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Maximising data and precision from detrital zircon U-Pb analysis by LA-ICPMS: The use of core-rim ages and the single-analysis concordia age[☆]

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ABSTRACT

U-Pb detrital zircon geochronology is a powerful and well-established tool in provenance studies. Modern analytical techniques (particularly LA-ICPMS) increasingly facilitate the rapid acquisition of large datasets. While improvements in data handling approaches have been explored in detail (e.g., more robust propagation of analytical uncertainties and inter-laboratory age reproducibility studies), there currently are no commonly established protocols for target spot location on polyphase detrital zircon grains: should the analyst ablate the zircon core, rim, or both? Here, we present two regional U-Pb detrital zircon datasets, one from the Banda Arc in Eastern Indonesia and one from the European Alps pro-foreland basin. We demonstrate that preferential ablation solely of cores or rim overgrowths results in a failure to detect age peaks, and also that generation of single-grain core-rim age pairs can permit additional characterisation of the source rock. Thus, both cores and rims should be analysed where possible, to maximise the data obtained from detrital zircon. In addition, we advocate the use of the single-analysis concordia age in visualizing and presenting U-Pb data, which is currently under-utilised in detrital provenance studies. We utilise a large (ca. 49,500 analyses) detrital zircon dataset to demonstrate that the single-analysis concordia age maximises precision throughout geological time (which removes the need to present ages derived from different isotopic ratios across an arbitrary age threshold), and obviates the necessity to separately assess discordance.

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1. Introduction

Recent developments in U-Pb zircon geochronology by means of laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) have allowed for the progressively more rapid and cost-effective acquisition of large datasets, with a significant increase in the amount of new publications every year (e.g., see Fig. 1 of Spencer et al., 2016). However, the ease by which large detrital zircon datasets can be acquired by the geoscience community has led to diverse data handling approaches and interpretations of geochronological data (see discussion by Spencer et al., 2016). Similarly, Gehrels (2014) highlighted how particular approaches to grain selection, isotopic analysis, and subsequent data reduction and filtering can result in interpretation biases. In this contribution,

we aim to improve on the lack of universally agreed protocols in the LA-ICPMS U-Pb zircon community for: (1) spot positioning on polyphase zircon in detrital provenance studies and (2) subsequent age calculation and discordance filtering.

The highly refractory nature of zircon, even when exposed to high-temperature geological processes such as anatexis or incorporation within magmatic bodies, means that rim overgrowths are common features of zircon grains (e.g., Nemchin and Pidgeon, 1997; Whitehouse and Platt, 2003). As thermally-activated Pb diffusion in non-metamict zircon occurs only at temperatures > ca. 900 °C and is thus negligible in most cases (Cherniak and Watson, 2000), this means that the core-rim textures observed in a single zircon grain can record multiple geological events that are routinely resolvable by in situ micro-beam U-Pb geochronometry. Such polyphase single-grain archives are frequently exploited by high-resolution crystalline basement studies targeting small numbers of grains (e.g., Chew et al., 2017a, b); in contrast, detrital provenance studies often texturally characterize zircon grains only to avoid simultaneously ablating multiple age zones during analysis, which would otherwise generate geologically meaningless mixed ages.

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Textural characterisation of zircon is typically conducted using the well-established technique of cathodoluminescence (CL) imaging, often coupled to a scanning electron microscope (SEM; e.g., Vavra, 1990; Vavra et al., 1996; Cavosie et al., 2004). In the case of magmatic zircons (e.g., Nemchin and Pidgeon, 1997), rim overgrowths are typically autocrysts linked to late-stage growth corresponding to crystallization from the final pulses of magma. The zircon cores may represent either antecrysts crystallized from an earlier pulse of melt in the magma plumbing system, or xenocrysts incorporated from the wall-rocks during magma generation and migration. However, it should be noted that in many magmas zircon inheritance does not just comprise inherited zircon cores but also entire inherited zircon grains, and hence zircon rims can also potentially pre-date incorporation into a given magmatic system. Zircon from high-grade metamorphic rocks often exhibits core-rim structures, with metamorphic zircon rims typically characterized by a structureless or patchily-zoned appearance in CL images overgrowing an inherited core (e.g., Gebauer et al., 1997; Whitehouse and Platt, 2003).

