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Evaluation of potential monazite reference materials for oxygen isotope analyses by SIMS and laser assisted fluorination

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ABSTRACT

Monazite can record several episodes of fluid/rock interaction within a single grain. Coupled in situ determination of age and oxygen isotope composition by SIMS (secondary ion mass spectrometer) may characterize such events. Yet, monazite reference materials for oxygen isotope analyses are scarce. Ion probe (CAMECA IMS 1280) and laser fluorination measurements of $\delta^{18}\text{O}$ values from four monazites are presented. Monazites (YREEPO₄) with variable cheralite [CaTh(PO₄)₂] and huttonite (ThSiO₄) substitutions, which span a wide compositional range covering most magmatic and metamorphic, as well as hydrothermal monazites were selected. Three monazites, Moacyr, Manangoutry and UNIL-Mnz1, have a homogeneous chemical (determined by electron microprobe analysis and back-scattered imaging) and oxygen isotopic composition with uncertainties (2 SD) in the range of 0.3 to 0.4‰ for ion probe measurements. These three samples are thus potentially suitable as reference materials, and sample UNIL-Mnz1 is available for inter-laboratory comparison. Sample UNIL-Mnz2 is less homogeneous, but it is still useful for internal monitoring. Uncertainties (2 SD) on the ion probe data are in the range of 0.5 to 0.6‰.

Using the investigated monazites as well as literature data, a new calibration curve has been established to account for instrumental mass fractionation (IMF) due to the solid solution in natural monazites. The data illustrate that the IMF is primarily a function of the YREEPO₄ content, while the influence of the Th-content seems to be less important.

The $\delta^{18}\text{O}$ values for the four studied monazites have been determined by laser fluorination (LF). They are as follows (1 SD): $1.5 \pm 0.1\%$ for Moacyr, $10.2 \pm 0.1\%$ for Manangoutry, $8.5 \pm 0.2\%$ for UNIL-Mnz1, and $9.5 \pm 0.3\%$ for the slightly less homogenous UNIL-Mnz2. The analytical protocol adopted here results in consistently high yields (>90%) and reproducible values, and hence it is argued that LF is a viable method for the calibration of phosphate reference materials.

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1. Introduction

Monazite is a ubiquitous accessory mineral. It is commonly used for U-Th-Pb dating in crustal rocks (Bingen et al., 1996; Harrison et al., 1999; Janots et al., 2006; Bosse et al., 2009; Rubatto et al., 2013). Though monazite is resistant to resetting of its age at high temperatures, (Cherniak et al., 2004; Gardés et al., 2006), it can be very sensitive to an exchange with fluids. Several natural and experimental studies (Poirasson et al., 1996; Seydoux-Guillaume et al., 2002; Bosse et al., 2009; Hetherington et al., 2010; Seydoux-Guillaume et al., 2012; Gasser et al., 2012; Didier et al., 2013) show that fluids can enhance the crystallization of new domains by dissolution–precipitation (Putnis, 2002). These newly formed domains can potentially record

the age of the fluid–rock interaction (Didier et al., 2014a). In addition, the fluid can leave an imprint of its isotopic and chemical composition in the recrystallized monazite. Consequently, coupled with U-Th-Pb dating, the chemical and oxygen isotope composition of monazite can be of interest to characterize fluid–rock interaction, especially for low-temperature conditions (<400 °C under high water activity conditions) when oxygen diffusion is too slow to enhance resetting (Cherniak et al., 2004). Monazite is more often than not chemically and isotopically zoned (Zhu and O’Nions, 1999; Franz et al., 1996; Pyle and Spear, 2003), hence it may record several events – including hydrothermal events – within a single grain (Allaz et al., 2013). In this context, in-situ analyses are indispensable and the ion probe is a suitable tool that allows for analyses of spot sizes as small as 10 μm. The monazite structure can accommodate an array of different cations resulting in a large range of chemical compositions. Breecker and Sharp (2007) and Rubatto et al. (2014) showed that the instrumental mass fractionation (IMF) is large, with up to 4‰ for $\delta^{18}\text{O}$, and is influenced by the chemical composition of monazite. Indeed, the study of Breecker and Sharp

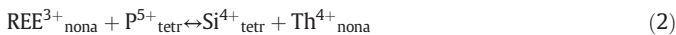
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(2007) performed on a SIMS1270 illustrates that the IMF is inversely correlated to the Th content of monazite. Rubatto et al. (2014) propose that the IMF depends on the fraction of cheralite ($\text{CaTh}(\text{PO}_4)_2$) and huttonite (ThSiO_4) components in monazite (work performed on SHRIMP). Finally, Ayers et al. (2006) do not report matrix effects for different monazite compositions. These contrasting studies demonstrate the need for new standards with a range in chemical composition large enough to cover the majority of monazites found in nature. In this context, potential monazite reference materials are investigated and a new calibration scheme to correct IMF due to matrix effects using a SIMS1280 is proposed. It is also suggested that the absolute $\delta^{18}\text{O}$ values of monazites can be accurately determined by laser-assisted fluorination (LF); using LF has so far been contested when applied to phosphate analyses (Breckner and Sharp, 2007).

