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Halogen and trace-element chemistry in the Gardar Province, South Greenland: Subduction-related mantle metasomatism and fluid exsolution from alkalic melts

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ABSTRACT

XRF analyses of 152 magmatic dyke samples from a broad area (150 × 60 km) of the Gardar Province in Southern Greenland span the time 1280 to 1163 Ma and represent a wide compositional range (transitional olivine basalts to trachytes, alkalinity index of 0.3 to 1.5). Among those, 16 dyke samples were additionally analysed for Cl and Br.

Generally, the dykes represent a continuous fractionation trend from relatively unfractionated basalts to more highly fractionated trachytes. Dykes from different areas exhibit a diverse geochemistry suggesting a heterogeneous and metasomatised mantle source. Enrichment in LILE, LREE and Sr and depletion in HFSE, Nb and Ti suggest that some of the metasomatism may have been associated with subduction processes pre-dating Gardar activity by some 600 Ma (Ketilidian orogeny).

The dykes are characterised by high F contents up to 1.2 wt.%, particularly in the vicinity of the Ivigtut fluoride deposit. F was probably derived from partial melting of lithospheric mantle enriched in F-apatite and F-phlogopite. High Cl/Br (>500) and low Cl/F (<1) ratios of the dykes point to a fluid degassing/separation process which is supported by mineral/rock and fluid inclusion data from the Ilímaussaq and Ivigtut intrusions. There, the analysed rocks and minerals generally show high Cl/Br (>300) and low Cl/F (<1) weight ratios whereas the fluid inclusions have complementary low ratios (Cl/Br ±100; Cl/F >10). Our investigations are in accordance with experimental data which show that F is preferentially enriched in the melt whereas Cl and especially Br are lost with the fluid phase. Accordingly, the halogens show an increase in incompatible behaviour in the magma in the order of F<Cl<Br.

1. Introduction

Halogens (F, Cl, Br) are useful geochemical tools and can provide constraints on the genesis of plutonic and volcanic rocks and their fluid evolution (Sigvaldason and Óskarsson, 1986; Kullerud, 1996; Markl and Schumacher, 1996; Bureau et al., 2000). Among the halogens, F is most soluble in (alumino)silicate melts (>10 wt.%) (Webster, 1990; Carroll and Webster, 1994). It generally remains in the residual magma and eventually enters hydroxyl-bearing minerals (Candela, 1986; Edgar et al., 1996). Of all rock types, alkaline rocks have the highest F content which increases with peralkalinity index [molar (Na + K)/Al] (Bailey, 1977). In alkaline magmas, F forms bonds with alkali elements rather than with Si or Al (Kogarko, 1974; Kogarko and Ryabchikov, 1978) and may even generate fluoridic alkaline melts which show immiscibility with a silicate melt (Bailey, 1977; Veksler, 2004; Dolejš and Baker, 2007a,b). In addition, F may play a crucial role in complexation processes in fluids and in the transport of ore-forming elements such as Li, Be, Sn and HFSE (Pan and Fleet, 1996; Salvi et al., 2000; Williams-Jones et al., 2000; Tagirov et al., 2002; Wood, 2003).

Cl can be highly concentrated in melts, but especially in fluids (e.g. Carmichael et al., 1974; Metrich and Rutherford, 1992; Lowenstern, 1994; Bailey et al., 2001). Cl solubilities in aluminosilicate melts vary from a few thousand ppm to more than 4 wt.% in peralkaline systems (Metrich and Rutherford, 1992; Bailey et al., 2001; Webster and DeVivo, 2002; Carroll, 2005). Cl is commonly lost from magmas either through degassing or partitioning into aqueous fluids (Nijland et al., 1993; Carroll and Webster, 1994). During late magmatic stages, a Cl-rich aqueous phase or even a salt melt may separate (Carmichael et al., 1974; Lowenstern, 1994).

