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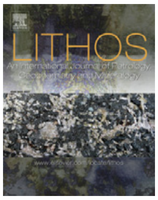

Chemical characteristics of zircon from A-type granites and comparison to zircon of S-type granites

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ABSTRACT

The trace element content in zircons from A-type granites and rhyolites was investigated by using back-scattered electron images and electron microprobe analyses. The studied Proterozoic (Wiborg batholith, Finland and Pará, Amazonas and Goiás states, Brazil) and Variscan (Krušné Hory/Erzgebirge, Czech Republic and Germany) plutons cover a wide range of rocks, from large rapakivi-textured geochemically primitive plutons to small intrusions of F-, Li-, Sn-, Nb-, Ta-, and U-enriched rare-metal granites. While zircon is one of the first crystallized minerals in less fractionated metaluminous and peraluminous granites, it is a late-crystallized phase in peralkaline granites and in evolved granites that may crystallize during the whole process of magma solidification. The early crystals are included in mica, quartz, and feldspar; the late grains are included in fluorite or cryolite or are interstitial. The zircon in hornblende–biotite and biotite granites from the non-mineralized plutons is poor in minor and trace elements; the zircon in moderately fractionated granite varieties is slightly enriched in Hf, Th, U, Y, and HREEs; whereas the zircon in highly fractionated ore-bearing granites may be strongly enriched in Hf (up to 10 wt.% HfO_2), Th (up to 10 wt.% ThO_2), U (up to 10 wt.% UO_2), Y (up to 12 wt.% Y_2O_3), Sc (up to 3 wt.% Sc_2O_3), Nb (up to 5 wt.% Nb_2O_5), Ta (up to 1 wt.% Ta_2O_5), W (up to 3 wt.% WO_3), F (up to 2.5 wt.% F), P (up to 11 wt.% P_2O_5), and As (up to 1 wt.% As_2O_5). Metamictized zircons may also be enriched in Bi, Ca, Fe, and Al. The increase in the Hf content coupled with the decrease in the Zr/Hf value in zircon is one of the most reliable indicators of granitic magma evolution. In the zircon of A-type granites, the Zr/Hf value decreases from 41–67 (porphyritic granite) to 16–19 (equigranular granite) in the Kymi stock, Finland, and from 49–52 (biotite granite) to 18–36 (leucogranite) in the Pedra Branca pluton, Brazil. In the in situ strongly fractionated Cínovec cupola (Erzgebirge), the Zr/Hf value decreases from 33–51 in the protolithionite granite at a depth of 1255 m to 7.5–25 in the zinnwaldite granite at a depth of 40 m. At the scale of individual crystals, the Zr/Hf value decreases from 86 to 68 from the cores to the rims of the zircons from the Teplice rhyolite and from 64 to 33 in the zircons from the biotite granite at Krupka, Erzgebirge. The contents of Hf and U in zircon are dependent mainly on the degree of granite fractionation and the nature and volume of the volatile phases and are independent of the A- or S-character of the parental melt. The zircon Zr/Hf ratios 55 and 25 are proposed to approximately distinguish common, moderately evolved and highly evolved granites. Zircons from the moderately and highly evolved granites of A- and S-type can be discriminated on the basis of their HREE content and the U/Th ratios. Nb, Ta, and W are present in zircon from the highly evolved granites from all studied areas, while high As, Bi, and Sc contents are typical only for the Erzgebirge.

1. Introduction

Zircon is an almost ubiquitous and relatively stable accessory mineral in the majority of types of granitoids and is often used for genetic considerations and geochronology (e.g., Hanchar and Hoskin, 2003, and references therein). In spite of its apparently simple chemical composition, $(Zr,Hf)SiO_4$, zircon is able to accept substantial amounts of a number of other minor and trace elements into its crystal lattice. Zircon crystals that are not affected by intense metamictization provide information about the chemical composition of the melt from which the granite crystallized. The metamictized crystals may accumulate substantial amount of nonformula elements adsorbed from hydrothermal and low-temperature fluids.

