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 Ions 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 (YREEPO_4) with variable cheralite $[\text{CaTh}(\text{PO}_4)_2]$ and huttonite (ThSiO_4) 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 ± 0.1 ‰ for Moacyr, 10.2 ± 0.1 ‰ for Manangoutry, 8.5 ± 0.2 ‰ for UNIL-Mnz1, and 9.5 ± 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.

Keywords: monazite, standard, oxygen isotopes, SIMS, laser fluorination, Moacyr, Manangoutry, UNIL-Mnz1.

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; Gardès et al., 2006), it can be very sensitive to an exchange with fluids. Several natural and experimental studies (Poitrasson 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, 1996; Pyle and Spear, 2003), hence it may record several events – including hydrothermal events – within a single grain (Allaz et al., 2014). 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 (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 (Breecker and Sharp, 2007).

2. The field of chemical compositions investigated and sample selection

Monazite is a light rare earth element phosphate (LREEPO₄). It may contain large concentrations of Th (up to 15%), Ca and Si, according to two substitutions:

Eq. (1) is the huttonite (ThSiO₄) substitution and Eq. (2) is the cheralite [CaTh(PO₄)₂] substitution. Both minerals have the same structure as monazite and thus form solid solutions with the end-member LREEPO₄ (Fig.1a). Besides these solid solutions, heavy rare earth elements (HREE) and Y (xenotime end-member YPO₄) can be incorporated in the same nonaedric crystalline site as LREE. The HREE rarely exceed 100 ppm and Y is typically less than 2 wt.%. In contrast, the LREE content can be up to 60 wt.%. They are thus all grouped together in the YREEPO₄ 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 hutonnite (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 Mnz₁₀₀ - Cher₂₀Mnz₈₀ - Hutt₂₀-Mnz₈₀ (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 mounts, and enough to be shared with other laboratory). 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 analysis. According to these criteria, four monazites have been selected: Moacyr, Manangoutry, UNIL-Mnz1 and UNIL-Mnz2.

For this study no pure monazite-cherilite solid solution could be found that would fulfill all the criteria: they are commonly too small ($<100\text{ }\mu\text{m}$) 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 globally more homogeneous (Rubatto et al., 2014) and cover a larger range of chemical compositions (Ayers et al., 2006) compared to previous studies.

3. Sample description, chemical and isotopic composition

Moacyr

Several cm-sized grains were used for the Moacyr monazite from the Itambe pegmatite district in Brazil (Cruz et al., 1997; Seydoux-Guillaume et al., 2002). The yellow-orange crystals are nearly free of fluid and solid inclusions. In the literature, Moacyr is also called “the French monazite” (Fletcher et al., 2010) or Itambe (Rubatto et al., 2014). Moacyr is commonly used as reference material for in-situ dating. It has a reversely concordant U-Th-Pb age with weighted mean dates of 504-507 Ma for $^{208}\text{Pb}/^{232}\text{Th}$ and 511-516 Ma for $^{206}\text{Pb}/^{238}\text{U}$ (Mahan et al., 2006; Gasquet et al., 2010; Fletcher et al., 2010; Palin et al., 2013). Moacyr locally contains common Pb (Didier et al., 2014b). Although all studies report the same U-Th-Pb age, Moacyr grains have a large range of chemical composition with, for example, up to 1 wt% variation in Th. This suggests that there are different batches or crystals used in the community. The Moacyr grains used in this study have been provided by A.M Seydoux-Guillaume, and come from the same batch as the grains described by Seydoux-Guillaume et al. (2002) and Gasquet et al. (2010).

Manangoutry

The Manangoutry monazite is a piece of a large crystal, several centimeters in size, from an apatite-, biotite-, and monazite-bearing lens in the Anosyan granite-charnockite from the Adroyan complex in Madagascar (Paquette et al., 1994). The orange-brown crystal is nearly free of inclusions. The specimen was cut into mm-sized fragments. Manangoutry is commonly used as a secondary reference material for in-situ dating. It has slightly discordant U-Pb ages with an upper intercept at 555-559 Ma (Horstwood et al, 2003; Paquette et Tiepolo, 2007; Palin et al., 2013). Montel et al. (1996) and Oelkers and Poitrasson (2002) showed that Manangoutry has a homogeneous chemical composition.

UNIL-Mnz1

The UNIL-Mnz1 monazite grains are from a *ca.* 5 cm large hand specimen consisting of monazite, as well as Fe-oxides, ilmenite in a carbonate groundmass. Monazites form several cm-sized grains. The specimen was donated by the Natural History Museum of Basel (Mineralogical Collection NHMB 40'346''). According to the museum records, the sample comes from a well-known monazite locality, the Farm Eureka 99, in Namibia, where carbonatites are exposed (Nidermayr, 2006). For this particular specimen, we have not yet determined a radiometric age. The U/Pb isotope study of Burger et al. (1965) on monazites from the Eureka locality gave an age of 500 Ma (for further discussions see also Dunai et al. 1998).

The hand specimen was cut into two pieces, the smaller one of which was crushed to yield several size fractions between >125 μm to <1000 μm . For three size fractions (250-500 μm , 500-800 μm , 800-1000 μm) a monazite pre-concentrate of >90 % purity was obtained by repeated cycles of panning and magnetite separation using a FRANTZ magnetic separator.

For the LF work a batch of monazite powder was prepared by handpicking from the 500-800 μm fraction. Honey-brown, inclusion-free crystals were chosen. Those grains were powdered in a small agate mortar to yield about 140 mg of powder. Grains from the 250-500 μm fraction were chosen for SIMS analysis. After initial tests confirmed the homogeneity of these monazite grains, the pre-concentrate was hand-picked to remove inclusion-rich pieces.

