Equilibrium partitioning and subsequent re-distribution of halogens among apatite–biotite–amphibole assemblages from mantle-derived plutonic rocks: Complexities revealed

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ABSTRACT

The concentration of halogens in apatite, biotite and amphibole is investigated for a large variety of mantle-derived plutonic rocks (gabbros, diorites, monzonites, olivine- and pyroxene-bearing monzonitic to granitic rocks, syenites, carbonatites and a phoscorite). In all rocks studied, apatite occurs as an early magmatic phase, whereas biotite and amphibole may occur either as a late magmatic phase or as late-stage, potentially hydrothermal product replacing precursor olivine, pyroxene and Fe–Ti oxides (ilmenite and magnetite).

Based on electron microprobe analyses for F and Cl and detailed textural observations, we test existing models of halogen partitioning between apatite and biotite. Bromine concentration data for apatite, biotite and amphibole are used to further refine our understanding of the geochemical similarities and differences between Cl and Br during magmatic and hydrothermal processes.

Our data suggests that F and Cl contents in apatite, biotite and amphibole can indeed be useful monitors of the halogen systematics in magmas, but they may also be subject to post-magmatic changes to variable extents. The relatively small radius and compatible F cation seems to be less prone to post-magmatic alteration and is likely to best reflect the original magmatic halogen abundances — especially in apatite. However, the larger and probably more incompatible Cl anion, is more easily re-mobilized as reflected by strong redistribution of Cl in biotite and amphibole which have been clearly overprinted by hydrothermal fluids. In certain cases, the ability of halogens to re-distribute themselves after magmatic equilibrium partitioning (as emphasized by our data) suggests that observed partitioning (especially between apatite and biotite) may also be used as a very sensitive indicator for post-magmatic hydrothermal processes.

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1. Introduction

Halogens (F, Cl and Br) influence the physical properties of natural melts (e.g., density, viscosity and crystallization temperature) and are important for many magmatic and hydrothermal processes such as the transport of metals in melts and hydrothermal fluids. Their potential environmental impacts are related to volcanic eruptions due to the release of these elements into the atmosphere (see the recent reviews of Aiuppa et al., 2009; Pyle and Mather, 2009).

In most plutonic rocks apatite, micas and amphibole are the major halogen-bearing phases (e.g., Speer, 1984; Markl and Piazolo, 1998; Piccoli and Candela, 2002; Zhang et al., 2012; Teiber et al., 2014), although titanite, fluorite, topaz, epidote, sodalite or scapolite may be important in some cases (Breiter and Siebel, 1995; Teertstra and Sherriff, 1997; Förster

et al., 1999; Frost et al., 2000; Frindt et al., 2004; Gieré and Sorensen, 2004; Krumrei et al., 2007; Gioncada et al., 2014). Because of the similar ionic radii of F$^-$ (1.33 Å; Shannon, 1976) and OH$^-$ (1.32–1.37 Å), F$^-$ is much easily incorporated into OH-bearing minerals than the larger Cl$^-$ (1.81 Å) and Br$^-$ (1.95 Å). Consequently, in mineral-melt systems, F is less incompatibly during magmatic differentiation than the heavier halogens Cl and Br (e.g., Pyle and Mather, 2009). Furthermore, in melt-fluid systems, Cl and Br preferentially partition into the fluid phase, whereas F is largely retained in the melt, resulting in the fractionation of F from Cl and Br during fluid-present magmatic processes (e.g., Fuge, 1977; Webster and Holloway, 1990; Carroll and Webster, 1994; Villemant and Boudon, 1999; Bureau et al., 2000; Webster et al., 2009; Wang et al., 2014a).