Thus, in detrital studies, U-Pb zircon rim data records the last zircon-forming tectonothermal event (either magmatic or high-temperature metamorphic) in the original source rock, while core age data can record inheritance from the local country rocks or co-genetic magmatic ages derived from earlier melt pulses in the magma plumbing system.

However, despite abundant evidence that complex polyphase zircons with clear core-rim age differences are formed in a variety of geological settings (e.g., Carter and Moss, 1999; Whitehouse and Platt, 2003; Wu and Zheng, 2004; Wan et al., 2006; Zhang et al., 2007) and are thus commonly observed in the sedimentary record, there is no consensus on how such grains should be treated during U-Pb detrital provenance analysis. During the discussion sessions at the 3rd meeting of the Working Group on Sediment Generation on which this special volume is based, there was also no consensus between different geochronology laboratories on target spot location for detrital zircon grains.

Within the literature examples can be found with the ablation spot preferentially sited on the zircon core (e.g., Goldstein et al., 1997; DeGraaff-Surpless et al., 2002; Amidon et al., 2005; Zimmermann et al., 2015); both the zircon rim and core (e.g., Cawood and Nemchin, 2000; Gehrels, 2014; Spencer et al., 2016), or alternatively the zones with the most homogeneous CL response (e.g., Cao et al., 2015;

Zimmermann and Hall, 2016). In provenance studies from a specific, well-characterized source region where the polyphase growth history of detrital zircon detritus is known, such preferential siting of ablation spots may be justified (i.e. analysts may target cores to trace the contribution of old inherited zircon from different basement massifs, or rims to provide maximum age constraints on deposition). However, given that zircon core and rim age data can yield significantly different provenance information, we propose that both rims and cores should be targeted during routine provenance studies, subject to the physical sampling limits of the analytical procedure employed (micron-thick rim overgrowths are not datable by conventional LA-ICPMS spot analysis on polished grain mounts, for example). To illustrate this, Fig. 1 shows a hypothetical tectonothermal history, and the idealized detrital zircon spectra that would result (Fig. 1A–C). Selective targeting of either rims or cores leads to a less informative dataset than if both are targeted: either tectonothermal events are not identified (Fig. 1B), or are identified but not characterized (Fig. 1C).

We also argue for the routine calculation of single-analysis concordia ages, which utilises information from three isotopic systems (^{206}Pb - ^{238}U , ^{207}Pb - ^{235}U , and ^{207}Pb - ^{206}Pb) to minimize uncertainty, permit simultaneous assessment of discordance, and also remove the necessity of presenting ages derived from different isotopic ratios (e.g., ^{206}Pb - ^{238}U and ^{207}Pb - ^{206}Pb ; Ludwig, 1998). Thus, in this contribution we initially document the utility of the concordia age (Ludwig, 1998) for U-Pb age determinations of single-grain detritus. We use a large, previously published zircon U-Pb dataset (Voice et al., 2011) to demonstrate that single-grain concordia ages yield uncertainties which are both significantly lower in absolute terms than ages derived from a single isotope ratio and are also more uniform over time, as stated by Ludwig (1998). In contrast, ages calculated from single isotope ratios typically show either decreasing (^{207}Pb - ^{206}Pb) or increasing (^{206}Pb - ^{238}U) age uncertainties with increasing age, which in turn requires an analyst to decide which of these two age systems is the most geologically appropriate when presenting U-Pb detrital zircon age data (e.g., see discussion in Spencer et al., 2016).