Br data may be used to constrain magmatic degassing (e.g. Villemant et al., 2008; Bureau and Métrich, 2003). The high potential solubility of Br in silicate melts also makes it a sensitive tracer of the interaction of a magma with seawater or other Br-rich material (Bureau and Métrich, 2003).

Finally, the combination of these halogens, i.e. using their ratios (Cl/Br; Cl/F), allows investigation of the relation of samples to certain reservoirs in detail (primitive mantle, crust, sea water; Dreibus et al.,

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1979; Bottomley et al., 2005) and can provide helpful constraints on the unmixing of a fluid phase from a magma, fluid–fluid or fluid–rock interactions (e.g. Villemant and Boudon, 1999; Bureau et al., 2000; Bureau and Métrich, 2003). However, until now, very few data especially on the Br concentration in rocks exist.

Therefore, this study combines halogen data from whole-rock samples as well as fluid inclusion data from the literature in order to obtain information on magmatic- and fluid-evolution processes in natural samples.

For these purposes, rocks from the Gardar Province are particularly suited for a detailed halogen analysis. The Gardar Province hosts (or hosted, prior to its exploitation) the world's largest fluoride deposit at Ivigtut (Pauly and Bailey, 1999). The importance of F in the petrogenesis of the Gardar magmas has been highlighted by Upton and Emeleus (1987) and Upton et al. (2006) and recent publications provide the first insights into the halogen contents of the Gardar rocks and fluids (Bailey et al., 2001; Krumrei et al., 2007; Köhler et al., 2008; Graser et al., 2008; Schönenberger and Markl, 2008). In order to provide more quantitative data on the subject of halogens in the Gardar magmas, 152 samples of dykes were investigated. The majority of these are of relatively unfractionated basaltic dykes, sufficiently fine-grained as to reflect compositions of the host magmas. Furthermore, the majority of the dykes crystallised under pressures sufficiently high to prevent vesiculation.

The results help us to understand the timing, distribution, source and significance of halogen enrichment and distribution in the Gardar rocks and their sources, particularly the sub-continental mantle.

Throughout the present article, the 1980s revised spelling of Greenlandic place names is use. However, traditional geological spelling is used for stratigraphic names (e.g. igneous intrusions).

2. Geology

The Gardar Province in South Greenland is situated across the Archaean craton in the north and the Ketilidian mobile belt in the south (Fig. 1). The Gardar Province represents a failed rift structure where magmatic activity lasted from 1350 to 1160 Ma (Blaxland et al., 1978). The country rocks mainly consist of the calc-alkaline, 1855–1795 Ma old Julianehåb batholith (Garde et al., 2002) which was intruded by 12 major alkaline igneous complexes. Among the earliest Gardar rocks are those of the syn-rift Eriksfjord Formation (>1280 Ma) comprising clastic sediments and lavas.

All over the province, numerous dyke swarms of different ages and highly variable chemical composition traverse the basement rocks. The oldest, WNW–ESE trending dykes are called “Brown Dykes” (BD 0) due to their brown alteration colour. Their composition ranges from lamprophyric to (trachy)doleritic and gabbroic (Upton and Emeleus, 1987; Goodenough, 1997). The BD 0 have an average U–Pb age of 1280 Ma and are succeeded by the “Giant Dykes” (GD) which are younger than 1200 Ma (Upton et al., 2003). The GD follow an ENE–WSW trend, have a width of 200–800 m and are mainly concentrated in the area around Nunarsuit–Isortoq and on Tuttutoq. The latter comprises the Older and Younger Giant Dyke Complexes (OGDC and YGDC, respectively; Upton, 1962; Upton and Thomas, 1980; Martin, 1985). The OGDC has an age of 1184 ± 5 Ma and acted as a precursor to the larger, 1163–1166 Ma old YGDC (Upton et al., 2003). Generally, the GD are composed of augite syenite, quartz syenite and alkali granite. Where they are composite, the dykes have a mafic (gabbroic) margin and a salic centre (Upton and Emeleus, 1987; Halama et al., 2004). Due to their broadness, the GD can be regarded as the transitional link between the dykes and the igneous complexes (Upton and Emeleus, 1987).

