Chemical Geology 363 (2014) 185–199

Contents lists available at ScienceDirect

Chemical Geology

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

U–Pb LA–ICPMS dating using accessory mineral standards with variable common Pb

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ARTICLE INFO

Article history:
Received 29 June 2013
Received in revised form 9 November 2013
Accepted 11 November 2013
Available online 19 November 2013

Editor: K. Mezger

Keywords:
U–Pb dating
Common Pb
LA–ICPMS
Apatite
Rutile
Titanite

ABSTRACT

Precise and accurate U–Pb LA–ICPMS dating of many U-bearing accessory minerals (e.g. apatite, allanite, titanite and rutile) is often compromised by common Pb. LA–ICPMS dating of these U-bearing accessory phases typically requires a matrix-matched standard, and data reduction is often complicated by *variable* incorporation of common Pb not only into the unknowns but also particularly into the reference material. We present here a general approach to common Pb correction in U–Pb LA–ICP–MS dating using a modified version of the VizualAge U–Pb data reduction package for Iolite (VizualAge_UcomPbine). The key feature of the method is that it can correct for *variable* amounts of common Pb in any U–Pb accessory mineral *standard* as long as the standard is concordant in the U/Pb (and Th/Pb) systems following common Pb correction. Common Pb correction of the age standard can be undertaken using either the ^{204}Pb, ^{207}Pb or ^{208}Pb$_{(\mathrm{no\ Th})}$ methods, and the approach can be applied to raw data files from all widely used modern multi-collector and single-collector ICPMS instruments.

VizualAge_UcomPbine first applies a common Pb correction to the user-selected age standard integrations and then fits session-wide “model” U–Pb fractionation curves to the time-resolved U–Pb standard data. This downhole fractionation model is applied to the unknowns and sample-standard bracketing (using a user-specified interpolation method) is used to calculate final isotopic ratios and ages. ^{204}Pb- and ^{208}Pb$_{(\mathrm{no\ Th})}$-corrected concordia diagrams and ^{204}Pb-, ^{207}Pb- and ^{208}Pb$_{(\mathrm{no\ Th})}$-corrected age channels can be calculated for user-specified initial Pb ratio(s). All other conventional common Pb correction methods (e.g. intercept or isochron methods on co-genetic analyses) can be performed offline.

The approach was tested on apatite and titanite age standards (for which there are independent constraints on the U–Pb crystallization age) using a Thermo Scientific iCAP-Qc (Q-ICP–MS) coupled to a Photon Machines Analyte Excite 193 nm ArF Excimer laser. Madagascar apatite, OLT1 titanite and R10 rutile were used as primary standards and were corrected for variable common Pb using the new VizualAge_UcomPbine DRS. The secondary Durango (31.44 ± 0.18 Ma) apatite standard yielded a U–Pb TW concordia intercept age of 31.97 ± 0.59 Ma (MSWD = 1.09; primary standard corrected by the ^{207}Pb-method) and a U–Pb concordia age of 31.82 ± 0.40 Ma (MSWD = 1.4; primary standard corrected by the ^{204}Pb-method). McClure Mountain (523.51 ± 1.47 Ma) yielded a U–Pb TW concordia intercept age of 524.5 ± 3.7 Ma (MSWD = 0.72) while the Fish Canyon Tuff (28.201 ± 0.046 Ma) and Khan (522.2 ± 2.2 Ma) titanite standards yielded U–Pb TW concordia intercept ages of 28.78 ± 0.41 Ma (MSWD = 1.4) and 520.9 ± 3.9 Ma (MSWD = 4.2) respectively. The suitability of the ^{208}Pb$_{(\mathrm{no\ Th})}$-correction is demonstrated by the agreement between a U–Pb TW concordia intercept age of 452.6 ± 4.7 Ma (MSWD = 0.89) and a ^{208}Pb$_{(\mathrm{no\ Th})}$-corrected TW concordia age of 448.6 ± 4.5 Ma (MSWD = 1.4) on a c. 450 Ma rutile which exhibits variable incorporation of common Pb.

