Chemical Geology 414 (2015) 109–123

Contents lists available at ScienceDirect

Chemical Geology

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

U–Pb zircon geochronology by LAICPMS combined with thermal annealing: Achievements in precision and accuracy on dating standard and unknown samples

L.A. Solari *, C. Ortega-Obregón, J.P. Bernal

Universidad Nacional Autónoma de México, Centro de Geociencias, Campus Juriquilla, 76230 Querétaro, Mexico

ARTICLE INFO

Article history:
Received 28 November 2014
Received in revised form 9 September 2015
Accepted 11 September 2015
Available online 16 September 2015

Keywords:
LAICPMS
Thermal annealing
Zircon
U–Pb geochronology
Isotopic composition

ABSTRACT

U–Pb zircon dating by LAICPMS is one of the most popular geochronological techniques, however it still suffers from some accuracy and precision problems. These are mostly due to the slight differences in behavior between zircons, and differential coupling with the laser radiation, probably the result from crystal damage induced by the radioactive decay of U and Th. These result in difficult-to-predict and even irreproducible matrix effects, impinging on the precision and accuracy of the technique.

Here, we explore the effect that thermal annealing has on the analysis of zircons by LAICPMS, to improve U–Pb age results obtained We document the advantages of thermal annealing by means of two experiments on standard and several igneous zircons, spanning different degrees of crystallization history complexity. In general, pretreatment of zircons by thermal annealing yields more accurate ages (e.g., 336.87 $\pm$ 0.49 Ma for the annealed Plešovice standard zircon, vs 340.24 $\pm$ 0.49 Ma when not annealed) with significantly less dispersion (e.g., MSWD decreasing as much as 80%). We also demonstrate that thermal annealing significantly reduces the scatter of the trace element data in zircon, yet they preserve the primary characteristics (such as REE anomalies, Hf isotopes, igneous fluctuations and differences in overgrowth composition). This method allows the production of more accurate U–Pb ages, but also has implication for petrogenesis and geothermometry studies.

1. Introduction

During the last 15 years U–Pb geochronology on accessory minerals using laser ablation inductively-coupled plasma mass spectrometry (LAICPMS) has been the fastest-growing analytical technique in geosciences (more than 2800 documents found in Scopus, searching for a combination of U–Pb + laser ablation + ICPMS keywords, growing from 3 to 9 documents per year from 1995 to 2000, to 575 documents in 2014 alone). This is due to a combination of factors, such as the increased availability of laser ablation systems (both excimer and solid-state lasers, e.g. Eggins et al., 1998; Horn et al., 2000; Guillong et al., 2003; Košler and Sylvester, 2003; Chang et al., 2006; Frei and Gerdes, 2009; Solari et al., 2010; Kylander-Clark et al., 2013), which allows fast (<2 min) and precise (< 2%) U–Pb dating in several accessory minerals. Zircon is the most commonly dated mineral, due to its abundance in many igneous and sedimentary rocks and its physicochemical properties (see Harley and Kelly, 2007, for a comprehensive review). Despite the increasing number of zircon LACIPMS U–Pb ages published, there is still an ongoing debate with respect to the analytical protocols employed and, importantly, the factors that limit precision and accuracy to ~2% age discrepancy with respect to TIMS (thermal ionization mass spectrometry) ages (e.g., Hanchar, 2009; Klotzli et al., 2009; Košler et al., 2013). For example, it has been suggested that the concentration of incompatible elements in zircon impinges on the precision of the analysis by LAICPMS (Black et al., 2004). Additional factors affecting the accuracy and precision of zircon analysis by LACIPMS are related to the laser-induced elemental fractionation (Košler et al., 2005, 2014), the presence of variable amounts of oxygen during ablation (Košler et al., 2014), or even associated to differences in ablation rates due to crystallographic orientation, and/or slight variations in focal plane distance before ablation (Marillo-Sialer et al., 2014). Moreover, differences in radiation damage due to the natural decay of U and Th between reference zircons and unknowns has also been suggested as an important source of bias, and discussed in depth by previous authors (e.g., Murakami et al., 1991; Nasdala et al., 2001; Allen and Campbell, 2012). The bias introduced by these factors is such that, if two different standard zircons are used as primary and secondary standard, then the latter often yields U/Pb ages which are significantly different (more than 2%) to those obtained by TIMS, (e.g., Allen and Campbell, 2012). It is important to underline, however, that this can also be dependent on the data-reduction scheme, as it will be discussed further below.

