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LGC-1: A zircon reference material for *in-situ* (U-Th)/He dating

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ABSTRACT

A pairwise *in-situ* (U-Th)/He dating method has been proposed for mitigating matrix-related bias in U and Th measurements using synthetic reference materials. This method requires a natural zircon reference material whose (U-Th)/He age should be homogeneous on the scale (~10–100 μm) to be used in such dating experiments. A newly characterized zircon LGC-1 megacryst fulfils this requirement. This pale-yellowish, flawless Sri Lanka *gem* specimen is about 1.2 $*$ 0.8 $*$ 0.8 cm in size. Optical microscopy, cathodoluminescence-imaging, X-ray elemental mapping, and Raman spectroscopy on a large number of random shards did not reveal any detectable textural and compositional heterogeneity. Laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) analyses on a large number of randomly selected fragments yield 266 measurements of U, Th and Pb concentrations, which are within the corresponding experimental uncertainties. The weighted mean U, Th and Pb concentrations are 357.7 ± 1.8 ppm, 740.9 ± 5.0 ppm, and 39.06 ± 0.18 ppm, respectively, with a weighted mean Th/U ratio of 2.07 ± 0.01, indistinguishable from Isotope Dilution ICP-MS (ID-ICP-MS) and Thermal Ionization Mass Spectrometry (ID-TIMS) results. ID-TIMS U/Pb ages are concordant within uncertainties of decay constants, with a concordia age of 541.70 ± 0.70 Ma. Conventional (U-Th)/He dating on 28 random shards from the crystal in different laboratories gives a central age of 476.4 ± 5.7 Ma. Six *in-situ* (U-Th)/He analyses yield consistent ^{4}He concentrations and ages with weighted mean values of 1248 ± 46 nmol/g and 462 ± 21 Ma, respectively. Fractions of this zircon have been shared with several laboratories in the Australia, China, UK and US, and are expected to serve as a reference for both *in-situ* and conventional (U-Th)/He analyses. The combination of analytical methods used to characterize LGC-1 zircon may be used as a template for future age reference calibration.

1. Introduction

Zircon is an extremely durable mineral, which is commonly found in siliciclastic rocks and is rich in U and Th. These properties make zircon uniquely well suited for sedimentary provenance studies. Using micro-analytical methods such as laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) or secondary ion mass spectrometry (SIMS), it has become routine practice to determine the probability distribution of ~100 detrital zircon U/Pb ages as a characteristic fingerprint to trace the flow of sand through modern and ancient sediment routing systems. Dozens of papers employing this method are published each year. The power of such provenance studies would greatly increase if it were possible to routinely double-date detrital zircons with the *in-situ* U/Pb and (U-Th)/He methods (Evans et al., 2015; Horne et al., 2016; Rahl et al., 2003; Reiners et al., 2005).

Several research groups around the world are currently pursuing this goal using a variety of approaches. While the *in-situ* U/Pb method has been well-established, the *in-situ* (U-Th)/He method is still under development. Boyce et al. (2006), Tripathy-Lang et al. (2013) and Horne et al. (2016) used a 'first principles' approach, in which the absolute concentrations (*e.g.*, in units of ppm or fmol/μm^{3}) of U, Th and ^{4}He are measured by laser ablation. Vermeesch et al. (2012) proposed an alternative approach, in which the raw mass spectrometric measurements are normalized to a standard of known ^{206}Pb/^{238}U, ^{208}Pb/^{232}Th and ^{206}Pb/^{238}U, ^{208}Pb/^{232}Th and ^{208}Pb/^{206}Pb and (U-Th)/He ages. A recent study by Evans et al. presented a modified version of a 'pairwise' dating method proposed by Vermeesch et al. (2012). The modified method uses a 'Kappa' calibration constant derived from multiple

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standard analyses for age calculation of unknown samples. The method is similar to the zeta calibration factor for fission-track (Hurford and Green, 1983) or the J-factor for $^{40}Ar/^{39}Ar$ dating (Mitchell, 1968).

The pairwise dating method crucially depends on the availability of a well behaved age reference material that is spatially homogeneous in its U, Th and He content. This condition in turn requires large, unzoned crystals with a simple thermal history. Previous *in-situ* dating studies by Vermeesch et al. (2012) and Evans et al. (2015) employing the pairwise dating methods have used Sri Lanka zircon crystals (RB140 and B188) from Nasdala et al. (2004) as age references. These cm-sized gem-quality zircons are an attractive option for three reasons. First, they are old (>400 Ma) and rich in actinides. This is important because the analytical uncertainty of the reference's U, Th and He measurements is propagated into the sample's age uncertainty. By being very rich in the three elements of interest, this error component is kept very small. Second, Sri Lanka zircons are often of centimeter-size, so that a single crystal can supply enough material to last several laboratories for many years. Third and finally, although all Sri Lanka zircons are found as pebbles in alluvial sediments, their ultimate source is likely to be found in pegmatitic rocks that have undergone a simple cooling history. Being tectonically inactive, Sri Lanka is characterised by extremely low erosion rates that have kept the zircons near the Earth's surface for hundreds of millions of years (Von Blanckenburg et al., 2004). As a result, the *gem* quality zircons lack the helium depleted rims that characterise most natural zircons. Furthermore, by virtue of having been transported and abraded during transport and deposition, Sri Lanka zircons have generally lost any diffusively depleted rim that might have existed.

