NOTA BREVE

Hafnian zircon as a tracer for rare metal exploration

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Abstract The major difficulty for the application of tracer minerals as mineralogical tool in geological exploration is to differentiate, in geochemical samples (like soil or stream sediment), the ore-related resistant indicator minerals from the barren-related grains. Hafnian zircon or high hafnium zircon can be such a tool to prospect rare metal granite and pegmatite bodies. Here we present some habits of the Hf-rich zircon associated to granites and pegmatites from the southeastern Brazil. Some particular characteristics of the mineral, like its luster, colour and especially its crystal forms, would allow the separation, with a simple visual analysis under a stereomicroscope, of the possible hafnian zircon from the common zircon grains. Microprobe or SEM/EDS analysis are still necessary to confirm the hafnium content in zircon crystals.

Keywords: hafnian zircon, rare metal, pegmatite, granite.

Resumo *Zircão hafnífero como um traçador para a exploração de metais raros.* A maior dificuldade para utilizar minerais traçadores como ferramenta na exploração geológica é a de diferenciar, nas amostras geoquímicas (solo ou sedimento de drenagem), os relacionados a depósitos minerais dos grãos comuns. Zircão hafnífero e/ou zircão rico em háfnio pode ser utilizado para prospectar corpos graníticos e pegmatitos a metais raros. São apresentados alguns hábitos de zircões ricos em háfnio associados a granitos e pegmatitos da região sudeste do Brasil. Algumas características particulares dos minerais tais como brilho, cor e especialmente as formas de cristais podem ajudar a separar, a partir de uma simples análise em lupa binocular, os cristais de zircão hafnífero dos zircões comuns. Análises por microsonda ou MEV/EDS são necessárias para confirmar o conteúdo de háfnio nos cristais de zircão.

Palavras-chave: zircão hafnífero, metais raros, pegmatito, granito

INTRODUCTION Weathering accounts for the destruction of mineral deposits and the country rocks, covering everything with autochthonous and allochthonous soils. In this way, the geochemical or mineralogical signatures of rocks and ores are masked and dispersed. In tropical environments, like in most of Brazil, the deep soil mantle, reaching over 60 m in some Brazilian regions, is the major impediment to mineral exploration and often the principal obstacle to construct reliable geological maps, as the simple identification of the country rocks is not possible.

Various resistant minerals, on the other hand, are not destroyed by weathering, remaining stable under adverse chemical and physical conditions at the earth surface. Such minerals, as tourmaline, zircon, ilmenite, magnetite, to name just a few, are dispersed in the regolith and preserved in soil samples. Even when the overburden is eroded, the resistant minerals are carried by waters fluxes and dispersed downstream, protected from erosion by the favourable natural traps (riffles, pot holes, meanders, etc.) of the rivers and creeks. In both condi-

tions, in soil or in stream samples, these heavy minerals may be retrieved during routine geochemical surveys.

Some of these resistant minerals, as tourmaline and rutile, are usual gangue phases of different types of mineral deposits. In these conditions, they assume specific chemical signatures (the wide range of major and trace elements) that permit to distinct them from the same minerals formed in barren rocks (Koval *et al.* 1991, Slack 1996, Smith *et al.* 1986, Scott *et al.* 1999). Others minerals are ordinary petrographic minerals, as zircon and monazite, and are found in the accessories assemblage of the most frequent rocks of the crust. In both cases, the principal problem of the prospector is to identify, in the regolith or in the stream sediment samples, the resistant minerals that could be related to ores among the population of grains present in a geochemical sample. Usually the minerals are identified under the stereomicroscope, after being hand-picked from the heavy pan assemblage, and its discrimination as mineral indicator requires more accurate, but time- and resource-consuming microanalysis techniques, as energy dispersive X-ray spectrometry

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coupled to a scanning electron microscope (SEM/EDS) or electron microprobe.

