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Abstract

Quantifying the rates of landscape evolution in response to climate change is inhibited by the difficulty of dating the formation of continental detrital sediments. We present uranium isotope data for Cooper Creek palaeochannel sediments from the Lake Eyre Basin in semi-arid South Australia in order to attempt to determine the formation ages and hence residence times of the sediments. To calculate the amount of recoil loss of ^{234}U , a key input parameter used in the comminution approach, we use two suggested methods (weighted geometric and surface area measurement with an incorporated fractal correction) and typical assumed input parameter values found in the literature. The calculated recoil loss factors and comminution ages are highly dependent on the method of recoil loss factor determination used and the chosen assumptions. To appraise the ramifications of the assumptions inherent in the comminution age approach and determine individual and combined comminution age uncertainties associated to each variable, Monte Carlo simulations were conducted for a synthetic sediment sample. Using a reasonable associated uncertainty for each input factor and including variations in the source rock and measured ($^{234}\text{U}/^{238}\text{U}$) ratios, the total combined uncertainty on comminution age in our simulation (for both methods of recoil loss factor estimation) can amount to $\pm 220\text{--}280$ ka. The modelling shows that small changes in assumed input values translate into large effects on absolute comminution age. To improve the accuracy of the technique and provide meaningful absolute comminution ages, much tighter constraints are required on the assumptions for input factors such as the fraction of α -recoil lost ^{234}Th and the initial ($^{234}\text{U}/^{238}\text{U}$) ratio of the source material. In order to be able to directly compare calculated comminution ages produced by different research groups, the standardisation of pre-treatment procedures, recoil loss factor estimation and assumed input parameter values is required. We suggest a set of input parameter values for such a purpose. Additional considerations for calculating comminution ages of sediments deposited within large, semi-arid drainage basins are discussed.

Keywords

sediment, times, residence, constrained, uranium, series, isotopes, critical, appraisal, comminution, approach

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Sediment residence times constrained by uranium-series isotopes: A critical appraisal of the comminution approach

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Quantifying the rates of landscape evolution in response to climate change is inhibited by the difficulty of dating the formation of continental detrital sediments. We present uranium isotope data for Cooper Creek palaeochannel sediments from the Lake Eyre Basin in semi-arid South Australia in order to attempt to determine the formation ages and hence residence times of the sediments. To calculate the amount of recoil loss of ^{234}U , a key input parameter used in the comminution approach, we use two suggested methods (weighted geometric and surface area measurement with an incorporated fractal correction) and typical assumed input parameter values found in the literature. The calculated recoil loss factors and comminution ages are highly dependent on the method of recoil loss factor determination used and the chosen assumptions. To appraise the ramifications of the assumptions inherent in the comminution age approach and determine individual and combined comminution age uncertainties associated to each variable, Monte Carlo simulations were conducted for a synthetic sediment sample. Using a reasonable associated uncertainty for each input factor and including variations in the source rock and measured ($^{234}\text{U}/^{238}\text{U}$) ratios, the total combined uncertainty on comminution age in our simulation (for both methods of recoil loss factor estimation) can amount to ± 220 – 280 ka. The modelling shows that small changes in assumed input values translate into large effects on absolute comminution age. To improve the accuracy of the technique and provide meaningful absolute comminution ages, much tighter constraints are required on the assumptions for input factors such as the fraction of α -recoil lost ^{234}Th and the initial ($^{234}\text{U}/^{238}\text{U}$) ratio of the source material. In order to be able to directly compare calculated comminution ages produced by different research groups, the standardisation of pre-treatment procedures, recoil loss factor estimation and assumed input parameter values is required. We suggest a set of input parameter values for such a purpose. Additional considerations for calculating comminution ages of sediments deposited within large, semi-arid drainage basins are discussed.

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1. INTRODUCTION

The uranium-series (U-series) isotopes provide invaluable time chronometers for quantification of the rates of Earth's surface processes over the last several 100 ka, such as silicate weathering and soil and sediment residence in the

landscape (e.g., Osmond and Ivanovich, 1992; Vigier et al., 2001; Dequincey et al., 2002; Maher et al., 2004; Dosseto et al., 2008; Andersen et al., 2009 and see Chabaux et al., 2003; Vigier and Bourdon, 2011, for recent comprehensive reviews). Quantification of such rates is crucial to improve our understanding of the relationship between climate change, tectonics and landscape evolution throughout the Quaternary. Recent studies (e.g., DePaolo et al., 2006; Dosseto et al., 2010; Lee et al., 2010) of the fractionation between ^{234}U and ^{238}U in fine-grained sediment have