Secondly, we investigate how LA-ICPMS spot positioning can affect provenance interpretations in U-Pb detrital zircon studies. We present two regional detrital zircon datasets: one from the outer Banda Arc of eastern Indonesia (Fig. 2A) and a second from the pro-foreland basin of the European Alps (Fig. 2B). Both regions are tectonically complex,

Fig. 1. Cartoon illustrating hypothetical detrital provenance scenario. Panels A–C show snapshots of the evolving zircon population through time. In panel B, identification of both tectonothermal events is only possible if both cores and rims are targeted during U-Pb analysis. In panel C, all three events could be identified by analysis of cores alone, but characterisation of the youngest peak as likely recording an igneous event (i.e. indistinguishable core and rim ages) is only possible if both cores and rims are targeted.

Fig. 2. Location of individual datasets from selected Triassic clastic units along the Banda Arc Islands in eastern Indonesia (A) and Oligo-Miocene clastic units of the European Alpine foreland (B).

comprising terranes originally accreted to the margins of major continents (Eurasia and Gondwana, respectively) during the late Neoproterozoic and Phanerozoic. Both areas have been studied in detail, and a summary of their complex geological history is beyond the scope of this study. The reader is directed to [Matte \(2001\)](#) and [Stampfli et al. \(2013\)](#) (Alps), and [Charlton \(2001\)](#), [Barber et al. \(2003\)](#) and [Zimmermann and Hall \(2016\)](#) (Banda Arc) for detailed reviews. Each dataset is of a size typical for regional detrital zircon U-Pb studies (six and eleven samples respectively, each comprising ca. 100 analyses), and includes multiple pairs of core-rim ages. The two datasets were acquired using similar LA-ICPMS protocols and yield a range of ages indicative of a mixed provenance. As only a subset of grains from each study yielded rim overgrowths amenable to conventional LA-ICPMS spot dating and thus to generation of core-rim pairs, the samples from each study were each amalgamated into two large datasets, one for each study area. Both datasets thus comprise several samples of different stratigraphic age and geographical location within each deposystem. We investigate whether employing U-Pb zircon core vs rim ages systematically shifts individual age populations and hence

affects subsequent provenance interpretations, and evaluate the additional provenance information obtainable by analysing core-rim pairs on single grains.

2. Background

The U-Pb zircon geochronometer exploits the ability of U^{4+} to substitute for Zr^{4+} in the zircon mineral lattice ($ZrSiO_4$). As the U-Pb isotopic system involves two separate decay schemes (^{235}U decaying to ^{207}Pb with a half-life of 0.704 Ga and ^{238}U decaying to ^{206}Pb with a half-life of 4.468 Ga), three separate isotopic ages can be calculated for a single analysis: ^{206}Pb - ^{238}U , ^{207}Pb - ^{235}U and ^{207}Pb - ^{206}Pb . This allows for the internal age consistency of each analysis to be assessed, and agreement of the ages (within error) is termed concordance ([Wetherill, 1956](#)). Due to the significantly shorter half-life and hence substantially lower present-day isotopic abundance of ^{235}U , young samples yield low radiogenic ^{207}Pb count rates during analysis, and hence ^{206}Pb - ^{238}U ratios are more precise than ^{207}Pb - ^{235}U and ^{207}Pb - ^{206}Pb

ratios for young samples (e.g., Košler and Sylvester, 2003; Nemchin and Cawood, 2005).

Solution of the two U–Pb age equations for time permits construction of an age evolution line, termed a concordia (as distinct from a concordia age). The two most commonly used concordia plots utilise ^{207}Pb – ^{235}U and ^{206}Pb – ^{238}U , or ^{238}U – ^{206}Pb and ^{207}Pb – ^{206}Pb as their respective axes (Wetherill, 1956; Tera and Wasserburg, 1972). Analyses which have experienced isotopic disturbance plot off the concordia line. Such so-called discordant analyses are typically interpreted either as recording intra-grain Pb mobility or Pb exchange with the external environment (Mezger and Krogstad, 1997; Cherniak and Watson, 2000), or may represent a mixture of two discrete age components. Because such processes may be caused by geological events, discordant ages can still record geochronologically useful information (e.g., Gehrels et al., 2006; Gehrels, 2014; Schoene, 2014; Reimink et al., 2016). However, in cases where discordant analyses do not form clear age arrays (discordia) with resolvable intercepts to the concordia line, there is no way to verify which (if any) of the discordant isotope ratios is geologically meaningful without additional independent information from the same source rock, such as ages derived from independent radioisotope systems. Thus, discordant ages are typically excluded from detrital datasets (e.g., Gehrels, 2012).