The routine use of electron microprobe analysis (EMPA) during the last 20 years has produced extensive data concerning the chemical composition of zircon (Breiter et al., 2006; Finch and Hanchar, 2003; Grimes et al., 2007; Hoskin and Schaltegger, 2003; Huang et al., 2002; Johan and Johan, 2005; Pérez-Soba et al., 2007; Pettke et al., 2005; Rubatto, 2002; Uher et al., 1998; Van Lichtervelde et al., 2009; Wang

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et al., 2000). However, in addition to Zr, Hf, and Si, only a few of the most abundant elements found in zircon, including U, Th, Y, some REE, Al, and Ca, are usually analyzed using this technique. Complete analyses for the 20 or more trace elements that contribute to the chemical composition of individual zircon grains are still scarce (Breiter and Škoda, 2012; Breiter et al., 2006, 2009; Förster, 2006; Förster et al., 2011; Uher et al., 2009). A broad trace element spectrum in zircon including the lower concentration elements may be obtained by using the LA-ICP-MS method (Belousova et al., 2002; De Liz et al., 2009; Nardi et al., 2012, 2013).

Although A-type granites have recently garnered more attention (cf. Bonin, 2007, 2008; Dall'Agnol and Rämö, 2009; Dall'Agnol et al., 2012; Frost et al., 2007; Rämö, 2005), especially for their potential rare-metal mineralizations (Bastos Neto et al., 2009; Bettencourt et al., 2005; Borges et al., 2009; Costi et al., 2009; Dall'Agnol et al., 2005, 2012; Haapala, 1995; Lamarão et al., 2012; Lenharo et al., 2002), the chemistry of zircon from these granites has not been reported extensively. It is also relevant to compare the characteristics of zircon found in A- and S-type mineralized granites to define an additional tool for the identification of these types of granites that can occur in the same province (Breiter, 2012) and to evaluate their potential as carriers of rare-metal mineralization.

The aims of this article are as follows:

(i) To characterize the contents of minor and trace elements in zircon from A-type granites from plutons of different ages, chemical compositions, grades of fractionation and ore fertilities, as represented by several tin mineralized provinces;
(ii) To identify the behavior of different elements related to areal specialization (protoliths) and magma typology (A-type vs. S-type granitoids);
(iii) To propose discrimination tools (diagrams) to distinguish zircon from ore-bearing and barren A-type plutons.

2. Chemical studies on zircon of A-type granites

Zircon from granitoids always contains some Hf. The Zr/Hf ratio in chondrites is 33–38 (Anders and Grevesse, 1989; Barrat et al., 2012), but this ratio in zircons varies considerably. A general rule is that the Zr/Hf ratio decreases with progressive fractionation of the melt (e.g., Černý et al., 1985). The content of Hf in zircon from rocks ranging from kimberlites to common granites remains almost the same (0.8–1.7 wt.% HfO_2) and increases significantly only in strongly fractionated granites (Belousova et al., 2002). The highest concentrations of Hf in zircon were found in the Tanco pegmatite in Manitoba, Canada (39 wt.% HfO_2, Van Lichtervelde et al., 2009) and in the Steward granitic pegmatite (44 wt.% HfO_2, Ma and Rossman, 2005). Hafnon, the Hf-dominant member of the zircon group, was found in a rare-metal pegmatite at Zambezia, Mozambique (Correia Neves et al., 1974) and in the Koktokay No.1 pegmatite, China (Yin et al., 2013).

Uher and Broska (1996) analyzed zircon from relatively less-fractionated post-orogenic A-type granites in the Slovak Republic and Hungary and found only low trace element content, with a maximum 1.8 wt.% HfO_2. Wang et al. (1996, 2000) reported Hf-rich zircon from A-type granites in Sushou and Laoshan, China. Kempe et al. (2004) noted that extreme Hf-enrichment is typical of zircons with patchy structure from P-poor (more commonly A-type) granites. Johan and Johan (2005) analyzed 16 chemical elements in zircon from the Cínovec granite cupola, Krušné Hory/Erzgebirge, and found important differences between zircons from the zinnwaldite and protolithionite granite facies. Förster (2006) described Th-, U-, and Y-rich zircon and intermediate solid solutions in the system zircon–xenotime–thorite–coffinite from A-type granites in the eastern Erzgebirge (Germany) and Jordan. Lamarão et al. (2010) published an overview of the Hf, Y, U, Th, Nb, and Ca content in zircon from A-type granites of the Amazonian craton and stressed the significance of the Zr/Hf ratio for granite classification.

