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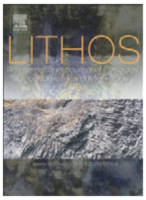

Isotope, major, minor and trace element geochemistry of late-magmatic fluids in the peralkaline Ilímaussaq intrusion, South Greenland☆

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The persodic, 1.16 Ga old Ilímaussaq intrusion consists of alkali granites, syenites, and agpaitic nepheline syenites. These rocks are cut by late-magmatic veins and lenses consisting of albite, aegirine, ussingite ($Na_2AlSi_3O_8(OH)$), fluorite, and occasionally quartz. Oxygen-isotope compositions of quartz indicates both orthomagmatic ($\delta^{18}O_{qtz}=8.5$‰) and country rock-influenced ($\delta^{18}O_{qtz}\sim10$‰) origin. While albite and aegirine do not contain fluid inclusions suitable for investigations, ussingite contains secondary hydrocarbon fluid inclusions, fluorite contains brine inclusions of primary and secondary origin with up to 26.3 wt.% $NaCl_{equiv.}$, and quartz contains predominantly secondary brine inclusions with up to 29.7 wt.% $NaCl_{equiv.}$ or CH_4–H_2O–NaCl mixtures. These fluids are interpreted to reflect fluids in equilibrium with late-stage melts at Ilímaussaq at ≤450 °C.

The carbon- and hydrogen-isotope composition of CH_4 in ussingite ($\delta^{13}C=-6$ to -3‰, $\delta D=\sim-121$‰) is indicative of a magmatic abiogenic origin. However, the isotopic composition of CH_4 in fluid inclusions in quartz veins resembles the signature of thermogenic CH_4 ($\delta^{13}C=-43$ to -23‰, $\delta D=-176$ to -121‰), but the higher hydrocarbons are mostly ^{13}C-depleted in relation to CH_4 (up to 7.3‰), which is typical of abiogenically-derived hydrocarbons.

Ion-chromatography of fluid inclusion leachates from the late-stage veins reveals Cl/Br ratios of ~100. As such values seem to be typical of peralkaline magmatic rocks, at least in the Gardar Province of South Greenland, it is suggested that this ratio is typical of Gardar magmatic fluids and may be characteristic of the Cl/Br ratio of the lithospheric mantle from which these alkaline melts are derived.

1. Introduction

Late-magmatic metasomatic processes in and around alkaline intrusions (e.g. Sørensen et al., 1974; Ranløv and Dymek, 1991; Boily and Williams-Jones, 1994; Finch, 1995; Sørensen and Larsen, 2001; Coulson, 2003; Salvi and Williams-Jones, 1996) are often responsible for the transport and enrichment of incompatible elements (e.g. Zr, REE, Nb or Ta, Salvi and Williams-Jones, 1990, 2006; Salvi et al., 2000). However, details of fluid unmixing, effect of redox conditions and fluid composition (e.g. H_2O–CO_2 vs. CH_4-dominated fluid), transport capability, metasomatic reactions and precipitation mechanisms are still poorly understood. Magmatic fluids in such systems may consist of H_2O–CO_2 or CH_4-dominated fluids depending on the redox state of the system (Petersilie and Sørensen, 1970; Markl et al., 2001; Potter et al., 2004; Nivin et al., 2005). Theoretical calculations (e.g. Ryabchikov and Kogarko, 2006) predict that at redox conditions close to the quartz-fayalite-magnetite buffer (QFM), a CO_2–H_2O fluid will produce significant amounts of CH_4 by simple closed-system cooling between 800 and 400 °C. On the other hand, a melt with redox conditions corresponding to QFM-3 will be in equilibrium with pure CH_4 at magmatic conditions of 900 °C and 1 kbar (Ryabchikov and Kogarko, 2006). Determining fluid production, chemical evolution and internal or external reactions in these late-stage fluids is therefore important to understand the transport and enrichment of incompatible elements in alkaline melts.

