Lithos 288–289 (2017) 156–174

Contents lists available at ScienceDirect

Lithos

journal homepage: www.elsevier.com/locate/lithos

The amphiboles of the REE-rich A-type peralkaline Strange Lake pluton – fingerprints of magma evolution

Karin Siegel *, Anthony E. Williams-Jones, Vincent J. van Hinsberg

Department of Earth and Planetary Sciences, McGill University, 3450 University St., FDA, room 238, Montréal, QC H3A 0E8, Canada

A R T I C L E I N F O

Article history:
Received 16 March 2017
Accepted 14 July 2017
Available online 20 July 2017

Keywords:
Amphibole
REE
Strange Lake
Peralkaline granite
Magma evolution

A B S T R A C T

Major and trace element compositions of amphibole in igneous environments commonly reflect evolving magma compositions. In this study, we use the amphibole-group minerals from the Strange Lake, REE-enriched peralkaline granitic pluton to gain insights into the evolution of the magma. This 1240 Ma old pluton consists of two main intrusive facies, an early hypersolvus granite, which occurs as separate northern and southern intrusions, and a more evolved transsolvus granite. In the hypersolvus granite the amphibole is a late interstitial phase, whereas in the transsolvus granite, it is present as phenocrysts. The amphibole compositions vary from calcic–sodic (ferro–ferri-katophorite) in the southern hypersolvus granite to sodic (arfvedsonite, ferro–ferri-leakeite) in the other, more evolved granitic units. High Na, Si, Li, and low Al and Ca concentrations in the amphibole phenocrysts of the transsolvus granite indicate formation from a more evolved magma compared to the hypersolvus granite, despite the fact that these crystals formed early. We interpret the increasing Fe^{3+}/Fe^{2+} ratios in the amphibole of the hypersolvus granite to reflect crystal chemical effects (Na/Ca-ratio) and increasingly oxidizing conditions in the magma, whereas in the phenocrysts of the transsolvus granite, the increasing ratio was the product of increasing proportions of F^- and OH^- in the melt. The amphiboles of all the granite units have elevated Nb, Zr, Hf and REE concentrations compared to the bulk rock, suggesting that these elements are compatible in amphibole. By contrast the much lower Ti concentration was due to saturation of the magma in sodium-titanosilicates. The amphibole REE concentrations vary greatly among the granite units. Amphibole of the southern and northern hypersolvus granite contains 0.16 and 0.07 wt.% $\sum$REE + Y, on average, respectively, and in the transsolvus granite, the average $\sum$REE content is only 0.01 wt.%, despite the more evolved nature of its host transsolvus granite. We intrepret this compositional difference to be due to the fact that the latter represents phenocrysts, which crystallized early, whereas the hypersolvus arfvedsonite is a late interstitial phase. Chondrite-normalized REE profiles emphasise the wide range in LREE-, and the narrow range in HREE-concentrations of the amphiboles. The variations in the LREE-profiles reflect the variable crystallization of primary LREE-bearing phases, including monazite-(Ce), pyrochlore group minerals and gagarinite-(Ce), prior to or contemporaneous with the amphibole, as well as the exsolution of a LREE-rich fluoride melt. The LREE are incompatible in the amphibole structure (apparent $D < 0.01$) and are preferably accommodated by the octahedral C-site, whereas the HREE occupy the B-site. The chondrite-normalized HREE profiles are steep and display an increasing relative enrichment that culminates in compatible behavior for Yb and Lu (apparent $D > 1$). Owing to their small ionic radius and their compatibility with the amphibole structure, HREE concentrations were more controlled by partitioning (crystal chemical effects) than by the concentrations in the corresponding magma. Large proportions of the bulk HREE content (up to 70%) reside in the amphibole, and their later release through hydrothermal replacement helps to explain the extreme and unusual HREE enrichment of the Strange Lake pluton.