Motivated by the above background information, we examined a number of commercially sourced gem-quality Sri Lanka zircon megacrysts, from which we selected five grains with different, but uniform colours for further detailed compositional analyses using a combination of methods, including optical microscopy, Cathodoluminescence-imaging, Raman Spectrometry, wavelength dispersive X-ray spectroscopy, Electron-probe Microanalysis (EPMA), LA-ICP-MS, Isotopic Dilution Thermal Ionization Mass Spectrometry (ID-TIMS) U/Pb dating, conventional (U-Th)/He dating, and *in-situ* (U-Th)/He dating. Results determined from a large number of randomly selected chips of LGC-1 grain did not reveal any remarkable textural zoning or compositional heterogeneity. The consistent (U-Th)/He ages fulfil the requirements for a high-quality age reference material for the pairwise *in-situ* (U-Th)/He dating methods of Vermeesch et al. (2012) and Evans et al. (2015).

2. Requirements for age references of the pairwise method

Similar to requirements for age references of other *in-situ* geochronological methods, an *in-situ* (U-Th)/He age reference needs to be homogenous in its (U-Th)/He age. An *in-situ* (U-Th)/He age analysis involves two ~10–50-μm laser ablation spots, one for ^{4}He analyses in an ultra-high vacuum noble-gas system, and the other for U-Th analyses using LA-ICP-MS, or SIMS. These two spots are positioned either spatially close, or one reoccupying (or inside of) the other (*e.g.*, Evans et al., 2015; Vermeesch et al., 2012). To produce a consistent age, the ^{4}He and U-Th measurements from the two spots should be representative of each other; it is thus required to have uniform ^{4}He and U-Th distributions at least at a scale of tens of micrometers. Otherwise, incomparable ^{4}He and U-Th results would be obtained, due to ^{4}He redistribution by alpha recoil (Farley et al., 1996).

Also, zircon samples that have experienced a complex thermal history may not be suitable as an *in-situ* dating reference material. This is because helium diffusion at elevated temperatures may produce a ^{4}He gradient from the grain margin to the core. To summarize, an *in-situ* (U-Th)/He age reference material should fulfil the following criteria. (1) The grain should be of a relatively considerable size to allow for sharing among laboratories. (2) No significant U and Th zoning and

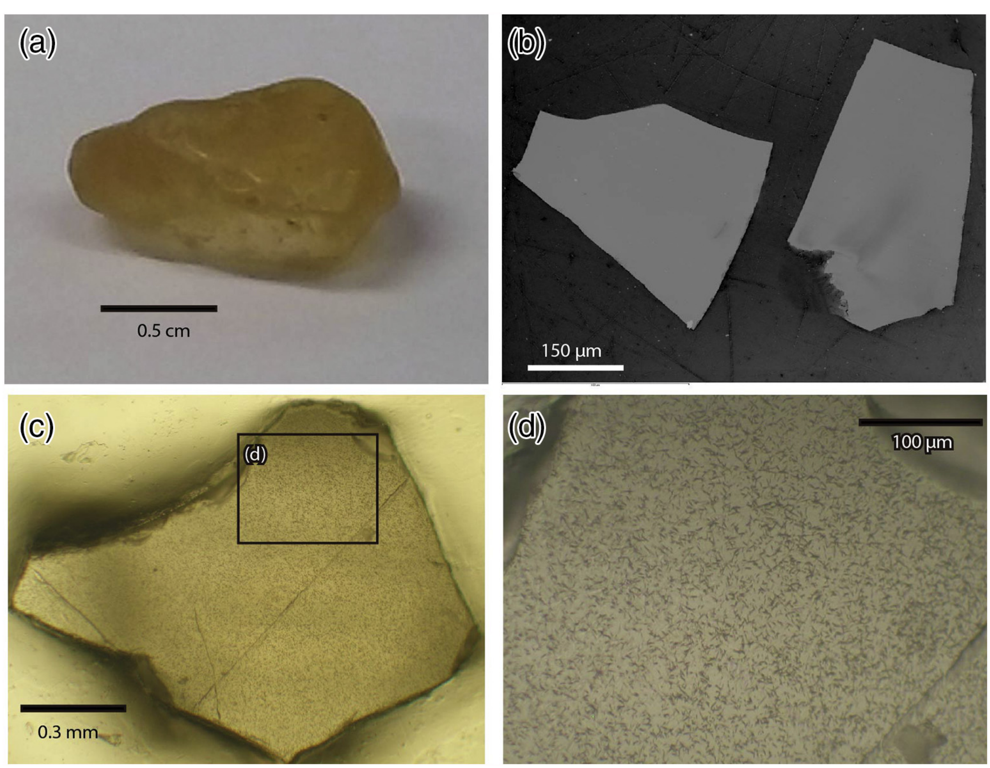

Fig. 1. (a) Appearance of LGC-1. (b) Representative CL images of two random shards showing textural homogeneity of LGC-1 zircon. (c) A representative spontaneous fission-track map of a randomly selected shard indicating the uniform distribution of ^{238}U, spontaneous fission of which formed the observed fission-tracks. (d) A close-up view of the upper portion of panel (c).

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