Geoscience Frontiers xxx (2015) 1–9

HOSTED BY
ELSEVIER

Contents lists available at ScienceDirect

China University of Geosciences (Beijing)

Geoscience Frontiers

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

Research paper

Strategies towards statistically robust interpretations of *in situ* U–Pb zircon geochronology

Christopher J. Spencer [a,*], Christopher L. Kirkland [b,c], Richard J.M. Taylor [a]

[a] *The Institute of Geoscience Research (TIGeR), Department of Applied Geology, Western Australian School of Mines, Curtin University, WA 6102, Australia*
[b] *Centre for Exploration Targeting – Curtin Node, Department of Applied Geology, Western Australian School of Mines, Curtin University, WA 6102, Australia*
[c] *Australian Research Council, Centre of Excellence for Core to Crust Fluid Systems, Perth, WA 6102, Australia*

ARTICLE INFO

Article history:
Received 15 September 2015
Received in revised form
17 November 2015
Accepted 19 November 2015
Available online xxx

Keywords:
Zircon
Geochronology
U-Pb
Geostatistics
MSWD

ABSTRACT

Zircon U–Pb geochronology has become a keystone tool across Earth science, arguably providing the gold standard in resolving deep geological time. The development of rapid *in situ* analysis of zircon (via laser ablation and secondary ionization mass spectrometry) has allowed for large amounts of data to be generated in a relatively short amount of time and such large volume datasets offer the ability to address a range of geological questions that would otherwise remain intractable (e.g. detrital zircons as a sediment fingerprinting method). The ease of acquisition, while bringing benefit to the Earth science community, has also led to diverse interpretations of geochronological data. In this work we seek to refocus U–Pb zircon geochronology toward best practice by providing a robust statistically coherent workflow. We discuss a range of data filtering approaches and their inherent limitations (e.g. discordance and the reduced chi-squared; MSWD). We evaluate appropriate mechanisms to calculate the most geologically appropriate age from both ^{238}U/^{206}Pb and ^{207}Pb/^{206}Pb ratios and demonstrate the cross over position when chronometric power swaps between these ratios. As our *in situ* analytical techniques become progressively more precise, appropriate statistical handing of U–Pb datasets will become increasingly pertinent.

1. Introduction

Since the advancement of *in situ* U–Pb geochronology (via secondary ionization or laser ablation) there have been significant discussions on appropriate methods to assign temporal constraint for geologic phenomena (e.g. maximum depositional age of sedimentary successions, timing of volcanic eruptions/plutonic emplacement/peak metamorphism). U–Pb geochronology has seen over 300% growth in publication of this method over the last 10 years (Harrison et al., 2015). Of the U–Pb chronometers zircon has by far seen the greatest uptake in its use (Fig. 1), likely in part due to its ubiquity in a wide range of lithologies and general ease of data reduction (e.g. due in part to minimal common-Pb). Although now widely adopted as the method of choice to assess the age of a wide range of geological processes the coherent application of a suite of statistical tests to demonstrate the veracity of calculated dates is important. This paper does not discuss issues related to natural or induced bias in sample selection and processing nor in hand-picking of zircons, location of analytical spots, and common-Pb correction as these up-stream issues are discussed at length elsewhere (Sircombe and Stern, 2002; Ludwig, 2003; Košler, 2012; Malusa et al., 2013). Rather, this paper highlights a series of other problematic issues that may degrade the interpretation of U–Pb geochronology data. Although much of the solutions to these issues are not in themselves new, we present them in a coherent workflow (see inline Supplementary Figure) that draws together these best practice approaches (e.g. see Horstwood, 2008; Condon and Bowring, 2011; Corfu, 2013).

2. Data reduction versus reducing the data

Converting the raw electrical signals during an analysis from a mass spectrometer to a usable datum is often referred to as "data reduction". Often included in this catch-all process is the correction of mass-bias, normalization to reference materials, and propagation of external and internal (systematic) uncertainties in

---

* Corresponding author.
E-mail addresses: cspencer@curtin.edu.au, spenchristoph@gmail.com (C.J. Spencer).
Peer-review under responsibility of China University of Geosciences (Beijing).

http://dx.doi.org/10.1016/j.gsf.2015.11.006

Please cite this article in press as: Spencer, C.J., et al., Strategies towards statistically robust interpretations of *in situ* U–Pb zircon geochronology, Geoscience Frontiers (2015), http://dx.doi.org/10.1016/j.gsf.2015.11.006

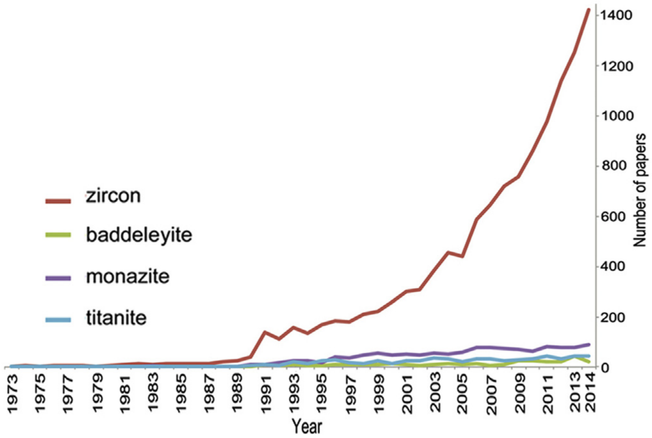


Figure 1. Plot of the number of geochronology papers dealing with a specified mineral phase published from 1973 to 2014 from ISI Web of Science (using keywords U–Pb and the mineral name).

quadrature. It is usually after this procedure when the data-handler assesses the acceptability of each datum. However, in many published datasets analytical results are often discarded if they fall out with an arbitrary discordance threshold or goodness of fit parameter. While discarding of data based on discordance alone should be discouraged, the level of such a filter is important and should be carefully set according to grouping independent criteria.

3. Dealing with discordance

An important filtering process is assessing the similarity of ages calculated from different decay schemes that have been measured. The discordance of a zircon U–Pb date can be defined as the percentage disagreement of isotopic dates from two or more isotopic systems (Wetherill, 1956). Discordance in the U/Pb system is generally due to Pb migration within the mineral lattice (Mezger and Krogstad, 1997; Cherniak and Watson, 2000). This is generally quantified either by using the ratio of the ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ages or the ^{206}Pb/^{238}U and ^{207}Pb/^{235}U ages. The resulting percentage difference provides a qualitative assessment of whether the isotopic ratios had experienced disturbance following the zircon crystallization (Eglington and Harmer, 1993; Gehrels, 2014). Although discordance is given as a numerical value the interpretation thereof is generally reduced to: ‘concordant’ or ‘discordant’. The level of acceptable discordance is a topic of minimal discussion and each worker/laboratory/study rarely justifies the chosen discordance filter. Typical discordance filters vary from 1% to 30% depending on the data processing techniques and level of interpretation desired, although 10% is more commonly used as the generally accepted filter. Once each datum has been categorized using the simple binary division, many workers treat the data within each category the same with no further attempt to discriminate their analyses. The arbitrary nature of the discordance filter can dramatically affect the ways in which data is interpreted (e.g. Nemchin and Cawood, 2005). Furthermore, the measure of discordance is a direct reflection of the analytical precision of the instrumentation used. That is, it is easier to have ‘concordant’ data when using an imprecise instrument when uncertainties are large, e.g. using a quadrupole ICP-MS.

A percentage age difference discordance filter provides a simple method to assess the distribution of detrital zircon dates without directly interpreting any individual dates and is therefore an effective way to assess a subset of data (e.g. in age spectra). However, it is important to present age spectra using a variety of discordance filters (including the unfiltered data) to assure robust interpretation of zircon populations (Fedo, 2003; Nemchin and Cawood, 2005). To assess the robustness of a discordance filter, Malusa et al. (2013) proposed using the similarity between the unfiltered data and filtered subsets using a Kolmogorov-Smirnov (K-S) test (Smirnov, 1939). Their philosophy is to “accept” the largest proportion of data without significantly altering the position of the age peaks in the least discordant subset. This approach, however, ignores the age-peak shift that is generally associated with minor amounts of Pb-loss.

