Chemical Geology 438 (2016) 11–24

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

An investigation of the laser-induced zircon 'matrix effect'

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ARTICLE INFO

Article history:
Received 28 January 2016
Received in revised form 12 May 2016
Accepted 18 May 2016
Available online 25 May 2016

Keywords:
Laser ablation
Zircon
Matrix effects
U–Pb geochronology
Annealing
Raman spectroscopy

ABSTRACT

This study aims to improve our understanding of the current limitations to high-precision U–Pb analysis of zircon by LA-ICP-MS by investigating the underlying causes of variation in ablation behaviour between different zircon matrices. Multiple factors such as: the degree of accumulated radiation damage; trace element composition; crystal colour; and crystallographic orientation are all systematically investigated. Due to the marked decrease in elastic moduli of natural zircon crystals with increasing radiation damage, the accumulation of this damage is the dominant factor controlling the rate of ablation for partially damaged to highly metamict zircon samples. There are slight differences, however, in ablation behaviour between highly crystalline matrices that cannot be attributed solely to differences in the degree of accumulated radiation damage. These differences are associated with structural weakening (i.e., decrease in elastic moduli and overall lower mechanical resistance) caused by an increasing degree of cation substitution in some of the zircon samples. Effects of crystallographic orientation and of crystal opacity (i.e., colour) on ablation behaviour are negligible compared to the combined influences of accumulated radiation damage and trace element substitution into the zircon structure. Experiments performed on natural and annealed zircon grains reveal that the reduction in ablation rates observed for the treated samples compared to the untreated grains is proportional to the degree of structural reconstitution achieved after annealing. Thermal annealing of natural zircon at temperatures >1000 °C results in much more uniform ablation characteristics. This 'homogenisation' of ablation behaviour between zircon matrices produces a decrease in the laser-induced matrix effects and subsequent improvement in the accuracy of $^{206}Pb/^{238}U$ ratio determinations by LA-ICP-MS.

1. Introduction

The uptake of laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) as an essential tool for rapid, cost-effective and high spatial resolution dating of zircon has been unprecedented (e.g., Schoene, 2014). Unfortunately, however, the matrix dependency of the ablation process remains a major drawback of the current method, limiting its accuracy and precision. Currently, LA-ICP-MS is routinely used to generate zircon U–Pb ages with an accuracy of ~2–3% (2σ) relative to the long-established benchmark thermal ionisation mass spectrometry (TIMS) U–Pb analysis of bulk zircon (e.g., individual grains or parts of grains; Schaltegger et al., 2015). The potential for any improvement in these figures appears to be influenced by systematic biases, which are associated with matrix differences between unknowns and the reference zircon materials used for standardization (e.g. Klötzli et al., 2009; Košler et al., 2013). These effects are further aggravated by the fact that it is unusual for 'unknown' natural zircon samples to share the traits that characterise a zircon reference material (i.e., well-ordered crystalline materials without many inclusions). It is now clear that the mitigation of these laser-induced 'matrix effects' will only be possible if the underlying causes are identified and understood.

Recent studies have linked the analytical bias between LA-ICP-MS dates and those determined by TIMS to the differential response of unknown and standard zircon materials to laser radiation (Marillo-Sialer et al., 2014; Steely et al., 2014). Although the underlying causes of this variable response have not yet been fully elucidated, a variety of factors are thought to influence the ablation efficiency (i.e., coupling of the laser to the material being ablated), such as crystal chemistry (Black et al., 2004), crystal colour (Kooijman et al., 2012), amount of accumulated radiation damage (Allen and Campbell, 2012; Steely et al., 2014) and crystal orientation (Mikova et al., 2009). The present study takes a systematic approach to investigating the relative importance of each of these factors.