1. Introduction

Our understanding of the genesis of intra-plate rift-generated intrusions that produce A-type granites is still incomplete. In particular, the reasons for the extremely high REE-, F- and other HFSE-concentrations in many of these peralkaline rocks are poorly known. In addition to the need for a highly fertile magma source, magmatic evolution by fractional crystallization appears to play a critical role in the enrichment of these elements (e.g., Kovalenko et al., 1995; Mungall and Martin, 1996). The chemistry of a major mineral, such as amphibole, which adapts to its *P*–*T*–*X* environment, and is capable of hosting most cation sizes and charges, can potentially record this and any other processes

* Corresponding author.
E-mail addresses: karin.siegel@mail.mcgill.ca (K. Siegel), ae.williams-jones@mcgill.ca (A.E. Williams-Jones), vincent.vanhinsberg@mcgill.ca (V.J. van Hinsberg).

http://dx.doi.org/10.1016/j.lithos.2017.07.012

that might have operated in the magma chamber. As a phenocryst, the amphibole would record the conditions prior to intrusion, and as a late crystallizing phase, the in-situ crystal fractionation processes.

The well-known ability of minerals of the amphibole super-group to accommodate a wide variety of elements with highly variable ionic radius and charge, including alkali elements, high field strength elements (HFSE) and the rare earth elements (REE), makes it an ideal monitor of magma evolution (Abdel-Rahman, 1994; Marks et al., 2004). In this study, we use the occurrence and composition of amphibole-group minerals in the Strange Lake pluton, Québec–Labrador, Canada, to trace the evolution of a peralkaline granitic magma that is unusually enriched in the REE, Zr and Nb. This magma was the source of a large REE/HFSE resource (indicated resources: 278 million tons grading 0.93 wt.% REE_2O_3, 0.18 wt.% Nb_2O_5 and 1.92 wt.% ZrO_2; Quest Rare Minerals Ltd., 2012) that is currently being considered for exploitation. In this study, the Na, Ca, Li, Fe^{3+} and REE contents of the amphibole-group minerals are used to gain information on the composition of the magma and conditions prior to, during and after its emplacement. The results show that fractional crystallization of a perthitic alkali feldspar, gravity settling of REE-minerals and zircon as well as the exsolution of a LREE-rich fluoride melt played a major role in the evolution of the magma and in concentrating the ore elements. They also show that the amphibole-group minerals host a significant proportion of the REE, and were the principal carriers of the HREE in some parts of the pluton.

2. Background information

A number of studies have traced evolutionary trends in alkaline rock suites using the crystal chemistry of the dominant mafic minerals (Davidson, 1982; Marks et al., 2004). In peralkaline rocks, which are defined by a molar excess of alkalis in respect to aluminum, the mafic minerals are usually of a sodic nature, e.g., amphiboles, such as arfvedsonite and riebeckite, or pyroxenes such as aegirine. The amphiboles of alkaline complexes generally trend from calcic through sodic-calcic to sodic members with differentiation, reflecting the increasing alkalinity of the melt from which they crystallized (Giret et al., 1980; Piilonen et al., 2013). They also display significant variations in REE and HFSE concentrations with magmatic differentiation, as shown, for example, by Marks et al. (2004) for the Gardar alkaline province (SW-Greenland). Similar conclusions have been reached for amphibole phenocrysts in alkaline basalts from the Rhine graben valley, Germany (Mayer et al., 2014).

Lithium has proven to be a particularly important constituent of alkali amphiboles (Camara et al., 2010; Hawthorne et al., 1993). Owing to its incompatible character in common rock-forming minerals, its concentration in amphibole may reflect the degree of melt differentiation. This case has been made for lithium-bearing amphiboles from Hurricane Mountain, New Hampshire, where the amphiboles vary from early Li-rich leakeite to late Li-poor riebeckite (Hawthorne et al., 1996). The progressive depletion in lithium in crystals growing into miarolitic cavities in granitic pegmatites is consistent with the idea that a highly evolved melt with a high Li content formed the earlier leakeite, and that progressive fluid exsolution resulted in the removal of lithium and the growth of Li-poor riebeckite.