Several studies have addressed the partitioning of F and Cl in melt-mineral-fluid systems and models have been developed to reconstruct F and Cl concentrations in melts and fluids using the halogen contents in apatite, biotite and amphibole to monitor the process (e.g., Stormer and

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Carmichael, 1971; Westrich, 1981; Munoz, 1984; Volfinger et al., 1985; Zhu and Sverjensky, 1991, 1992; Brenan, 1993; Icenhower and London, 1997; Villemant and Boudon, 1999; Piccoli and Candela, 2002; Mathez and Webster, 2005; Boyce and Hervig, 2008; Chevychelov et al., 2008; Webster et al., 2009; Patiño Douce et al., 2011; Zhang et al., 2012; Teiber et al., 2014). These studies show that F and Cl contents in apatite, biotite and amphibole are governed by several factors such as, melt composition, crystallization temperature, the presence of a fluid phase and the major element composition of biotite and amphibole. These factors are commonly interconnected, since relatively primitive rocks (e.g., gabbros) normally have relatively high Mg contents and crystallize at higher temperatures compared to more evolved rocks such as many granites. As a result the respective Mg-numbers of hydroxyl-bearing silicates may influence their ability to incorporate halogens in these two different magma types. Also, the degree of differentiation of a melt governs the relative abundance of F and Cl to a certain extent, Cl becoming relatively depleted compared to F during late-magmatic or hydrothermal stages due to its strong affinity for an evolving fluid phase (e.g., Zhang et al., 2012). Finally, it has been suggested that halogens may be re-distributed between apatite and hydroxyl-bearing silicates as a consequence of late-stage or post-magmatic hydrothermal fluid circulation (e.g., Brenan, 1994; Willmore et al., 2000; Teiber et al., 2014). Despite these potential complexities, studies generally show that F/OH and Cl/OH ratios are normally higher in apatite than in biotite and amphibole from the same rock. Also, amphibole tends to display higher F/OH than associated biotite, but for Cl/OH ratios to not show such a clear relationship (e.g., Stormer and Carmichael, 1971; Ekström, 1972; Westrich, 1981; Volfinger et al., 1985; Léger et al., 1996; Zhang et al., 2012; Teiber et al., 2014). Br is present at much lower concentrations than F & Cl, and there is little data for the distribution of this element, mainly due to analytical limitations (Ionov et al., 1997; O'Reilly and Griffin, 2000; Marks et al., 2012; Teiber et al., 2014; Wang et al., 2014b).

In the present study we have carefully measured the distribution of halogens (F, Cl and Br) between apatite, biotite and amphibole for a range of plutonic rocks including gabbros, diorites, monzonites, olivine- and pyroxene-bearing monzonitic to granitic rocks, syenites, carbonatites and a phoscorite. All rocks contain magmatic apatite that is clearly formed at an early stage in the crystallization sequence. Biotite and amphibole occur as subhedral to euhedral, probably magmatic phases and/or as texturally late overgrowths and reaction rims around orthomagmatic olivine and Fe–Ti oxides and/or as a replacement of pyroxene. This diversity allows us to investigate (i) the general applicability of existing halogen partitioning models between apatite and biotite and (ii) the potential susceptibility to alteration of magmatic halogen distribution patterns between apatite and hydroxyl-bearing silicates under late-magmatic to hydrothermal conditions during the final cooling of plutonic rocks. The combination of detailed textural observations with halogen distribution systematics allows us to distinguish the various episodes of halogen mobilization and the "footprint" of such events in the various minerals. Interpretation of these events is a prerequisite for modeling halogen distribution for an evolving magmatic-hydrothermal system.

2. Material and methods

The rock samples studied here are from five different localities. Selection was based on the abundance of apatite and most of them were previously investigated in previous petrological and geochemical studies (Table 1). Here we provide brief descriptions of geological settings and textures with a main focus on apatite, biotite and amphibole. A more detailed classification of apatite, biotite and amphibole group minerals is provided in Table 2.

2.1. Mont Saint-Hilaire

The Mont Saint-Hilaire complex (Canada) is one of many Cretaceous intrusive complexes of the alkaline Monteregian Hills Province and consists of gabbros, diorites and foid syenites, that crystallized from partial melts of an OIB-type mantle source (e.g., Eby, 1985; Currie et al., 1986; Foland et al., 1988; Darbyshire et al., 2007; Schilling et al., 2011b).