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demonstrated the potential in constraining the comminution age of continentally-derived sediments, that is, the time elapsed since physical weathering of the source rock into fine-grained ($<50\ \mu\text{m}$) particles (DePaolo et al., 2006; Fig. 1). The comminution age includes the time that a particle has been mobilised in transport, held in temporary storage (e.g., soils and floodplains) and the time elapsed since final deposition to present day (Fig. 1). Therefore, if the deposition age of sediment can be constrained independently, for example via optically stimulated luminescence (OSL) dating, the residence time of sediment (e.g., a palaeochannel deposit) can be computed from:

$$T_{\text{res}} = t_{\text{com}} - t_{\text{dep}} \quad (1)$$

where T_{res} is the sediment residence time (the time between the formation of the silt-sized grain and final deposition, or transport time), t_{com} the comminution age of the sediment and t_{dep} is the deposition age of the sediment.

Where it is possible to compare calculated comminution ages of detrital sediments with independent age estimates, the comminution data yield reasonable timescales but maybe offset from independently constrained ages by several 100 ka (e.g., Lee et al., 2010). Clearly the comminution method is still in its infancy and has only been applied in a handful of studies. The technique also remains to be tested and examined for more complex fluvial environments in order to assess its real value as a dating technique. For example, in large catchment areas with potentially much longer transport times, more complex sediment transport pathways and a wide range in source rock lithology. Nevertheless, using the U-series comminution approach, residence times calculated for palaeochannel sediments of the Murrumbidgee River in temperate, southeastern Australia (Dosseto et al., 2010) suggested a link between catchment erosion, climate and vegetation.

Fig. 1. Illustration of the comminution age concept and associated geomorphological processes (modified from Dosseto et al., 2010).

Here we present the first U-series study of palaeochannel sediments from Cooper Creek in the Lake Eyre Basin in central Australia. This study site affords a great opportunity to assess the comminution approach as the vast catchment area of the basin ($\sim 1.2 \times 10^6\ \text{km}^2$) drains a wide variety of lithology (including fine-grained sedimentary rocks) and furthermore, the deposition age of the deposits has already been determined independently by Cohen et al. (2010). The objectives of the study are twofold: (1) to determine comminution ages and residence times of Cooper Creek sediments using common assumptions of input parameter values found in the present literature and, (2) estimate both individual parameter and combined comminution age uncertainties for a synthetic sample.

2. ^{234}U – ^{238}U COMMUNITION AGE METHOD

2.1. Concept

The ‘comminution age’ dating model of DePaolo et al. (2006) hypothesises that measured disequilibria between U-series nuclides (^{234}U and ^{238}U) in fine-grained continental (detrital) sediments can be used to calculate the time elapsed since mechanical weathering of a grain to the threshold size ($\sim 50\ \mu\text{m}$). When ^{238}U undergoes alpha decay to ^{234}Th , the associated release of energy results in the physical displacement (recoil) of the ^{234}Th nuclide from the original position of ^{238}U . When this decay occurs in a mineral grain it can result in the physical ejection of ^{234}Th from the solid (e.g., into a pore fluid) and lead to the subsequent depletion of ^{234}U (the daughter of the ejected intermediate ^{234}Th nuclide) relative to ^{238}U (Kigoshi, 1971) (Fig. 2). In coarse-grained sediment (sand-sized particles and larger) ^{234}U – ^{238}U disequilibria is only measurable at grain edges as the grain radius is much larger than the recoil length of $\sim 30\ \text{nm}$ (theoretical α -recoil length of feldspar; Ziegler et al., 1996). However, in fine-grained silt-sized or smaller detrital sediments this process leads to measurable ^{234}U – ^{238}U disequilibria in bulk samples comprising fine-grained particles (Fig. 2). This disequilibrium can be used to calculate the comminution age (time since mechanical weathering) of the sediment (t_{com}) using the following equation (DePaolo et al., 2006):

$$t_{\text{com}} = -\frac{1}{\lambda_{234}} \ln \left[\frac{A_{\text{meas}} - (1 - f_{\alpha})}{A_0 - (1 - f_{\alpha})} \right] \quad (2)$$

where λ_{234} is the ^{234}U decay constant ($2.82629 \times 10^{-6}\ \text{yr}^{-1}$, using $t_{1/2}(^{234}\text{U})$ of 245,250 yr, from the compilation of Bourdon et al., 2003), A_{meas} is the measured ($^{234}\text{U}/^{238}\text{U}$) activity ratio (parenthesis around U-series isotopic ratio denotes activity ratio) of the sediment, f_{α} is the recoil loss factor, defined as the fraction of ^{238}U decays that result in the recoil loss of the intermediate nuclide ^{234}Th , and A_0 is the initial ($^{234}\text{U}/^{238}\text{U}$) of the source rock.