While a dataset filtered for extremely discordant analyses is useful when visualizing and comparing age spectra (e.g. in sedimentary systems), it is severely limited in its ability to define ages of individual geologic events that require greater attention when assessing the possibility of Pb-loss. When defining these temporal constraints more stringent criteria must be used to assure the usability of a given subset. For this reason a potentially more powerful technique is to accept data that are within analytical uncertainty of concordia at a specified confidence level (e.g. 2σ). The assessment of whether an age from a given analysis is concordant can be conducted using the covariance of uncertainties of McLean et al. (2011) or Ludwig (2003) within Isoplot. Those analyses that fall along the 1:1 age line are within uncertainty of concordia and following this definition ‘concordant’. If analyses fall off this line, even by a small margin, they cannot be considered ‘concordant’. In such discordant cases, radiogenic lead loss or some other isotopic disturbance cannot be discounted. Unlike recent lead loss, in which stoichiometric loss of total lead maintains the ^{207}Pb/^{206}Pb system, dealing with discordance in rocks interpreted to have undergone metamorphism must be done with care. In such a case a spread of ages may be expected, all of which are meaningful and should not necessarily be discounted for not forming a statistical population. While it is not within the scope of this paper to deal with these complexities, it is recommended that in such a scenario that all the data is presented, and any description of ‘filtering’ is given in full so the reader can understand the interpretation.

4. Selecting the “best age”

In the radium and actinium series decay chains, three ages can be calculated using lead and uranium isotopes, namely the ^{206}Pb/^{238}U, ^{207}Pb/^{235}U, and the ^{207}Pb/^{206}Pb. Additionally, the thorium series decay can be used to calculate the ^{208}Pb/^{232}Th age although this is rarely used in zircon geochronology. Given the relative imprecision of the ^{235}U and ^{207}Pb measurements, the ^{207}Pb/^{235}U age is also rarely used and often ^{235}U is not measured by the mass spectrometer, rather this isotope is calculated using the fixed ^{238}U/^{235}U ratio of ~137.8 (see Hiess et al., 2012) and is primarily used to measure the discordance of an analysis. Therefore in zircon analyses there are effectively two isotopic ages (^{206}Pb/^{238}U, and ^{207}Pb/^{206}Pb) from which the ‘best age’ is chosen. It is common practice to use the ^{207}Pb/^{206}Pb age for zircons older than ~1.2 Ga (although the strict cutoff varies significantly within the literature) and to use ^{206}Pb/^{238}U ages for those younger (Gehrels et al., 2008). The analysis of ^{207}Pb exhibits greater imprecision and nearly an order of magnitude lower count rate relative to the ^{206}Pb (despite dwell times as much as 3–4 times longer). This often leads to greater imprecision to the ^{207}Pb/^{206}Pb age for younger zircons hence the ~1.2 Ga cutoff. A compilation of ~38,000 LA-ICP-MS zircon analyses (Voice et al., 2011) and ~5000 SIMS zircon analyses (Wingate et al., 2015) that pass the test for concordance described above reveal a cross over point of ^{207}Pb/^{206}Pb and ^{206}Pb/^{238}U ages and respective uncertainties at ~1.5 Ga (Fig. 2). Although ^{207}Pb/^{206}Pb ages may offer a more correct age for discordant data if recent Pb-loss has occurred, nonetheless filtering data for a more robust measure of concordance provides a less assumptive approach. Hence, utilizing a ~1.5 Ga cross over point from ^{207}Pb/^{206}Pb ages to ^{206}Pb/^{238}U is preferable given the change in

Please cite this article in press as: Spencer, C.J., et al., Strategies towards statistically robust interpretations of *in situ* U–Pb zircon geochronology, Geoscience Frontiers (2015), http://dx.doi.org/10.1016/j.gsf.2015.11.006

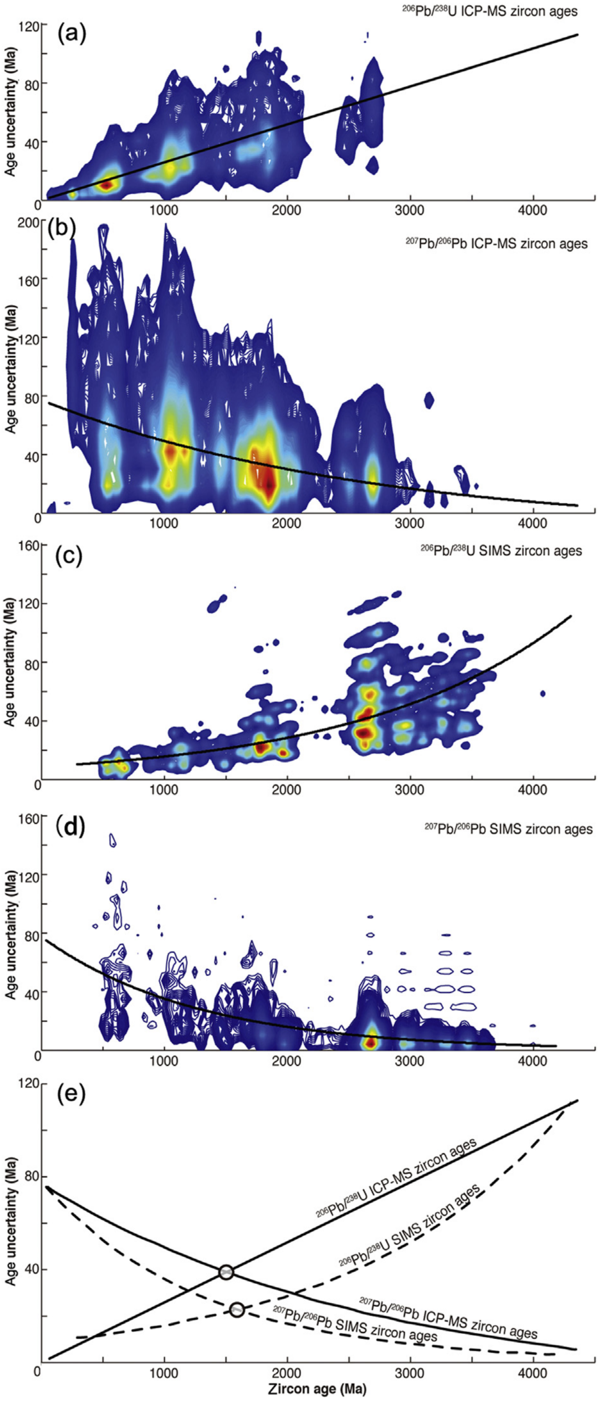


Figure 2. (a–d) Respective bivariate kernel density estimation diagrams (after Botev et al., 2010) of ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ages from a compiled ~38,000 LA-ICP-MS zircon analyses (Voice et al., 2011) and ~5000 SIMS zircon analyses (Wingate et al., 2015) that pass the test for concordance (see text for explanation). (e) Best-fit trend-lines reveal a cross over point of ^{207}Pb/^{206}Pb and ^{206}Pb/^{238}U ages at ~1.5 Ga.

chronometric power. This cross over point is equivalent for both LA-ICP-MS and SIMS analyses. Fortuitously, the 1.5 Ga cross over-point generally falls within a trough between the major zircon age peaks in global compilations and provides a natural break in many datasets (see e.g. Voice et al., 2011; Roberts and Spencer, 2014). However, if there is a detrital zircon population in the environs of the ~1.5 Ga cutoff, rather than splitting a single population with different isotopic ages, the cutoff should be shifted to a gap in the detrital age spectra.