We investigate two gabbroic (MSH17 and 18) and three dioritic (MSH12, 75 and 119) samples, which contain variable amounts of plagioclase, alkali feldspar, nepheline, olivine, clinopyroxene, Fe–Ti oxides, apatite, amphibole and biotite. Typical accessories are baddeleyite/ zircon and pyrrhotite (Table 1). Apatite occurs in all samples as sub- to euhedral inclusions (20–300 μm) in orthomagmatic olivine, clinopyroxene and Fe–Ti oxides. Where present, biotite and amphibole appear as mm sized, subhedral grains (presumably magmatic) and as texturally late, fine-grained reaction rims around Fe–Ti oxides in contact with feldspar and in places intergrown with each other. Amphibole further occurs as replacement of pyroxene (Fig. 1a–c).

2.2. Ilímaussaq

The Ilímaussaq complex (South Greenland) is part of the Mid-Proterozoic alkaline Gardar Province. Its major rock units comprise augite syenites, peralkaline granites and nepheline syenites. Melting of lithospheric mantle followed by prolonged fractionation processes is assumed to be responsible for the origin of these rocks (e.g., Larsen and Sørensen, 1987; Marks and Markl, 2001, in press; Marks et al., 2004a,2004b; Upton, 2013).

Five samples of augite syenite were chosen for this study, representing a traverse from the fine-grained margin (GM1858) towards the central part of the complex (GM1333, 1332, 1330 and 1857; see details in Marks and Markl, 2001; Zirner et al., submitted). They consist of apatite, alkali feldspar ± nepheline, olivine, clinopyroxene, Fe–Ti oxides, amphibole and biotite along with accessory baddeleyite/zircon, and pyrite ± pyrrhotite. All samples contain euhedral apatite (50–700 μm) enclosed in alkali feldspar, olivine, clinopyroxene, Fe–Ti oxides, amphibole and biotite (Fig. 1d–f). Brown amphibole occurs as poikilitic grains up to 3 mm in size, usually associated with alkali feldspar, apatite and Fe–Ti oxides (Fig. 1f). Red amphibole is present as a replacement of clinopyroxene and as fine-grained reaction rims around Fe–Ti oxides (in the latter case often associated with fine-grained biotite). A green amphibole forms and overgrows on olivine, and in places is intergrown with tiny biotite flakes (Fig. 1g–i).

2.3. Ardnamurchan

The Ardnamurchan complex (Scotland) is part of the Paleogene North Atlantic magmatic province and mainly consists of gabbroic and monzonitic rocks. The rocks formed by combined fractional crystallization of a tholeiitic magma and assimilation of country rocks (Walsh, 1975; Walsh and Henderson, 1977; Geldmacher et al., 1998; Emeleus and Bell, 2005; O'Driscoll, 2007).

For this study a monzonite (ARD16) and a quartz-monzonite (ARD17) were investigated in detail. Both rock samples consist of plagioclase, alkali-feldspar, quartz, Fe–Ti oxides and apatite. ARD16 contains additional clinopyroxene, amphibole and rare biotite. In contrast, ARD17 is rich in biotite but lacks amphibole. Apatite in both samples (10–300 μm) occurs as euhedral to subhedral inclusions in feldspars, Fe–Ti oxides and in biotite and amphibole, if present. Euhedral to subhedral biotite (up to several mm) in ARD17 (0.2–3 mm) and subhedral amphibole (0.2–1.5 mm) and rare subhedral biotite (0.2 mm) in ARD16 appear to be of magmatic origin (Fig. 1j and k). Additionally, ARD16 contains abundant fine-grained reaction rims of biotite surrounding Fe–Ti oxides (Fig. 1l).

2.4. Lofoten Islands

The Lofoten Islands (Norway) mainly consist of Proterozoic gabbroic, dioritic, as well as associated olivine- and (ortho-)pyroxene-bearing monzonitic to granitic rocks. For convenience, the latter are grouped