However, what criteria should be used to assess discordance and justify exclusion? The level of acceptable discordance is seldom discussed and the choice of discordance filter (^{207}Pb – ^{235}U vs ^{206}Pb – ^{238}U age or ^{206}Pb – ^{238}U vs ^{207}Pb – ^{206}Pb age) in a study is rarely justified (Spencer et al., 2016), yet discordance assessment and age rejection can significantly influence data interpretations (Nemchin and Cawood, 2005). Typically, discordance filters are set between 5 and 10% above and below the concordia, but discordance filters as large as 30% have also been used in the literature (cf Reimink et al., 2016).

2.1. The single analysis concordia age calculation

In this study, we utilise concordia ages (Ludwig, 1998) to present our detrital zircon data. Concordia ages are rarely used in detrital provenance studies, (although see McAteer et al., 2010 for one such example), but are advantageous because: (1) they make optimum use of both U–Pb decay schemes, resulting in smaller age uncertainties extending back through geological time compared to ages calculated from the single isotope ratios ^{207}Pb – ^{235}U , ^{206}Pb – ^{238}U or ^{207}Pb – ^{206}Pb (Ludwig, 1998); (2) this improved precision in turn removes the need to choose a “preferred” single isotope ratio for an age determination (or an age threshold to switch from ^{206}Pb – ^{238}U ages to ^{207}Pb – ^{206}Pb ages) as they are invariably more precise than an age derived from a single isotopic system; and (3) they eliminate the need for a separate discordance calculation, as the probability and MSWD of concordance can be calculated simultaneously. The Isoplot add-in for Microsoft Excel (Ludwig, 2008) can calculate either conventional (Wetherill) or Tera–Wasserburg concordia ages for single or multiple analyses. For multiple analyses of a single age population (e.g., a magmatic rock), the Isoplot concordia age dialog box only returns a concordia age if both the probability of data-point equivalence and the probability of concordance are >0.001 . For single analyses (relevant to U–Pb detrital provenance studies), it should be noted the concordia age function always returns an age, which must then be assessed for concordance. This is simply achieved using a threshold value of 0.001 for the probability of concordance value returned by the Isoplot function, and is the same threshold value employed in concordia age calculations of multiple analyses in Isoplot (Ludwig, 2008).

To examine how the uncertainty of the concordia age calculation compares to that of ^{206}Pb – ^{238}U , ^{207}Pb – ^{235}U and ^{207}Pb – ^{206}Pb ages through geological time, we utilised the large global detrital zircon U–Pb dataset of Voice et al. (2011) comprising $>200,000$ analyses, along with more recent U–Pb zircon studies added to their dataset. Data were initially screened for analyses made using LA–ICPMS instruments and for

which ^{206}Pb – ^{238}U , ^{207}Pb – ^{235}U and ^{207}Pb – ^{206}Pb isotope ratios were reported, and concordia ages were calculated. The dataset was then filtered for a probability of concordance >0.001 , resulting in ca. 49,500 LA–ICPMS acceptable single-analysis zircon concordia ages. Best-fit trendlines were then fitted to each of the two-dimensional density estimation diagrams of age uncertainty vs age (Fig. 3A–D).