There is still some debate on the utility of thermal annealing for improving accuracy and precision of U–Pb ages obtained by LAICPMS;

* Corresponding author.
E-mail address: solari@unam.mx (L.A. Solari).

http://dx.doi.org/10.1016/j.chemgeo.2015.09.008
0009-2541/

Allen and Campbell (2012) employ thermal annealing, and suggest that differences in the radiation damage (alpha dose) between zircons is one of the main sources of age offset. This is at odds with Marillo-Sialer et al. (2014) who suggests that the chemical annealing recovery method does not improve the $^{206}Pb/^{238}U$ age accuracy in zircons. In contrast two recent papers focused on the effect that crystal-lattice damage of zircon has upon precision and accuracy and the use of a combination of thermal annealing and chemical abrasion to minimize it (von Quadt et al., 2014; Crowley et al., 2014), which are broadly based on the methodology developed by Mattinson (2005, and references therein) to improve precision and accuracy during TIMS dating. Additionally, von Quadt et al. (2014) suggest that the chemical abrasion removes those domains in which occurred Pb loss, therefore improving precision and accuracy.

In this paper, we performed two experiments to investigate the effect of thermal annealing on LAICPMS U–Pb ages, trace element composition and Hf-isotope compositons. In the first set of experiments, carried out on both standard and igneous zircons ranging in age between ca. 1000 to ca 10 Ma, we focus on thermal annealing as a method to repair the crystal damage and improve age concordance. In the second experiment we investigate the behavior of very complex zircons (multiple episodes of growth during repeated metamorphism, from ca. 1200 Ma in cores, to ca. 220 Ma in rims), to see whether thermal annealing has any effect on their U/Pb ages and elemental composition. The results presented here demonstrate the efficency of Thermal annealling to repair the crystal lattice of radiation-damaged zircons, and yield U–Pb ages and trace element compositions with improved accuracy and precision.

2. Sample selection and preparation

Two widely used standard zircons were employed for this work, 91500 (Wiedenbeck et al., 1995, 2004) and Plešovice (Sláma et al., 2008). Whereas other standard zircons are not always available, 91500 and Plešovice are used in most laboratories around the world, and are thus thoroughly characterized. Both are concordant, with TIMS ages of 1065.4 $\pm$ 0.6 and 337.13 $\pm$ 0.37 Ma, respectively.

Currently, three methods, in which multiple analyses of a known, standard zircon are used to bracket unknown zircons, are typically used by the laser ablation community: a) the Tzero method, which interpolates the $^{206}Pb/^{238}U$ ratios measured during the whole ablation, regressing it to the start of the analysis (e.g., Košler et al., 2002); b) the Mean method, in which the mean ratio is calculated, and its deviation from the true value is then applied to the unknowns (e.g., Fisher et al., 2010; Solari and Tanner, 2011); c) modeling the down-hole fractionation, according to either linear, exponential or more complex curves (Paton et al., 2010). The differences of the three methods are such that, if applied to the same dataset, the resulting age is slightly different. An example is provided in Fig. 1 (and data included in the Table 1 of the Supplementary material), where we used 91500 zircon as reference and Plesovice as unknown and reduced the same dataset using the three different approaches, which yield biases of 1.65%, 1.91% and 2.03% from the the true age (337.13 $\pm$ 0.37 Ma, Sláma et al., 2008) for Tzero, to Mean, and down-hole fractionation modeling, respectively. The down-hole fractionation modeling method is thus the one that mostly evidences differences in matrix behavior during laser ablation, and will be employed hereafter. We have been measuring 91500 and Plešovice in our laboratory for over seven years, without thermal annealing, either as a primary standard, and/or control standard (e.g., Solari et al., 2010). During this period, these zircons have yielded age offset from true ages from 0 to $\pm$2% (see an example in Fig. 1).

