fluid/melt partitioning and/or magmatic differentiation processes. The Motzfeldt rocks formed at oxygen fugacities below the
Therefore, comparing the Ilmaussaq intrusion (the type locality of agpaitic melts, cancrinite) with the Motzfeldt intrusion formed from these very highly fractionated, late-stage melts. The syenites in the Motzfeldt intrusion are related to the high-temperature fluid phase was methane-dominated (Krumrei et al., 2007) and carbonates are absent at orthomagnatic conditions. Marks et al. (2003) showed that the granitic to syenitic Puklen intrusion crystallized at ~ΔFMQ ±0-0 to ~−2 and c. 800°C. Consequently, Puklen contains carbonate as a late-stage (alteration) product (Marks et al., 2003). No evidence of CO₂ was found in the fluid inclusions (Köhler, 2004). However, in syenitic samples, which crystallized at oxygen fugacities of ΔFMQ −0 to −2.3 (Marks et al., 2003), Köhler (2004) detected subordinate amounts of methane. In samples from the Puklen alkali granite, which formed at higher fO₂, only methane-free H₂O-NaCl fluid inclusions were observed. Grønnedal-Ika and Puklen lack any sign of agpaitic minerals such as eudialyte.

Globally, agpaitic rocks occur from early magmatic, as in the Ilmaussaq intrusion or Lovozero and Khibina (Kramm & Kogarko, 1994; Zaitsev et al., 1998), to hydrothermal stages of crystallization (agpaitic pegmatites; e.g. in Langenfeldsfjord, Tamazeght and Mont St. Hilaire; Brogger, 1890; Bouabdli et al., 1988; Horvath & Gault, 1990; Marks et al., 2008). We propose that these differences may be related to the T-fO₂ evolution of the respective intrusions. In this respect, it is interesting to note that in terms of fO₂ evolution during magmatic differentiation, Motzfeldt is similar to but slightly more reduced than the Puklen intrusion; this may be related to the stronger contamination effects detected in the Puklen melts (Marks et al., 2003). This slight change in redox (and crustal contamination) conditions to the more reducing side is just enough to allow the melt to enter the field of agpaitic mineral stability in the very last magmatic stage SM6. In the highly reduced Ilmaussaq intrusion, contrasts, eudialyte is found as an early crystallizing liquidi phase, which may be attributed to the reduced character.

This study demonstrates that fluid inclusion chemistry, particularly the speciation of a C–O–H fluid (CO₂ or CH₄) may serve as an excellent tracer for the redox conditions of the melt and help to understand the transition from miasitic to agpaitic rocks. The transition from miasitic to agpaitic rocks can be explained in terms of a continuous magmatic differentiation sequence in peralkaline systems. Several features are common to all agpaitic intrusions: (1) an extreme peralkaline composition, which causes the high solubility of trace elements such as Zr and other HFSE; these elements are complexed with Na and Si, forming the precursor species to the complex minerals of agpaitic rocks (eudialyte, rinkite); (2) an extremely long crystallization interval down to temperatures as low as 450°C; (3) redox reactions involving the speciation of Fe³⁺/Fe²⁺ and C (CO₂/CH₄); (4) no (or very late) exsolution of a characteristically methane-bearing fluid phase.

**Comparison with other intrusions**

On the basis of Nd and O isotope data, the source of the Motzfeldt magmas seems to be similar to that of the other Gardar intrusions (Ilmaussaq: Marks et al., 2004; Puklen: Marks et al., 2003; Grønnedal-Ika: Halama et al., 2005). Therefore, comparing the T-fO₂ conditions of the Motzfeldt rocks with those of other Gardar intrusions can reveal underlying mechanisms of alkaline to peralkaline magmatic differentiation (Fig. 14). The syenites in the Grønnedal-Ika complex crystallized at higher oxygen fugacities (~ΔFMQ +3 to +4; 700–900°C, Halama et al., 2005) where only CO₂-bearing phases are stable (carbonates, cancrinite). In contrast, Markl et al. (2001) showed that the Ilmaussaq intrusion (the type locality of agpaitic rocks) crystallized under very reduced conditions (~ΔFMQ −3 to −4); consequently, the stable low-temperature fluid assemblage to form. The similar fluid isotopic composition of the miaskitic and agpaitic rocks indicates that not only the minerals or rocks but also all the Motzfeldt fluids were derived from a similar source. Combining the carbon isotopic composition, which partially reflects a mantle origin, with the hydrogen and oxygen isotope compositions of the inclusion water, which imply a meteoric origin, a fluid mixing model best explains the fluid assemblage observed in the Motzfeldt rocks. This seems to be similar to the case of the South Greenland Ivigtut complex (Köhler et al., 2008) and at least the late-stage hydrothermal fluids in the Ilmaussaq intrusion (Graser et al., in press).

We suggest that the association of a reduced mineral assemblage (Fe³⁺-dominated minerals) and an oxidized fluid (CO₂, calcite) progressively changes during magmatic differentiation to an oxidized mineral assemblage (Fe³⁺-bearing; aegirine) and a reduced fluid (CH₄) in the last crystallizing rock unit (SM6). These changes are probably mainly driven by respeciation during temperature decrease and the increasing alkaline content of the melt. The lujavrites in the Motzfeldt intrusion formed from these very highly fractionated, late-stage melts.

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