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Trace element homogeneity from micron- to atomic scale: Implication for the suitability of the zircon GJ-1 as a trace element reference material

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A B S T R A C T

The quality of a chemical reference material relies on the fact that the composition of the material is homogeneous across all scales. A series of different techniques have been used to evaluate the trace element homogeneity of the GJ-1 reference zircon from the micron- to atomic scale. Cathodoluminescence imaging was conducted along with quantitative crystallographic orientation analysis and trace element analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). The nanometre-scale homogeneity was evaluated by analysing five mineral tips using atom probe tomography, which provides atomic scale three dimensional chemical reconstructions with unprecedented spatial resolution. Results show that the GJ-1 reference zircon is homogeneous at all scales, both structurally and chemically. Crystallographic orientation data confirms that this *gem* quality zircon has no detectable internal crystallographic orientation changes such as crystal-plastic deformation features or cracks. No mineral inclusions were found. Atom probe tomography shows that there is a lack of any chemical clustering or other modes of spatially defined elemental accumulation or depletion for the most abundant trace elements such as Y, Yb and Hf. This finding is supported by LA-ICPMS data revealing homogeneity within the analytical precision. Trace elements of significant abundance include P, Yb, Y, U and Hf, with contents of 30 ± 6, 65 ± 2, 238 ± 5, 284 ± 14 and 6681 ± 57 ppm, respectively. Hence, the GJ-1 zircon used as a reference zircon for U—Pb and Hf-isotopic studies is also a suitable zircon reference material for trace element analyses.

1. Introduction

The accuracy of trace element (including rare earth element) data in zircon is of increasing importance in geoscience as zircon ($ZrSiO_4$) is now commonly used, not only as a reliable geochronometer utilizing the U—Th—Pb isotope systems, but also as a trace element monitor. The tendency of the accessory mineral zircon to incorporate trace elements (including radionuclides) and its robustness against both chemical and physical alteration after growth as well as extremely sluggish diffusive re-equilibration at high temperatures contribute to the high fidelity of the zircon trace element record (e.g. Cherniak et al., 1997a; Cherniak et al., 1997b; Watson and Cherniak, 1997; Cherniak and Watson, 2003; Hoskin and Schaltegger, 2003). Many trace elements tend to participate in a coupled substitution within the zircon crystal structure and therefore behave relatively coherently. Phosphorus concentrations, for example, correlate positively with Y and REEs (rare earth elements), reflecting the so-called xenotime substitution (REE, $Y)^{3+} + P^{5+} = Zr^{4+} + Si^{4+}$ (Belousova et al., 2002). Many other coupled substitutions may occur within zircon (e.g. Reid et al., 2011), although it has also been shown that elements such as Li and Al tend to occur interstitially (Bouvier et al., 2012).

In recent years, the usefulness of zircon trace element data has been rigorously tested and developed into a tool used in igneous source rock determination (Belousova et al., 2002; Grimes et al., 2007; Grimes et al., 2015; Chapman et al., 2016) as well as petrogenetic modelling (Belousova et al., 2006). In addition, trace element ratios become increasingly important. For example, zircon incorporates ~1 wt% of Hf into its crystal structure (e.g. Patchett and Tatsumoto, 1981; Claiborne et al., 2006). As Hf is nearly exclusively incorporated into zircon, it controls the Hf budget of most crustal rocks (Wark and Miller, 1993). At the same time, Lu occurs in relatively low concentrations in the range of a few tens of ppm; hence zircons usually have a low Lu/Hf ratio. Because of this very low Lu/Hf ratio, zircon can preserve the $^{176}Hf/^{177}Hf$ of its parental magma at the time of crystallization and, when combined with U—Pb analysis, this mineral has provided unprecedented insight into crustal evolution (e.g. Vervoort and Blichert-Toft, 1999; Amelin et al., 2000; Griffin et al., 2000; Kemp et al., 2005; Belousova et al., 2006; Scherer et al., 2007; Belousova et al., 2010) and sedimentary

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provenance (e.g. Andersen, 2005; Griffin et al., 2006). Routine zircon analyses of U—Pb, Hf-isotope and other trace elements using LA-ICPMS and LA-MC-ICPMS have increased dramatically in recent years (Blichert-Toft et al., 1997; Belousova et al., 2010).

The increase in this type of analysis has created a need within the geological community of well-characterized reference materials to monitor instrumental drift and to define external reproducibility. Such a reference material is a material that is "sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in measurement or in examination of nominal properties" (Potts, 2012). While geochemical analysis is becoming increasingly common mainly using in-situ LA-ICPMS analysis, this type of analysis is highly destructive. Consequently, there is an ever increasing demand for chemically homogeneous, well-characterized reference material for zircons. Over the decade, the GJ-1 reference zircon developed at GEMOC/CCFS (Macquarie University, Sydney, Australia) has been widely distributed as a reference zircon for U—Pb geochronology and Hf-isotope analyses (e.g. Jackson et al., 2004; Elhlou et al., 2006; Morel et al., 2008; Nasdala et al., 2008; Frei and Gerdes, 2009; Matteini et al., 2010; Cottle et al., 2012; Košler et al., 2013).

At the same time, over the last decade it has been shown that elements within zircon can be heterogeneously distributed at the micrometre scale (e.g. Reddy et al., 2006, 2007, 2009; Timms et al., 2006; Piazolo et al., 2012; Hofmann et al., 2009, 2014). In addition, recent studies using now commonly available advanced techniques such as scanning ion imaging have revealed that zircons previously thought to be homogeneous in isotopic and trace elemental composition can exhibit significant elemental clustering at the submicron scale (e.g. Kusiak et al., 2013a, 2013b; Kovaleva et al., 2015).