Zircons from peralkaline rocks contain in general fewer trace elements. Smith and de St. Jorre (1991) reported Hf-poor (<0.30 wt.% HfO_2), but Nb-enriched (up to 6.6 wt.% Nb_2O_5) zircon from the Thor Lake alkali syenite. In peralkaline A-type granites from eastern coastal China, Xie et al. (2005) distinguished two types of zircon: an early crystallized Th-rich zircon (1–10 wt.% ThO_2) and a late recrystallized Th-poor zircon (<1 wt.% ThO_2) with thorite microinclusions. Nardi et al. (2012) analyzed zircons from several varieties of A-type granites of the Pitinga tin province of Brazil, including the peralkaline Madeira albite granite, and found that the Madeira granite contains exceptionally high average contents of HfO_2 (2–5 wt.%), Nb (8–825 ppm), Th (200–6649 ppm), U (456–2975 ppm) and Y (2003–9211 ppm).

3. Geology of the studied plutons and sampling

For our study, we chose three areas with well-known A-type granite magmatism: (i) the Wiborg batholith, the classic area of Proterozoic rapakivi-type granites in southern Finland, (ii) the Proterozoic A-type granite plutons of Xingu (Pará state), Pitinga (Amazonas state), and Goiás tin provinces in Brazil, and (iii) the Krušné Hory/Erzgebirge area in the Czech Republic and Germany with Variscan volcanoplutonic complexes containing Sn–W-bearing A-type rhyolites and granites.

All selected plutons are composed of typical A-type granites (Bonin, 2007; Dall'Agnol et al., 2012; Eby, 1990, 1992; Haapala and Rämö, 1992; Loiselle and Wones, 1979). The studied granite complexes are generally metaluminous to marginally peraluminous, ferroan (Frost et al., 2001), both reduced and oxidized (cf. Dall'Agnol and Oliveira, 2007), and are post-orogenic or within-plate (Pearce et al., 1984) granites with relatively high Fe/Mg ratios and high HFSE content (Breiter and Škoda, 2012; Haapala and Rämö, 1992; Rämö and Haapala, 2005). The studied granites are derived predominantly from crustal sources (Anderson and Bender, 1989; Breiter, 2012; Creaser et al., 1991; Dall'Agnol et al., 2005; Heinonen et al., 2010a; Rämö and Haapala, 2005). They belong to the A2 subtype, according to the classification of Eby (1992). Its Alumina saturation index (ASI) generally varies between 0.9 and 1.1, except for greisenized and/or hydrothermally altered rocks. Peralkaline rocks were not included in this study. The only exception is the Pitinga cryolite granite, which is associated with the metaluminous to peraluminous dominant facies of the Madeira pluton (Costi et al., 2009).

Most complexes consist of voluminous early non-mineralized facies of geochemically ‘normal’ granites and/or rhyolites followed by smaller later intrusions of fractionated geochemically specialized rare-metal granites, with different grades of enrichment in F, Li, Rb, Sn, W, Nb, Ta, and U. However, some barren plutons are also presented for comparison.

3.1. The Proterozoic A-type Wiborg batholith, Finland

The Wiborg batholith is the largest and the most petrologically diversified Proterozoic (1.67–1.54 Ga) rapakivi-type batholith crosscutting the Paleoproterozoic Svecofennian (1.9–1.8 Ga) basement in southern Finland (Heinonen et al., 2010b; Sederholm, 1891, Fig. 1). Wiborgite is the most typical member of the entire rapakivi suite. It is a porphyritic coarse-grained biotite–hornblende granite with cm-sized ovoids of alkali feldspars mantled by plagioclase rims. The ‘dark wiborgite’ differs from the wiborgite s.s. in containing fewer alkali feldspar ovoids and additionally containing megacrysts of basic plagioclase and larger modal contents of mafic minerals. Equigranular biotite, partly hornblende-bearing, granite forms smaller, relatively younger bodies. The contacts between the mentioned rock types are sharp and intrusive, locally with magmatic brecciation (Heinonen et al., 2010b). Samples of the most typical and widespread granite varieties were collected in the southern part of the batholith near the town of Hamina (sample #4717) and the island of Ristisaari (#4711 and 4712). The Ahvenisto complex located at the NW margin of the Wiborg batholith