In cases where the true location of the mean data point can be assumed to fall on the concordia curve or at least within analytical uncertainty of it, there are some workers who use a ‘concordia age’ (Ludwig, 1998), which makes the best use of all ^{207}Pb/^{206}Pb and ^{238}U/^{206}Pb ratios. This approach will typically yield a more precise mean age than can be obtained using either ratio alone, and also yields an objective and quantitative measure of concordance, additionally it is logically consistent with filtering data based on the overlap of their error ellipse on concordia. It should be noted however, that utilizing the concordia age in either single grains or single populations of ages assumes that the uncertainties of both the ^{238}U and ^{235}U decay constants are equal, which is not the case.

5. Weighted mean and the reduced chi-squared

In a scenario where one isotopic system is determined to provide the most robust results, a weighted mean of that data may provide a more applicable solution than calculating concordia ages. When a set of data appears to form a single population, a mean whose uncertainty is weighted with the uncertainties of the individual analyses can be calculated to represent the data with a single value and uncertainty. It is calculated using the following equation:

$$\bar{x} = \frac{\sum_{i=1}^{n}(x_i/\sigma_i)^2}{\sum_{i=1}^{n}\sigma_i^2} \text{ or } \bar{x} = \frac{(x_1/\sigma_1 + x_2/\sigma_2 + \mathrm{L} + x_n/\sigma_n)^2}{(\sigma_1 + \sigma_2 + \mathrm{L} + \sigma_n)^2}$$

where x_i and σ_i are the analyses and uncertainties, respectively. The weighted uncertainty is calculated with

$$\sigma_{\bar{x}} = \sqrt{\frac{1}{\sum_{i=1}^{n} 1\big/\sigma_i^2}} \text{ or } \sigma_{\bar{x}} = \sqrt{\frac{1}{1\big/(\sigma_1 + \sigma_2 + \cdots + \sigma_n)^2}}$$

The reduced chi-squared statistic (X^2_{red}; also known as the mean square weighted deviation or MSWD; Wendt and Carl, 1991) is used to indirectly assess the degree to which the weighted average and uncertainty represent a single population. This statistic is the chi-squared statistic divided by the number of degrees of freedom and is calculated using the following equation:

$$X^2_{\text{red}} = \frac{1}{\nu} \times \sum \frac{(O - E)^2}{\sigma^2}$$

where ν is the degrees of freedom (n−1), O is the observed data, E is the theoretical or expected data (i.e. the weighted average of the observed data/model that represents the data), and σ^2 is the variance of the observed data.

The X^2_{red} statistic is most generally used to assess the appropriate propagation of random and systematic uncertainties (Wendt and Carl, 1991; Horstwood, 2008; Condon and Bowring, 2011). Where a X^2_{red} statistic of 1 indicates the observed values and the weighted average neither under- nor overestimate the associated uncertainties. A value greater than 1 reflects that either the uncertainties have been significantly underestimated or that the scatter represented is natural variation whereas those less than 1 indicate the uncertainties have been overestimated or that the weighted average uncertainty has not captured the actual variation in the data. An underutilized metric demonstrates how the acceptable values of the X^2_{red} are related to the number of analyses used in the weighted mean and is expressed as $1 + 2\sqrt{2/f}$ where f is the degrees of freedom (n−1) (Wendt and Carl, 1991). If the X^2_{red} is greater than $1 + 2\sqrt{2/f}$, there is only a 5% probability that the data form a single statistical population (Fig. 3). Therefore, with an n of 20 the acceptable reduced chi-squared is 0.35–1.65, whereas with an n of 10 the acceptable range is 0.1–1.9 (at the 2σ level). Weighted averages with X^2_{red} values that fall outside of this range should not be used; rather the range of analyses should be given with the caution that the population either does not represent a single population (if the $X^2_{\text{red}} > 1$) or does not fully represent the accurate level of uncertainty (if the $X^2_{\text{red}} < 1$). Condon and Bowring (2011) also pointed out that even when the X^2_{red} does equal 1, this merely indicates that if there is variation in the given population then it cannot be resolved within the observed precision. Hence, the X^2_{red} should only be used when a single population can be identified within a given uncertainty in which the X^2_{red} does not violate the $1 + 2\sqrt{2/f}$ rule at 2σ (see Fig. 3) and the identification of a single population does not violate the geologic context of the sample (detrital zircons versus primary igneous/metamorphic zircons). It should be noted that to cull data of a presumed single population simply to achieve an acceptable X^2_{red} should be avoided unless other evidence supports classifications of these analyses as ante- or xenocrystic.

6. Maximum depositional ages

Various strategies have been employed to define the maximum depositional age including: the youngest single grain age, youngest "peak" of dates, mean (or weighted mean) dates of the youngest two or more grains with overlapping 1σ uncertainties, or mean (or weighted mean) dates of youngest three or more grains (see Dickinson and Gehrels, 2009). Using the youngest age peak or a weighted mean raises some significant issues as it assumes the detrital zircons source represents a single zircon growth event (e.g. a volcanic eruption). Defining such an event in a detrital system is not possible for many sediments and defining ancient catchments is fraught with uncertainty (e.g. see Horton and DeCelles, 2001). Even within a given catchment (modern or ancient) the temporal span of magmatism with a given unit is often poorly understood. Additionally, when defining the maximum depositional age the concordance of the youngest detrital zircon analysis must be taken into account, which should be within analytical uncertainty of concordia (e.g. overlap at 2 standard deviations of the 1:1 age line of concordance as discussed above). More precise data thus require more stringent criteria to define maximum depositional ages.

Dickinson and Gehrels (2009) proposed that a weighted arithmetic mean of the youngest population of zircons ($n > 3$) that overlap in age at 2σ as a statistically robust measure for a maximum depositional age. This method has been utilized to extract a single age from several individual analyses (recent examples include: Tucker et al., 2013; Amarasinghe et al., 2015; Hu et al., 2015; Yokelson et al., 2015). As discussed above, it is common practice to use a weighted arithmetic mean of a group of analyses to reduce a population of analyses into a single age. However, the weighted arithmetic mean can only be used when dealing with analyses from a single population (e.g. a volcanic eruption or rapidly emplaced pluton), therefore, this method is only acceptable within a presumed single zircon growth event (within uncertainty). This method, in many cases, may not be valid for detrital zircon grains within clastic sedimentary rocks, despite their age similarity, as these zircon cannot *a priori* be considered to have been derived from a single zircon growth event without further chemical or isotopic verification. Based on age data alone it cannot be assumed that the youngest detrital population is volcanic in nature nor can detrital zircons be definitively tied to a single source. There are several geologic complications associated with this grouping exercise. Consider a suite of detrital zircon crystals collected from a single pluton. Even if it can be assumed the detritus was sourced from a single pluton (which in ancient sedimentary systems is virtually impossible), it cannot be assumed that the pluton is characterized by a single age without detailed geochronologic data. Magmatic systems are often shown to be characterized by protracted events. For example, the Idaho Batholith has been shown to contain primary magmatic zircons that span ~50 Myr (Bickford et al., 1981; Toth and Stacey, 1992; Foster and Fanning, 1997; Gaschnig et al., 2012). Other examples include the ~40 Myr spread in the Florida Mountains granite (Amato and Mack, 2012), ~20 Myr spread in the Ladakh Batholith (Weinberg and Dunlap,

