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An assessment of monazite from the Itambé pegmatite district for use as U–Pb isotope reference material for microanalysis and implications for the origin of the “Moacyr” monazite

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ABSTRACT

Large quantities of monazite from different pegmatite bodies of the Itambe pegmatite district were investigated to assess their suitability as U–Pb and Sm–Nd isotope reference materials for LA-ICP-MS and to track the origin of a piece of the Moacyr monazite (termed here Itambé), a widely used reference material for LA-ICP-MS U–Pb geochronology. Monazite from the largest pegmatite bodies in the district (the Bananeira, Coqueiro and Paraíso pegmatites) are Ce-monazite, with negligible amounts of the huttonite and brabantite components. They are homogeneous in major and trace elements, which makes them potential candidates as compositional reference materials. U–Pb LA-ICP-MS and ID-TIMS analyses yielded identical ages within error. Although the ID-TIMS ages (507.7 ± 1.3 ($^{207}Pb^{*}/^{235}U$) and 513.6 ± 1.2 Ma ($^{206}Pb^{*}/^{238}U$)) were reversely discordant, spot ages determined by LA-ICP-MS geochronology were concordant at ca 508 Ma. The Bananeiro monazite was assessed as a LA-ICP-MS U–Pb primary reference material against other known reference materials (treated as unknowns). This approach successfully reproduced the previously published ages of the reference materials. MREE/HREE fractionation (ie, $(La/Gd)_N$ and $(Gd/Lu)_N$ values), Eu/Eu^{*} and the chondrite-normalized REE patterns suggest that the “Itambé” monazite aliquot is very similar to that from the Coqueiro pegmatite. This similarity is likewise apparent in their Sm–Nd isotope compositions. Moreover, the εNdi values of the “Itambé” monazite fragment ($\varepsilon Ndi = -4.2$) and those from all the major pegmatites in the district, are distinct from other reference materials (eg, Managountry; $\varepsilon Ndi = -22.3$) as well as gem-quality monazite from c. 490–520 Ma pegmatites from the Araçuaí Orogen, further to the south. The εNdi can provide a further distinction for tracing Brazillian gem-quality monazite reference materials.

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1. Introduction

Monazite (Ce, La, Nd, Th) PO_4 is a monoclinic light rare earth element (LREE; Ni et al., 1995) orthophosphate, with a general formula given by ABO_4, where A = Bi, Ca, Ce, La, Nd, Th, U and B = As, P, Si (Back and Mandarino, 2008). Due to its high concentration of U (hundreds to thousands ppm) and Th commonly >50,000 ppm (Parrish, 1990, Heaman and Parrish, 1991) and low concentrations of common Pb, monazite has proven useful for constraining the timing of geological events using U–Th–Pb geochronology (Hawkins and Bowring, 1997; Kosler et al., 2001; Harrison et al., 2002; Williams et al., 2007, Kohn and Vervoort, 2008; Warren et al., 2011; Goudie et al., 2014). In addition, owing to its high concentration of Sm and Nd (e.g., ~10^4 to 10^5 ppm; Tomascak et al., 1998; McFarlane and McCulloch, 2007), monazite has also been shown to be useful for isotopic tracing because the original Sm–Nd isotopic composition of the source rock may be preserved despite high-temperature overprinting (Rapp and Watson, 1986; Montel and Seydoux, 1998; Hammerli et al., 2014). Clearly, the combination of U–Th–Pb ages, Sm–Nd isotope compositions and chemical composition variation of monazite provides a powerful tool for

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studying crustal evolution (McFarlane and McCulloch, 2007; Thöni et al., 2008; Gregory et al., 2009).

Monazite has a high closure temperature for Pb (> 900 °C; Cherniak et al., 2004; Gardes et al., 2006), which means that the diffusion of this cation is negligible, even at high-grade conditions (e.g., Cherniak et al., 2004; Gardes et al., 2006). The low diffusivity of major and trace elements also allows the preservation of compositional domains that can record the geological processes that have influenced the host rock (Foster et al., 2000, 2002; Catlos et al., 2002; Williams et al., 2007), e.g., sub-solidus vs. suprasolidus growth in polymetmorphosed metapelitic rocks (Buick et al., 2010). One disadvantage of using monazite for U–Th–Pb dating is its ability to recrystallize under the presence of fluid, potentially causing resetting of the U–Th–Pb system (Harlov et al., 2011; Williams et al., 2011).

Sm–Nd isotope systematics in monazite resides in the fact that those elements are relatively immobile (DePaolo, 1988) and that the chemical similarities of Sm–Nd makes the ratio of the two elements difficult to fractionate during most crustal processes (Rapp and Watson, 1986; Montel and Seydoux, 1998; Goudie et al., 2014). Moreover, the very high partition coefficients for those elements in monazite make the system difficult to reset (Stepanov et al., 2012). Recently, Sm–Nd isotopic analyses on monazite have been successfully undertaken by laser ablation-multicollector-inductively plasma-mass spectrometry (LA-MC-ICP-MS; McFarlane and McCulloch, 2007; Yang et al., 2008; Fisher et al., 2011; Iizuka et al., 2011; Liu et al., 2012), greatly improving the use of this systematics due to high-spatial resolution, fast data acquisition and low cost, in comparison to solution techniques.