HIGH HAFNIUM ZIRCON Hafnium is a rare element in nature, usually associated to zirconium and known as Zr substitute in the zircon structure. Hafnian zircons (HfO_2 contents may reach up to 35 wt%) have been described associated to pegmatites from Norway, Africa, India and Canada (Levinson & Borup 1960, Knorring & Hornung 1961, Correia-Neves *et al.* 1974, Pal *et al.* 2007). In rare metals granites, hafnium-rich zircon was identified in the Beauvoir, Suzshou, Laoshan and Yichun granites (Wang *et al.* 1992, 1996, 2000; Huang *et al.* 2002). Granite-derived zircon usually contains from 4 to 8 wt% HfO_2 , but may reach up to 22 wt% at the rim of the crystals.

In Brazil (Fig.1), hafnian zircon has been described from the Sn-Ta-rich São João del Rei Pegmatite Province (Volta Grande and Cascalho Preto pegmatites) (Pereira *et al.* 2004), and from the Mixiriqueira (Cassedanne *et al.* 1985) and Golconda pegmatites (the latter a gemstone-bearing pegmatite) of the Eastern Brazilian Pegmatite Province, both in Minas Gerais

State. A-type granites of the Serra do Mar Intrusive Suite (Guaraú/Desembarque Pluton, Mandira and Graciosa granites) of São Paulo and Paraná State also presented hafnian zircon (Pereira *et al.* 2003a,b, 2005).

The Brazilian hafnian zircon occurs in millimetre-sized euhedral crystals (grain sizes vary from less than 1 up to 3 mm), with prismatic and bi-terminated forms that resemble the G2 zircon of Pupin's (1980) typology (Fig. 2). Flabelliform habit is related to the Mixiriqueira and Golconda pegmatites, and bipyramidal crystals to the Mandira alkaline riebeckite-granite. Colors range from reddish over brownish to milky white, although it could be due to metamictization. Hafnian zircon is opaque and has a greasy luster.

Electron microprobe and particularly SEM/EDS analysis of several zircon grains show high HfO_2 content (≥ 10 wt%) and atomic ratios $(100\text{Hf}/\text{Hf}+\text{Zr}) > 10\%$ (mol). The zircon is commonly zoned. The SEM/BSE images differentiate between lighter Hf-enriched portions, usually located on the crystal's border, and darker regions with lower contents of such element in the inner zones (Fig. 3). Other type of hafnium-rich zircon is characterized by a porous core and a relatively homogeneous

Figure 1 - Schematic map of the Brazilian areas with rare metal mineralizations and hafnian zircon: I = Araçuaí Pegmatite District; II = Governador Valadares Pegmatite District; 1 = Capivari-Pardo area / Graciosa granite; 2 = Mandira alkaline riebeckite-granite; 3 = Desembarque Pluton; 4 = Volta Grande pegmatite; 5 = Mixiriqueira pegmatite; 6 = Golconda pegmatite. Brazil's States: MG = Minas Gerais; SP = São Paulo; RJ = Rio de Janeiro; PR = Paraná; ES = Espírito Santo.

Figure 2 - SEM/BSE images of the habits of hafnian zircon crystals from Brazilian pegmatites and granites. Pegmatite: Volta Grande = A; Golconda = C; Granite: Desemborque = B; Mandira = D).

Figure 3 - SEM/BSE images of hafnian zircon from granites (Desemborque= A; Mandira = B) and pegmatites (Volta Grande = C and D), on polished sections.

like pseudo-colloform aspects, that indicate hydrothermal crystallization (Sáez *et al.* 2005), can occur in some crystals. The hafnian zircon related to pegmatites shows higher HfO₂ values (17 - 35 wt. %), dropping to lower values (10 - 17 wt. %) if it is related granite plutons. Thorite and uraninite are the main exsolutions found in hafnian zircon. Cassiterite, microlite, niobotantalates, xenotime and chernovite are the inclusions hosted in the crystals from the pegmatites. Magnetite, uraninite, monazite, xenotime and bastnaesite are the main inclusions of the granitic hafnian zircons.

CONCLUDING REMARKS Hafnian zircon related to pegmatitic and alkaline granitic intrusions in south and southeastern Brazil are potential resistate indicator minerals for rare metal exploration. Particular properties of the mineral, like its luster, colour and especially its crystal forms (Fig. 2), allows the separation of possible hafnian zircon from the common zircon grain, in a simple visual analysis under a stereomicroscope,

and Hf-rich rim. Oscillatory zoning and other features,

although microanalytical data on polished sections are necessary to confirm the hafnium content.

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