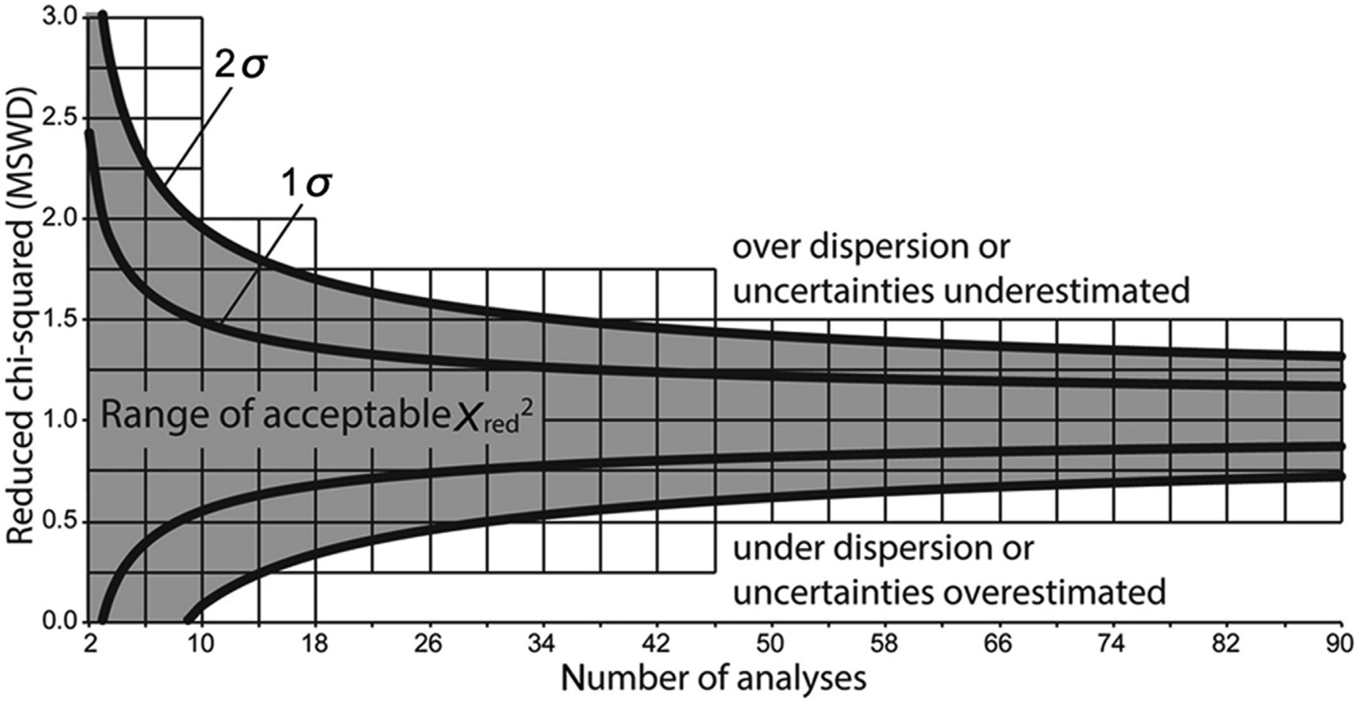


Figure 3. Range of acceptable X^2_{red} values as a function of sample size at 1σ and 2σ. This range of acceptability is calculated using the $\sqrt{2/f}$ rule of Wendt and Carl (1991).

2000), ~10 Myr spread in the Tuolumne Intrusive Suite (Coleman et al., 2004), ~10 Myr spread in the Adamello Batholith (Schaltegger et al., 2009; Schoene et al., 2012). Thus, given the confounding variables in the provenance of a detrital suite of zircons, weighted arithmetic means of analyses from multiple detrital zircons should not be used to define the maximum depositional age. The proposed alternative(s) will vary based upon the apparent ages of the youngest detrital zircons. For zircons older than the late-Paleozoic Era where identification of lead-loss is unambiguous, it is proposed that multiple *in situ* analyses of youngest concordant zircons be performed within the same age zone (as determined by cathodoluminescence imaging) either with an adjacent spot or on top of the original spot following repolishing (see also Gehrels, 2012). By performing multiple analyses of the same grain, it can be assured that the resulting age is 'real' and does not represent mixing of two isotopic zones (Spencer et al., 2014). For zircons where lead-loss cannot be discounted, multiple analyses of these grains might reveal different degrees of lead loss and thus the discounting of that grain. Alternatively, chemical abrasion of the youngest grains to remove the metamict regions of the zircon followed either by *in situ* or ID-TIMS analysis will provide a more reliable result (Mattinson, 2005; Kryza et al., 2012). It should also be noted that when utilizing the multiple analyses of the youngest grain, the resulting age will be an underestimate of the maximum depositional age (assuming a normally distributed true maximum depositional age) (see inline Supplementary Figure).

When constraining a maximum depositional age only data within analytical uncertainty of concordia (2σ) should be used. However, establishing how concordant a datum must be in order to be considered valid is generally established using an arbitrary discordance filter. Although a 10% discordance filter might be useful when visualizing and comparing detrital age spectra using a zircon that is 10% discordant to constrain the timing of deposition can deliver an errant result. For example, Dehler et al. (2010) and Spencer et al. (2012) reported a very small proportion of zircon ages (<3% of the total analyses) that are used to define the maximum depositional age of presumably Neoproterozoic sediments deposited along the western margin of Laurentia during the rifting of Rodinia. The youngest analyses are variably discordant (3%–19%) and have ages that span over 100 Myr. Dehler et al. (2010) reported eleven analyses of ten zircons all of which passed their chosen discordance filter (20%) with an age ~300 Myr younger than the next oldest population in an attempt to define the maximum depositional age of a sedimentary succession. Spencer et al. (2012) also reported two zircons from correlative sedimentary rocks with the same discordance filter. Despite all of them passing the arbitrary discordance filter and incorporating the uncertainty covariance (McLean et al., 2011), only six of the thirteen analyses overlap with the 1:1 concordance line (Fig. 4). Excluding analyses that do not overlap the 1:1 concordance line (within analytical uncertainty of concordia) seems a more conservative approach as lead-loss (or if reverse discordance lead-gain or U/Pb calibration imprecision or fractionation) is indicated. Therefore, these discordant analyses should not be used to define a discrete maximum depositional age for this sedimentary succession. Furthermore, in both of these studies the ^{207}Pb/^{206}Pb age was chosen as the 'best age' with no further mention of the other isotopic systems despite the greater precision and concordance of the ^{206}Pb/^{238}U and the ^{207}Pb/^{235}U ratios/ages (see Fig. 4).

7. Phanerozoic Pb-loss

Discordance is relatively easy to evaluate for zircon dates older than the late Paleozoic Era (>~400 Ma). For zircons younger than the late Paleozoic Era, the limited curvature of concordia combined with the imprecision of the ^{207}Pb measurement (compounding the imprecision of the ^{207}Pb/^{235}U and ^{207}Pb/^{206}Pb ages) significantly limits the identification of discordance (Bowring and Schmitz, 2003; Ireland and Williams, 2003). This becomes a significant problem when dealing with Phanerozoic units that have potentially experienced lead loss. For these particular situations, any level of lead loss is masked by the uncertainty of the analysis.

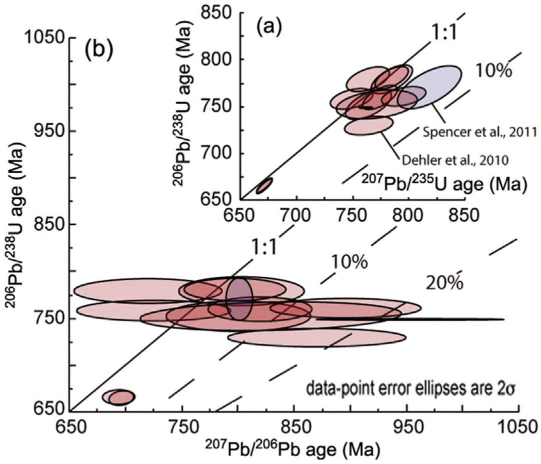


Figure 4. (a) ^{207}Pb/^{235}U age versus ^{206}Pb/^{238}U age of Neoproterozoic zircons from the Big Cottonwood and Little Willow Formations (Dehler et al., 2010; Spencer et al., 2012). (b) ^{207}Pb/^{206}Pb age versus ^{206}Pb/^{238}U age of the same. Covariance of uncertainties is calculated from McLean et al. (2011). The 1:1 line represents equivalent isotopic ages (0% discordance) with the dashed lines representing respectively 10% and 20% discordance. Although in these two studies, the ^{207}Pb/^{206}Pb ages were used for these Neoproterozoic zircons, given the degree of discordance and the analytical imprecision these analyses should not be used to constrain the timing of deposition as lead loss cannot be discounted.

