Open-system behaviour of detrital zircon during weathering: an example from the Palaeoproterozoic Pretoria Group, South Africa

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Abstract

Detrital zircon in six surface samples of sandstone and contact metamorphic quartzite of the Magaliesberg and Rayton formations of the Pretoria Group (depositional age c. 2.20–2.06 Ga) show a major age fraction at 2.35–2.20 Ga, and minor early Palaeoproterozoic – Neoarchaean fractions. Trace-element concentrations vary widely, with Ti, Y and light rare earth elements (LREEs) spanning over three orders of magnitude. REE distribution patterns range from typical zircon patterns (LREE depletion, heavy REE enrichment, well-developed positive Ce and negative Eu anomalies) to patterns that are flat to concave downwards, with indistinct Ce and Eu anomalies. The change in REE pattern correlates with increases in alteration-sensitive parameters such as Ti concentration and (Dy/Sm) + (Dy/Nd), U–Pb discordance and content of common lead, and with a gradual washing-out of oscillatory zoning in cathodoluminescence images. U and Th concentrations also increase, but Th/U behaves erratically. Discordant zircon scatters along lead-loss lines to zero-age lower intercepts, suggesting that the isotopic and chemical variations are the results of disturbance long after deposition. The rocks sampled have been in a surface-near position (at least) since Late Cretaceous time, and exposed to deep weathering under intermittently hot and humid conditions. In this environment, even elements commonly considered as relatively insoluble could be mobilized locally, and taken up by radiation-damaged zircon. Such secondary alteration effects on U–Pb and trace elements can be expected in zircon in any ancient sedimentary rock that has been exposed to tropical–subtropical weathering, which needs to be considered when interpreting detrital zircon data.

1. Introduction

Crystalline zircon is a robust and non-reactive mineral that can survive abrasion during repeated events of erosion and transport, and whose U–Pb system can be preserved even at high-grade metamorphic conditions (e.g. Williams, 2001; Bindeman et al. 2018). The crystal structure of zircon will, however, suffer radiation damage from the decay of U and Th incorporated at the time of crystallization, and their radioactive decay products. Over geological time, this will cause gradual transformation of the mineral into an amorphous substance known as metamict zircon. Whereas radiation damage itself does not cause changes in chemical composition or discordance of the U–Pb isotope system, metamict zircon is mechanically weakened (e.g. Salje, 2006) and reactive when exposed to fluids, for example during diagenesis or weathering (Balan et al. 2001; Willner et al. 2003; Hay & Dempster, 2009; Pidgeon et al. 2013, 2019; Andersen et al. 2019b). When interacting with fluids, metamict zircon commonly loses radiogenic lead causing normal U–Pb discordance; in the process, the contents of common lead and non-structural elements such as titanium, light rare earth elements (REEs) and hydrogen will increase (Stern et al. 1966; Black, 1987; Nasdala et al. 2001; Belousova et al. 2002; Hoskin & Schaltegger, 2003). Even elements such as yttrium, uranium and thorium can be introduced during weathering of metamict zircon (Pidgeon et al. 2017, 2019).

The favourable properties of crystalline zircon have made U–Pb ages from detrital zircon in clastic sediments a much-used tool for provenance identification and correlation of sedimentary strata (e.g. Zimmermann, 2018). Furthermore, the trace-element signature can be used to identify the types of igneous rocks contributing material to a basin (Belousova et al. 2002; Griffin et al. 2004; Veevers & Saeed, 2007). Zircon grains whose composition has been modified during diagenesis or weathering of the host sediment are less useful for these purposes. When dating igneous or metamorphic rocks by U–Pb in zircon, grains that are influenced by secondary processes can commonly be avoided by careful selection of single grains for analysis, and altered parts of grains can be removed by mechanical or chemical abrasion (Krogh, 1982; Mattinson, 2005). In detrital zircon geochronology, the priority is to establish an unbiased estimate of the zircon population in the samples studied. This is commonly achieved by random sampling from a bulk
zircon mineral separate, and selective methods used in isotope dilution–thermal ionization mass spectrometry (ID-TIMS) U–Pb geochronology are generally not applicable. For meaningful interpretations of sedimentary provenance, stratigraphic correlation or basin filling history to be extracted from detrital zircon data, it is important that no significant age fraction is overlooked and no spurious fraction added to the dataset. To preserve such ‘qualitative representativity’ (in the sense of Andersen et al. 2019a), it is essential that the observed age, isotopic or trace-element distributions are not modified by alteration processes after deposition, that is, that detrital zircon has behaved as a closed system. Different data filtering criteria have been suggested to exclude analyses that have been compromised by alteration processes from detrital zircon datasets, the most common of which is to remove analyses that deviate from the U–Pb concordia curve by more than a given percentage (a discordance filter). This has the disadvantage that it may also exclude grains which are discordant only due to recent lead loss, whose $^{207}\text{Pb}/^{206}\text{Pb}$ age still retains a valid memory of the age of the protosource rock, while it may be inefficient against bias-inducing lead loss caused by processes in the past (Andersen et al. 2019a). Other filtering criteria that have been proposed are based on trace-element parameters (Bell et al. 2019) or common lead content (Andersen et al. 2019b). The main concern when using such data filters should be to remove grains whose U–Pb isotope systematics have been affected, while retaining as much of the valid information in the randomly sampled dataset as possible.

The vulnerability of zircon to alteration depends on the degree of structural damage, which is related to the alpha radiation dose accumulated over the lifetime of a zircon grain. At time $t$, a crystal formed at $t_i > t$ will have accumulated an alpha radiation dose given by:

$$D_{\alpha}(t) = x_9 \frac{N_4}{10^9} \left[ 8A_{238} \text{Cu} \frac{e^{x_{238}t_i} - e^{x_{238}t}}{M_{238}} + 7A_{235} \text{Cu} \frac{e^{x_{235}t_i} - e^{x_{235}t}}{M_{235}} + 6C_{238} \frac{e^{x_{238}t_i} - e^{x_{238}t}}{M_{232}} \right],$$

(1)

where $A_{238}, A_{235}$ are the natural isotopic abundances of $^{235}\text{U}$ and $^{238}\text{U}, M_{235}, M_{238}, M_{232}$ are the atomic masses of $^{235}\text{U}$, $^{238}\text{U}$ and $^{232}\text{Th}$, $C_{238}$ and $C_{232}$ are the concentrations (in parts per million) of $\text{U}$ and $\text{Th}$, and $N_4$ is the Avogadro constant. The formula was first defined for $t = 0$ by Holland & Gottfried (1955); here it is generalized as a function of $t$ from the version given by Nasdala et al. (2004). The corresponding weight fraction of metamict material ($f_m$) in a zircon grain is given by the empirical relationship:

$$f_m = 1 - e^{-B_D_{\alpha}},$$

(2)

in which $B_D = 2.7 \times 10^{-18}$ g/α (Zhang & Salje, 2001).

