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An improved EPMA analytical protocol for U-Th-Pb$_{total}$ dating in xenotime: Age constraints from polygenetic Mangalwar Complex, Northwestern India

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ABSTRACT

EPMA U-Th-Pb$_{total}$ dating in U- and Th bearing minerals (e.g., monazite, zircon, and xenotime) is a low-cost and reliable technique used for retrieving age information from detrital, diagenetic and low to high-T metamorphic, as well as magmatic rocks. Although, the accuracy on measured ages obtained using EPMA is considered to be poor compared to isotopic ages, the superior spatial resolution, ability to integrate textural and age information by in-situ measurement, lack of sample damage and easier and cheaper data generation in EPMA make chemical dating a very valuable tool to decipher diverse petrological processes.

This contribution presents an improved analytical protocol to obtain precise estimates of U, Th and Pb concentrations in xenotime. Results were tested on monazite standard (Moacyr pegmatite, Brazil; TIMS age: 487 ± 1 Ma) as the reference material. The proposed analytical protocol has been successfully applied to achieve an analytical uncertainty of less than 10% in U, Th and Pb measurements in xenotime. The protocol was further used to resolve polygenetic xenotime ages (ca. 1.82, 1.28 and 0.93 Ga) in metapelite samples from the Mangalwar Complex, Northwestern India. Monazites in the same samples were also analyzed and found to preserve the two younger ages (i.e., ca. 1.28 and 1.0 Ga). The obtained ages from the xenotime and monazite very well corroborate with the earlier published ages from the area validating the proposed analytical protocol.

1. Introduction

Xenotime [Y(HREE)PO$_4$] is a common accessory mineral that hosts significant concentration of heavy rare earth elements (HREEs) and can grow in a wide range of P-T conditions (Palache et al., 1951; Giere, 1996; Spear and Pyle, 2002; Rasmussen, 2005; Rasmussen et al., 2005; Hetherington et al., 2008; Suzuki and Kato, 2008). The mineral hosts >100 parts per million (ppm) of uranium (Rasmussen et al., 2011) and excludes Pb during its growth, and once formed, it is extremely resistant to diffusional Pb loss over geological time scales at temperatures <750°C (Dahl, 1997; Cherniak, 2006). These features make xenotime an ideal mineral for U–Th–Pb geochronology (Fletcher et al., 2000, 2004; Harrison et al., 2002; Hetherington et al., 2008; Suzuki and Kato, 2008). The ability of the mineral to record processes in wide metamorphic conditions ranging from lower greenschist to upper amphibolite facies

(Hetherington et al., 2008; Rasmussen et al., 2011) and igneous events (Förster, 1998) endorses it as a robust geochronometer. Additionally, recent studies reveal that xenotime can grow in diagenetic environment (Rasmussen, 1996; Rasmussen et al., 1998) having potential to be used as a chronometer for diagenetic and low temperature hydrothermal events.

Understanding the evolution of high grade polymetamorphic terrains requires detailed petrological, geochemical and geochronological studies. Delineating geochronological evolution of polymetamorphic terrains is not straight forward, and complexities may arise as a consequence of overprinting by latest event, erasing earlier tectono-metamorphic records (e.g., Holdsworth et al., 2001; Dutch et al., 2005). Nevertheless, a promising approach to this problem is to integrate age information from growth zones of geochronometers (viz., zircon, monazite, and xenotime), which can be best approached by in-situ dating methods. In particular, monazite has received greater appreciation for preserving multiple events because of its significant response to changing metamorphic condition, while the same is not true for zircon, due to its meager response to weaker tectono-thermal events (e.g., Schenk et al.,

2005; Boniface et al., 2012). In spite of being competent, or indeed an alternative to monazite and/or zircon in geochronological studies, xenotime is not extensively used for dating (e.g., Suzuki and Adachi 1991; Griffin et al., 2000; Asami et al., 2002; Grew et al., 2001; Hetherington et al., 2008; Suzuki and Kato, 2008).

High spatial resolution achievable by in-situ U-Th-Pb$_{total}$ dating using electron probe micro analyzer (EPMA) (Suzuki and Adachi, 1991) aids in obtaining texturally constrained precise age information from individual micro-domain in zoned grains (Hetherington et al., 2008). The observed concordancy in Th-Pb and U-Pb systems in monazite and xenotime (e.g., Köppel and Grünenfelder, 1971; Grauert et al., 1974; Köppel, 1974; Hawkins and Bowring, 1997) stimulate the potential of these minerals for U-Th-Pb$_{total}$ dating. Unlike isotope methods, the accuracy and precision in the chemical ages are contentious (Cocherie et al., 2005; González-Álvarez et al., 2006; Spear et al., 2009; Jercinovic et al., 2012). However, with the understanding of appropriate limitations and taking proper precautionary measures, EPMA chemical dating can be successfully used in decoding complex tectonic events (Finger et al., 1998; Montel et al., 2000). The recent developments in chemical dating such as: (i) introduction of spectrometer incorporating larger crystals (e.g., VLPET crystal of Cameca SX-Geochron/Ultrachron, Williams et al., 2006, 2007; Hetherington et al., 2008), (ii) upgraded softwares for simultaneous analysis of U, Pb and Th in multiple spectrometers (Jercinovic and Williams, 2005; Williams et al., 2006, 2007; Spear et al., 2009), and (iii) "sub-counting" method to obtain a more precise and accurate analysis of U, Th and Pb (Spear et al., 2009; Prabhakar, 2013) are critical in order to achieve better analytical accuracy and precision. Several workers have tested and proposed improved techniques for measuring trace element concentrations in monazite (e.g., Suzuki and Adachi, 1991; Jercinovic and Williams, 2005; Williams et al., 2006, 2007; Spear et al., 2009; Jercinovic et al., 2012; Prabhakar, 2013), and have enhanced the accuracy and precision on age determinations. Because of ubiquitous occurrence of monazite in most pelitic/quartzofelspathic rocks, monazite chemical dating has received greater attention, whereas xenotime, being relatively sparse in occurrence, has not gained much consideration. Further, chemical ages obtained from xenotime have always been associated with larger errors (Chatterjee et al., 2007; Das et al., 2015) because of lower concentrations of U, Th and Pb and consequential low analytical precision. In a recent study, Hetherington et al. (2008) developed a novel analytical protocol for xenotime chemical dating and achieved very low uncertainties (≤3%) on measured ages. The use of very large pentaerythritol (VLPET) crystal installed in the Cameca SX-Ultrachron at University of Massachusetts allowed the authors to achieve very high analytical precision for U, Th and Pb in the xenotime. However, it is unrealistic to acquire such high analytical precision using common electron probe micro-analyzers (Cameca SX-100, Cameca SX-Five and Jeol JXA-8230 SuperProbe) because of the absence of very large crystals, which enhance counting statistics.