To illustrate the issues associated with lead loss and discordance in young zircons, a series of synthetic zircon datasets are generated using assumed single zircon growth events at 1000, 500, 300, 100, and 50 Ma (Fig. 5). The "analyses" of these hypothetical populations form a normally distributed population centered at the true age within the typical uncertainties of *in situ* analytical techniques. These single populations are then subjected to a random degree of lead loss ranging from 0 to 100% along a discordia anchored at 0 Ma (modern radiogenic-Pb loss). These are grouped into a single "detrital" dataset to represent a metasedimentary rock with five discrete sources mentioned above using the ^{206}Pb/^{238}U ages for those analyses <500 Ma and ^{207}Pb/^{206}Pb for those >1000 Ma. Using the typical 10% discordance filter the "concordant" subset includes varying amounts of each population from 40% of the 1000 Ma to 100% of the 100, and 50 Ma populations despite a significant degree of lead loss. The resulting age spectrum presents a meaningless spread of data with peaks at 5, 20, 165, and 350 Ma (^{206}Pb/^{238}U) and an accurate peak at ~1000 Ma (^{207}Pb/^{206}Pb) (Fig. 5). Although this illustrates the worst-case scenario, it provides a stark look at the difficulty when interpreting detrital zircon age spectra in (meta)sedimentary units with zircon that have been affected by Pb-loss. When collecting U–Pb data of detrital zircons in sedimentary units potentially derived from metamorphic rocks or those that have experienced lead-loss these issues should be taken into account. One potential way to overcome these issues is to assess the clustering of age populations and the nature of the negatively skewed tail in the youngest zircon population (Fig. 6). Although the highest point in an 'age peak' might correspond to the approximate age of a given zircon source, as illustrated in Fig. 6, the youngest set of analyses are often used to constrain the maximum depositional age in

Please cite this article in press as: Spencer, C.J., et al., Strategies towards statistically robust interpretations of *in situ* U–Pb zircon geochronology, Geoscience Frontiers (2015), http://dx.doi.org/10.1016/j.gsf.2015.11.006

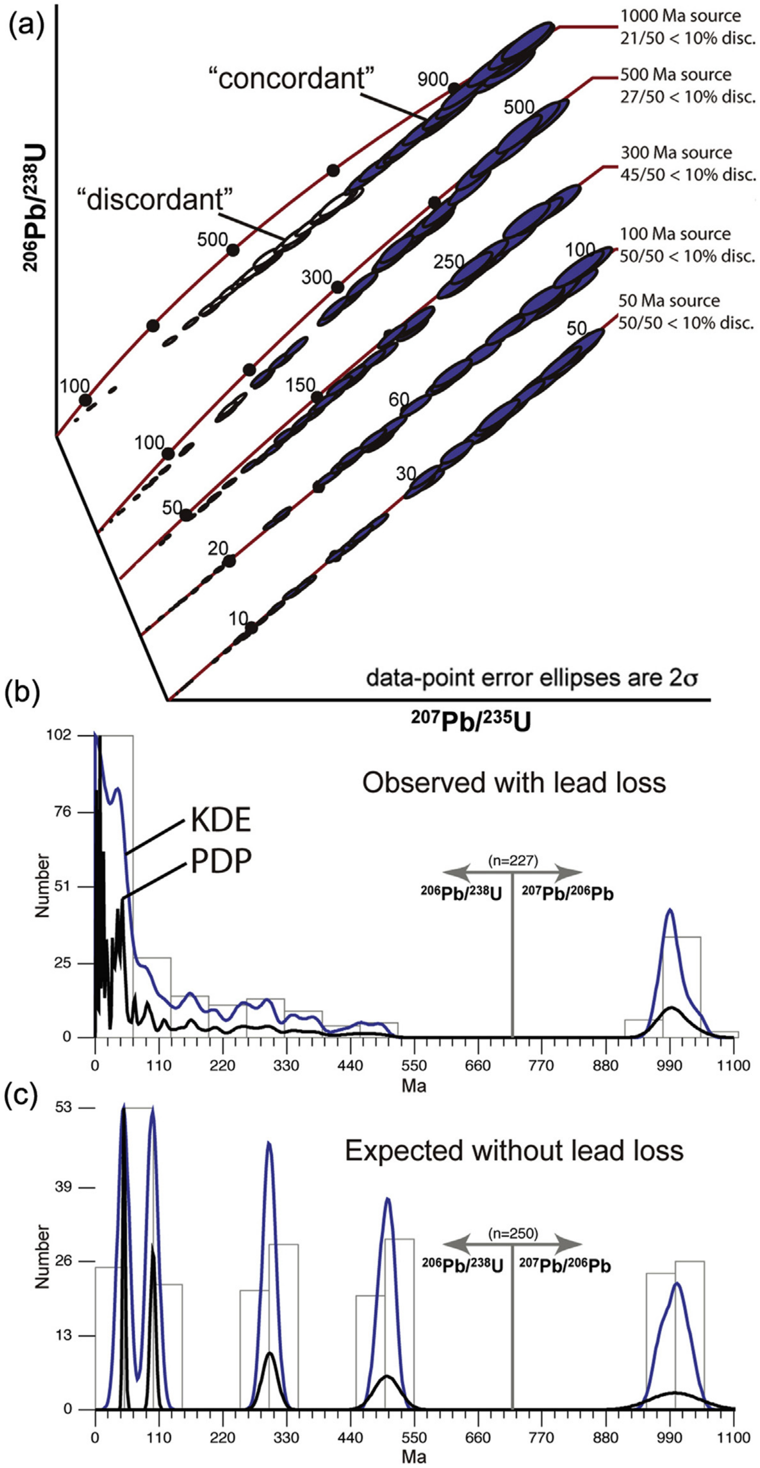


Figure 5. (a) Normally distributed synthetic data centered at 50 Ma. Random amounts of lead loss are superimposed on 30% of the data creating a negatively skewed tail. (b) Concordia plot of the synthetic data in (a). Despite lead loss each analysis overlaps with concordia. (c) Synthetic data from (a) and along with weighted averages, 2σ uncertainty, and X^2_{red} of the youngest three, five, and eight analyses. Red analyses are those with random lead loss and blue analyses are those without lead loss. In this scenario, none of the previously proposed strategies to define the maximum depositional age would provide a meaningful age within a normally distributed population with a negatively skewed tail.

detrital samples or the latest stage of zircon growth in magmatic and metamorphic samples. However, if a zircon age population is negatively skewed with a tail towards younger ages, this may relate to lead-loss undetectable with a discordance filter. Therefore, the youngest zircons within a negatively skewed age population should not be used in calculation of a maximum age of deposition.

8. Conclusions

It is proposed that constraining the timing of geologic events using *in situ* zircon analyses can benefit from the following criteria:

(1) Only analyses that overlap within 2σ covaried uncertainty of the concordia curve should be used.