X-ray and spectroscopic studies have shown that the change from a fully crystalline to an amorphous state in zircon is a continuous transition process in which the crystal passes through a stage with crystalline ‘islands’ in a continuous, amorphous matrix, which is reached at what is known as the percolation point (Salje et al. 1999). A critical alpha dose of $D_{\alpha} \approx 3.5 \times 10^{18}$ g/α has been shown to be necessary to transform a fully crystalline zircon to this intermediate state (Salje et al. 1999), at which 61 weight percent of a grain will consist of metamict zircon according to Equation (2). Such zircon grains have lost much of their mechanical strength and resistance against chemical alteration; zircon with $D_{\alpha} > 3.5 \times 10^{18}$ α/g has been shown to be depleted in sediments relative to their source rocks (Markwitz & Kirkland, 2018). Further radiation damage will lead to complete metamictization at $D_{\alpha} \geq 8 \times 10^{19}$ α/g (Ewing et al. 2003).

As an example of the extent of radiation damage expected in ancient zircon, the distribution of $D_{\alpha}$ at the present day ($D_{\alpha}(0)$) expected from a suite of 2.2 Ga zircon with $\text{U}$ and $\text{Th}$ concentrations following the distribution patterns observed for granitic zircon by Belousova et al. (2002) is illustrated in Figure 1. In this example, only c. 22% of the zircon grains would be expected to contain less than 61% metamict material at the present time ($D_{\alpha}(0) < 3.5 \times 10^{18}$ α/g), whereas c. 50% of the grains would be completely metamict with $D_{\alpha}(0) \geq 8 \times 10^{19}$ α/g. A similar distribution based on data for zircon in a wider range of igneous rocks (gabbro to alkali granite) by Kirkland et al. (2015) gives a similar total range of $D_{\alpha}$, but with a lower median value and hence lower accumulated alpha dose (23% with $D_{\alpha}(0) \geq 3.5 \times 10^{18}$ α/g, and 6% with $D_{\alpha}(0) \geq 8 \times 10^{19}$ α/g).

A consequence of this example is that a significant fraction of zircon grains from a 2.2 Ga granitic source rock would be unlikely to survive erosion, transport and deposition to make it into a sedimentary basin at the present time. Another consequence is that detrital zircons in old sedimentary rocks that were fully crystalline at the time of deposition may have acquired sufficient structural damage while residing in their host sedimentary rock, making their U–Pb and trace-element systems vulnerable to reaction with fluids in a near-surface weathering environment. Such damaged detrital grains may survive physically, as long as the host sediment is not eroded and recycled. However, both their U–Pb isotope composition and trace-element distributions may be modified.

To get a better understanding of the effects of post-depositional, in situ weathering on detrital zircon in ancient sedimentary rocks, and its consequences for detrital zircon geochronology, we have undertaken a U–Pb and trace-element study of zircon in samples of quartz arenites of the Magaliesberg and Rayton formations of the Palaeoproterozoic Pretoria Group in part of the Transvaal Basin of South Africa (Fig. 2). These rocks have remained undisturbed since deposition some time before 2.06 Ga (Zeh et al. 2015, 2016, 2020), but have been in a surface-near position and exposed to weathering since Late Cretaceous time (e.g. Partridge & Maud, 1987; Partridge, 1998).

2. Geological setting

The late Archaean – Palaeoproterozoic Transvaal Supergroup (Eriksson et al. 2006) comprises shales, sandstones, carbonate rocks and minor volcanic rocks, deposited on a basement of Archaean gneisses and supracrustal cover successions of the Kaapvaal Craton. It is preserved in three different basins, the Transvaal and Griqualand West basins of South Africa and the Kanye Basin of Botswana. Correlations between the successions in these basins as outlined by, for example, Eriksson et al. (2006), have been questioned from more recent geochronological data (Mapeo et al. 2006; Moore et al. 2012; Gumsley et al. 2017).

The Pretoria Group is the youngest part of the Transvaal Supergroup in the Transvaal Basin; a simplified, general stratigraphic column is given in Figure 2a. The Pretoria Group comprises two unconformity-bounded sequences, deposited in fault-controlled basins on the Kaapvaal Craton (Eriksson et al. 2006). Only the younger of the two sequences is of interest to the present study. In the Transvaal Basin, this succession started with terrestrial sedimentation (Boshoen Formation) and andesitic
volcanism (Hekpoort Formation), followed by lacustrine deposition  
(Dwaalheuwel and Strubenkop formations), marine transgression  
(Daspoort and Silverton formations) and regression during  
deposition of the Magaliesberg Formation. The Magaliesberg  
Formation consists of sandstone with minor lenses of  
mudrock, overlying the marine shale of the Silverton  
Formation. It has variously been interpreted as shallow-marine,  
or as a succession of regression-related shore, tidal and  
braided delta deposits (Eriksson et al. 2006). The younger, ‘Post-  
Magaliesberg’ formations of the Pretoria Group are represented  
by the Rayton Formation in the area of this study (Fig. 2), and  
by several formations in the eastern part of the Transvaal Basin  
(Schreiber & Eriksson, 1992). These strata comprise mainly sand-  
stones and shales, with subordinate carbonates and volcanic rocks,  
deposited in non-marine, probably isolated sub-basins (Eriksson  
et al. 2001). In the southern exposure area in Figure 2b, in the  
Potchefstroom syncline, the Magaliesberg formation occurs as  
discontinuous erosional remnants, and stratigraphically higher units  
are not preserved.

Deposition of the Pretoria Group in the Transvaal Basin must  
have started slightly before 2300 Ma (Hannah et al. 2004;  
Rasmussen et al. 2013), and terminated before eruption of the lavas  
of the overlying Dullstroom Formation and Rooiberg Group, the  
latter of which has been dated to 2061 ± 2 Ma (Walraven, 1997).  
Deposition was followed by emplacement of the Bushveld  
Complex at 2056.0 ± 0.3 Ma (Zeh et al. 2016) and the Vredefort  
depositional impact event at 2.02 Ga.  