While these trends, summarised on Fig. 3E, are somewhat influenced by both the choice and goodness-of-fit of the trendline, it is immediately apparent that the ^{207}Pb – ^{206}Pb age is more precise than the ^{206}Pb – ^{238}U age for U–Pb ICPMS zircon analyses older than ca. 1.5 Ga (an identical finding to the similar analyses of Spencer et al., 2016 on the same dataset). However, we also show that the ^{207}Pb – ^{235}U age is typically more precise than the ^{207}Pb – ^{206}Pb age for analyses younger than ca. 1.9 Ga, and is additionally more precise than the ^{206}Pb – ^{238}U age for analyses older than ca. 1 Ga (Fig. 3E). This is because although the abundance of radiogenic ^{206}Pb is always greater than the abundance of radiogenic ^{207}Pb in terrestrial zircon, the vast majority of detrital zircon data (including that in the Voice et al., 2011 dataset) are produced using single-collector (either quadrupole or sector field) LA–ICPMS systems. These systems cannot simultaneously analyse ^{207}Pb , ^{206}Pb or ^{238}U , and so individual dwell times are set for each isotope. As most analysts use longer dwell times (up to 3 or 4 times longer, Spencer et al., 2016) for the low abundance ^{207}Pb isotope, the resultant ^{207}Pb – ^{235}U uncertainty can be less than that for ^{206}Pb – ^{238}U in old, radiogenic zircons (e.g., Fig. 3E). This clearly would not be the case for zircon data acquired using instruments equipped for simultaneous isotope detection (e.g., LA–ICPMS multi-collector systems).

Most importantly, our analysis shows that the concordia age is the most precise U–Pb age calculation through geological time, which thus removes the need to choose a “preferred” single isotope ratio (e.g., ^{206}Pb – ^{238}U vs ^{207}Pb – ^{206}Pb) for an age determination. The apparent slight improvement in the precision of ^{206}Pb – ^{238}U ages compared to the concordia age calculation for very young samples (Fig. 3E) is a minor artefact caused by the trendline fit at very young ages. The uncertainties on the ^{206}Pb – ^{238}U and concordia age are essentially identical for ages younger than Late Palaeozoic (Ludwig, 1998, 2008), as the concordia age uncertainty is heavily influenced by the superior precision on the ^{206}Pb – ^{238}U ratio for young samples.

2.2. Core–rim ages from new zircon U–Pb data

2.2.1. SE Asia samples

The samples presented derive from selected Triassic clastic units along the outer Banda Arc Islands (Zimmermann and Hall, 2016), which are part of a larger dataset reported by Zimmermann and Hall (2016). The 63–250 μm non-magnetic heavy mineral fraction was extracted using standard crushing, sieving, magnetic- and density separation techniques. Individual zircon grains were hand-picked, mounted in epoxy resin and polished to reveal internal surfaces. Selected samples were imaged by SEM CL (Jeol8100 Superprobe) at University College London, and texturally homogenous cores and rims targeted for ablation. U–Pb analyses were acquired at University College London using an Agilent Technologies 7700 Series quadrupole ICPMS, coupled to a New Wave NWR 193 nm laser ablation system (1-volume cell); He gas was utilised for transfer of the aerosol to the plasma. Parameters used were a spot size of 20–35 μm ; pulse repetition of 8–10 Hz; ablation time of 25 s with a warm-up of 10–15 s (background measurement at the start of each analysis) and wash-out of 18 s. The Plešovice zircon (Sláma et al., 2008) and reference glass NIST SRM 612 (Pearce et al., 1997) standards were used to correct for instrumental mass bias, intra-session drift, and depth-dependent inter-element fractionation of Pb, Th and U. Data reduction was performed using the Glitter software package (Griffin et al., 2008). Concordia ages were calculated with the Isoplot add-in for Microsoft Excel (Ludwig, 2008) and kernel density plots were generated with DensityPlotter (Vermeesch, 2012). See Supplementary Information A1 for the sample