UNIL-Mnz2

The UNIL-Mnz2 monazite is a 2 cm long, brown crystal-fragment from a pegmatite collected in Madagascar and provided by the Museum of Geneva (n° MHNG 489.080). It was crushed in mm-sized fragments. U-Th-Pb_{tot} dating by EMPA performed on another monazite crystal from the same pegmatite gives a preliminary age around 502 Ma (unpublished data by Dr. E. Gnos).

USGS-44069

The USGS-44069 sample was taken as a batch of grains, 100-200 μm in size, from an amphibolite- to granulite-facies psammitic layer within the Wissahickon formation in the central part of the Appalachian orogeny (Aleinikoff et al., 2006). It is commonly used as reference material for in-situ dating (U-Pb age of 424 Ma; Aleinikoff et al., 2006). Crystals are yellowish to orange. USGS-44069 contains variable amounts of cheralite (0.36-0.77 wt.% of Ca) and negligible huttonite substitution (<0.15 wt.% of Si) (Rubatto et al., 2014). Oxygen isotope ratios of USGS-44069 have been investigated by Rubatto et al. (2004). They obtained an average $\delta^{18}\text{O}$ value of $7.67 \pm 0.13 \text{ ‰}$ (1 SD). These analyses have been done by LF at the University of Lausanne (Switzerland) on grain separates.

4. Analytical setup

The homogeneity of major elements was assessed by back-scattered electron imaging (BSE) and electron microprobe quantitative analysis (EMPA). Oxygen isotope compositions were determined by and laser fluorination (LF); $\delta^{18}\text{O}$ homogeneity and IMF calibrations by Secondary ion mass spectrometry (SIMS).

Monazite grains were mounted in epoxy for imaging and in-situ analyses (BSE, EMPA, and SIMS). The mounts were polished using diamond paste, decreasing the diamond size fraction from 15 to 0.5 μm to obtain a good polish. A very low relief is essential for reproducibility of SIMS analyses (e.g., Kita *et al.* 2009). Finally, mounts were coated with carbon for BSE and EMPA analyses or gold for SIMS analyses. A total of four mounts (Mount 1: Manangoutry, UNIL-Mnz2, Moacyr and UNIL-Mnz1; Mount 2: Manangoutry, UNIL-Mnz2, Moacyr, UNIL-Mnz1 and USGS; Mount 3: Manangoutry and Moacyr; Mount 4: Manangoutry, Moacyr and UNIL-Mnz1) were used during seven SIMS sessions (Table 3). They contain two to five of the studied monazites and a grain of quartz standard UNIL-Q1 from Seitz et al., (2016). The seven sessions were used to test the homogeneity of the potential reference materials and three of them to determine the calibration curve.

4.1. Imaging and microprobe analyses

Backscattered electron imaging of the monazite grains was done using a Tescan Mira LMU at the University of Lausanne (Switzerland). Quantitative microprobe analyses used a Cameca SX100 at the Laboratoire Magmas et Volcans, Clermont Ferrand (France) for Moacyr and Manangoutry monazites, and a JEOL Superprobe at the University of Lausanne (Switzerland) for USGS 44069, UNIL-Mnz1 and UNIL-Mnz2 monazites. Operating conditions were 15 kV as accelerating voltage and a 40 nA beam current. Counting times were adjusted to the element concentrations and varied from 10 to 75s. X-ray lines, background offsets and standards (Zircon, CePO_4 ; LaPO_4 ; PrPO_4 ; NdPO_4 ; SmPO_4 ; GdPO_4 ;

YPO₄; Apatite; ThO₂; UO₂) followed the procedure outlined by the study of Montel *et al.* (1996).

4.2. SIMS oxygen isotope analysis

Oxygen isotope ratios were measured using the CAMECA IMS 1280 multi-collector-ion microprobe at the SwissSIMS facility, Lausanne (Switzerland). All the SIMS sessions followed the same analytical protocol. A +10 kV Cs⁺ primary Gaussian beam with 2 nA current was used, resulting in a typical spot size of about 10 µm. A raster of 10 µm was applied to homogenize the crater bottom. A small beam size was chosen because monazite commonly presents zonation smaller than 20 µm. Secondary ions were extracted from the sample at -10 kV and admitted via high magnification transfer optics (magnification of 200 between the sample surface and the field aperture) to the mass spectrometer, operating at a mass resolution (M/ΔM) of 2400. Charge compensation on the sample is provided by a vertical incident electron gun. This general protocol follows Kita et al. (2009).

A 30 s pre-sputter period was followed by automated centering of the secondary ion beam. Counts were accumulated during 20 cycles of 5 s for each analysis. The internal error (as 2 × standard error; 2 SE) also called within-spot reproducibility, and corresponding to the standard error of the mean during an individual analysis, was generally between 0.1-0.2 ‰ (2 SE).

The different sessions lasted more than 10 hours each, and were designed to regularly alternate between reference material: every 4-5 spots a different reference material was analyzed. The quartz standard, UNIL-Q1 (Seitz et al., 2016) and/or the Moacyr monazite was used to monitor the homogeneity and give an external reproducibility (also called spot-to-spot uncertainty in 2 standard deviation) of ±0.3 ‰ (2 SD). The ¹⁸O/¹⁶O ratio is reported in

standard $\delta^{18}\text{O}$ per mil notation relative to VSMOW. Minor linear drift corrections have been applied to the data sets, where necessary.