In general, when using a single wavelength of pulsed laser light at constant laser fluence, differences in ablation rates arise from differences in absorptivity between samples (Horn et al., 2001). The absorption of radiation by accessory minerals, such as zircon, is strong in the ultraviolet (UV). For this reason, either excimer lasers operating at 193 nm (ArF) or solid state lasers operating at 213 nm (Nd:YAG) are

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http://dx.doi.org/10.1016/j.chemgeo.2016.05.014
0009-2541/

now the norm for the analysis of these materials. However, slight changes in the degree of absorptivity between different zircon samples due, for example, to the presence of an increasing concentration of trace elements absorbing in the UV range of the laser, could lead to differences in the optical penetration depth of the laser beam and thus result in significant variations in rates of material removal. Horn et al. (2001) reported such variations in ablation behaviour among the NIST SRM 61× series glasses and correlated this with absorptivity of the sample, i.e., sample colour. This effect was noted when using a 266 nm Nd-YAG laser, but no apparent variation in ablation efficiency was observed when using a 193 nm excimer laser.

Structural damage produced by the process of alpha-decay also imparts a pronounced effect on the crystal structure and properties of natural zircon which could, in principle, alter the response to laser radiation. It is known that properties such as density, birefringence, hardness, compressibility and thermal conductivity, among others, change as a function of increasing radiation dose (Holland and Gottfried, 1955; Özkan, 1976; Chakoumakos et al., 1991; Oliver and McCallum, 1994; Ewing et al., 2003; Salje, 2006). Thus, for example, Steely et al. (2014) reported a close relationship between the degree of crystallinity of zircon samples and their laser penetration depth. However, an exclusive dependence of the ablation behaviour on the degree of structural distortion caused by alpha radiation could not be confirmed since the variations in ablation rates could also have been caused by other factors including the change in crystal colour, and thus be triggered by variations in the degree of optical absorption of the laser light. Furthermore, zircon shows different optical and mechanical properties on different crystallographic planes (Finch and Hanchar, 2003) that might also affect the rate at which the zircon ablates.

It is clear from the above that there are a multiplicity of factors potentially influencing the extent of laser coupling to the zircon target. It is therefore highly probable that the observed variability in ablation behaviour between zircon matrices is due to a combination of some or all the factors listed above and that no simple generalization is possible. This study represents a first attempt to systematically investigate the multiple variables affecting the rate of material removal as a function of the zircon properties. Our approach was designed to simplify the highly complex physical phenomena of laser-material interaction to a one-dimensional case. This was achieved by careful consideration of experimental design, as well as appropriate zircon sample selection, as detailed below.

2. Analytical approach, instrumentation and methods

Our study is composed of three parts. In the first part, the amount of accumulated radiation damage is used to evaluate the extent to which zircon matrices with different properties respond to laser radiation. In the second part, we investigate the role played by trace element composition on the different optical absorption properties of zircon crystals, and thus on their ablation behaviour. Finally, we evaluate the role that crystallographic orientation and crystal colour play on the ablation behaviour.

2.1. Zircon samples and sample preparation

Several well-characterized zircon reference materials from various rock types were selected in order to study the relationship between crystal structure and ablation behaviour. These included the 02123 (295 ± 1 Ma, 2σ; Ketchum et al., 2001), 91500 ($^{206}Pb/^{238}U$ age 1062.4 ± 0.8 Ma, 2σ; Wiedenbeck et al., 1995), AS-3 ($^{206}Pb/^{238}U$ age 1099 ± 0.7 Ma, 2σ; Schmitz et al., 2003), FC-1 ($^{206}Pb/^{238}U$ age 1099.9 ± 1.1 Ma, 2σ; Paces and Miller, 1993), Mt. Dromedary ($^{206}Pb/^{238}U$ age 99.12 ± 0.02 Ma, 2σ; Schoene et al., 2006), Plešovice ($^{206}Pb/^{238}U$ age 337.13 ± 0.37 Ma, 2σ; Sláma et al., 2008), QGNG ($^{206}Pb/^{238}U$ age 1842 ± 3.1 Ma, 2σ; Black et al., 2003), Qinghu ($^{206}Pb/^{238}U$ age 159.38 ± 0.12 Ma, 2σ; Li et al., 2013), R-33 ($^{206}Pb/^{238}U$ age 419.26 ± 0.39 Ma, 2σ; Black et al., 2004), Seiland (531 ± 2 Ma, Pedersen et al., 1989), and Temora-2 ($^{206}Pb/^{238}U$ age 416.4 ± 0.4 Ma, 2σ; Black et al., 2004) zircons. These materials encompass a wide range of U–Pb ages, U and Th contents and thus, accumulated radiation damage. U and Th contents range from ~30 to 3000 μg g^{-1} and ~20 to 1200 μg g^{-1}, respectively. Several grains of each zircon were mounted in epoxy-discs. The epoxy mounts were diamond polished and cleaned using standard techniques. Zircon grains were then examined by means of scanning electron microscope (SEM) and imaged with cathodoluminescence (CL). The images were used to identify inclusions and fractures within the zircon grains and to reveal internal zonation patterns and irregular domains. Additionally, optical inspection of the zircon samples was done by conventional reflected and transmitted microscopy.