The 1240 Ma Strange Lake pluton (Miller et al., 1997) is an extraordinary example of hyper- REE-, Zr-, and Nb-enrichment in a peralkaline granite, and is composed of a sequence of granitic intrusions, two earlier hypersolvus granites and a later transsolvus granite (this study). The last of these intrusions is host to numerous NYF-type pegmatites with extremely high concentrations of the REE, particularly the heavy REE (HREE), Zr and Nb. Most of the previous studies of the pluton have focused on the hydrothermal alteration and the rare-metal mineralized pegmatites (Gysi and Williams-Jones, 2013; Gysi et al., 2016; Kerr and Rafuse, 2012; Salvi and Williams-Jones, 1990, 1992, 1996, 1997, 2006; Vasyukova et al., 2016). Several studies, however, have addressed its magmatic evolution. Boily and Williams-Jones (1994) proposed that the REE-enrichment was due to a combination of fractional crystallization, and the heterogeneous distribution of F-rich residual melts, in which the REE and HFSE were transported as fluoro-complexes. Vasyukova and Williams-Jones (2014, 2016) provided evidence for the early separation of a REE- and Y-rich immiscible fluoride melt from the silicate melt, which accumulated in the highly evolved residual melts that formed the mineralized pegmatites.

Previous studies of the mafic minerals of the Strange Lake pluton concluded that the amphiboles are enriched in Li and Zn, are associated with Ti-silicates and crystallized under relatively low fO_2 (Pillet et al., 1993; Roelofsen, 1997). Hawthorne et al. (2001) showed that Li is an essential component of the amphiboles and identified lithian arfvedsonite and lithian manganoan arfvedsonite.

3. Geologic setting

The Strange Lake pluton is part of the Nain Plutonic AMCG suite, which comprises anorthosites, mangerites, charnockites and granites (Gower and Krogh, 2002; Miller, 1996). Rocks of the Nain suite were emplaced along the boundary between the Archean Nain province and the Archean to Early Paleoproterozoic Churchill province (Emslie et al., 1994), more recently referred to as the Core Zone (James and Dunning, 2000). The Nain Plutonic Suite covers an area of ~19,000 km^2, and was emplaced between 1460 and 1240 Ma, with the Strange Lake pluton (1240 ± 2 Ma) representing the youngest intrusive body (Gower and Krogh, 2002).

To the south and west, the Strange Lake pluton intrudes the Napeu Kainiut quartz monzonite, which is interpreted to represent a satellite body of the Mistastin batholith (Miller et al., 1997). The Napeu Kainiut intrusion, which is composed mainly of quartz, K-feldspar, plagioclase and biotite, also occurs within the Strange Lake pluton as xenoliths and large roof pendants. The Mistastin batholith consists of pyroxene- and fayalite-bearing Rapakivi-textured granites, which were cut by younger biotite-hornblende-bearing granites and minor syenitic intrusions, such as the Misery Lake syenite, which hosts abundant REE mineralization (Petrella et al., 2014). Dated at 1420 Ma (Emslie and Stirling, 1993), the Mistastin batholith represents one of the oldest members of the Nain Plutonic Suite. The other host rock to the Strange Lake pluton is an Archean to Paleoproterozoic gneiss complex belonging to the Core Zone (Churchill Province), comprising quartzofeldspathic augen–gneiss, banded biotite gneiss and minor garnet-bearing paragneiss and mafic gneiss.

3.1. The Strange Lake pluton

The circular (in outcrop), ~6 km in diameter, Strange Lake pluton is located on the border between Québec and Labrador, and consists of a sequence of alkaline granitic intrusive units (Fig. 1). The earliest phase of the pluton is a hypersolvus granite (Pillet et al., 1992), implying its formation at conditions above those for the alkali feldspar solvus (Tuttle and Bowen, 1958). The hypersolvus granite occurs in the center and southern part of the pluton, and has been subdivided into a northern and a southern unit, based on bulk rock and mineral compositional differences. The third major unit, formerly classified as subsolvus granite (Boily and Williams-Jones, 1994; Gysi and Williams-Jones, 2013; Salvi and Williams-Jones, 1996), is now classified as transsolvus granite, and contains perthite phenocrysts as well as separate albite and K-feldspar crystals in the groundmass. It occupies much of the pluton, and has been strongly affected by hydrothermal activity. A smaller, unaltered part of the transsolvus granite is exposed in the center of the pluton and provided the samples for this study. The transsolvus granite commonly contains dark grey, fine-grained ovoid enclaves and barren pegmatite pockets; the altered transsolvus granite is host to highly REE/HFSE-enriched pegmatites. A dark grey porphyritic microgranite with a fine-grained matrix occurs in contact with