4.3. Oxygen isotope analysis by laser fluorination

Oxygen isotope analyses of monazite were measured as reference $\delta^{18}\text{O}$ values for the SIMS analyses. They were performed in the stable isotope laboratory of the University of Lausanne. Analyses were made, in general, on powdered monazites, crushed from small individual grains and chips. Initial tests were made directly on individual grains (see supplementary material S2). Clean, inclusion- and intergrowth-free pieces were selected from larger crystal fragments (Moacyr, Manangoutry, UNIL-Mnz2) or pre-concentrates (UNIL-Mnz1). The monazites were washed with distilled water, but underwent no further treatment with acids (e.g., Brecker and Sharp, 2007; in their study monazites were soaked in HF for several days).

Laser-assisted fluorination (LF) of monazite analyses follows the method initially described by Sharp (1990). For details of the exact procedure used see Lacroix and Vennemann (2015). Samples between 1 to 2 mg were loaded into small pits of a Pt sample holder. Pre-fluorination occurred in several cycles. After a first long pre-fluorination (between 10 and 12 h; overnight), followed by a 10 min pre-fluorination, the sample was heated by a CO_2 laser in about 50 mbar F_2 to yield O_2 . The gas was purified and analyzed as O_2 in a dual-inlet gas source mass-spectrometer (Finnigan MAT 253). Replicate analyses of NBS-28 quartz (9.64 ‰, Coplen et al., 1983) or LS-1 quartz (in-house-reference material Lausanne quartz 18.1 ‰) have a precision (1 SD) better than ± 0.1 ‰ for NBS-28 and ± 0.2 ‰ for LS-1. The accuracy relative to the accepted value is routinely < 0.1 ‰ for NBS-28 and < 0.2 ‰ for LS-1. But there were several runs between February and October 2014 that had systematically

lower values for LS-1, thus a lower accuracy, related to a problem with heating of the molecular sieve (see Supplementary material S2).

Initial tests revealed that reproducible analyses and high oxygen yields were only obtained for a specific analytical procedure. Notable modifications compared to other silicates and oxides are the use of slightly higher F_2 -pressures of about 100 mbar. Only the samples in question and the standard quartz were loaded into the sample chamber to avoid any interference or cross-contamination during the reaction. Samples were as far away from each other as possible on the Pt-tray to avoid contamination due to sputtering from other samples of monazite. It was found that monazite powders lase quite smoothly, whereas grains or single chips are more difficult to lase and tend to “sputter” during the reaction with fluorine while heating, resulting in lower yields too.

LF analysis of monazites requires experience. As is the case for many Ca-silicates, laser heating and reaction with fluorine gas produces melt beads. These beads continue to melt and emit bright light during lasing, even after the reaction to liberate oxygen is complete. This is likely due to a weak absorption of the laser beam by the CaF_2 . Laser heating was stopped once the melted sphere is clear throughout and does not decrease in size anymore. This approach provided high oxygen yields when applied carefully (see Table 2). Residual pressures after extraction are slightly higher than for silicates (50 μm of Hg instead of about 35 to 40 μm of Hg), reflecting the presence of non-condensable gases that are also not adsorbed onto the molecular sieve.

The tests showed that only analyses of powdered monazite gave reproducible results (see discussion). For Moacyr, for example, two clean crystal fragments were crushed to obtain three batches of 1.0 to 2.5 mg of powder for each fragment, sufficient material for about 6 analyses (for details see Table 2 and supplementary material S2). It was possible to prepare a larger quantity of powder for the UNIL-MNZ1 monazite using a pre-concentrate of the size

fraction 500-800 μm . This fraction was sufficiently clean to facilitate handpicking. For LF work several fragments were crushed to give about 140 mg of fine powder.

5. RESULTS

5.1. Chemical composition and homogeneity

New chemical analyses have been obtained by EMPA for all reference materials in order to determine the homogeneity and the chemical composition of each individual batch of monazite used in the study. This way, analytical bias between laboratories is avoided. All variations are quoted with 2 SD. Overall, Moacyr, Manangoutry, UNIL-Mnz1 and UNIL-Mnz2 monazite have homogeneous chemical compositions, in contrast to USGS-44069 that has variations in Th larger than 3 % but presents an interestingly unique chemical composition (elevated contents of the cheralite and xenotime components).

Moacyr

BSE images reveal no chemical zoning (Fig. 2). Indeed, Moacyr has a homogeneous chemical composition within a single grain but also from one grain to another (Table 1): 6.5 ± 0.4 wt.% Th, 0.3 ± 0.1 wt.% Ca, 0.6 ± 0.1 wt.% Si, and $Y=0.6 \pm 0.1$ wt.%. LREE and MREE (medium rare earth elements) account for 52 wt.% (La: 12.0 wt.%; Nd: 9.2 wt.%). Analyses ($n = 64$) have been performed on five different pieces of Moacyr and the results are identical to those previously published by Seydoux-Guillaume et al., 2002 and Fletcher et al., 2010. End-member calculation after Pyle et al. (2001) give a composition of 6 % huttonite (ThSiO_4), 3 % cheralite [$\text{CaTh}(\text{PO}_4)_2$] and 91 % monazite (YREEPO_4) (Fig.1b, 2 and 3).

Manangoutry

BSE images do not show any chemical zoning or evidence for recrystallization (Fig. 2). Manangoutry has clearly a homogeneous chemical composition within a single (Table 1): the

Th content is relatively high (12 ± 0.2 wt.%) accompanied by high Ca (0.7 ± 0.1 wt.%) and Si (1.1 ± 0.1 wt.%) contents according to cheralite and huttonite substitutions (Fig. 3). Consequently, lower REE contents (47.2 ± 0.2 wt.%) were measured relative to Moacyr. The La content is 11.5 wt.%, Nd 8.2 wt.%. Y is low at 0.02 wt.%. Analyses ($n = 20$) have been performed on a mm-sized grain and are identical to those previously published (Oelker and Poitrasson, 2002), which further confirms its homogeneity. Manangoutry is composed of 9 % huttonite end-member, 9 % cheralite end-member and 82 % monazite end-member (Fig. 1b).