Please cite this article in press as: Spencer, C.J., et al., Strategies towards statistically robust interpretations of *in situ* U–Pb zircon geochronology, Geoscience Frontiers (2015), http://dx.doi.org/10.1016/j.gsf.2015.11.006

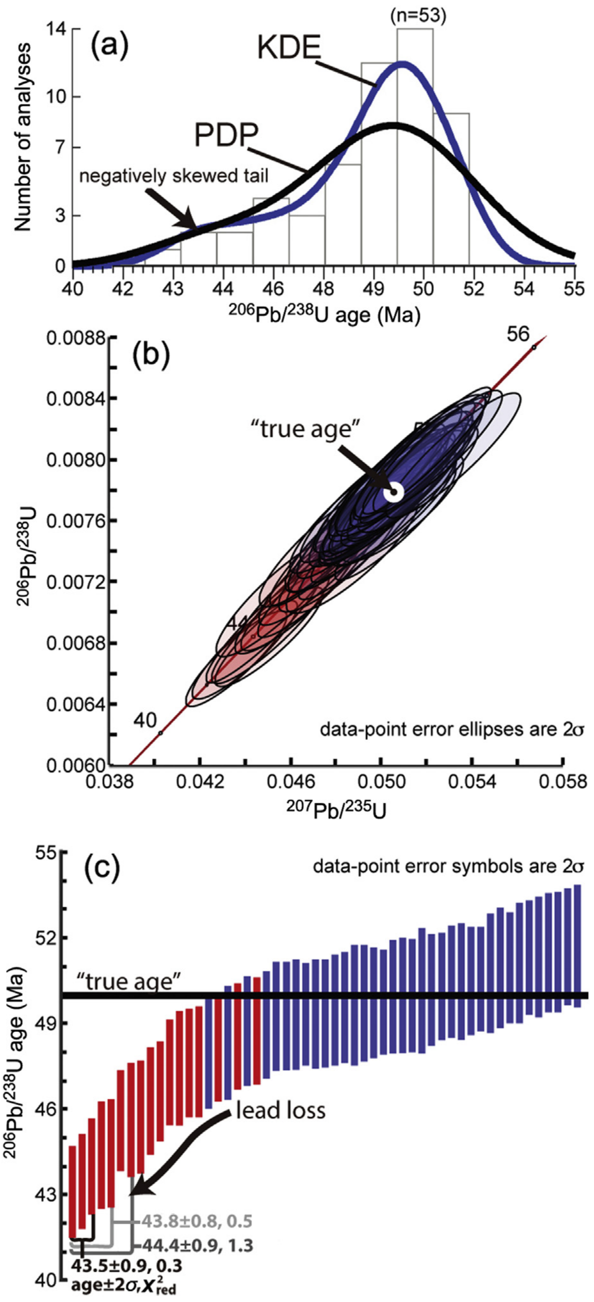


Figure 6. (a) Synthetic data of five hypothetical units with initial unimodal age distributions that have experienced a random degree of lead-loss. Blue ellipses are data that are <10% discordant and white ellipses are >10% discordant. Ma = millions of years, disc. = discordant. Figure constructed with Isoplot (Ludwig, 2003). (b) Combined observed detrital age spectra from "concordant" data in Fig. 1a. For ages smaller and greater than ~700 Ma, the ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ages are used respectively. Blue line = kernel density estimation (KDE), black line = probability density plot (PDP). (c) Same as Fig. 6b but with expected age spectra without and lead-loss. Fig. 6b and c is constructed using density plotter (Vermeesch, 2012).

(2) Weighted averages and X^2_{red} of multiple analyses within individual grains should not violate the $1+2\sqrt{2/f}$ rule at the 2σ level.
(3) When maximum depositional ages are sought, it is best practice to perform multiple analyses on the youngest individual zircon either in spots within the same textural domain or on a repolished surface to assure the validity of the analysis, given the potential difficulty of distinguishing radiogenic-Pb loss.
(4) Weighted averages of single detrital grains should not be combined unless chemical or other isotopic data (e.g. U concentration, Hf isotopes) has been used to independently verify that the detrital zircon population represents a single zircon-forming event. Rather, when age data alone exists then the weighted average of multiple analyses of the youngest zircon is preferred.
(5) In young zircon crystals (post-late Paleozoic Era) the lack of lead loss can be established through the lack of a negatively skewed age probability curve, by multiple re-analysis, and the lack of correlation between U (and Th) content and age.
(6) To assure that the youngest detrital grain is not a contaminant, reproducibility from a separate aliquot would be ideal.
(7) Additionally, we suggest that defining spot level interpretations of U–Pb geochronology for all analyzed grains, within the reported data table and using a consistent nomenclature is a profitable approach aiding the utility of datasets and allowing easy compilation. The following is one scheme, which we have found to satisfactorily accommodate all interpretations needed over multiple years of campaign style U–Pb geochronology. D = outside discordance threshold or age information regarded as geologically meaningless; P = concordant but interpreted to have undergone radiogenic-Pb loss (e.g. high alpha dose or correlation with uranium or F206 content); M = metamorphic (subscripts for multiple generations if present); I = magmatic; X = xenocryst/inheritance; Y = youngest detrital analyses; S = other detrital; Z = other growth mechanism not otherwise defined.

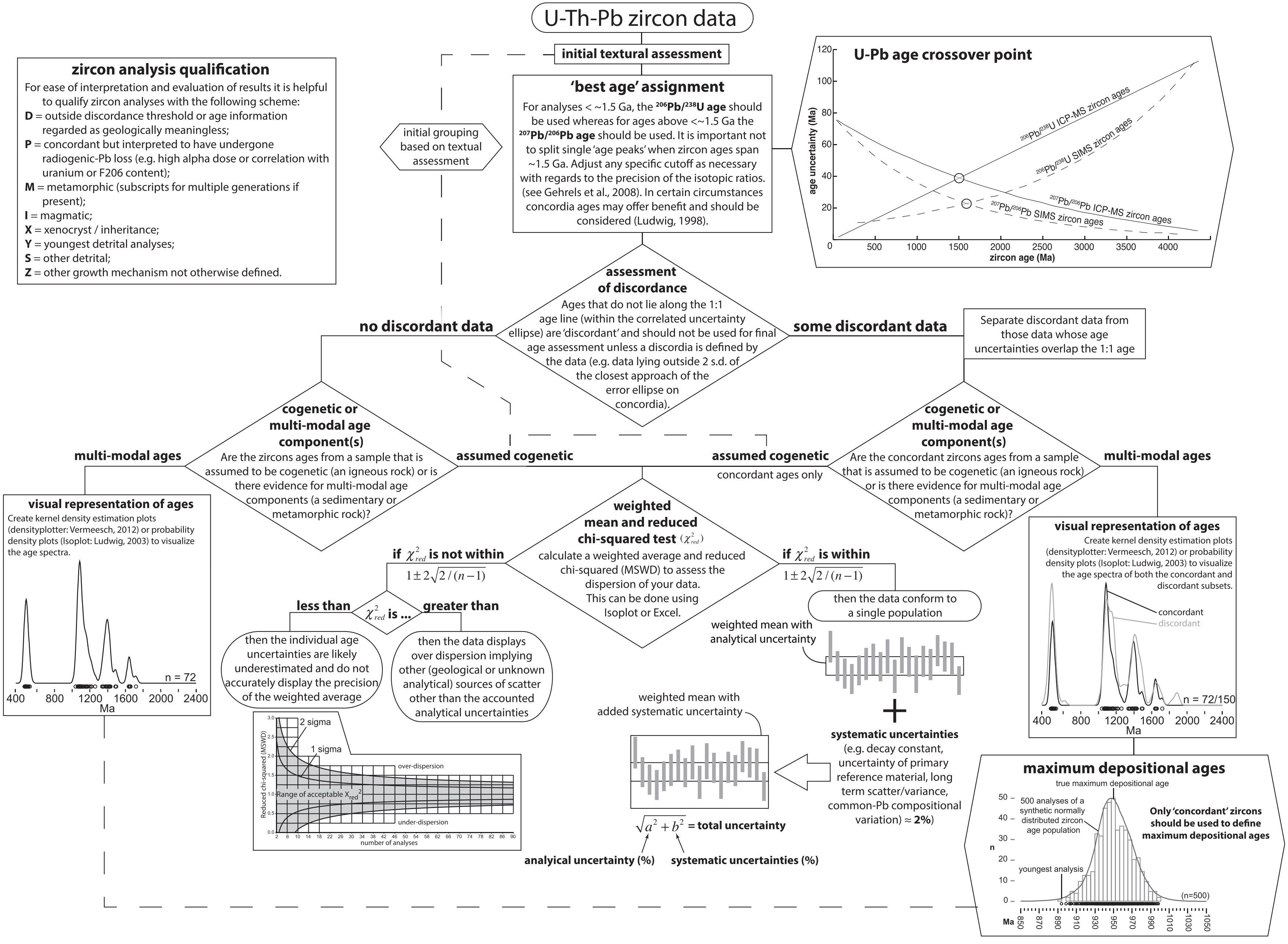
Because of population statistics the youngest detrital zircon age may in many cases post-date the true *maximum* depositional age. If the latest zircon-forming event to contribute detritus to a sedimentary succession could be determined, multiple analyses of zircon from this event would form a normal distribution centered at the true depositional age; that is, the youngest zircon is the minimum of the maximum depositional age. Lastly, many of the issues dealt within this paper are specifically related to *in situ* analytical techniques when uncertainties are relatively large (>1%). When using analytical techniques whose precision is significantly lower than 1% (e.g. ID-TIMS) many of these issues are not relevant to data assessment as the precision achieved is approaching and in some cases exceeding the constraints of the decay constants that control the usage of geochronology (Boehnke and Harrison, 2014). Indeed, the measurement uncertainty of high-precision (e.g. ID-TIMS) U–Pb geochronology is assumed much less than the timescale over which the geological process responsible for zircon generation may be occurring. That is with infinite analytical resolution, zircon growth will not be geologically instantaneous and hence the assumption of a normal distribution will become increasingly less palatable as our analytical precision improves (e.g. Schoene et al., 2012).