The Magaliesberg and Rayton formations were deposited some  
time before emplacement of the Bushveld complex, of which they  
form the intrusion floor (Cawthorn et al. 2006). The age of deposi-  
tion is somewhat controversial: Schröder et al. (2016), Beukes  
et al. (2019) and Andersen et al. (2019a) have suggested a maxi-  
mum depositional age of c. 2.2 Ga for the Magaliesberg  
Formation, based on the youngest, major age fraction of detrital  
zircons observed, whereas Zeh et al. (2016, 2020) interpreted zircon  
ages as young as 2080 Ma as protosource ages unmodified by  
post-depositional metamorphic resetting, and therefore prefer a  
correspondingly younger depositional age. No detrital zircon data  
have been published from the Rayton Formation.

The strata of the Transvaal Supergroup have been downwarped  
by emplacement of the Bushveld complex, with increasing dip towards the contact. In the south, the Vredefort meteorite  
impact formed a series of concentric synforms and antiforms and  
trust sheets around the central dome, including the  
Potchefstroom Syncline (Fig. 2b; Brink et al. 1997; Therriault et  
al. 1997).

Emplacement of the Bushveld complex caused significant contact  
metamorphism in the Transvaal Supergroup, mainly in the  
floor rocks. Metamorphism locally reached anatectic grade in pel- 
itic lithologies (Harris et al. 2003), and sandstones are transformed  
to coarse-grained, glassy quartzite in the inner part of the contact  
aureole (Cawthorn et al. 2006). Outside of the contact aureole  
(Fig. 2b), metamorphism is restricted to low-grade regional meta-  
morphism in events dated to c. 2150 Ma and 2040 Ma (Alexandre  
et al. 2006). Thermally induced lead loss and other effects of post-  
depositional metamorphism in the detrital zircon would therefore  
be of Palaeoproterozoic age, and no younger than the age of the  
Vredefort impact event at c. 2.02 Ga.

In the northeastern part of the area shown in Figure 2, the  
Rayton Formation is unconformably overlain by the Wilge River  
Formation of the Palaeoproterozoic Waterberg Group in the  
Middelburg Basin, comprising red-bed sandstones and conglomerates,  
with minor volcanic rocks (Barker et al. 2006). These rocks  
post-date the Transvaal Supergroup, Rooiberg Group and  
Bushveld Complex, all of which have contributed material to con-  
glemerates in the Middelburg Basin (Barker et al. 2006).

During Carboniferous–Jurassic time, southern Africa and  
adjacent parts of the Gondwana supercontinent were covered by  
sedimentary rocks of the Karoo Supergroup, followed by lavas of  
the Drakensberg Group. After break-up of the supercontinent,  
the southeastern margin of Africa remained a topographic high. By  
the end of the Cretaceous Period, the inland parts of southern  
Africa were denuded to a high-standing, gently W-sloping erosion  
surface bounded by a marked escarpment to the south and east  
(Partridge & Maud, 1987; Partridge, 1998; Partridge et al. 2006).  
In this process, the Phanerozoic cover was almost completely  
removed from the area of interest, so that only local relics remain;  
towards the east, the lower part of the Karoo succession is still  
intact (Fig. 2b). The erosion surface formed in this denudation  
cycle is partly preserved as the ‘African Surface’. Regional uplift  
events in the Miocene and Pliocene triggered new denudation  
cycles represented by two younger erosion surfaces of regional  
importance, of which only the older ‘Post African I’ surface,  
formed in response to Miocene uplift, is of relevance for the present  
study (Fig. 2b). The regional denudation history implies that the  

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**Fig. 1.** Distribution of accumulated alpha dose at t = 0 Ma experienced by 2.2 Ga zircon with U and Th concentrations similar to those reported for zircon in granitic rocks by Belousova et al. (2002), represented by percentile points and a log-norm distribution compatible with these, and for a wider compositional range of igneous rocks by Kirkland (2001); log-normal distribution based on data from their supplementary table A1. The dip towards the contact. In the south, the Vredefort meteorite impact formed a series of concentric synforms and antiforms and trust sheets around the central dome, including the Potchefstroom Syncline (Fig. 2b; Brink et al. 1997; Therriault et al. 1997).

Emplacement of the Bushveld complex caused significant contact metamorphism in the Transvaal Supergroup, mainly in the floor rocks. Metamorphism locally reached anatectic grade in pelitic lithologies (Harris et al. 2003), and sandstones are transformed to coarse-grained, glassy quartzite in the inner part of the contact aureole (Cawthorn et al. 2006). Outside of the contact aureole (Fig. 2b), metamorphism is restricted to low-grade regional metamorphism in events dated to c. 2150 Ma and 2040 Ma (Alexandre et al. 2006). Thermally induced lead loss and other effects of post-depositional metamorphism in the detrital zircon would therefore be of Palaeoproterozoic age, and no younger than the age of the Vredefort impact event at c. 2.02 Ga.

In the northeastern part of the area shown in Figure 2, the Rayton Formation is unconformably overlain by the Wilge River Formation of the Palaeoproterozoic Waterberg Group in the Middelburg Basin, comprising red-bed sandstones and conglomerates, with minor volcanic rocks (Barker et al. 2006). These rocks post-date the Transvaal Supergroup, Rooiberg Group and Bushveld Complex, all of which have contributed material to conglomerates in the Middelburg Basin (Barker et al. 2006).

During Carboniferous–Jurassic time, southern Africa and adjoining parts of the Gondwana supercontinent were covered by sedimentary rocks of the Karoo Supergroup, followed by lavas of the Drakensberg Group. After break-up of the supercontinent, the southeastern margin of Africa remained a topographic high. By the end of the Cretaceous Period, the inland parts of southern Africa were denuded to a high-standing, gently W-sloping erosion surface bounded by a marked escarpment to the south and east (Partridge & Maud, 1987; Partridge, 1998; Partridge et al. 2006). In this process, the Phanerozoic cover was almost completely removed from the area of interest, so that only local relics remain; towards the east, the lower part of the Karoo succession is still intact (Fig. 2b). The erosion surface formed in this denudation cycle is partly preserved as the ‘African Surface’. Regional uplift events in the Miocene and Pliocene triggered new denudation cycles represented by two younger erosion surfaces of regional importance, of which only the older ‘Post African I’ surface, formed in response to Miocene uplift, is of relevance for the present study (Fig. 2b). The regional denudation history implies that the...
units sampled for the present study have been in a surface-near position and exposed to weathering under variable climatic conditions for 20–70 Ma (Partridge, 1998).