UNIL-Mnz1

No chemical zoning (Fig. 2) or evidence of recrystallization has been observed in the UNIL-Mnz1 sample; it has a homogeneous chemical composition within a single grain and from one grain to another (11 grains analyzed; $n = 84$). Among all studied monazite, UNIL-Mnz1 has the lowest Th content (0.6 ± 0.3 wt. %) and consequently the lowest Ca and Si content (respectively 0.06 and 0.01 wt.%), and hence the highest REE content (59.0 ± 0.8 wt.%) following the cheralite and huttonite substitutions (Fig. 2 and 3). Nevertheless, among REEs, the strong LREEs enrichment is correlated with a MREEs and Y depletion (La: 19.0 wt.%; Nd: 7.04 wt.%; Y: 0.02 wt.%). UNIL-Mnz1 has very low cheralite component (<1 %) and high monazite component (99 %) (Fig. 1b).

UNIL-Mnz2

BSE images (Fig. 1) show that UNIL-Mnz2 has alteration zones of micrometric size, composed of newly formed thorite and monazite. No additional zoning is apparent. The unaltered domains are less homogeneous within a single grain and from a grain to another than the other monazites studied. Analyses ($n = 209$) have been performed on a total of thirteen grains. Thorium content is 9.4 ± 1.0 wt.%; Ca: 0.24 ± 0.17 wt.%; and Si: 1.1 ± 0.2 wt.%. MREE+LREE are 50.6 ± 1.3 wt. % with 11.7 wt. % of La, 6.9 wt. % of Nd. Altered

domains are Th-depleted (<5 % Th) and REE-enriched (Table 1). The unaltered parts of UNIL-Mnz2 are composed of 9 % huttonite end-member, 3 % cheralite end-member and 88 % monazite end-member (YREE) (Fig. 2b).

USGS-44069

USGS-44069 can display concentric and patchy zoning (Fig. 1) resulting from chemical heterogeneities (10 analyzed grains; n = 30): Th content ranges from 2 to 5.5 wt.%, Ca from 0.4 to 1.1 wt.%, Si from 0 to 0.2 wt.%. The Y content is exceptionally high (1.4-3.0 wt.%), i.e., higher than in the other studied monazites. MREE+LREE range between 49.5 to 54.5 wt.%. USGS-44069 does not contain huttonite, but 5-12 % cheralite and 89-95 % monazite (YREE) (Fig. 2b). The xenotime-component (YPO₄) is not negligible in this monazite, around 4-7 %. Most of chemical variation is due to the cheralite substitution (Fig. 3).

5.2. Oxygen isotope analyses by laser fluorination

The oxygen isotope ratios measured by laser fluorination of the monazites are listed in Table 2. Care was taken to bracket monazite analysis by quartz standards. The $\delta^{18}\text{O}$ values average as follows: for Moacyr 1.5 ± 0.1 ‰ (n = 6); for Manangoutry 10.2 ± 0.2 ‰ (n = 6) ; for UNIL-Mnz1 8.5 ± 0.4 ‰ (n = 13) and for UNIL-Mnz2 9.5 ± 0.6 ‰ (n = 8). All uncertainties quoted are two standard deviations. For more details, see Supplementary materials S2.

Between 6 to 13 replicates were measured for each monazite. The analyses of powdered monazite fragments or grains (1.0-2.5 mg) replicate well (0.1 to 0.3 ‰, 2 SD) and give consistently high yields with $>95 \pm 5$ %.

Using powdered material rather than grains or chips was found to be more precise, resulting in consistently high yields and best reproducibility. For the initial studies on

monazite in the Lausanne laboratory (see also Rubatto et al. 2014), single chips or 2 to 5 smaller fragments (i.e. grain separates) were used. Results were less reproducible, although a few results with high yields were obtained, also giving reproducible values. Yet, it was not possible to predict which sample – using the same analytical set-up during laser heating and extraction – will give good yields. It became also clear that low yields are not simply related to sputtering. More systematic tests with the UNIL-MNZ1-monazite and other phosphate samples (not shown here) using both grains and powder showed that less than 50 % of the >250 μm to 800 μm size fraction were reproducible to better than 0.3 ‰. This is due to the difficulty to quantitatively react the samples with laser heating and powders of the monazite reference materials were also found to sputter less than chips or grains of the same sample.

As was previously noted (e.g., Brecker & Sharp 2007, Rubatto et al. 2014) a clear correlation exists between low yields and lower absolute $\delta^{18}\text{O}$ values. Hence, only analyses with yields >90 % were taken into account (Table S2). Low-yield results tend to be about 0.5 ‰ lower than the high-yield analyses.

5.3. Reproducibility of oxygen isotope analyses by SIMS

The reproducibility of $\delta^{18}\text{O}$ values of the potential reference materials has been tested during seven sessions between July 2014 and November 2015, first on the same grains and fragments as those used for microprobe measurements, and then on supplementary ones set in other epoxy mounts. For each investigated potential reference material, between five to fifteen grains or fragments have been investigated to test homogeneity from one grain/fragment to another (five mm-sized pieces of Moacyr and Manangoutry; fourteen μm -sized grains (250-500 μm) of UNIL-Mnz1; ten mm-sized pieces of UNIL-Mnz2; fifteen grains of USGS44069). Between 5 and 35 SIMS analyses (including traverses) have been performed in each

individual grain or fragment to test their internal homogeneity (Table 3 and supplementary material S3).