A range of LA–ICPMS U–Pb dating applications are presented and include U–Pb dating of apatite from >3.8 Ga gneisses from Akilia, SW Greenland. These apatites host ^{13}C-depleted graphite inclusions that are interpreted as biogenic in origin and representing the oldest indications of life on Earth. The U–Pb age profiles on single apatite grains presented here are characteristic of Pb loss by volume diffusion with core–rim age differences of up to 300 Ma. These data explain the scatter and poor precision of earlier U–Pb apatite age determinations on Akilia apatite. Other LA–ICPMS dating applications include U–Pb apatite dating as a rapid method for determining the age of mafic intrusions, U–Pb titanite and apatite dating of ash fall tuffs, determining temperature–time histories using multiple U–Pb thermochronometers and improving concordance in LA–ICPMS primary zircon standard datasets by analysing young, common Pb-bearing primary zircon standards that have not accumulated significant radiation damage.

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http://dx.doi.org/10.1016/j.chemgeo.2013.11.006

1. Introduction

U–Pb dating of accessory minerals has been revolutionised in the last decade by substantial improvements of the LA–ICPMS technique, which offers low-cost, rapid data acquisition compared to the ID-TIMS or ion microprobe U–Pb methods (e.g., Košler and Sylvester, 2003). The high sample throughput afforded by LA–ICPMS has made it a routine tool in sedimentary provenance studies, particularly in U–Pb dating of detrital zircon. Recent analytical developments in mass spectrometer and laser ablation systems (e.g. McFarlane and Luo, 2012) have facilitated progressively smaller spot sizes and shorter analysis times (e.g. Cottle et al., 2012) with a precision approaching that of ion microprobe analysis.

The challenges involved in U–Pb dating of accessory minerals such as zircon by LA–ICPMS include the problem of laser-induced U–Pb downhole fractionation during an analysis, and instrument drift (the change in sensitivity with time) during the course of an analytical session. The various strategies employed for correcting for downhole U–Pb fractionation are discussed in detail later, but generally involve using an external standard of known age to derive an empirical downhole correction factor that can then be applied to the unknown sample (e.g., Jackson et al., 1996). Instrument drift during an analytical session can also be corrected for using the sample-standard bracketing approach.

For this reason, the LA–ICPMS U/Pb dating method is particularly reliant on high-quality reference materials. These materials must be homogenous in terms of their U/Th/Pb age systematics and free of (or at very least homogenous in terms of) common Pb, such as the zircon standard 91500 (Wiedenbeck et al., 1995). Many other U/Pb age reference materials have been proposed but many suffer to variable extent from issues such as occasional localized discordance, and occasional and variable localized incorporation of common Pb (e.g. SL 13 zircon, Kinny et al., 1991; R33 zircon, Black et al., 2004; Khan titanite, Heaman, 2009). Apart from zircon, monazite and baddelyite, many common U- and Th-bearing accessory minerals typically accommodate significant amounts of common (or initial) Pb in their crystal structure (e.g. apatite, titanite, allanite and rutile). As such, these phases often have low U and Pb concentrations and low radiogenic Pb/common Pb ratios which necessitate common-Pb correction. This is either achieved in concordia or isochron plots of a suite of co-genetic grains with a large spread in radiogenic Pb/common Pb ratio or alternatively a Pb-correction is applied to individual analyses based on an appropriate choice of initial Pb isotopic composition. The need to correct for common Pb, U–Pb downhole fractionation and instrument drift makes U–Pb dating of common Pb-bearing accessory minerals challenging.

Although there have been several successful LA–ICPMS U–Pb dating studies (on both single collector and multi-collector instruments) of apatite (e.g. Storey et al., 2007; Chew et al., 2011; Thomson et al., 2012), titanite (e.g. Kohn and Corrie, 2011; Sun et al., 2012; Spencer et al., 2013) and rutile (e.g. Zack et al., 2011) to date there has been no universal approach to U–Pb dating of common Pb-bearing accessory minerals by LA–ICPMS. The method presented here uses a modified version of the VizualAge U–Pb data reduction package (Petrus and Kamber, 2012) for Iolite (Paton et al., 2011). The chief advantage of the chosen Iolite-based approach is that it can employ any accessory mineral standard, even if it contains significant and *variable* amounts of common Pb, and it can be applied to raw data files exported from the majority of modern ICPMS instruments.