The complex chemical and age zonation commonly preserved in individual monazite grains requires high spatial resolution analytical techniques, such as secondary ionization ion mass spectrometry (SIMS; Harrison et al., 1995; Stern and Berman, 2001), laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS; Machado and Gauthier, 1996; Poitrasson et al., 2000; Kosler et al., 2001; Horstwood et al., 2003; Gehrels et al., 2008; Paquette and Tiepolo, 2007; Kohn and Vervoort, 2008; Liu et al., 2012; Goudie et al., 2014) or electron probe microanalysis (EPMA; Suzuki and Adachi, 1991; Montel et al., 1996; Catlos et al., 2002, Williams et al., 2007). Although the three techniques require well-calibrated primary and secondary (quality control) reference materials, LA-ICP-MS has shown both the greatest increase in application to geochronology and isotope geochemistry, but is the most inherently destructive technique; it requires a constant supply of well-characterized reference materials in order to correct mass bias, elemental fractionation and instrumental drift. In general, relatively few U–Pb or Sm–Nd isotope reference materials are available for international distribution to high spatial resolution instruments and, of these, only a small subset have been distributed widely to LA-ICP-MS laboratories because only small amounts of the reference material are available and the destructive nature of the LA-based technique. Facilities otherwise develop in-house reference materials that are not widely available. For the case of LA-ICP-MS, the most commonly distributed U–Pb reference material is 44,069 monazite (c. 425 Ma - Aleinikoff et al., 2006), and Managountry monazite (Paquette et al., 1994) is also commonly used. Managountry monazite (Liu et al., 2012), Namaqualand monazite (also known as Steenkampskraal) (Liu et al., 2012) and 16-F-16 monazite (Iizuka et al., 2011) have all been proposed as reference materials for Sm–Nd isotope tracing.

One widely distributed reference material used for LA-ICP-MS or SIMS U–Pb geochronology and EPMA chemical dating comes from the Itambé pegmatite district of Bahia State (E Brazil; Silva et al., 1996; Fig. 1). Monazite from this source is described as either “Moacyr” or “Moacir” monazite in the literature (e.g. Seydoux-Guillaume et al., 1999, 2002; Paquette and Tiepolo, 2007; Dumond et al., 2008; Kohn and Vervoort, 2008; Gasquet et al., 2010; Palin et al., 2013; Harley and Nandakumar, 2014), but the exact location of those monazite crystals remains unclear. An initial TIMS age determination suggested that this monazite was concordant at c. 474 Ma (Seydoux-Guillaume et al., 1999). Subsequent TIMS age determinations have suggested that the Moacyr monazite is reversely discordant, with best-estimate crystallization (^{207}Pb/^{235}U) ages in the range c. 504–508 Ma (unpublished data quoted in Dumond et al., 2008, and Kohn and Vervoort, 2008; published data in Gasquet et al., 2010). The TIMS ^{207}Pb/^{235}U crystallization age estimates for Moacyr monazite do not entirely overlap, within error, and it is unclear whether this is an inter-laboratory analytical effect, or other unknown factor i.e. different sources. Compounding this uncertainty is the fact the Itambé pegmatite district contains three different large pegmatite bodies (the Bananeira, Coqueiro and Paraíso pegmatites; Fig. 2), all of which contain large quantities of monazite.

The main goal of this study is to assess the suitability of the monazites from the Itambe district as reference material for U–Pb geochronology. We furthermore attempt to identify the origin of a c. 50 g crystal fragment of Moacyr monazite (termed hereafter Itambé) that has previously been proposed as a SIMS oxygen isotope reference material by Rubatto et al. (2014) and its origin has been investigated by comparing new data on its age, Nd-isotope composition and chemical composition with those of monazite sampled for this study.

2. Sample description and geological setting

The Itambé pegmatite district occurs in the northernmost portion of the Eastern Brazilian Pegmatite Province (EBPP), a NNE-SSW belt of approximately 150,000 km^2. The EBPP consists of pegmatites that were

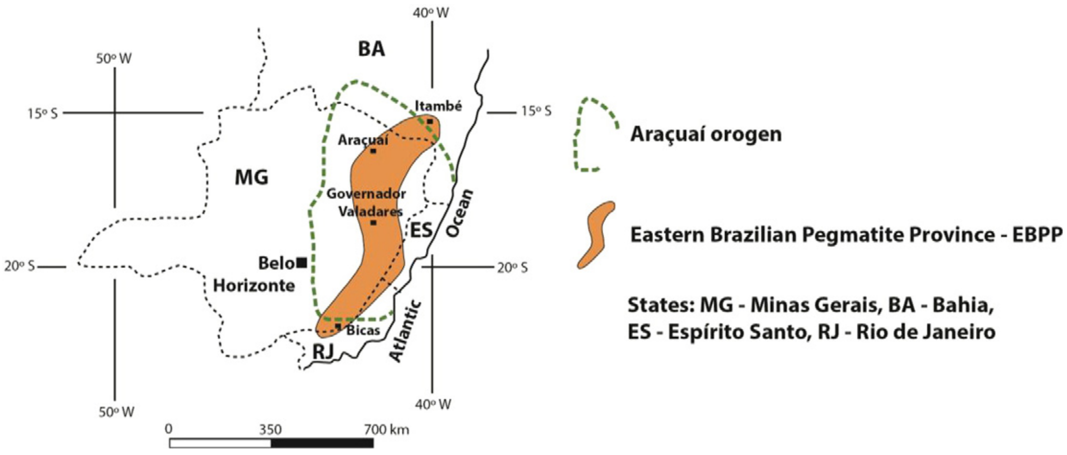

Fig. 1. Position of the Itambé pegmatite district, the northern tip of the Eastern Brazilian Pegmatite Province—EBPP, in relation to the Araçuaí orogen.

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