Moacyr, Manangoutry and UNIL-Mnz1 show homogeneous $\delta^{18}\text{O}$ at the scale of individual grain (or fragment) with a standard deviation (2SD) around 0.2-0.3 ‰ and rarely exceeding 0.45 ‰ (See supplementary material S3). Moreover, for each monazite, all tested grains have identical oxygen isotope composition within the uncertainty. Globally, Moacyr, Manangoutry and UNIL-Mnz1 have a good external reproducibility for each session with standard deviations (2 SD) ranging respectively from 0.24 to 0.45 ‰; 0.21 to 0.36 ‰; and 0.28 to 0.40 ‰ (Table 3). In contrast, for UNIL-Mnz2, the reproducibility is lower (but not unacceptable), typically within 0.36 to 0.56 ‰, except for one session with 0.25 ‰, due to larger heterogeneities within a single grain, even if all tested grains have similar range of isotopic composition. (Table 3 and S3). The reproducibility of USGS 44069 is between 0.45 to 0.73 ‰. Most of variations are intra-crystalline, but surprisingly there is no particular relationship between the variations in $\delta^{18}\text{O}$ values and chemical composition. For comparison, Rubatto et al. (2014) report a similar reproducibility of 0.4 to 0.6 ‰ for the USGS 44069 using SHRIMP and consider it as satisfying for routine analyses.

To summarize: Moacyr, Manangoutry, and UNIL-Mnz1 are chemically and isotopically homogeneous and appear to be suitable as reference materials for standardization, while this is not the case for UNIL-Mnz2, nor likely for USGS.

6. DISCUSSION

6.1. Accuracy of oxygen isotope data obtained by laser fluorination

In this study the oxygen isotope compositions, which serve as reference for the interpretation of the SIMS data, have been obtained by laser fluorination. It has been

questioned to which extent laser assisted fluorination produces reliable oxygen isotope measurement of monazite or phosphates in general. Brecker and Sharp (2007) argued that only conventional fluorination in Ni reaction vessels (CF) give accurate oxygen isotope compositions for monazite. They noted an offset of their LF-value with respect to the CF-data and suggest a correction of 1.1 ‰. Kohn et al. (1996) used a similar high correction of +1.4 ‰ to be added to the LF value measured.

Indeed, analyses of phosphates can be challenging. Phosphate analyses by fluorination are often hampered by low yields. One of the difficulties is that fluorination of phosphates may result in the production of POF_3 gas (in addition to other probably metastable intermediates of P-O-F) in addition to O_2 , a reaction which could plague both techniques. This may result in a fractionation between the metastable phosphorus-oxygen compounds that are retained in the liquid nitrogen traps and the evolved O_2 .

Using LF with F_2 as reagent as described above, replicate analyses of powdered monazite fragments or grains are found to be precise to within 0.2 ‰ when the oxygen yields are higher than 90 %. Indeed, Vennemann et al. (2002, 2012) showed in their comparison of analytical techniques for apatite – and their Ag_3PO_4 equivalents – that laser data can be exact. Good agreement between LF with yields >90 % and CF values can be obtained with careful lasing. Additional confirmation of the accuracy of the LF values comes from comparison with a completely different technique – the high-temperature reduction of phosphate. This method, abbreviated TC-EA (high temperature conversion elemental analyzer), is based on continuous flow techniques and the high-temperature reaction of Ag_3PO_4 to form CO as analyte gas. Vennemann et al. (2002, 2012) report good agreement between values using (1) both the TC-EA and the LF method and (2) TC-EA and CF method. TC-EA analysis, in addition, has the advantage, that it circumvents the problem of formation of POF_3 gas.

The above demonstrates the viability of LF analysis for phosphates, provided high yields (>90 %) are obtained. We are confident in the rigor of our analysis, and given that data obtained by laser assisted fluorination in the Lausanne laboratory show consistent high yields of > 90 % and a good reproducibility of the analyses introducing a correction factor is not considered necessary. Thus, the LF data (as listed in Table 2) without any further correction are used below.

Further work to address the questions related to fluorination of monazites and phosphates in general, including biogenic phosphates is in progress, and UNIL-mnz1 can at this stage be made available for a comparison of the CF and LF methodology. One of the main problems is the formation of metastable POF_3 gases, which is in fact intrinsic to fluorination, and thus to both LF and CF analysis. In addition, an important drawback for conventional fluorination analyses is the large amount of sample material needed (ca. 6-10 mg).

Analysis of monazite using the TC-EA method is promising. This method only requires small amounts of phosphate (≤ 1 mg equivalent of Ag_3PO_4). Work in progress focuses on establishing a protocol for the isolation of the PO_4^{3-} from monazite. While the isolation of PO_4^{3-} (a necessary step for TC-EA analysis) from natural apatite (see e.g. Sun et al. 2016) follows well-established techniques (e.g., Crowson et al., 1990; O'Neil et al., 1994; Stephan 2000, Vennemann et al. 2002), there is at present no protocol for the dissolution and precipitation of monazites (Vennemann, personal communication).