In light of the advancements in analytical techniques and requirement of a protocol to date xenotime in easily accessible EPMAs (without very large crystals), in this contribution we intend to improve the analytical precision of U, Th and Pb measurements. For the same, we aim to incorporate the improved methodologies suggested by Spear et al. (2009), some of which were successfully adopted by Prabhakar (2013) for improving the analytical precision in monazite. Further, in this contribution, we present ages recorded by coexisting monazite and xenotime in same sets of samples and document the disparities in preserved age information. The comparable crystal-chemical properties of xenotime and monazite, along with negligible initial Pb content suggest that EPMA methodologies applied to monazite dating are also applicable to xenotime (Hetherington et al., 2008). Therefore, in the absence of an established xenotime standard, the protocol was

tested in monazite from Moacyr pegmatite (Brazil). The small difference in matrix between LREE dominated monazite and HREE dominated xenotime should not affect U, Th and Pb measurement. This was tested by comparing results obtained for Moacyr monazite using our new protocol (for xenotime analysis) and the improved protocol of Prabhakar (2013) for monazite analysis. The calculated ages obtained using our new xenotime protocol and existing monazite protocol (Prabhakar, 2013) show significant consistency. The weighted mean ages obtained for Moacyr monazite (TIMS age = 487 ± 1 Ma; Crowley et al., 2005) using new xenotime protocol and Prabhakar's (2013) monazite protocol are 478 ± 8 Ma (n = 14) and 485 ± 8 Ma (n = 21), respectively (Fig. 1; data in Supplementary Appendix A1). The improved analytical protocol was used to resolve three age populations in xenotime at ~1.82 Ga, ~1.28 Ga, and ~0.93 Ga for the metapelites of polymetamorphic Mangalwar Complex (MC) within central Aravalli-Delhi Fold Belt (ADFB), NW India. Monazites in the same samples yielded two distinct ages at ~1.28 Ga and ~1.00 Ga. The preservation of three events in xenotime compared to two in monazite in the same samples suggests the requirement of multi-mineral chemical dating for comprehensive geochronological studies. The obtained ages and their implications are discussed in detail in later sections.

2. Analytical techniques and conditions

Three samples of metapelite from the Mangalwar Complex rocks of the ADFB were selected for the present study. Well-polished thin sections were observed under a JEOL JSM-6490 scanning electron microscope (SEM) to understand textural settings of xenotime and monazite in the samples. Major and trace element analyses of xeno-
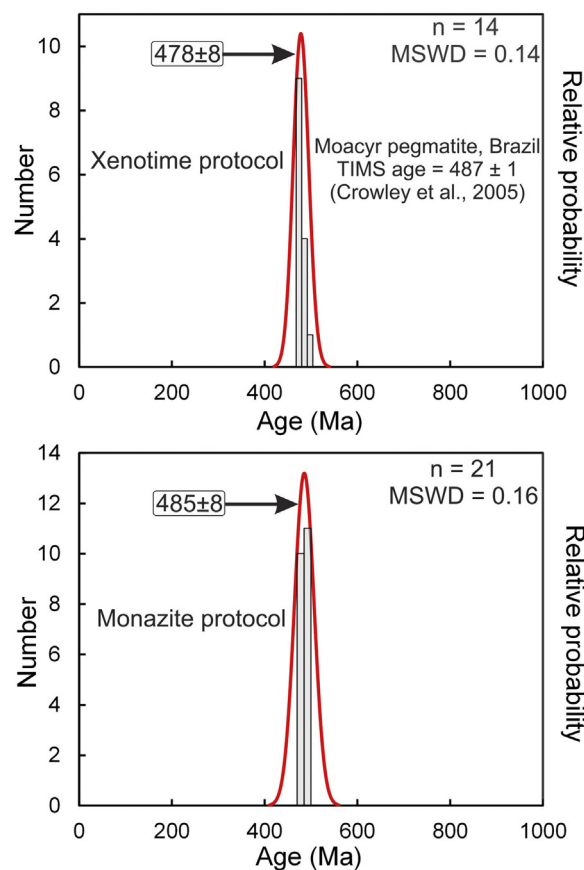

Fig. 1. Relative probability and histogram plots showing statistically significant age peak for monazite standard (Moacyr pegmatite, Brazil) using xenotime (a) and monazite protocol (b).