Acknowledgments

C. Spencer would like to thank Dan Condon, Carl Hoiland, Matt Horstwood, Noah Mclean, Steve Noble, Nick Roberts, and Pieter Vermeesch who provided many stimulating discussions and encouragement to write this manuscript. George Gehrels provided a very helpful review that improved the quality of this manuscript.

Please cite this article in press as: Spencer, C.J., et al., Strategies towards statistically robust interpretations of *in situ* U–Pb zircon geochronology, Geoscience Frontiers (2015), http://dx.doi.org/10.1016/j.gsf.2015.11.006

Appendix



Inline Supplementary Figure. Flowchart outlining the recommended workflow from reduced and corrected U-(Th-)Pb zircon data to interpretable results.

References

Amarasinghe, U., Chaudhuri, A., Collins, A.S., Deb, G., Patranabis-Deb, S., 2015. Evolving provenance in the Proterozoic Pranhita-Godavari Basin, India. Geoscience Frontiers 6, 453–463. http://dx.doi.org/10.1016/j.gsf.2014.03.009.

Amato, J.M., Mack, G.H., 2012. Detrital zircon geochronology from the Cambrian-Ordovician Bliss Sandstone, New Mexico: evidence for contrasting Grenville-age and Cambrian sources on opposite sides of the Transcontinental Arch. Geological Society of America Bulletin 124, 1826–1840. http://dx.doi.org/10.1130/B30657.1.

Bickford, M., Chase, R., Nelson, B., 1981. U–Pb studies of zircon cores and overgrowths, and monazite: implications for age and petrogenesis of the northeastern Idaho batholith. The Journal of Geology 89 (4), 433–457.

Boehnke, P., Harrison, T.M., 2014. A meta-analysis of geochronologically relevant half-lives: what's the best decay constant? International Geology Review 56, 905–914. http://dx.doi.org/10.1080/00206814.2014.908420.

Botev, Z.I., Grotowski, J.F., Kroese, D.P., 2010. Kernel density estimation via diffusion. Annals of Statistics 38, 2916–2957.

Cherniak, D.J., Watson, E.B., 2000. Pb diffusion in zircon. Chemical Geology 172, 5–24.

Condon, D.J., Bowring, S.A., 2011. Chapter 9 a user's guide to Neoproterozoic geochronology. Geological Society, London, Memoirs 36, 135–149. http://dx.doi.org/10.1144/M36.9.

Corfu, F., 2013. A century of U-Pb geochronology: the long quest towards concordance. Geological Society of America Bulletin 125, 33–47. http://dx.doi.org/10.1130/B30698.1.

Coleman, D.S., Gray, W., Glazner, A.F., 2004. Rethinking the emplacement and evolution of zoned plutons: geochronologic evidence for incremental assembly of the Tuolumne Intrusive Suite, California. Geology 32, 433. http://dx.doi.org/10.1130/G20220.1.

Dehler, C.M., Fanning, C.M., Link, P.K., Kingsbury, E.M., Rybczynski, D., 2010. Maximum depositional age and provenance of the Uinta mountain group and big cottonwood formation, northern Utah. Paleogeography of Rifting Western Laurentia: Geological Society of America Bulletin 122 (9-10), 1686–1699. http://dx.doi.org/10.1130/B30094.1.

Dickinson, W.R., Gehrels, G.E., 2009. Use of U–Pb ages of detrital zircons to infer maximum depositional ages of strata: a test against a Colorado Plateau Mesozoic database. Earth and Planetary Science Letters 288 (1-2), 115–125. http://dx.doi.org/10.1016/j.epsl.2009.09.013.

Eglington, B.M., Harmer, R.E., 1993. A review of the statistical principles of geochronometry; II, Additional concepts pertinent to radiogenic U-Pb studies. South African Journal of Geology 96, 9–21.

Fedo, C.M., 2003. Detrital zircon analysis of the sedimentary record. Reviews in Mineralogy and Geochemistry 53, 277–303. http://dx.doi.org/10.2113/0530277.

Foster, D., Fanning, C., 1997. Geochronology of the northern Idaho batholith and the bitterroot metamorphic core complex: magmatism preceding and contemporaneous with extension. Geological Society of America Bulletin 109 (4), 379–394. http://dx.doi.org/10.1130/0016-7606(1997)109<0379.

Gaschnig, R.M., Vervoort, J.D., Lewis, R.S., Tikoff, B., 2012. Probing for Proterozoic and Archean crust in the northern U.S. Cordillera with inherited zircon from the Idaho batholith. Geological Society of America Bulletin 125 (1-2), 73–88. http://dx.doi.org/10.1130/B30583.1.

Gehrels, G., 2012. Detrital zircon U-Pb geochronology: current methods and new opportunities, in tectonics of sedimentary basins. In: Busby, C., Azor, A. (Eds.), Recent Advances. Wiley-Blackwell Publishing, pp. 47–62.

Gehrels, G., 2014. Detrital zircon U-Pb geochronology applied to tectonics. Annual Review of Earth and Planetary Sciences 42, 127–149. http://dx.doi.org/10.1146/annurev-earth-050212-124012.

Gehrels, G.E., Valencia, V.A., Ruiz, J., 2008. Enhanced precision, accuracy, efficiency, and spatial resolution of U-Pb ages by laser ablation-multicollector-inductively coupled plasma-mass spectrometry. Geochemistry, Geophysics, Geosystems 9. http://dx.doi.org/10.1029/2007GC001805 n/a–n/a.

Harrison, T.M., Baldwin, S.L., Caffee, M., Gehrels, G.E., Schoene, B., Shuster, D.L., Singer, B.S., 2015. It's About Time: Opportunities and Challenges for U.S. Geochronology. Institute of Geophysics and Planetary Physics Publication 6539, University of California, Los Angeles, p. 56.

Hiess, J., Condon, D.J., McLean, N., Noble, S.R., 2012. 238U/235U systematics in terrestrial uranium-bearing minerals. Science 335, 1610–1614. http://dx.doi.org/10.1126/science.1215507.