3. The samples

In this study, detrital zircon has been analysed in six samples from two different exposure areas of the Pretoria Group, at different distances from the contact to the Bushveld complex (Fig. 2, Table 1). The samples were collected from roadcuts and isolated field exposures, guided by published 1:250 000 geological maps (Council for Geoscience, Pretoria). All samples were of sandstone or quartzite.

Two samples of the Rayton Formation were collected inside the limit of the contact aureole. Sample 726 is a quartzite with a distinct, pale-green colour and glassy appearance in hand specimen. Rounded detrital grains are cemented by quartz; thin rims of fine-grained chlorite around the grains are responsible for the green colour. Quartz grain boundaries are interlocking, but with sparse development of 120° triple junctions. Sample 728 is a quartz-cemented quartz-arenite. Both of the samples of the Rayton Formation contain minor (<3%) chert fragments. Sample 730 of the Magaliesberg Formation was collected at the limit of the contact aureole. This sample is a partly recrystallized quartzite–quartz arenite showing graded bedding. Quartz grains are well rounded with undulose extinction and locally sutured grain contacts, with quartz cement. Samples 733, 734 and 735 come from outcrops of the Magaliesberg Formation in the central part of the Potchefstroom Syncline (Fig. 2). Sample 733 is a feldspar-free quartz arenite. Samples 734 and 735 contain up to 7% K-feldspar and minor, heavily altered lithic fragments, including chert; sample 734 also contains minor mica and apatite. All are quartz cemented, and show brown staining due to Fe-hydroxide films along grain boundaries. Zircon is a minor to accessory mineral in all of the samples (less abundant in 728 than in the other samples), occurring as well-rounded, detrital grains, without obvious post-depositional (i.e. diagenetic or metamorphic) overgrowths.

4. Methods

Samples were crushed in a steel jaw crusher, sieved to <250 μm using a sieve with disposable cloth. Heavy mineral separates were produced by manual washing using plastic gold-washing pans. Zircon grains were picked from these separates in alcohol under a binocular microscope, mounted on two-sided adhesive tape.
and cast into epoxy disks, which were ground to expose the zircon grains and polished. Care was taken to produce zircon fractions that were as non-selective as possible. The zircon mounts were imaged in cathodoluminescence (CL), using a Hitachi SU5000 field emission scanning electron microscope with a Delmic Spark-Advanced CL System at the Department of Geoscience, University of Oslo.

U–Pb and trace elements were analysed simultaneously, using a Bruker Aurora Elite quadrupole mass spectrometer with a CETAC LS 213G2+ Nd:YAG laser microprobe, also at the Department of Geosciences, University of Oslo. Trace elements were analysed using a fast scanning protocol with dwell times as given in Table 2. NIST SRM 610 was used as calibration standard, with 26Si as internal standard. Glitter software (Griffin et al. 2008) was used for off-line, time-resolved integration and calculation of element concentrations. Trace-element concentrations for the GJ-1 reference zircon run as an unknown are given in Table 2.

U–Pb was analysed in the same ablation runs as trace elements, with real-time integration and calibration using in-house software based on Microsoft Excel. Natural zircon reference samples GJ-1 (600.5 ± 0.4 Ma, Schaltegger et al. 2015), 91500 (1065 ± 1 Ma, Wiedenbeck et al. 1995), A382 (1875 ± 2 Ma, Huhma et al. 2012) and OGC (also called OGI; 3465.4 ± 0.6 Ma, Stern et al. 2009) were used for standardization, and the U/Pb ratio was internally standardized by 91Zr/29Si. 238U was used for geochronology and was calculated from 238U, assuming 238U/235U = 138.77 (e.g. Ludwig, 2002). Raw data were reduced using an interactive spreadsheet program written in Visual Basic for Microsoft Excel. Common lead was estimated from Hg-corrected measurement of 204Pb, using a common lead composition defined by the Stacey & Kramers (1975) model at the observed 206Pb/238U age of the zircon. Discordance is calculated from isotopic ratios rather than from ages (Guitreau & Blichter-Toft, 2014; Andersen et al. 2019a). Note that discordance values calculated by the two methods are neither identical nor linearly related.

Thirty-one analyses of an in-house reference zircon (A44, Kapinsalmi tonalite, Finland, ID-TIMS U–Pb age 2719 ± 4 Ma, Hellem et al. 2007) gave a weighted average 207Pb/206Pb age of 2723 ± 4 Ma (95% confidence, MSWD = 1.5).

A complete listing of U–Pb and trace-element data is given in the online Supplementary Table S1 (available at http://journals.cambridge.org/geo).

5. Results

5.a. Zircon petrography

Cathodoluminescence images of a selection of zircon grains are shown in Figures 3–5 to illustrate the range of variation observed in the samples studied. Detrital zircon grains are rounded, short-prismatic to elongated grains, and grain fragments. Many of the grain fragments show rounded edges cross-cutting the internal zoning pattern of the zircon, indicating that they have been abraded after breaking up (e.g. 733-67 in Fig. 4), showing that the fragmentation happened prior to final deposition. However, there are also grain fragments cut by sharp edges, which were most likely broken during crushing (e.g. grain 730-47 in Fig. 3). No systematic relationship between grain morphology or internal zoning pattern and grain size was observed, but any such relationship may have been obscured by fragmentation of the larger grains.

The internal CL structure ranges from short-wavelength–low-amplitude oscillatory zoning (730-53 in Fig. 3; 733-67, 733-93 in Fig. 4; 726-08, 728-08 in Fig. 5), typical of unmodified igneous zircon (Corfu et al. 2003), to uniformly CL-dark with only ghost-like CL-brighter inner zones (733-97 in Fig. 4; 728-15 in Fig. 5), suggesting post-crystallization modification that can be related to metamorphism in the protosource or in sedimentary precursors, or to processes after deposition. Between these extremes, there are grains showing more irregular, oscillatory zoning (730-47 in Fig. 3; 733-61 in Fig. 4; 728-25 in Fig. 5), probably still a primary feature of the zircon grain; grains with oscillatory zoning whose contrast has been enhanced, in that CL-dark zones have become darker and apparently also broader (730-47 in Fig. 3; 733-01 in Fig. 4; 728-10 and 728-31 in Fig. 5); and grains with completely irregular internal variations (730-46 in Fig. 3). CL-bright domains overprinting the oscillatory zoned zircon are relatively rare (730-52 in Fig. 3), and there is no evidence of growth of new zircon that can be attributed to diagenesis/metasomatism of the host sediment. These observations apply to zircon in both Magaliesberg and Rayton formations, regardless of the degree of recrystallization of the host rock.