6.2. Instrumental Mass Fractionation and calibration curve

Measured $\delta^{18}\text{O}$ values on monazite need to be corrected for the instrumental mass fractionation (IMF) of the ion probe. IMF results from the instrumental bias due to the sputtering process that is mineral matrix dependent, and the transmission into the flight tube

and finally collectors of the mass spectrometer (Eiler et al., 1997). This means that IMF correction implies standardization for each session with a material of similar crystalline structure and similar chemical composition as the unknown. Ideally, IMF can be calculated as the difference between the absolute value of a standard (as measured by LF) and the measured (raw or uncorrected) value by SIMS: Using the α -notation this is:

$$\alpha_{\text{IMF}} = \alpha_{\text{LF}} / \alpha_{\text{SIMS}} \quad (3),$$

which is approximated by the well-known linear relationship between the individual delta values for the small isotopic fractionation observed (e.g. Rumble, 1982):

$$\text{IMF} = \delta^{18}\text{O}_{\text{LF}} - \delta^{18}\text{O}_{\text{SIMS}} \quad (4).$$

IMF obtained for the different monazites presented here vary by up to 3 ‰. This is outside the uncertainty of the measurements, on average of about 0.4 ‰ between two reference materials. Hence, it is necessary to establish a calibration curve using the available reference materials. This functional dependence is often assumed to be linear, but recent work on garnet (e.g. Ickert and Stern, 2013) or carbonates (Sliwinski et al., 2015) show the need for more complex functional relationships between composition and IMF.

To determine the influence of the chemical composition of the monazite on the IMF, the Mount 2 contained the five different potential reference materials, so that they were all analyzed during the same SIMS sessions without the need for an exchange of the sample holder. Moacyr, Manangoutry, and UNIL-Mnz1, as well as UNIL-Mnz2, and USGS 44069 were measured in three distinct runs, with similar analytical conditions from March to November 2015. The same mount was polished and cleaned in-between two analytical

sessions, in order to remove craters and any surface deposit. Although, UNIL-Mnz2 and USGS44069 are too heterogeneous in their $\delta^{18}\text{O}$ values for standardization, they were taken into account in the evaluations of the matrix effect, because (1) of their specific chemical composition, and (2) for the sake of comparison with the results of Rubatto et al. (2014) who have used USGS as the primary reference material.

Within a single session IMF varied from one monazite to another. Variations were as high as 3 ‰ (Table 3) for monazites with different chemical composition. The IMF-values of the individual monazites are always arranged in the same order in each individual session (from low to high): Manangoutry, UNIL-Mnz2, Moacyr, USGS, and UNIL-Mnz1 (Fig. 5). It is important to note, that absolute IMF-values changed between different sessions by up to 2 ‰, clearly showing the need for a complete calibration for each session.

The measured IMF variations contrast with the results of Ayers et al. (2006), who did not note any matrix effects, perhaps because the monazite reference materials used have a very restricted chemical composition (between Mnz_{100} - Mnz_{90}). In our study though, monazites plotting in this narrow compositional space (USGS; UNIL-Mnz1; Moacyr) have IMF variations in excess of 1.9 ‰. Although only a few details about analytical conditions are given in Ayers et al. (2006), it questions if whether the difference in IMF between the two studies might be related to the beam size used. Ayers et al. (2006) use a larger beam (25 μm) compared to the 10 μm beam-size used in the present study. However, tests using a 25 μm rastered beam appear to only slightly reduce the IMF variation (< 0.5 ‰) (see supplementary material S4). Most probably, e-gun tuning, which can strongly differ from SIMS to SIMS, as well as from one session to another, and/or a slightly different secondary beam alignment, could explain the differences observed between the results of Ayers et al. (2006) and this study.

In order to correct the IMF due to matrix effects, it is necessary to determine which elements control the IMF. Rubatto et al. (2014) propose three equations to perform matrix corrections, which are related to the cheralite and huttonite component in monazite. These were applied to Moacyr, Manangoutry, UNIL-Mnz1, and UNIL-Mnz2, using USGS as standard (to be consistent with Rubatto et al., 2014). Scatter is considerable and a difference of 0.4 to 1.3 ‰ is noted between IMF calculated with the equations of Rubatto et al. (2014) and the measured IMF values. These deviations for the reference materials set presented here are outside the measurement precision. Hence, other linear correction schemes were applied. In Figure 4, monazites analyses plotted in an IMF vs Ca + Si 3D-diagram define a planar linear regression. However, R^2 is not satisfying, with a range from 0.85 to 0.89 between sessions indicating that scatter is not negligible. With our setting, IMF correlates better with the Th content, or the monazite end-member content (YREEPO_4), certainly because chemical variations in monazite are affected by Th that is balanced by REE and Y variations. These correlations have been measured during three different sessions separated by several months (Fig. 5). The weighted linear regression of IMF vs. Th is robust (Fig. 5) with a R^2 ranging from 0.86 to 0.97 from one session to another. This result is in agreement with the results of Brecker and Sharp (2007). However, the USGS 44069, does not fit very well, resulting in a difference up to 0.5 ‰ between the predicted and the observed IMF of USGS (Δ_{IMF} in Fig.5). Note that USGS 44069-monazite plots along the cheralite-monazite solid-solution and has the highest xenotime component.

The calibration curve given as a function of the monazite component (YREEPO_4) describes the measured isotopic variations even better: the R^2 of the linear regression has a range from 0.96 to 0.97 depending on the particular session. Moreover, for each monazite, the difference between the predicted and the measured IMF rarely exceeds 0.3 ‰, even for the high variance session (06.11.15 in Fig. 5), a value that is close to the external reproducibility.

As indicated previously, USGS 44069 contains the highest xenotime component (4-8 %) balanced by a lower LREE content. Nevertheless, USGS is well defined by the XREEY calibration, which means that Y has little effect on IMF. This might be due to the fact that Y substitutes in the same nonaedric site as REE, without simultaneous intake or loss of elements in the tetrahedral site.

Finally, it is important to recognize that the slope of Th and YREEPO₄ calibration curves (Fig. 5) can vary from one session to another, suggesting that a new calibration curve must be determined for each analytical session.