2.2. Uncertainties in the comminution age calculation

2.2.1. ($^{234}\text{U}/^{238}\text{U}$) of the sediment source, A_0

The ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the source rock, A_0 , has been assumed by previous authors (e.g., DePaolo et al.,

Fig. 2. (a) Diagram showing the time dependent (since the onset of weathering) evolution of $(^{234}\text{U}/^{238}\text{U})$ as a function of sediment grain size (modified from DePaolo et al., 2006). Note the potential to form 'out of secular equilibrium' source rocks from aged, fine-grained sediments (dashed arrow). (b) Schematic illustration of the recoil loss of ^{234}Th from spherical grains and grains with surface roughness. For sand-sized grains (cf. silt-sized grains), recoil lost ^{234}Th (i.e., $(^{234}\text{U}/^{238}\text{U}) < 1$) will only be measurable at the grain rim due to the small recoil length ($\sim 30 \text{ nm}$) relative to the radius of a sand grain ($> 62.5 \mu\text{m}$) (modified from DePaolo et al., 2006). Right hand sketch shows the same sand-sized grain with surface roughness to illustrate that increased surface area translates to increased recoil loss of ^{234}Th .

2006; Lee et al., 2010; Dosseto et al., 2010) to be 1, i.e., in secular equilibrium. While this may be expected for unfractured, fresh, crystalline source rocks (e.g., Zeilinski et al., 1981; Rosholt, 1983), it is unclear whether sedimentary rock such as siltstone, formed of silt-sized 'out-of-secular-equilibrium' grains, will achieve secular equilibrium after 1 Ma (5 times the half-life of the daughter nuclide, ^{234}U) (Fig. 2a). If the source rock is porous, permeable and/or fractured then it is possible that ^{234}Th produced by post-depositional α -recoil may continue to be lost, via removal by pore and migrating fluids. In this scenario, A_0 will never achieve secular equilibrium and therefore, possess $(^{234}\text{U}/^{238}\text{U}) < 1$ (Fig. 2a). The age of the source rock is also important to constrain as any source rock younger than 1 Ma could potentially be out of secular equilibrium. Furthermore, if the source rock is chemically weathered or if ^{234}U has been preferentially leached from damaged α -recoil sites (see Section 2.3.1), measurable fractionation of ^{234}U from ^{238}U may occur prior to physical comminution to the threshold grain size. In such a scenario, the residence time of a particle would represent the time between its isotopic alteration, in a profile, and the time of its final deposition. Whether the source rock is in ^{234}U – ^{238}U secular equilibrium needs to be tested for each study. $(^{234}\text{U}/^{238}\text{U})$ activity ratios significantly less than 1 (0.912–0.971) have been measured in siltstone, shale and quartzite bedrock from the Flinders Ranges in South Australia (Handley et al., in press). This adds uncertainty to the calculated comminution ages for sediments, particularly in vast catchment areas that drain a wide range of bedrock types (e.g., that of the study area). Therefore the present study will assess the effects of variation in source rock $(^{234}\text{U}/^{238}\text{U})$

activity ratios upon the calculated comminution age of a synthetic sample.

2.2.2. Recoil loss factor, f_α

The largest source of uncertainty in the comminution age calculation is attributed to difficulties in the estimation of f_α , the fraction of ^{234}Th lost via α -recoil in a bulk sample. Even slight variations in estimated f_α values can significantly affect inferences about weathering rates and comminution ages (e.g., DePaolo et al., 2006; Lee et al., 2010). Several approaches have been used to estimate f_α , and these are summarised in Maher et al. (2006) and Lee et al. (2010). Previous research (e.g., Maher et al., 2006; DePaolo et al., 2006; Lee et al., 2010) suggests that reasonable approximations of f_α can be obtained by: (1) weighted geometric estimation of f_α using sample grain size distributions and assumptions for surface roughness and grain aspect ratio, and (2) measurements of specific surface area (e.g., Brunauer–Emmett–Teller (BET) gas adsorption measurements) with an incorporated fractal correction to account for the significant difference between the size of the adsorbed gas molecule and the recoil length scale (Semkow, 1991; Bourdon et al., 2009).