In the second part of this study, we made use of synthetically grown zircon crystals thereby eliminating the accumulated radiation damage component. The synthetic samples include undoped, Hf-doped, Gd^{3+}- and P-doped, Dy^{3+}-and P-doped, Er^{3+}-and P-doped, Yb^{3+}-and P-doped, Y^{3+}-and P-doped zircon crystals, as well as zircon crystals doped with Gd^{3+}, Dy^{3+}, Er^{3+}, Yb^{3+}, Y^{3+}-and P at two different doping levels. Details regarding synthesis and the properties of these materials can be found in Finch et al. (2001); Hanchar and Finch (2001); Fisher et al. (2011). Using synthetic zircon crystals to evaluate the effects of chemical composition on the ablation behaviour of zircon has certain advantages over the use of natural zircon samples. These include the absence of U and Th in their structure, and therefore the lack of radiation-induced damage; the availability of crystals doped with individual rare-earth elements (REE) and Hf, and the high level of doping achievable. The latter may provide a means of augmenting any effect that the trace element composition may have on the ablation behaviour, thus making it more noticeable. As with their natural counterparts, the synthetic samples were mounted in a single epoxy disc, polished and cleaned using the standard procedures. It was ensured that the crystals were mounted with their *c*-axis parallel to the surface of the epoxy mount to avoid potential variations in the ablation behaviour arising from different crystallographic orientations.

For the third part of this study, we selected four relatively large (centimeter-size) zircon crystals derived from the Mud Tank carbonatite suite (U–Pb TIMS age of 731.65 ± 0.49 Ma; Horstwood et al., 2016). These were chosen due to their high degree of crystallinity, i.e., negligible structural damage, in order to avoid the ambiguity that may occur in the simultaneous analysis of two or more variables (e.g., radiation damage and crystal orientation) that could potentially affect the ablation behaviour. The selected crystals have well-developed faces and colours ranging from nearly colourless to brown (Fig. 1a). The colour of each crystal has been visually estimated using the following colour and intensity coding: pale orange (MT0), orange (MT1), red (MT2) and brown (MT3). Preliminary crystal orientation was defined using the well-developed (100) or (010) faces of the zircon crystals. The crystals were cut parallel and perpendicular to the *c*-axis using a diamond saw as depicted in Fig. 1b. The prepared sections were mounted in epoxy resin and their exact crystallographic orientation was then determined by electron backscatter diffraction (EBSD) as described below. The remaining section of each crystal was crushed and a few shards of <3 mm length were separated, weighed and digested for solution ICP-MS analysis. Dissolution was achieved in high-pressure PTFE reaction vessels in an oven at 185 ºC with HF-HNO_3 followed by HCl acids, and then finally taken up in HNO_3. An aliquot of each resultant solution was further diluted with a 1.8% HNO_3 solution containing an internal standard mixture (see below for details) to give a total dilution factor of 4000.

2.2. Solution-ICP-MS analyses

The chemical composition of the Mud Tank zircon samples was determined by solution ICP-MS analysis on an Agilent 7700× instrument.