2. The field of chemical compositions investigated and sample selection

Monazite is a light rare earth element phosphate (LREEPO_4). It may contain large concentrations of Th (up to 15%), Ca and Si, according to two substitutions:



Eq. (1) is the huttonite (ThSiO_4) substitution and Eq. (2) is the cheralite [$\text{CaTh}(\text{PO}_4)_2$] substitution. Both minerals have the same as monazite and thus form solid solutions with the end-member LREEPO_4 (Fig. 1a). Besides these solid solutions, heavy rare earth elements

(HREE) and Y (xenotime end-member YPO_4) can be incorporated in the same nonaedic crystalline site as LREE. The HREE rarely exceed 100 ppm and Y is typically <2 wt.%. In contrast, the LREE content can be up to 60 wt.%. They are thus all grouped together in the YREEPO_4 end-member of the solid-solution called “monazite” (Mnz) in the rest of the paper. Hence, monazite solid-solution can be described by three main end-members: monazite (Mnz), cheralite (Cher) and huttonite (Hutt), as illustrated by the grey domain in the ternary diagram in Fig. 1a. This study focuses on the most widespread monazite compositions found in metamorphic, igneous, and hydrothermal environments. Most natural monazite plots in a field delimited by $\text{Mnz}_{100}\text{-Cher}_{20}\text{Mnz}_{80}\text{-Hutt}_{20}\text{-Mnz}_{80}$ (see Fig. 1b).

A dozen monazite was selected initially (see Supplementary material S1). A more detailed investigation focused on monazites that (1) are as homogeneous as possible in major element and in oxygen isotope composition; (2) have a composition in the range of common variations in the monazite group outlined above; (3) are available in sufficient amount to be used as standards (i.e., enough material to have at least one fragment of standard on each unknown mount, and enough to be shared with other laboratories). Ideally, monazites with known U-Th-Pb ages were selected with the objective of providing standards that can be used for both age and oxygen isotope analyses. According to these criteria, four monazites have been selected: Moacyr, Manangoutry, UNIL-Mnz1 and UNIL-Mnz2.

For this study, no pure monazite-cheralite solid solution could be found that would fulfill all the criteria: they are commonly too small (<100 μm) and heterogeneous. Consequently, USGS 44069 - already used as an oxygen isotope standard for in-situ analysis by Rubatto et al. (2014) - has been chosen in addition to represent this specific chemical composition. The selected monazites are

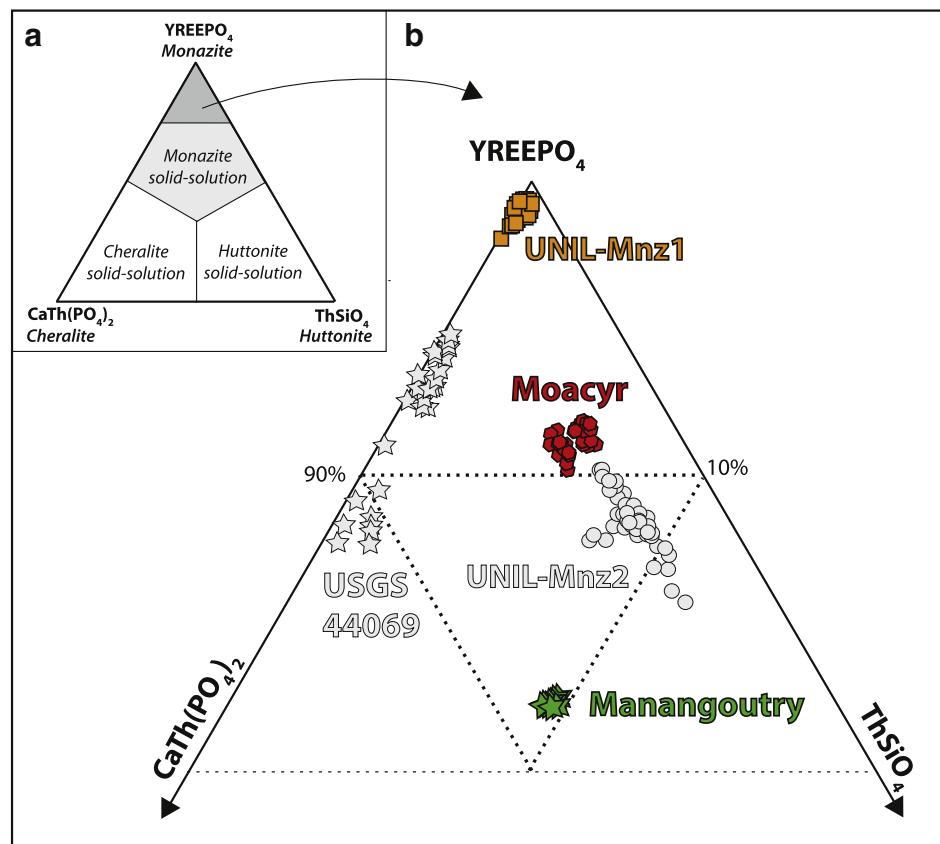


Fig. 1. a. Chemical composition space of monazite solid-solution. b. Ternary diagram showing the distribution of Moacyr, Manangoutry, UNIL-Mnz1, UNIL-Mnz2 and USGS monazites among the main end-members: cheralite, huttonite and YREEPO_4 . End-members are calculated according to Pyle et al. (2001).

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