5.b. Trace-element distributions: Ti, Y, REE, Hf, U and Th

Chondrite-normalized REE patterns are illustrated for the grains shown as examples in Figures 3–5. These suggest a connection between REE distribution and CL structure, in the sense that REE patterns typical for unaltered magmatic zircon (low LREE, continuously increasing patterns towards Yb and Lu, positive Ce anomaly and negative Eu anomaly; Belousova et al. 2002; Hoskin & Schaltegger, 2003) are restricted to grains that show reasonably well preserved oscillatory zoning patterns. The levels of light and middle REEs increase with increasing disturbance of the CL zoning pattern and, in grains with the most severely modified structure in CL images, the REE patterns are nearly flat in the middle to heavy REE range. These grains can show concentrations above 10⁴ chondrites for the most extreme cases, and some grains even show a broad maximum in the range of Sm to Dy. These

Table 1. Samples analysed for the present study

| Sample  | Formation          | Locality       | S (°)  | E (°)  | Rock type    |
|---------|--------------------|----------------|--------|--------|--------------|
| SA19-726| Rayton Formation   | N. Cullinan    | 25.6454| 28.4697| Quartzite    |
| SA19-728| Rayton Formation   | S. Bronkhorstspruit| 25.8574| 28.7389| Quartz arenite|
| SA19-730| Magaliesberg Formation | R25 roadcut | 25.8651| 28.6268| Quartz arenite|
| SA19-733| Magaliesberg Formation | SE Potchefstroom | Surface exposure | 26.8215 | 27.1126 | Quartz arenite |
| SA19-734| Magaliesberg Formation | SE Potchefstroom | Surface exposure | 26.5937 | 27.5488 | Subarkose |
| SA19-735| Magaliesberg Formation | SE Potchefstroom | Surface exposure | 26.6191 | 27.6307 | Quartzite |

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features are representative of the whole set of analysed grains, as is more conveniently illustrated in element versus element plots of the pooled dataset shown in Figure 6.

Titanium has a range of concentrations from near the detection limit at circa 2 to 4890 ppm. Y and REE concentrations are positively correlated with Ti (Fig. 6a, b), with the largest relative variation (over 4–5 orders of magnitude) for Nd and Pr (La falls under the detection limit for some grains). Th and U are also positively correlated with Ti, whereas Hf remains close to 1.5 × 10⁴ ppm over the whole range of Ti (Fig. 6c). Because of the increasing trend in heavy REEs, the Lu/Hf ratio also increases with increasing Ti (Fig. 6d). In contrast, the chondrite-normalized Yb/Sm and Yb/Dy ratios decrease with increasing Ti, approaching or falling below 1.0 at high Ti. This reflects the tendency towards flat patterns in the middle to heavy REEs seen in some of the examples in Figures 3–5; patterns with (Yb/Dy)CH < 1.0 have a maximum in the Dy-range. ²⁰⁶Pb ranges from below detection limit (< 0.1 ppm) to c. 10 ppm, and is positively correlated with Ti, although less so than the REE (Fig. 6c). The Th/U ratio varies from 0.16 to 4.7, with a huge majority of grains having ratios between 0.3 and 3, generally increasing with increasing concentrations (Fig. 7). This is a range in which compositions of igneous and metamorphic zircon overlap (Kirkland et al. 2015; Yakymchuk et al. 2018).

### 5.c. U–Pb systematics

The unfiltered, common-lead-corrected U–Pb data show a range from mildly inversely discordant to almost 100% normally discordant (Fig. 6f). The discordant grains spread widely in the concordia diagram, but with a concentration of points along a lead-loss line from c. 2200 Ma to zero (Fig. 8a). Analyses that show a ²⁰⁶Pb signal above the background level defined by common-lead-free reference zircons have been corrected for common lead using an average crustal lead composition according to Stacey & Kramers (1975) at the ²⁰⁶Pb/²³⁸U age of the zircon. This composition may not be optimal for correction for unsupported lead in zircon, causing bias towards low ages at corrections for more than 0.2–0.5% common ²⁰⁶Pb (Andersen et al. 2019). The cumulative age distribution (Fig. 8b) of the unfiltered, common-lead-corrected dataset (297 grains) shows minimum ages of c. 2000 Ma, and a continuously increasing trend towards older, early Palaeoproterozoic and Archaean ages, with a poorly defined age fraction in the 2200–2400 Ma range. Some highly discordant grains with ²⁰⁶Pb/²³⁸U ratios below 100 give spurious ages above 4 Ga (online Supplementary Table S1); these are completely dominated by common lead that cannot be adequately corrected for, and carry no age significance. Excluding data more than 10% discordant