2. Challenges in U–Pb dating of common Pb-bearing accessory minerals

2.1. Downhole U–Pb fractionation

Elemental fractionation is an important consideration in U–Pb dating of accessory minerals by LA–ICPMS. Several strategies have been employed to both minimise this fractionation and to correct for it, primarily in U–Pb dating studies of zircon, and the reader is referred to Košler and Sylvester (2003) for a detailed account of these techniques. Approaches for minimizing U–Pb fractionation include generating a large, shallow laser pit by either spot ablation (Eggins et al., 1998) or by rastering (Košler et al., 2002), to ablate in He instead of Ar, and to use a 2-volume sample cell.

One approach to correct for U–Pb downhole fractionation is that of Košler et al. (2002). Termed the intercept method, it is based on the premise of Sylvester and Ghaderi (1997) that laser-induced, volatile/refractory element fractionation is a linear function of time and can therefore be corrected by extrapolating the measured U–Pb ratios back to the start of ablation. This approach eliminates potential matrix differences between external standards and unknown samples because the measured ratios at the start of ablation are calculated from the data for each individual sample. This method has been applied to U–Pb LA–ICPMS dating of zircon (Košler et al., 2002), monazite (Košler et al., 2001) and apatite (Chew et al., 2011) and is well suited to target minerals for which no well characterised matrix-matched standard exists.

The most commonly used approach to correcting for U–Pb downhole fractionation in LA–ICPMS dating of accessory minerals is to characterise the downhole U–Pb signal response using a matrix-matched standard (e.g., Jackson et al., 1996). A matrix-matched standard is usually required because different accessory minerals (e.g., apatite, titanite and zircon) show different time-resolved U–Pb signals during ablation (e.g., Gregory et al., 2007). Early studies have typically assumed that the pattern of fractionation with hole depth was linear but recent studies (e.g. Paton et al., 2010) have demonstrated that nonlinear, session-specific models of downhole fractionation are more appropriate.

2.2. Instrument drift and instrumental U/Th/Pb fractionation

Although modern LA–ICPMS systems generally yield relatively stable signals for extended periods of time, instrument drift during analytical sessions does occur and has to be corrected for to ensure good quality quantitative analyses. Solution-based measurements by ICPMS generally employ an internal and/or external standardisation where all data are normalised to an isotope present in known concentrations in all samples and standards (e.g. Eggins et al., 1997). A similar strategy is behind the intercept method of Košler et al. (2002) where variations in sensitivity during a U–Pb LA–ICPMS analytical session are corrected for by aspirating a tracer solution (e.g. Tl–U–Bi–Np) with the sample into the plasma. However simultaneous aspiration of a tracer solution to correct for instrument drift results in decreased sensitivity and increased oxide production when compared to "dry" LA–ICPMS analyses. The sample-standard bracketing approach used to correct for U–Pb downhole fractionation is also the most commonly used method to correct for instrument drift in U–Pb dating by LA–ICPMS, as drift in U–Pb ratios caused by variations in sensitivity during an analytical session can be accounted for by interspersing the unknown samples with matrix-matched external U–Pb age standards.

An important premise of successful U–Pb dating with the matrix-matched sample-standard bracketing method is the lack of even subtle matrix effects. Theoretically, for stoichiometric minerals such as zircon, there should be no significant matrix differences between different grains of zircon. However, because U-bearing minerals have variably radiation damaged lattices, it is possible and indeed likely that the UV-laser beam will interact slightly different with grains of variable lattice damage. The resulting aerosol may therefore contain particle size distributions that are different from one mineral to the next, even when the matrix is identical in terms of its chemistry. Because Th, U and Pb have different first ionisation potentials, particle size does affect the extent to which these elements are ionised. To minimise the effect of particle size distribution on effective ionisation and hence apparent U/Th and U/Pb ratios, ICP–MS instruments are tuned to yield near-equal response for Th and U. This involves ablation of a glass standard with identical Th