Fig. 3. Two-dimensional density estimation diagrams of age uncertainty vs age for $^{206}\text{Pb}/^{238}\text{U}$ (A), $^{207}\text{Pb}/^{235}\text{U}$ (B), $^{207}\text{Pb}/^{206}\text{Pb}$ (C) and concordia age (D), calculated from the [Voice et al. \(2011\)](#) dataset along with more recent U-Pb zircon studies added to their dataset. The dataset plotted here comprises 49,651 LA-ICPMS zircon analyses. The best-fit trendlines are (A, B) 2nd order polynomial, (C) logarithmic and (D) spline fit respectively, and all four trendlines are plotted in panel (E). Also note the reduced age error scale in the concordia age plot (D).

locations, deposition ages, and fully tabulated reduced isotope data and U-Pb ages.

2.2.2. European Alps samples

Samples were collected from Oligo-Miocene clastic units of the Alpine pro-foreland basin ([Ford and Lickorish, 2004](#)). The sub-300 μm non-magnetic heavy mineral fraction was extracted from rock samples via standard crushing, sieving, and magnetic and density separation techniques. Zircon grains were hand-picked using a Nikon SMZ 1500 binocular microscope. To avoid sample bias, no attempt was made to exclude anhedral grains. Samples were mounted in epoxy resin, ground to reveal internal surfaces, and polished. Grain textures were characterized using a CL imaging system mounted to a Tescan MIRA SEM. All U-Pb

analyses were made using a Thermo Scientific iCAP Qc quadrupole mass spectrometer, coupled to a Photon Machines Analyte Excite 193 nm ArF excimer laser at Trinity College Dublin. Spot sizes of 30 and 36 μm diameter were used with a fluence of 3.9 J cm^{-2} , a pulse rate of 5 Hz, and total analysis time of 70 s, comprising 45 s of ablation followed by a 25 s background measurement. Downhole fractionation and intra-session analytical drift were corrected for using either the 91,500 or Plešovice as the primary and the Temora zircon as the secondary zircon mineral standard, together with NIST glass SRM 612 ([Wiedenbeck et al., 1995](#); [Pearce et al., 1997](#); [Black et al., 2003](#); [Sláma et al., 2008](#)). Data reduction was carried out using the VizualAge data reduction scheme for the IOLITE extension to the Igor Pro analytical software package ([Paton et al., 2011](#); [Petrus and Kamber, 2012](#)). Calculation of concordia

ages and generation of concordia plots was performed using the Isoplot add-in for Microsoft Excel (Ludwig, 2008), and kernel density plots and peak ages were generated using DensityPlotter (Vermeesch, 2012). Data for a subset of these samples was previously reported by Mark et al. (2016). See Supplementary Information A2 for sample locations, depositional ages, and fully tabulated reduced isotope data and U-Pb ages.

3. Results

For the Banda Arc, we present data from 1560 zircon analyses derived from eleven samples with Triassic depositional ages. A total of 995 acceptable (probability of concordance > 0.001) zircon U-Pb concordia ages (Fig. 4A) were obtained (pass rate of 64%); while 1297 grains pass at a 10% conventional discordance filter and 1074 grains pass using a 5% conventional discordance filter (pass rate of 69%, similar to the concordia age pass rate). Hence this dataset is characterized by appreciable discordance, but would not be atypical of many detrital datasets. The dataset comprises 51 rim overgrowth ages (Fig. 4B) with 36 core-rim age pairs presented here (Fig. 5A), as 15 rim ages derive from zoned zircons yielding discordant core ages and were excluded.

From the Alps, we present a total of 579 acceptable (probability of concordance > 0.001) zircon U-Pb concordia ages on 482 separate grains from six samples deposited during the Oligo-Miocene, including 97 rim overgrowth ages (Fig. 4C). Grains yielding core-rim age pairs which were indistinguishable at the 2σ level were interpreted as recording magmatic zoning, leaving 41 core-rim age pairs (Fig. 4D) interpreted as recording metamorphic or magmatic overgrowths on antecrystic or xenocrystic cores (Fig. 5B).