### Table 2. Trace-element analyses of the GJ-1 reference zircon

| Element | Isotope | Dwell time (ms) | GJ-1 (yellow) | Published |
|---------|---------|----------------|--------------|-----------|
|         |         |                | Mean 2SD n   | Zhao et al. (2016) | Piazolo et al. (2017) |
| Ti      | 49      | 2              | 5 6 176      | 4.63      | 3.35       |
| Y       | 89      | 2              | 350 58 193   | 207       | 238        |
| La      | 139     | 10             | 0.02 0.04 137| 1.2       | 0.003      |
| Ce      | 140     | 2              | 20 2 193     | 16.0      | 15         |
| Pr      | 141     | 10             | 0.04 0.02 216| 0.2       | 0.03       |
| Nd      | 146     | 10             | 0.9 0.2 216  | 0.7       | 0.6        |
| Sm      | 147     | 10             | 2.3 0.5 216  | 1.2       | 1.4        |
| Eu      | 153     | 10             | 1.5 0.3 216  | 0.9       | 1.0        |
| Gd      | 157     | 2              | 11 2 216     | 5.7       | 6.6        |
| Tb      | 159     | 2              | 2.9 0.5 216  | 1.7       | 1.88       |
| Dy      | 163     | 2              | 30 5 216     | 16.9      | 20         |
| Ho      | 165     | 2              | 9.8 1.6 216  | 5.8       | 6.7        |
| Er      | 166     | 2              | 43 7 216     | 24.9      | 28.7       |
| Tm      | 169     | 2              | 9.1 1.4 216  | 5.3       | 6.4        |
| Yb      | 172     | 2              | 86 13 216    | 53.9      | 64.8       |
| Lu      | 175     | 2              | 17 2 216     | 10.9      | 11.52      |
| Hf      | 178     | 2              | 8374 940 216 | 6538      | 6681       |
| Pb      | 204     | 20             | 0.004 0.010 151| 6.6      | 25.3       |
| Pb      | 206     | 20             | 25 3 151     | 10        | 10         |
| Pb      | 207     | 30             | 1.53 0.19 151| 10        | 10         |
| Pb      | 208     | 10             | 0.29 0.06 151| 10        | 10         |
| Pb Total|         |                | 28 4 216     | 6.6       | 25.3       |
| Th      | 232     | 10             | 14 3 216     | 10        | 10         |
| U       | 238     | 10             | 320 43 216   | 255       | 284        |
reduces the useful dataset to 78 grains, with a major age fraction in the range 2200–2400 Ma and a smaller, late Mesoarchaean fraction at 2200–2400 Ma. A 'tail' of young ages between 2000 Ma and 2200 Ma persists. These apparently young grains have been corrected for common lead, and their 207Pb/206Pb ages are most likely affected by bias due to common-lead correction (cf. Andersen et al. 2019). Using 206Pb/204Pb > 2000 as a limit instead of discordance (Andersen et al. 2019) reduces the dataset further, to 47 useful analyses. The width of the main age fraction is reduced to 2225–2350 Ma, and a second Neoarchaean fraction at 2750–2800 Ma is indicated. The 'tail' of ages < 2200 Ma disappears.

The relationship between 207Pb/206Pb age and U concentration is illustrated in Figure 9a, compared with 0, 25, 50, 75 and 100 percentiles in the granitic zircon data of Belousova et al. (2002), and to critical limits of present-day \(D_\alpha\) as a function of zircon age at 3.5 \(\times\) \(10^{-19}\) \(\alpha\)/g and 8.0 \(\times\) \(10^{-19}\) \(\alpha\)/g. All but six of the analysed grains plot below the 75 percentile of the concentration range of granitic zircon, but a very significant proportion will still have \(D_\alpha > 3.5 \times 10^{-19} \alpha/g\), indicating that they will be significantly radiation damaged. This can be further illustrated by the cumulative distribution of \(D_\alpha (0)\) (Fig. 9b), which suggests that 68% of the zircon grains have passed the percolation limit and 39% are completely metamict. The figure also shows that the structural damage due to U and its radioactive daughters exceeds that of Th and its daughters by an order of magnitude.

6. Discussion

Detrital zircon in the samples of Magaliesberg and Rayton formations analysed in this study has suffered structural damage and disturbance to the U–Pb isotope system. Zircon of this state of preservation has limited geochronological value, and the only observations of that kind to be made with any confidence from the dataset is that the overall age distribution pattern resembles those previously reported from the Pretoria Group (Schröder et al. 2016; Zeh et al. 2016, 2020; Andersen et al. 2019a; Beukes et al. 2019). Dating of deposition or provenance identification are not the concern of this study, however. The observation that grains younger than 2200 Ma are removed by the common-lead-based data filter (Section 5.c) suggests that apparent 207Pb/206Pb ages less than 2200 Ma reflect bias induced by common lead correction (Andersen et al. 2019a) rather than a Palaeoproterozoic metamorphic overprint.

6.a. Primary and secondary features of the detrital zircon

Elevated Ti concentration is a characteristic feature of altered zircon (Belousova et al. 2002; Bell et al. 2019). In the present samples, the Ti concentration varies over almost 5000 ppm. The primary concentration of Ti in magmatic zircon is a function of temperature and TiO2 activity (Watson et al. 2006), and the maximum
temperatures calculated from the observed Ti concentrations would be of the order of 2000°C, which is clearly unrealistic for zircon-fertile, felsic magmatic protosource rock. This indicates that the variation in Ti is indeed due to alteration rather than to primary differentiation in the protosource(s) of detrital zircon. The lack of correlation between Ti and Hf (Fig. 6c) indicates that the Hf concentration even in heavily altered zircon has not been affected. This suggests that the Hf concentration is a feature inherited from the protosource, perhaps the only parameter analysed in this study that is preserved in the most heavily altered detrital zircon grains in these samples.

In studies of the trace-element chemistry of ancient detrital zircon in the Jack Hills conglomerate, and suites of magmatic zircon from granites of different ages, Bell et al. (2016, 2019) found that the sum of un-normalized ratios (Dy/Sm) + (Dy/Nd) (their LREE-I parameter) was a convenient index to distinguish primary magmatic zircon from zircon that has undergone fluid-induced alteration. Zircon with low values typically shows other evidence of secondary disturbance (high Ti, Fe, Mn, Th/U). A distinct change of slope in plots of ‘foreign’ elements versus (Dy/Sm) + (Dy/Nd) in their data at c. 50 suggested that this could be a useful limit between zircon grains that have retained their primary composition and those that have been significantly modified after crystallization. For the zircons in our study, trends in plots of, for example, U and Ti versus (Dy/Sm) + (Dy/Nd) (Fig. 10a) show a change in slope similar to that observed by Bell et al. (2019), but at a much lower (Dy/Sm) + (Dy/Nd) value (at c. 8, Fig. 10a), for reasons that may be related to differences in conditions (temperature, composition of fluid) or extent of alteration between the two studies. The turnover value of 8 corresponds to maximum concentrations of c. 300 ppm U and 40 ppm Ti (yielding a Ti-in-zircon temperature of c. 900°C), but with quite considerable overlap between the altered and unaltered groups, especially for U. Again, Hf concentrations show no systematic variation with (Dy/Sm) + (Dy/Nd).