It has been known for a long time, that halogens were important components of the Gardar magmas. The extraordinary concentration of F at Ivigtut in the western part of the Province has been apparent since Hans Giesecke's investigations some two hundred years ago. A small, A-type granite stock, ~350 m in diameter, hosted a zoned pegmatite deposit largely composed of about 12 million tons of cryolite (Na_3AlF_6) and siderite (Pauly and Bailey, 1999; Goodenough et al., 2002; Köhler et al., 2008) before it was mined out by 1962. In the

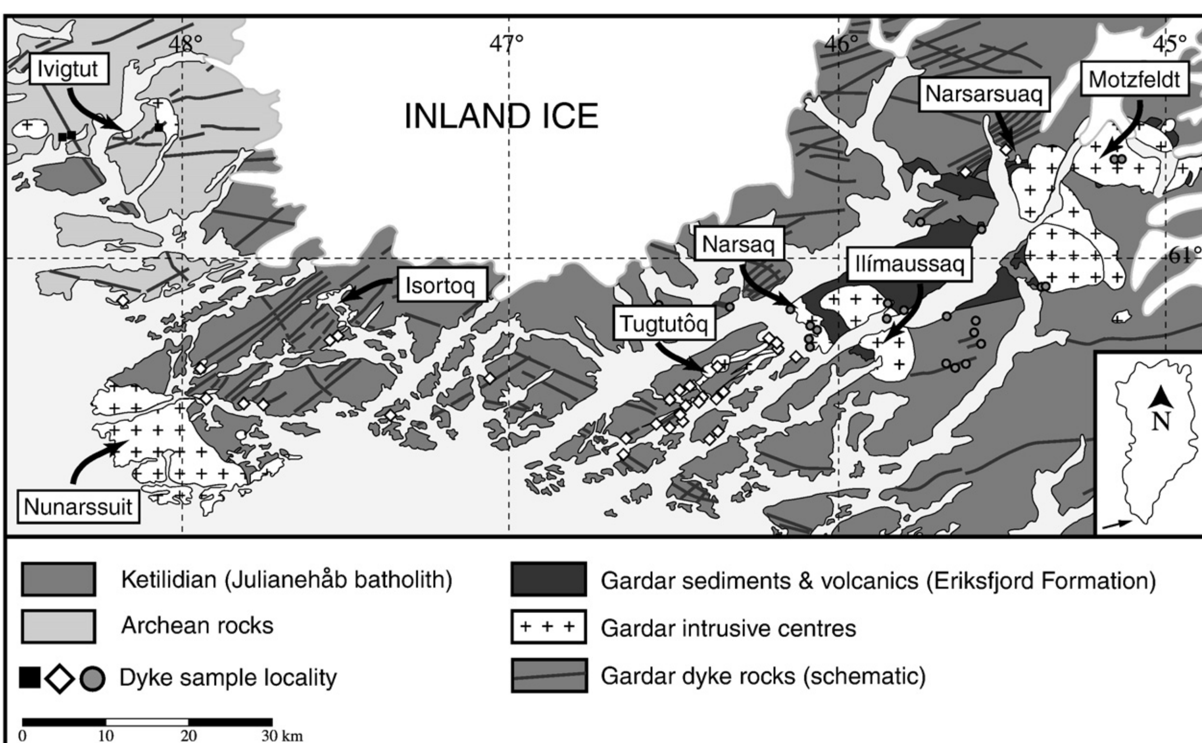

Fig. 1. Overview of the Gardar Province and the localities of the analysed dykes (except for Ivittuut) with respect to the different intrusive complexes. Map modified after Escher and Watt (1976). [rhomb: TuIsNunNar = Tuttutoq–Isortoq–Nunarsuit–Narsarsuaq; circle: IlmNarsMotz = Ilimmaasaq–Narsaq–Motzfeldt; square: Ivittuut].