4. Discussion

4.1. Core vs rim analyses and core-rim age pairs

The Banda Arc dataset (Fig. 4A) records peaks at ca. 1847 Ma, indicating Northern/Central Australian provenance; 1540 Ma and 1140 Ma populations associated with Western Australian origin (Southgate et al., 2011; Lewis and Sircombe, 2013); and a series of peaks between 600 and 402 Ma and a major, composite Permo-Triassic peak between 312 and 240 Ma which records prolonged magmatic activity in the Bird's Head region of New Guinea (Gunawan et al., 2012; Zimmermann and Hall, 2016). Age peaks generated only from rim overgrowths generally do not show major differences to the complete dataset (<3% in almost all cases; Fig. 4B). However, there are four exceptions. Neither the Paleoproterozoic (ca. 2348 Ma), nor the Mesoproterozoic peak at ca. 1145 Ma, nor the late Neoproterozoic peak (ca. 600 Ma) observed in the complete dataset are recorded by the rim overgrowth dataset. The otherwise close agreement between age peaks of the complete dataset and rim overgrowth dataset suggests that these differences are not sampling artefacts arising from differences in sample size. Between acceptable core-rim age pairs (Fig. 5A), it is noticeable that in most cases the core and rim ages are indistinguishable at the 2σ level. A distinctive difference can be seen in grain T13–14/15 which yields an Archean core with a Paleoproterozoic overgrowth rim. In summary, ablation of grain rims only would have excluded detection of Meso- and Neoproterozoic events.

In the Alpine pro-foreland samples (Fig. 4C), the complete dataset records a minor Grenville-age peak at ca. 1012 Ma; a series of peaks between ca. 688 Ma and 535 Ma which likely record Cadomian arc magmatism and collision with Gondwana; a prominent Caledonian-age (Eo-Variscan) peak at ca. 449 Ma; Variscan-age peaks at ca. 328 Ma and

Fig. 4. KDE plots of concordia ages of zircon igneous cores of the whole dataset (A, C) and a second curve integrating rim overgrowths (B, D) for datasets from the eastern Indonesian Banda Arc and the European Alps pro-foreland.

Fig. 5. Zircon core-rim-pairs for the Banda Arc (A) and the Alpine (B) samples. Inset shows acceptable Alpine zircon ages separated by Th/U ratio, excluding six grains younger than 200 Ma. Grains with Th/U ≥ 0.5 are likely igneous; grains with Th/U ≤ 0.1 are likely metamorphic.

311 Ma; and a minor peak at ca. 289 Ma which likely records end-Variscan magmatism (Matte, 2001; Linnemann et al., 2007; Stampfli et al., 2013; Rivers, 2015; and references therein). Despite all samples being collected from the pro-foreland basin of the Alpine orogen, only a very minor Alpine-age peak at ca. 31 Ma is observed, comprised of just four analyses. These likely record Periadriatic volcanism, widespread in the central Alps but also reported from the western Alps (Waibel, 1993; Jourdan et al., 2013; Mark et al., 2016). Separation of rim overgrowths from the remainder of the dataset (Fig. 4D) does not result in significant changes to most peak ages observed in the complete dataset ($\leq 1\%$ in all cases), although the Grenville-age peak is not recorded by the rim overgrowths. In addition, one new peak is detected at ca. 508 Ma by the rim overgrowths. Although a minor peak in the rim dataset, it corresponds to a minima in the complete dataset (Fig. 4D). Ablation of grain cores

only would have failed to detect this peak, which likely records either the final accretion of the Cadomian arc to Gondwana, generally accepted as of mid-Cambrian age, or post-Cadomian magmatism associated with rifting of the Gondwanan margin (Linnemann et al., 2007; Stampfli et al., 2013). The fact that only the rim overgrowths record the 508 Ma event suggest it may be a metamorphic rim, rather than magmatic.