Recent advances in atom probe tomography (APT) now allow analysis of non-conductive minerals such as zircon in terms of trace element homogeneity or heterogeneity at the nanometre scale. More specifically, ATP provides three-dimensional visualization and chemical identification of materials at the atomic scale (Gault et al., 2012). In this technique, ions are successively field-ionised from the tip of a needle shaped sample (approximately 160–240 nm width, 800–1200 nm length), collected by a position sensitive detector and their mass-to-charge ratios recorded by time-of-flight spectrometry. From this data, a three dimensional reconstruction of the field-evaporated volume is obtained consisting typically of millions of atoms. Due to the successive field evaporation of atoms from the end of the atom probe tip, the sample tip is destroyed during the analysis. Valley et al. (2014) utilized APT to investigate zircon from the oldest known zircon suite (Jack Hills zircons). They found that trace elements such as Y and Pb could cluster at the nanometre scale due to inferred prolonged heating. Recently, APT has been used to observe deformation-induced redistribution of trace elements within zircon grains from the Archean Napier Complex, Antarctica (Piazolo et al., 2016). In their study, Piazolo et al. (2016) successfully explain the origin of reverse and normal discordance commonly observed in zircons and their link to structural variations induced by crystal-plastic deformation. They found that dislocations that move through the crystal lattice of zircons tend to accumulate Al, Y, and U, while pipe diffusion along dislocation arrays can lead to preferential removal of certain elements (e.g. Pb) resulting in enriched chemical or structural sinks towards the end of dislocation arrays. As a result of this process, trace elements are redistributed and thus their spatial distribution is heterogeneous at the atomic to micrometre scale.

Here, we analyse in detail the GEMOC GJ-1 zircon reference material (crystal #81) in order to assess its chemical and structural homogeneity from the micron to the atomic scale. GJ-1 zircons have been used since 2002 (e.g. Spetsius et al., 2002), primarily as a zircon reference material for U—Pb dating (e.g. Jackson et al., 2004; Gerdes and Zeh, 2006; Zheng et al., 2006), but also for Hf-isotope analysis (e.g. Elhlou et al., 2006; Gerdes and Zeh, 2006; Griffin et al., 2006; Yuan et al., 2008; Matteini et al., 2010). Individual grains are commonly between 0.7 and 1 cm in size and are thought to originate from African pegmatites with a crystallization age of 608.5 ± 0.4 Ma (Jackson et al., 2004; Elhlou et al., 2006).

We show that the GJ-1 zircon reference material is exceptionally homogeneous even at the atomic scale and is therefore not only a reliable reference material for U—Pb dating and Hf-isotope studies but also for trace and rare earth element analysis. Therefore, we envisage that users will utilize GJ-1 not only as a reference material for U—Pb and Hf isotope analysis but also for trace element analysis; an analysis more and more frequently used. In addition, our study demonstrates that APT which provides three-dimensional atomic scale elemental reconstructions is an appropriate technique to assess the suitability of analytical reference materials at the nanometre scale.

2. Methods

2.1. Cathodoluminescence (CL) imaging and quantitative crystallographic orientation analysis

To evaluate the homogeneity of the zircon, CL imaging was performed on a Zeiss EVO SEM with a tungsten source operated at 15 kV under high vacuum.

We conducted two sets of quantitative crystallographic orientation analyses, namely electron backscatter diffraction (EBSD) and transmission Kikuchi diffraction (TKD), to test if there was any distortion of the crystallographic lattice at the micron and nanometre scale, respectively. ESBD analysis was conducted on the polished reference zircon embedded in epoxy, while TKD analysis was conducted on the ATP tip before ATP analysis (for details of the preparation of the atom probe tip see below). To prepare for EBSD analysis a colloidal silica–water solution (mixed in proportion 80:20) was used at the final stage of polishing for 3–5 min to reduce surface damage produced by mechanical polishing. Subsequently the sample was carbon-coated. We used the HKL NordlysNano high sensitivity Electron Backscatter Diffraction (EBSD) detector and indexed with AzTec analysis software (Oxford

Table 1
Results from analysis on BCR-2 Columbia River Basalt reference material, which was analysed during this work versus U.S. Geological Survey Recommended/Information values.

Element	Mean (this study) ppm	1 sigma	USGS values[a] ppm	±
Li	9.88	0.50	9	2
Mg	21,534	702	21,600	300
Al	74,448	2514	71,400	1000
P	1266	204	1500	100
Ti	13,694	453	13,500	300
V	433	14	416	14
Cr	14.6	0.5	18	2
Y	32.05	3.25	37	2
Mo	238.79	7.53	248	17
La	24.80	0.79	25	1
Ce	51.78	1.61	53	2
Pr	6.50	0.21	6.8	0.3
Nd	28.80	0.94	28	2
Sm	6.43	0.25	6.7	0.3
Eu	1.98	0.07	2	0.1
Gd	6.03	0.23	6.8	0.3
Tb	0.98	0.04	1.07	0.04
Ho	1.23	0.04	1.33	0.06
Tm	0.48	0.02	0.54	
Yb	3.39	0.14	3.5	0.2
Lu	0.50	0.02	0.51	0.02
Hf	4.70	0.18	4.8	0.2
Th	5.88	0.19	6.2	0.7
U	1.79	0.06	1.69	0.19

[a] https://crustal.usgs.gov/geochemical_reference_standards/basaltbcr2.html#information.

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