In the geometric estimation, the amount of recoil is related to the size, sphericity and surface area (roughness) of the grain. A SEM image (Fig. 3) of the Cooper Creek palaeochannel sediment shows that mineral grains are rarely spherical or perfectly smooth and therefore, in reality, f_α will be larger than would be assumed for the simple case of a spherical grain (Fig. 2b). Consequently, a weighted geometric model is preferred to yield reasonable estimations of f_α (DePaolo et al., 2006):

Fig. 3. (a) SEM backscattered electron image of sample GT2 (gold-coated) after sieving (to $<53 \mu\text{m}$), sequential leaching and clay removal. Note the wide variation in grain morphology and the elongated (non-spherical) nature of some grains. A grain with an aspect ratio of 2:1 is highlighted. (b) Enlargement of the area delimited by the white rectangle in *a*, highlighting the range in surface roughness observed between grains of similar size and the presence of a relatively euhedral zircon grain.

$$f_{\alpha} = \int_{\frac{r}{L}}^{r_{\text{max}}} X(r) \beta(r) \lambda_s(r) \frac{3}{4} \left(\frac{L}{r} - \frac{L^3}{12r^3} \right) dr \quad (3)$$

where r is the grain radius, L is the ^{234}Th recoil distance (in nm), $X(r)$ is the volume fraction of grains with radius r , β is the aspect ratio of the grain and λ_s is the surface roughness factor. Assumptions are required for the surface roughness factor (λ_s), which is expected to increase with grain size, and for the aspect ratio (β), which is commonly taken to range between 1 for the largest grain and 10 for smallest grain (e.g., DePaolo et al., 2006; Dosseto et al., 2010).

Direct measurements of bulk sediment specific surface area determined by BET gas adsorption methods circumvent the necessity to assume a surface roughness factor and aspect ratio. α -Recoil loss is related to surface area by the following equation (Kigoshi, 1971; Luo et al., 2000; DePaolo et al., 2006):

$$f_{\alpha} = \frac{1}{4} L \cdot S_{\text{BET}} \cdot \rho \quad (4)$$

where S_{BET} is the measured BET total surface area and ρ is the bulk density of the solid. However, due to the large difference in the size between the adhering gas molecule ($\sim 0.35 \text{ nm}$) and the length of α -recoil ($\sim 30 \text{ nm}$), this

method can significantly overestimate f_{α} , as noted by DePaolo et al. (2006) and Maher et al. (2006). To overcome this scale issue, Bourdon et al. (2009) incorporated the theoretical fractal recoil model of Semkow (1991) that predicts f_{α} based on the BET surface measurements according to the following equation:

$$f_{\alpha} = \frac{1}{4} \left[\frac{2^{D-1}}{4-D} [a/L]^{D-2} \right] L \cdot S_{\text{BET}} \cdot \rho \quad (5)$$

where D is the fractal dimension of the surface (which can be determined via BET data, see Bourdon et al., 2009 for details) and a is the diameter of the adsorbate gas molecule (N_2 in most BET measurements). This means of estimating the recoil ejection factor has yielded ice core ages (based on the accumulation of ^{238}U decay recoil products from dust trapped within the ice) comparable to independently obtained ages (Aciego et al., 2011).

Both the weighted geometric and BET surface area methods described above will be used to estimate and compare values of f_{α} , comminution age and sediment residence timescale for Cooper Creek palaeochannel sediments, employing the assumed input parameter values found in previously published comminution studies. A synthetic sample will also be used to constrain the comminution age uncertainty associated with the weighted geometric and surface area measurement (with fractal correction) methods.

2.3. Additional considerations

The comminution age of a sediment records the time since production of silt-sized material. The question of whether ($^{234}\text{U}/^{238}\text{U}$) activity ratios are modified in the source rock prior to reduction of material to the fine grain size also requires consideration. Furthermore, after the threshold size is reached, dissolution of grain edges via chemical weathering or further physical weathering e.g., via attrition in the river, may remove the grain rims. Removal of the rims (which store the largest disequilibrium between ^{238}U and ^{234}U) could effectively reset the U-series clock, producing ($^{234}\text{U}/^{238}\text{U}$) ratios closer to secular equilibrium than appropriate for that particle's true comminution age. Future experiments are required to fully assess the importance of these processes on calculated comminution ages. For comminution age studies of palaeochannel sediments of the Lake Eyre Basin, and other areas, it is important to consider: (1) preferential loss of ^{234}U through leaching, (2) addition of aeolian material, (3) influence of clay pellet aggregates, and (4) sample mineralogy and the effect of zircon.