The Th/U ratio shows a more complex behaviour. A large proportion of grains have Th/U between 0.3 and 1, regardless of

![CL photomicrographs of selected zircon grains from sample SA19-733, with chondrite-normalized REE patterns. See Figure 3 for abbreviations.](https://www.cambridge.org/core/journals/journal-of-the-south-african-geological-society/article/temperatures-calculated-from-the-observed-ti-concentrations-would-be-of-the-order-of-2000c-which-is-clearly-unrealistic-for-zircon-fertile-felsic-magmatic-protosource-rock)
For $(Dy/Sm) + (Dy/Nd)$ (Fig. 10b). For $(Dy/Sm) + (Dy/Nd) > 8$, there are only few grains with Th/U > 1, up to a maximum value of c. 2.5. In contrast, a significant number of grains with lower $(Dy/Sm) + (Dy/Nd)$ have higher Th/U ratios, ranging to 3 and above.

Grains showing $(Dy/Sm) + (Dy/Nd) > 8$ have REE concentrations in the lower part of the overall range (Fig. 11), and these grains do not show any of the anomalous features with flat middle to heavy REE patterns, maxima in the middle REE range, and at least traces of positive Ce and negative Eu anomalies. The REE distributions of these grains are likely to reflect the composition of a magmatic protosource rock. In contrast, grains with $(Dy/Sm) + (Dy/Nd) < 8$ have high REE concentrations (up to $> 4 \times 10^4$ chondrites in the heavy to middle REE range) and anomalous distribution patterns (see also Figs 3–5). REE patterns that are flat in the Gd to Lu range, and even relatively depleted in heavy REEs, are well known from metamorphic zircon that has grown in the presence of garnet, but such zircon will generally have heavy REE levels of 100 times chondrite or less, with distinct, positive Ce and negative Eu anomalies, and depletion in La, Pr and Nd (e.g. Hoskin & Schaltegger, 2003; Whitehouse & Platt, 2003; Skublov et al. 2012; Johnson et al. 2015; Jiao et al. 2017). None of these features are seen in the present high-REE zircon. Partitioning of heavy and middle REE into xenotime during Palaeoproterozoic diagenesis or metamorphism (e.g. Rasmussen et al. 2011) may cause a flattening of the heavy REE pattern in coexisting zircon, but would also be expected to cause a depletion rather than the observed increase in middle to heavy REE concentrations.
6.b. The origin of U–Pb discordance: lead loss or uranium gain

Normal discordance in zircon can in principle have four different reasons: loss of radiogenic lead, gain of uranium, incorporation of common lead and accidental mixing of concordant domains of different ages. The last of these is an analytical artefact that can normally be avoided when using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in time-resolved mode, and which will not be considered further. The present data have been corrected for common lead where required, so the third mechanism can also be disregarded, although the danger of correction-induced bias towards low ages exists, as discussed in Section 5.c. The preferred interpretation of normal discordance has always been loss of radiogenic lead, which may be induced by thermal overprint or interaction with fluids (e.g. Metzger & Krogstad, 1997; Geissler et al. 2003). Low-temperature weathering processes may induce loss of radiogenic lead from radiation-damaged zircon (Stern et al. 1966; Pidgeon et al. 2017). On the other hand, Pidgeon et al. (2017, 2019) found evidence of weathering-induced U–Pb discordance in metamict zircon that must have been due to U introduction rather than to lead loss. At surface-near conditions, uranium is highly mobile as the uranyl ion ($\text{UO}_2^{2+}$) (Murphy & Shock, 1999). Hexavalent uranium can form its own minerals (e.g. uranyl phosphates, Dal Bo et al. 2016), and can be absorbed by metamict zircon or precipitate as secondary minerals along fractures in zircon (Pidgeon et al. 2017, 2019). If a concordant zircon with $^{206}\text{Pb}/^{238}\text{U}$ age $t$ acquires $D$ normal discordance in a recent process, the percentage discordance is given by

$$D\% = 100 \left( \frac{\lambda_{238}}{\lambda_{206}} \frac{\text{observed}}{\text{equilibrium}} - 1 \right)$$

where $J_{238}$ is the decay constant of $^{238}\text{U}$ and $e^{\lambda t} - 1$ is the $^{206}\text{Pb}/^{238}\text{U}$ ratio of a concordant zircon with age $t$. Since the change of the $^{206}\text{Pb}/^{238}\text{U}$ ratio can result from reduction of radiogenic lead content by a factor $x = \frac{^{206}\text{Pb}_{\text{after}}}{^{206}\text{Pb}_{\text{before}}}$ or by an increase in the uranium concentration by a factor $y = \frac{^{238}\text{U}_{\text{after}}}{^{238}\text{U}_{\text{before}}}$, a discordance of $D\%$ can be expressed by either...
Depending on which process is responsible. Although increases of uranium concentration by up to an order of magnitude in the most altered zircon grains are permitted by the present data (Fig. 10a), which can generate up to 90% of normal discordance, the inverse relationship between $x$ and $y$ makes uranium gain less efficient than lead loss to generate such high degrees of normal discordance. Most likely, both U gain and Pb loss have contributed to the discordance pattern of the detrital zircon studied here.

### 6.c. Conditions of alteration

The increase in concentration of any element in altered detrital zircon requires input of the element from some source external to the...
zircon itself. Titanium is a high-field-strength element that has low solubility in aqueous solutions under most low-pressure and -temperature conditions (van Baalen, 1993), and will tend to behave as a locally immobile element during weathering of detrital Ti-minerals such as titanite (Tilley & Eggleton, 2005). Inorganic ligands other than fluoride have negligible effect on titanium solubility at low temperature (van Baalen, 1993). Elevated fluorine concentration may be important in hydrothermal systems, but is unrealistic for most near-surface weathering scenarios. On the other hand, titanium shows enhanced low-temperature solubility at low pH, and in the presence of organic ligands (Cornu et al., 1999). The excess Ti is likely to be absorbed into the amorphous, metamict zircon, or precipitated as poorly crystalline Ti- or Fe-Ti oxides or hydroxides along fractures, as was envisaged for other non-formula elements in low-temperature altered zircon by Pidgeon et al. (2019).

Th has generally been regarded as immobile in low-temperature aqueous fluids (e.g. Braun et al. 1992), but there is evidence for at least local remobilization of Th during weathering under hot and humid conditions (Braun et al. 2005; Du et al. 2012). At pH < 7, Th forms stable, soluble complexes with phosphate-, sulphate- and organic ligands, which enhances its solubility under acid conditions (Langmuir & Herman, 1980). Pidgeon et al. (2017, 2019) found that Th can indeed be introduced into radiation-damaged zircon during weathering, and that introduction of Th and U may be at least partly independent processes. This is also indicated by our data, with a general increase in Th/U seen in the more altered zircon, suggesting that Th is introduced to a greater extent than U.