Studies on the peralkaline complexes of Khibina, Lovozero, and Kovdor in northwest Russia (Potter et al., 1998, 2004; Beeskow et al., 2006), and the Strange Lake Complex, Canada (Salvi and Williams-Jones, 1990, 1992, 1997, 2006), as well as the Ilímaussaq complex in Greenland (e.g. Konnerup-Madsen, 2001), indicate that hydrocarbon-bearing fluid inclusions are a typical feature of agpaitic rocks. The origin of these highly reduced fluids has been controversial. Petersilie and Sørensen (1970), Konnerup-Madsen and Rose-Hansen (1982), and Konnerup-Madsen (2001) proposed a late-magmatic reduction of a primary CO_2–H_2O fluid in the Ilímaussaq intrusion, while Salvi and Williams-Jones (1997), Potter and Konnerup-Madsen (2003), Potter et al. (2004), and Salvi and Williams-Jones (2006) proposed a Fischer-Tropsch (FT)-type reaction in the Strange Lake complex, Canada, and the

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☆ Contribution to the mineralogy of Ilímaussaq No. 137.
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Khibina and Lovozero complexes, Russia. Both models require a primary magmatic CO_2-rich fluid, which is later reduced to methane and higher hydrocarbons. However, neither in Ilímaussaq nor in Khibina have remnants of a CO_2-rich fluid been found in the quantities one would expect if such models were applicable (e.g. Beeskow et al., 2006). Furthermore, a CO_2-rich fluid is not stable at the low fO_2 conditions in the Ilímaussaq (QFM-2 to -5; Markl et al., 2001) and Khibina magmas (close to QFM; Ryabchikov and Kogarko, 2006). Furthermore, Krumrei et al. (2007) recently demonstrated that at least some of the hydrocarbon-rich fluid inclusions in the core of large sodalite crystals in the Ilímaussaq intrusion are of primary high-temperature magmatic origin and Beeskow et al. (2006) described primary inclusions in nepheline from rocks in the Khibina intrusion.

In this study, we investigate the geochemistry of hydrocarbon- and water-bearing fluids entrapped during late-magmatic stages of the highly reduced, agpaitic Ilímaussaq complex. Most of the veins in the Ilímaussaq complex are silica undersaturated, quartz-bearing ones are rare. The fluids were investigated in the available minerals most suitable for inclusion studies, which are quartz, fluorite and ussingite, by using petrography, microthermometry, laser-Raman spectroscopy, ion-chromatography and gas chromatography-mass spectrometry. This study is restricted to late-magmatic phenomena and thereby augments the study of Krumrei et al. (2007), who described early, high-temperature fluids in Ilímaussaq, and extends earlier studies by Konnerup-Madsen (1980, 2001), Konnerup-Madsen and Rose-Hansen (1982), and Konnerup-Madsen et al. (1979, 1988), who investigated fluid inclusions in late-magmatic to hydrothermal Ilímaussaq veins, but did not constrain their geochemical composition in terms of major, minor and trace elements.

2. Geological setting

The 1.16 Ga Ilímaussaq intrusive complex belongs to the Gardar failed rift province, South Greenland (Upton and Emeleus, 1987; Krumrei et al., 2006). During a period of ~200 Ma, ten major and several minor intrusions were emplaced in the granitic Julianehåb batholith. The mantle melts parental to the Ilímaussaq magmas were emplaced at 3 to 4 km depth (Konnerup-Madsen and Rose Hansen, 1984; Larsen and Sørensen, 1987) into early Proterozoic Ketilidian (1.7–1.8 Ga) basement granites and sandstones and basalts of the late-Gardar Eriksfjord Formation (Fig. 1; Poulsen, 1964).

The rocks show a strong fractionation trend of an initially silica-saturated alkaline magma towards silica-undersaturation. Four magma batches intruded successively producing first an alkaline, barely silica-saturated augite syenite, second a peralkaline granite, and finally two sets of silica-undersaturated agpaitic nepheline syenites (Fig. 1; Sørensen et al., 2006; Krumrei et al., 2007). The agpaites form the major part of the intrusion and are divided into sodalite foyaite and naujaite of stage three, and the layered kakortokites and the lujavrites of stage four. All of them are texturally different varieties of nepheline or sodalite syenites consisting of nepheline, sodalite, eudialyte, alkali feldspar, arfvedsonite, and aegirine in various proportions. The lujavrites are believed to be the main source of late-stage fluids, which led to the formation of Na-rich veins in all other rock types (Engell et al., 1971). The late-magmatic to hydrothermal veins are commonly peralkaline and silica undersaturated and contain aegirine, arfvedsonite, albite, analcime, ussingite, or rare Be-silicates like chkalovite or tugtupite (Engell et al., 1971). In rare cases, aegirine-quartz veins are found in both the augite syenite in the southern part of the intrusion and in the alkali granite in the northern part. The veins are a few millimetres to several centimetres thick and up to several metres long. Some veins occur in faults or cracks, others formed by fluid-rock interaction between Na-rich autometasomatic hydrothermal fluids and Ilímaussaq rocks (Markl and Baumgartner, 2002). Depending on the rock type the fluid reacted with, the fluid could evolve completely differently with regard to pH and salinity and, hence, could precipitate variable mineral assemblages (Markl and Baumgartner, 2002). Previous studies indicate vein formation temperatures between 200 to 500 °C at 1 kbar for various types of these veins (Sobolev et al., 1970; Konnerup-Madsen and Rose-Hansen, 1982; Markl, 2001; Markl and Baumgartner, 2002).