To explore the effects of zircon annealing, two 3 mm-size Plešovice zircons, and three fragments of 91500, were handpicked and air-annealed in Corning® ceramic crucibles, for 48 h in a muffle heated at 850 °C. Five additional samples, ranging in ages (from 1000 to ca. 12 Ma) and complexity were also annealed:

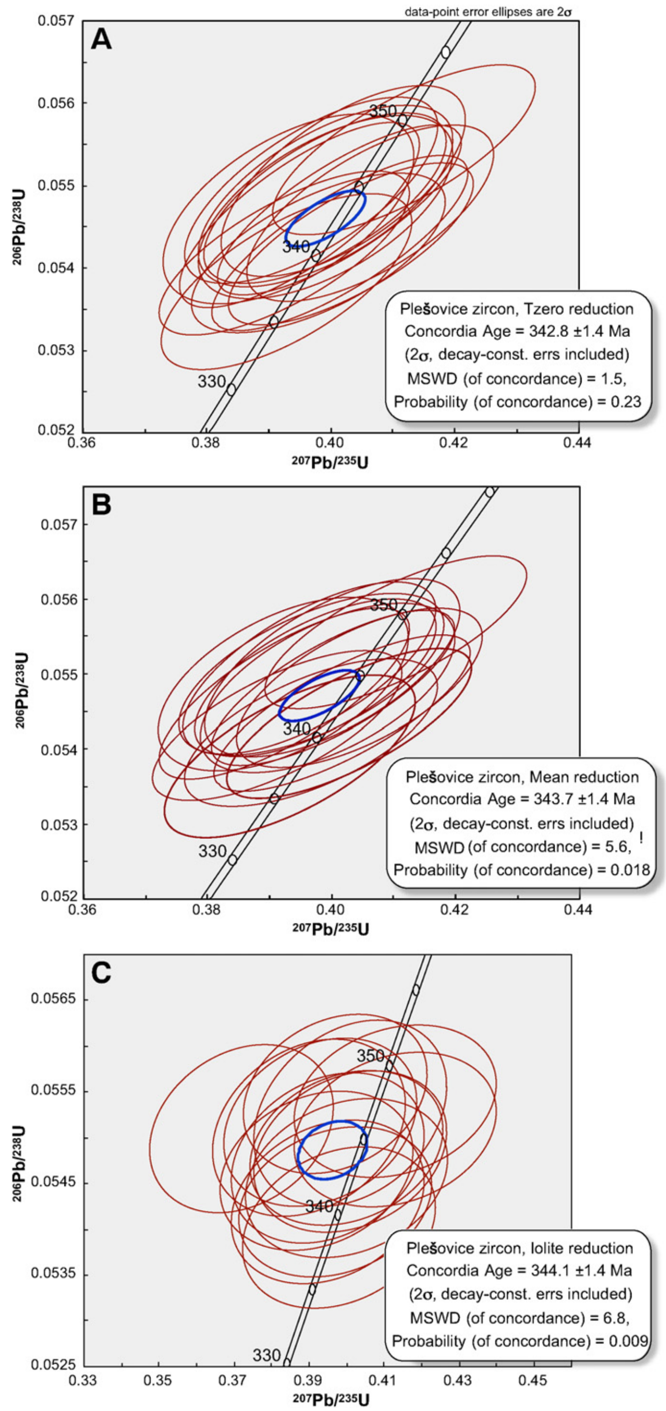

Fig. 1. A comparison of U–Pb LA-ICPMS data reduction, using three different methods. A) Tzero; B) Mean; C) Iolite. A) and B) data reductions were performed using UPb.Age, an R script written by Solari and Tanner (2011). Iolite uses the UPb_Geochronology data reduction scheme of Paton et al. (2011). The initial data are identical in the three cases, consisting of a run in which 91500 (not abraded) acted as reference standard, whereas Plešovice (also not abraded) was considered as unknown. The reduced data are presented in Table 1 of the Supplementary Material.

- La Panchita pegmatite, approximately 2 cm in size, cut from a larger crystal. La Panchita crops out in southern Mexico, and zircons larger than 10 cm in size are not uncommon; initially dated by alpha-Pb by Fries et al. (1966) to an age of 950 $\pm$ 50 Ma, it has been classified as