7. Conclusions

The monazites Moacyr, Manangoutry, and UNIL-Mnz1 have a homogeneous chemical and oxygen isotope composition. The external uncertainty of the $\delta^{18}\text{O}$ values for these samples is better than 0.4 ‰. We thus suggest that they can be used as primary references material for oxygen isotope analyses by SIMS. In contrast, UNIL-Mnz2 and USGS are less homogeneous in their chemical and isotopic composition (because of small alteration zones or chemical zonation, respectively). They are consequently not recommended for use as reference materials. It is demonstrated that with the present analytical settings and using a wider range of chemical compositions, the IMF is best correlated with the YREEPO₄ end-member of monazite. Hence, this new calibration opens up the possibility of applying oxygen isotope measurements of monazites to a wider range of questions regarding fluid-rock interactions in earth sciences. It is also suggested that laser-assisted fluorination allows for precise and accurate oxygen isotope analyses of monazites (and phosphates in a wider sense). UNIL-Mnz1 monazite is available for sharing between laboratories.

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Figure and table captions

Figure 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 amongst the main end-members: cheralite, huttonite and YREEPO₄. End-members are calculated according to Pyle et al. (2001).

Figure 2: Back scattered electron images obtained by SEM of the studied monazites. These images demonstrate the homogeneity of Moacyr, Manangoutry and UNIL-Mnz1 (see also Table 1). In contrast, USGS 44069 is compositionally zoned along growth sectors, while some alteration zones are visible in UNIL-Mnz2. The latter are zones filled by Th-poor secondary monazite and thorite.

Figure 3: (U+Th+Pb) versus (Ca-Si) diagram showing the relative proportion of cheralite and huttonite substitutions in the monazites (calculated on a 4 oxygen per formula unit basis).

Figure 4: A 3-D plot of IMF vs. (Ca and Si) showing the linear regression plane. The dashed lines represent the regression plane, while measured values are represented by the symbols and the vertical anchor line indicating the distance of each point from the plane.

Figure 5: Plots showing regression lines for the IMF of three individual SIMS sessions. The graphs on the left show the fits with respect to Th, while the fits on the right are for the sum of the XREEY. The fits for XREEY provide systematically better MSWD's and R^2 than the Th-calibration curve. Data reduction and regression lines were generated using Isoplot/Ex v 4.15 (Ludwig, 2001) to take into account the observed chemical variations in major elements during the fitting.

Table 1: Representative chemical analyses measured by electron microprobe. End-member calculations were done according to Pyle et al. (2001). XREEY, Xcher, Xhutt correspond respectively to the fraction of YREEPO₄, cheralite and huttonite end-members. The number of electron microprobe analyses is 62 for Moacyr, 20 for Manangoutry, 84 for UNIL-Mnz1, 209 for UNIL-Mnz2 and 30 for USGS 44069.

Table 2: Oxygen isotope composition of monazite Moacyr, Manangoutry, UNIL-Mnz1, and UNIL-Mnz2, determined by laser fluorination (LF). Oxygen isotope composition reported in standard $\delta^{18}\text{O}$ notation as per mil variation relative to V-SMOW.

Table 3: External reproducibility of SIMS oxygen isotope values (2SD) for Moacyr, Managoutry, UNIL-Mnz1, UNIL-Mnz2, and USGS monazites during several sessions and corresponding Instrumental Mass Fractionation (IMF).

Table 4: Summary of chemical and oxygen isotope data of the investigated monazites: Moacyr, Manangoutry, UNIL-Mnz1, UNIL-Mnz2 and USGS monazite.

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Figure1

Figure2

Figure3

Figure4

Table1

wt.%	Moacyr		Manangoutry		UNIL-Mnz1		UNIL-Mnz2			USGS	
							pristine	altered			
CaO	0.32	0.32	0.91	0.93	0.06	0.07	0.32	0.33	0.38	0.78	0.60
SiO ₂	1.32	1.44	2.28	2.34	0.02	0.00	2.03	2.19	0.36	0.09	0.13
P ₂ O ₅	28.13	28.01	26.48	26.61	29.98	30.22	26.19	26.32	29.30	29.59	30.13
Y ₂ O ₃	0.67	0.75	0.25	0.27	0.02	0.11	0.75	0.87	0.30	2.88	2.53
Ce ₂ O ₃	29.64	29.58	27.70	27.52	21.99	20.27	32.25	32.61	36.97	28.30	29.62
La ₂ O ₃	14.07	14.15	13.41	13.50	35.15	34.80	13.60	13.61	15.40	12.57	13.31
Pr ₂ O ₃	3.50	3.70	2.84	2.87	2.64	2.95	3.05	2.94	3.39	3.28	3.13
Nd ₂ O ₃	10.97	10.70	9.57	9.68	8.59	9.58	8.26	8.40	9.04	13.26	13.44
Sm ₂ O ₃	2.40	2.32	1.37	0.89	0.67	0.88	1.53	1.55	1.71	2.64	2.57
Gd ₂ O ₃	0.81	1.12	0.51	0.32	0.10	0.22	0.45	0.33	0.47	1.85	1.78
ThO ₂	7.41	7.59	13.84	13.94	0.56	0.74	11.10	10.61	2.53	3.99	2.78
UO ₂	0.22	0.20	0.26	0.32	0.01	0.03	0.05	0.08	0.00	0.26	0.25
PbO	0.15	0.21	0.39	0.40	0.04	0.00	0.28	0.24	0.09	0.07	0.05
Tot	99.60	100.08	99.81	99.59	99.82	99.88	99.85	100.08	99.94	99.55	100.32
XREEY	0.91	0.91	0.83	0.82	0.99	0.99	0.88	0.89	0.96	0.93	0.95
Xcher	0.03	0.03	0.08	0.08	0.01	0.01	0.03	0.03	0.03	0.06	0.05
Xhutt	0.06	0.06	0.10	0.10	0.00	0.00	0.09	0.09	0.01	0.01	0.00