Horstwood, M., 2008, Data reduction strategies, uncertainty assessment and resolution of LA-(MC-) ICP-MS isotope data, *in* Mineralogical Association of Canada Short Course 40, p. 283–303.

Horton, B.K., DeCelles, P.G., 2001. Modern and ancient fluvial megafans in the foreland basin system of the central Andes, southern Bolivia: implications for drainage network evolution in fold-thrust belts. Basin Research 13, 43–63. http://dx.doi.org/10.1046/j.1365-2117.2001.00137.x.

Hu, X., Wang, J., BouDagher-Fadel, M., Garzanti, E., An, W., 2015. New insights into the timing of the India–Asia collision from the Paleogene Quxia and Jialazi formations of the Xigaze forearc basin, South Tibet. Gondwana Research. http://dx.doi.org/10.1016/j.gr.2015.02.007 (in press).

Košler, J., 2012. U-Pb geochronology and Hf-isotope geochemistry of detrital zircon in sedimentary systems. Short Course Series, 42. In: Quantitative mineralogy and microanalysis of sediments and sedimentary rocks. Mineralogical Association of Canada, pp. 185–202.

Ludwig, K.R., 1998. On the treatment of concordant uranium-lead ages. Geochimica Et Cosmochimica Acta 62, 665–676. http://dx.doi.org/10.1016/S0016-7037(98)00059-3.

Ludwig, K.R., 2003. User's Manual for a Geochronological Toolkit for Microsoft Excel. Berkeley Geochronology Center Special Publication, pp. 1–75.

Kryza, R., Crowley, Q.G., Larionov, A., Pin, C., Oberc-Dziedzic, T., Mochnacka, K., 2012. Chemical abrasion applied to SHRIMP zircon geochronology: an example from the Variscan Karkonosze Granite (Sudetes, SW Poland). Gondwana Research 21, 757–767. http://dx.doi.org/10.1016/j.gr.2011.07.007.

Malusà, M.G., Carter, A., Limoncelli, M., Villa, I.M., Garzanti, E., 2013. Bias in detrital zircon geochronology and thermochronometry. Chemical Geology 359, 90–107. http://dx.doi.org/10.1016/j.chemgeo.2013.09.016.

Mattinson, J.M., 2005. Zircon U–Pb chemical abrasion ("CA-TIMS") method: combined annealing and multi-step partial dissolution analysis for improved precision and accuracy of zircon ages. Chemical Geology 220, 47–66. http://dx.doi.org/10.1016/j.chemgeo.2005.03.011.

McLean, N.M., Bowring, J.F., Bowring, S.A., 2011. An algorithm for U-Pb isotope dilution data reduction and uncertainty propagation. Geochemistry, Geophysics, Geosystems 12, 1–26. http://dx.doi.org/10.1029/2010GC003478.

Mezger, K., Krogstad, E.J., 1997. Interpretation of discordant U–Pb zircon ages: an evaluation. Journal of Metamorphic Geology 15 (1), 127–140. http://dx.doi.org/10.1111/j.1525-1314.1997.00008.x.

Nemchin, A.A., Cawood, P.A, 2005. Discordance of the U–Pb system in detrital zircons: implication for provenance studies of sedimentary rocks. Sedimentary Geology 182 (1-4), 143–162. http://dx.doi.org/10.1016/j.sedgeo.2005.07.011.

Roberts, N.M.W., Spencer, C.J., 2014. The Zircon Archive of Continent Formation through Time. Geological Society, London, Special Publications. 389, 197–225. http://dx.doi.org/10.1144/SP389.14.

Schaltegger, U., Brack, P., Ovtcharova, M., Peytcheva, I., Schoene, B., Stracke, A., Marocchi, M., Bargossi, G.M., 2009. Zircon and titanite recording 1.5 million years of magma accretion, crystallization and initial cooling in a composite pluton (southern Adamello batholith, northern Italy). Earth and Planetary Science Letters 286, 208–218. http://dx.doi.org/10.1016/j.epsl.2009.06.028.

Schoene, B., Schaltegger, U., Brack, P., Latkoczy, C., Stracke, A., Günther, D., 2012. Rates of magma differentiation and emplacement in a ballooning pluton recorded by U–Pb TIMS-TEA, Adamello batholith, Italy. Earth and Planetary Science Letters 355-356, 162–173. http://dx.doi.org/10.1016/j.epsl.2012.08.019.

Sircombe, K., Stern, R., 2002. An investigation of artificial biasing in detrital zircon U-Pb geochronology due to magnetic separation in sample preparation. Geochimica Et Cosmochimica Acta 66, 2379–2397.

Smirnov, N.V., 1939. On the estimation of the discrepancy between empirical curves of distribution for two independent samples. Bulletin Mathematics University Moscow 2, 2.

Spencer, C.J., Hoiland, C.W., Harris, R.A., Link, P.K., Balgord, E.A., 2012. Constraining the timing and provenance of the Neoproterozoic Little Willow and Big Cottonwood Formations, Utah: expanding the sedimentary record for early rifting of rodinia. Precambrian Research 204-205, 57–65. http://dx.doi.org/10.1016/j.precamres.2012.02.009.

Spencer, C.J., Prave, A.R., Cawood, P.A., Roberts, N.M.W., 2014. Detrital zircon geochronology of the Grenville/Llano foreland and basal Sauk Sequence in west Texas, USA. Geological Society of America Bulletin, 126 (7–8), 1117–1128. http://dx.doi.org/10.1130/B30884.1.

Toth, M.I., Stacey, J.S., 1992. Constraints on the formation of the Bitterroot Lobe of the Idaho Batholith, Idaho and Montana, from U–Pb zircon geochronology and Feldspar Pb isotopic data. United States Geological Survey Bulletin 2008, 24.

Tucker, R.T., Roberts, E.M., Hu, Y., Kemp, A.I.S., Salisbury, S.W., 2013. Detrital zircon age constraints for the Winton formation, Queensland: contextualizing Australia's late cretaceous dinosaur faunas. Gondwana Research 24, 767–779. http://dx.doi.org/10.1016/j.gr.2012.12.009.

Vermeesch, P., 2012. On the visualisation of detrital age distributions. Chemical Geology 312-313, 190–194. http://dx.doi.org/10.1016/j.chemgeo.2012.04.021.

Voice, P.J., Kowalewski, M., Eriksson, K.A., 2011. Quantifying the timing and rate of crustal evolution: global compilation of radiometrically dated detrital zircon grains. The Journal of Geology 119, 109–126. http://dx.doi.org/10.1086/658295.

Weinberg, R., Dunlap, W., 2000. Growth and deformation of the ladakh batholith, Northwest Himalayas: implications for timing of continental collision and origin of Calc-Alkaline Batholiths. The Journal of Geology 108 (3), 303–320.

Wendt, I., Carl, C., 1991. The statistical distribution of the mean squared weighted deviation. Chemical Geology Isotope Geoscience Section 86, 275–285. http://dx.doi.org/10.1016/0168-9622(91)90010-T.

Wetherill, G.W., 1956. Discordant uranium-lead ages, I. Transactions American Geophysical Union 37, 320. http://dx.doi.org/10.1029/TR037i003p00320.

Wingate, M.T.D., Kirkland, C.L., Hartley, G.J., Hitchings, B.L., White, S.R., 2015. Compilation of Geochronology Information 2015. Geological Survey of Western Australia, digital repository.

Yokelson, I., Gehrels, G.E., Pecha, M., Giesler, D., White, C., McClelland, W.C., 2015. U-Pb and Hf isotope analysis of detrital zircons from Mesozoic strata of the Gravina belt, southeast Alaska. Tectonics 34 (10), 2052–2066. http://dx.doi.org/10.1002/2015TC003955.

Please cite this article in press as: Spencer, C.J., et al., Strategies towards statistically robust interpretations of *in situ* U–Pb zircon geochronology, Geoscience Frontiers (2015), http://dx.doi.org/10.1016/j.gsf.2015.11.006