When only the single-grain core-rim pairs which yield ages distinguishable at 2σ are considered (Fig. 5B), the age spread between core and rim appears to vary systematically. In particular, Variscan-age rims are in all cases developed on cores which are also Variscan in age, whereas Caledonian-age rims are mostly developed on Cadomian age cores. Cadomian-age rims are mostly developed on Cadomian-age cores. Although the small size of this dataset ($n = 41$) prevents a definitive conclusion, the observed spreads in core-rim ages are in

good agreement with the Th/U ratio of the grains from the complete Alpine dataset (Fig. 5B, inset). The Th/U ratio of zircon is a commonly employed criterion to discriminate between magmatic and metamorphic paragenesis, where Th/U > 0.1 usually indicates a magmatic origin and Th/U < 0.1 usually indicates a metamorphic origin (Lopez-Sanchez et al., 2016 and references therein). However, metamorphic zircon overgrowths can have Th/U values of >0.1 (e.g., Schaltegger et al., 1999), while most Th/U values in magmatic zircons are above 0.5 (Hoskin and Schaltegger, 2003). Hence, we employ a Th/U ratio ≥ 0.5 as indicating a magmatic origin and a Th/U ratio ≤ 0.1 as denoting a metamorphic origin, even though this excludes just over half the grains in our dataset (Fig. 5B inset). The Th/U data (Fig. 5B inset) indicate that the Variscan and Cadomian are dominated by igneous grains, but the Caledonian event is dominantly metamorphic. Of course, these conclusions apply only to the original source rocks contributing to our dataset, and cannot be extrapolated to the entire orogen.

Thus, observed spreads in core-rim ages may provide additional information on the tectonothermal history of the source. For example, higher temperature tectonomagmatic events may be less prone to preserve antecrystic or xenocrystic cores. Alternatively, this may reflect the tectonic environment and the availability of xenocrysts for scavenging, which is likely lower in arc settings than in continental orogens, for example (e.g., Hopkinson et al., 2017). In summary, analysis of zircon cores alone would have failed to detect the ca. 508 Ma event, and analysis of zircon rims alone would have failed to detect the Grenville-age event.

5. Conclusions

Our data demonstrate that selective ablation of only cores or rim overgrowths in texturally polyphase zircon means that some tectonothermal events may be missed. In the case of our Banda Arc dataset, a Paleoproterozoic, a Mesoproterozoic and a late Neoproterozoic age peak recorded by zircon cores were not observed in the rim overgrowth dataset. In the Alps, a minor mid-Cambrian age peak was recorded only by the rim overgrowths. Failure to detect source area age peaks is undesirable in detrital provenance studies; given the relative ease with which large numbers of detrital zircon from conventional samples can now be characterized by CL-SEM and analysed by LA-ICPMS, we urge researchers to consider routinely targeting *both* cores and rims where practicable. This can now be achieved with ultra-fast spot U-Pb LA-ICPMS analyses using rapid aerosol introduction systems (cf Chew et al., 2017a, b), which can be combined with other multi-proxy U-Pb datasets (e.g., apatite and rutile; O'Sullivan et al., 2016). Generation of comprehensive single-grain core-rim age pair datasets can also help characterize further tectonothermal episodes recorded in the zircon data (e.g., magmatic versus metamorphic events), and can yield additional provenance information if source rocks are well-characterized.

We also urge routine use of single-analysis concordia ages. Comparison of concordia and single isotope ratio ages (i.e., ^{206}Pb – ^{238}U , ^{207}Pb – ^{235}U and ^{207}Pb – ^{206}Pb) calculated for ca. 49,500 LA-ICPMS zircon U-Pb analyses demonstrates that the concordia age provides the greatest precision through geological time, and the precision varies less with age, as identified by Ludwig (1998, 2008). In contrast, single isotope ratio ages systematically display less (^{206}Pb – ^{238}U) or greater (^{207}Pb – ^{206}Pb) precision with decreasing age.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.sedgeo.2017.12.020>.

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