Table2

<i>Monazite</i>	<i>run ID</i>	<i>Date</i>	<i>Weight (mg)</i>	<i>Yield (%)</i>	<i>$\delta^{18}\text{O}$ (‰)</i>
Moacyr	58_2	25-Apr-15	1.56	112	1.37
	58_3	25-Apr-15	2.09	109	1.52
	58_6	25-Apr-15	0.70	103	1.47
	11_2	28-July-15	1.56	105	1.47
	11_3	28-July-15	1.21	103	1.45
	11_6	28-July-15	1.65	107	1.43
	Average		<u>1.45 ± 0.05 ‰ (1 sd; n=6)</u>		
Manangoutry	55_2	19-Apr-15	1.77	97	10.28
	55_3	19-Apr-15	2.46	101	10.25
	55_5	19-Apr-15	2.17	99	10.19
	64_3	04-March-16	1.73	98	10.15
	64_5	04-March-16	1.88	100	10.21
	64_6	04-March-16	2.10	101	10.06
	Average		<u>10.19 ± 0.08 ‰ (1 sd; n=6)</u>		
UNIL-Mnz1	26_2	02-July-13	1.22	100	8.38
	26_4	02-July-13	1.69	100	8.47
	26_7	02-July-13	1.68	102	8.31
	27_2	02-July-13	1.85	108	8.47
	27_4	02-July-13	1.84	108	8.52
	27_7	02-July-13	1.15	103	8.26
	49_2	23-June-14	1.24	91	8.30
	49_7	23-June-14	1.75	94	8.33
	99_3	15-Oct-14	1.85	95	8.62
	99_4	15-Oct-14	1.39	90	8.64
	99_6	15-Oct-14	2.06	96	8.82
	3_3	28-Oct-14	1.87	98	8.13
	3_4	28-Oct-14	1.29	97	8.57
	Average		<u>8.45 ± 0.19 ‰ (1 sd; n=13)</u>		
UNIL-Mnz2	4_3	09-Feb-14	3.19	109	9.68
	4_7	09-Feb-14	2.29	110	9.89
	11_3	01-Feb-14	3.03	97	9.68
	11_4	01-Feb-14	2.76	99	9.27
	11_7	01-Feb-14	2.34	93	9.23
	11_8	01-Feb-14	2.10	94	9.13
	17_2	19-March-14	3.03	95	9.59
	17_6	19-March-14	2.34	96	9.62

Table3

	Date	Reproducibility $\delta^{18}\text{O}$ (2SD)	n	IMF (‰)
Manangoutry				
Mount1	7/7/2014	0.36	10	-1.8
Mount1	8/1/2014	0.22	50	-1.3
Mount3	7/2/2015	0.46	6	0.5
Mount4	7/3/2015	0.32	6	0.0
Mount2	3/28/2015	0.34	18	-1.3
Mount2	4/11/2015	0.24	25	-0.5
Mount2	11/6/2015	0.21	25	-2.2
UNIL-Mnz2				
Mount1	7/7/2014	0.56	90	-0.8
Mount1	8/1/2014	0.36	52	-0.5
Mount2	3/28/2015	0.55	18	-0.6
Mount2	4/11/2015	0.49	20	0.0
Mount2	11/6/2015	0.25	25	-1.1
Moacyr				
Mount1	7/7/2014	0.29	66	-1.1
Mount1	8/1/2014	0.24	64	-0.4
Mount3	7/2/2015	0.35	19	1.8
Mount4	7/3/2015	0.35	6	0.8
Mount2	3/28/2015	0.29	22	-0.4
Mount2	4/11/2015	0.34	34	0.3
Mount2	11/6/2015	0.45	38	-1.2
USGS 44069				
Mount2	3/28/2015	0.73	18	0.0
Mount2	4/11/2015	0.67	23	0.7
Mount2	11/6/2015	0.45	16	-0.7
UNIL-Mnz1				
Mount1	7/7/2014	0.36	66	0.8
Mount1	8/1/2014	0.29	47	1.3
Mount4	7/3/2015	0.32	6	1.9
Mount2	3/28/2015	0.31	17	1.3
Mount2	4/11/2015	0.40	30	1.5
Mount2	11/6/2015	0.28	25	0.6

Table4

	Chemical composition				$\delta^{18}\text{O}$ (‰)		U-Pb age (Ma)
	XREEY	Xcher	Xhutt	Th (%)	LF $\pm$ 1SD	2SD SIMS	
Moacyr	0.91	0.03	0.06	6.5	1.45 $\pm$ 0.05 (n=6)	0.3	511 ¹
Manangoutry	0.82	0.09	0.09	12.1	10.19 $\pm$ 0.08 (n=6)	0.3	555 ²
UNIL-Mnz1	0.99	<0.01	<0.01	0.6	8.45 $\pm$ 0.19 (n=13)	0.3-0.4	n.d.
UNIL-Mnz2	0.88	0.03	0.09	9.4	9.51 $\pm$ 0.27 (n=8)	0.5-0.6	n.d.
USGS 44069	93	7	0	2.1-5.5	7.67 $\pm$ 0.13 (n=7) ⁴	0.4-0.6	424 ³

¹ Gasquet et al. (2010)

² Paquette and Tiepolo (2007)

³ Aleinikoff et al. (2006)