During Late Cretaceous time, the bedrock below the African Surface was deeply weathered under hot, humid and acidic (pH c. 4) conditions (Partridge & Maud, 1987; Partridge, 1998; Partridge et al. 2006). These are conditions that would favour local mobility of Ti and Th. Weathering has continued to the present day, under variable temperature and humidity conditions. The increase in Ti seen in the altered zircon may be due to millimetre- to centimetre-scale mobilization of Ti released by leaching of detrital titanite and ilmenite during deep weathering in periods of favourable climatic conditions during Cretaceous and Cenozoic time. The accompanying enrichment in light to middle REEs, Y, U and Th is most likely due to release by leaching of detrital apatite and possibly monazite in the same process.

6.d. Implications for detrital zircon geochronology

The U–Pb and trace-element characteristics of detrital zircon in the samples of Magaliesberg and Rayton formation analysed in this study are largely consequences of Cretaceous to recent alteration induced by weathering. Less than 20% of the grains analysed have retained a reliable memory of their protosource. A data-filtering routine based on a maximum level of common lead contamination removes noise from the 207Pb/206Pb age distribution, so that distinct age fractions can be identified. Alternative trace-element-based parameters may be used to filter data, using a minimum value for (Dy/Sm) + (Dy/Nd) as suggested by Bell et al. (2019), but with a limit at 8 in the present data, $D_\alpha(0) < 3.5 \times 10^{18}$ a/g.
or a maximum concentration limit for non-structural elements (e.g., Ti ≤ 40 ppm). These routines will remove grains whose trace-element chemistry has been altered, but will still allow grains with disturbed U–Pb systematics to pass, and will not reveal the pattern of age fractions suggested by the 206Pb/204Pb filtered data (Fig. 12). However, it can be a viable screening for datasets where 206Pb cannot be reported because of high mercury backgrounds during analysis.

As was pointed out by Pidgeon et al. (2017), the possibility that U has been introduced by late processes has the implication that the \( D_\alpha(0) \) calculated from observed concentrations by Equation (1), and hence also the degree of metamictization estimated from Equation (2), may overestimate the real alpha dose and radiation damage of the crystal structure. Uranium added to an old zircon in Cenozoic time has only been able to induce minor radiation damage on top of what has been accumulated throughout the lifetime of the crystal at the lower, primary concentrations of the radioactive elements. If so, the calculated \( D_\alpha(0) \) value would be less useful as a filtering criterion for detrital zircon data. Furthermore, calibration methods for LA-ICP-MS that use present-day U and Th concentrations or counting rates to compensate for radiation damage of the crystal structure (e.g., Sliwinski et al., 2017) may overestimate damage and thus introduce bias. Some studies have found that the degree of radiation damage in zircon estimated from present-day U and Th concentrations exceeds the structural damage that can be measured by Raman spectroscopy, which is commonly interpreted as evidence for late annealing of the crystal structure, even where there is no other evidence of thermal overprint (e.g., Wang et al., 2014). This may instead be a consequence of overestimation of \( D_\alpha(0) \) due to late introduction of U and Th. Although perhaps of less importance for detrital zircon studies, it must be noted that weathering-related change in U and Th contents also invalidates the common Pb-correction routine described by Andersen (2002).

The problems outlined here affect detrital zircon in old sedimentary rocks that have been exposed to chemical weathering under climatic conditions that favour element mobility. This would apply to any Precambrian sandstone in areas undergoing tropical or sub-tropical weathering today, or which has been exposed to such weathering in the past. The present samples were taken from natural exposures and roadcuts. As long as weathering extends far below the natural surface (several tens of metres in part of South Africa; Partridge & Maud, 1987), surface or near-surface samples are less useful for detrital zircon geochronology than drillcore and mine samples from well below the weathered zone. Data from surface samples should therefore be interpreted with great care. Trace-element data may provide information on the extent of alteration, and should therefore be included in analytical protocols whenever possible, but may not provide a sufficiently effective data filter to remove the effects of late weathering.

Hf isolate data have not been considered in the present study. The most significant effect on time-corrected \( ^{176}\text{Hf} / ^{177}\text{Hf} \) ratios or epsilon-Hf values is likely to be caused by shifts in the U–Pb age (Guitreau & Blichert-Toft, 2014). As a result of the elevated Hf concentration, and its apparent resistance to the late processes (Figs 6c, 10a), weathering is unlikely to affect the present-day \( ^{176}\text{Hf} / ^{177}\text{Hf} \) ratio. However, the change in Lu/U ratio due to REE gain in the most severely affected zircon grains (Fig. 6d) suggests that time-corrected \( ^{176}\text{Hf} / ^{177}\text{Hf} \) and epsilon-Hf(\( \text{r} \)) values may be modified, even when the true (i.e. protosource) age of the zircon can be estimated.

7. Conclusions

Sandstones and contact metamorphic quartzites belonging to the Magaliesberg and Rayton formations of the upper part of the Palaeoproterozoic Pretoria Group have been in a near-surface position since the Cretaceous Period, and exposed to chemical weathering under variable climatic conditions for 20–70 Ma. Whereas fully crystalline zircon has been able to survive such exposure without modification of its primary uranium–lead and trace-element characteristics, radiation-damaged zircon has been severely affected, causing increasing U–Pb discordance, increasing content of common lead and non-structural trace elements, and changing REE distribution patterns that are strongly enriched and flat to concave downwards in the middle to heavy REE range. U and Th concentrations were increased in the process, but the two elements are at least partly decoupled, resulting in a wide range of Th/U in zircon that has been affected. Late increases in U and Th have the additional consequence that the accumulated alpha dose that can be estimated from observed element concentrations is
likely to overestimate the real dose absorbed through the lifetime of the zircon. Only c. 15% of the detrital grains in the samples analysed in this study have escaped severe disturbance of their U-Pb and trace-element system. The use of data filters to such detrital zircon datasets is necessary. This study suggests that the conventional, discordance-based data filter, and alternatives based on trace-element analyses, are not sufficiently effective. Filtering the analyses on $^{206}\text{Pb}/^{238}\text{Pb}$ ratio or common lead content prior to element analyses, are not sufficiently effective. Filtering the datasets is necessary. This study suggests that the conventional, element system. The use of data filters to such detrital zircon

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