3. Previous work on fluid inclusions in Ilímaussaq

A variety of studies have dealt with fluids and fluid-rock interaction processes in alkaline rocks of the Gardar Province and especially the Ilímaussaq igneous complex (Sobolev et al., 1970; Petersilie and Sørensen, 1970; Konnerup-Madsen, 1980, 1984, 2001; Konnerup-Madsen and Rose-Hansen, 1982, 1984; Konnerup-Madsen et al., 1979, 1981, 1985, 1988; Larsen and Sørensen, 1987; Markl and Baumgartner, 2002; Schönenberger et al., 2006; Krumrei et al., 2007). These studies revealed a complex mineralogical and fluid compositional evolution in Ilímaussaq. The Ilímaussaq alkali granite contains moderate to highly saline aqueous inclusions (Konnerup-Madsen, 1984). However, inclusions in an associated alkali-granitic vein in a sandstone xenolith contains predominantly CH_4 with traces of CO_2, C_2H_6, and H_2S (Konnerup-Madsen and Rose-Hansen, 1984; Konnerup-Madsen et al., 1985).

In the nepheline syenites and their veins, CH_4 is the dominant volatile component (Konnerup-Madsen, 2001). The hydrocarbon inclusions are secondary, commonly aligned in healed fractures. Aqueous and mixed hydrocarbon-aqueous inclusions are scarce and occur in isolated patches. Hence, the aqueous inclusions are thought to be trapped earlier than most of the hydrocarbon inclusions. In hydrothermal vein minerals (e.g. chkalovite, $Na_2BeSi_2O_6$), the association of hydrocarbon-rich and highly saline aqueous inclusions indicates the simultaneous entrapment of immiscible fluids (Konnerup-Madsen and Rose-Hansen, 1982). Previous carbon-isotope studies of the gases in the vein fluid inclusion assemblages support an abiogenic origin for the CH_4 (−6 to −1‰; Konnerup-Madsen et al., 1988).

4. Localities and sample description

We investigated fluid inclusions in quartz, ussingite, and fluorite from veins and lenses distributed throughout the complex (Fig. 1). Quartz-bearing veins and lenses are rare in the Ilímaussaq intrusion, found in alkali granite, augite syenite, and in xenoliths (the latter investigated by Konnerup-Madsen and Rose-Hansen, 1982). The quartz veins studied by us come from within the augite syenite unit from the southern part of the complex (Fig. 1; samples ILM4, IlM169, ILM170 and KH2). The veins strike parallel to the contact and the intrusion's margin. Anhedral to euhedral quartz is either the main component of the veins, separated from the augite syenite by a seam of albite, aegirine, and occasionally amphibole, or it occurs intergrown with these minerals (sample KH2). In thin section, calcite is also visible in sample KH2. It occurs interstitially and is intergrown with the other minerals. Aegirine-albite veins lacking quartz are also present. One additional sample of a pure quartz vein (sample ILM190) comes from the alkali granite on the southwest slope of the Nakkaalaaq mountain in the northern part of the complex (Fig. 1).

The ussingite samples come from the north coast of the Tunulliarfik fjord (Fig. 1; GM1246, GM1382 and GM1384) and occur as metre-sized lenses in naujaite autoliths in lujavrites (Engell et al., 1971). The ussingite most probably formed during late-magmatic fluid-rock interaction as described by Markl and Baumgartner (2002).

Three samples of fluorite were taken (i) from the foot of the Nakkaalaaq mountain (ILM77) where the fluorite occurs as disseminated, mm-sized grains in a zone of altered naujaite, (ii) close to lake Taseq (ILM99), where it occurs as small flakes in association with late-magmatic to hydrothermal albite, and (iii) at Appat (ILM325), occurring as cm-sized masses in altered naujaite (Fig. 1). These