2.3.1. Preferential loss of ^{234}U due to leaching

Preferential loss of ^{234}U relative to ^{238}U may occur via leaching of loosely bound recoiled ^{234}U from damaged lattice sites (e.g., Fleischer, 1980; Andersen et al., 2009). This process could be of significance for both the initial source rock and the transported sediments themselves. Loss of ^{234}U relative to ^{238}U due to leaching, in addition to direct α -recoil ejection of ^{234}Th from the grain, complicates the assumptions underlying the comminution age method and

would generally lead to overestimates in the calculated ages. However, DePaolo et al. (2006) argue that it is possible to account for the observed range of f_{α} values in North Atlantic, Pleistocene deep-sea sediments by α -recoil alone without the need for preferential leaching of ^{234}U . Maher et al. (2006) demonstrate that all of the measured ^{234}U depletion in Pleistocene fluvial sediments from south central Washington can also be accounted for by the α -recoil process. Porcelli and Swarzenski (2003) suggest that, in practice, loss of ^{234}U via leaching along recoil tracks is only plausible when new surfaces are exposed or dry periods allow implantation of recoiled nuclides into adjacent phases. The quantification of the relative importance of leaching lost, versus recoil lost, ^{234}U in each sample studied is difficult to constrain and is not directly addressed in this study.

2.3.2. Addition of aeolian material

The impact of dust on calculated U-series isotope residence timescales of soil and fluvial sediment has received little attention in previous studies, despite the fact that the typical grain size of aeolian material overlaps with that of interest in the comminution approach ($<50\text{ }\mu\text{m}$). The potential of aeolian material to modify bulk soil or fluvial U-series signatures will depend on its ($^{234}\text{U}/^{238}\text{U}$) ratio and its volume percentage contribution to the deposit. Locally sourced dust from nearby floodplains may have a similar ($^{234}\text{U}/^{238}\text{U}$) activity ratio to the fluvial sediments themselves and therefore, be indistinguishable from the fluvial signature. On the other hand, substantial input of distally derived dust, that has been circulating in the environment over a longer timescale than is representative of the fluvial deposit, may modify the residence time significantly.

The impact of aeolian material input on ($^{234}\text{U}/^{238}\text{U}$) ratios is important to consider for the present study area as a prevalence of dust deposits are recorded in the sedimentary record throughout the Quaternary in southeast Australia (e.g., Butler, 1956; Chen et al., 2002; Hesse and McTainsh, 2003; Cattle et al., 2009; Marx et al., 2011). The rate of dust accumulation in Australia during the late Pleistocene is suggested to have been much greater than during the Holocene (e.g., Hesse, 1994; Chen et al., 2002; McGowan et al., 2008). In Australia, aeolian material is carried along two major pathways: to the east/southeast and northwest of the continent (Bowler, 1976; McTainsh, 1989; Hesse and McTainsh, 2003). Dust sourced from central Australia (e.g., Lake Eyre Basin (Fig. 4); Hesse and McTainsh, 2003) may be deposited either distally offshore in the Tasman Sea or in New Zealand (e.g., Hesse, 1994; Marx et al., 2009) or be deposited or more proximally on the Australian continent. The large catchment area of the Lake Eyre Basin and the westward/southwestward directed river discharge back towards Lake Eyre, means that flood events in Queensland and New South Wales will carry the top soil, including any recently deposited aeolian material (initially sourced from Lake Eyre, or further west of Lake Eyre), back to the interior. Multiple cycles of essentially eastward dust transport and westward fluvial drainage may therefore occur. The implication for U-series is that such long cycles of sediment transport and reworking in a fluvial-aeolian feedback

system, may (1) continually mix recently weathered fluvial material with older reworked material or (2) mean that long residence times do not simply represent the fluvial sediment residence within a fluvial system but rather the combined fluvial and aeolian system as a whole. U-series measurements of Australian dust are urgently required to increase our understanding of the effects of dust additions to calculated residence times of fluvial sediment.

2.3.3. Presence of clay pellets

The present day Cooper Creek floodplain and river valleys of the eastern part of the Lake Eyre Basin are characterised by clay-rich mud aggregates (Maroulis and Nanson, 1996). From the comminution perspective, the question raised is whether or not, if present, the silt- to sand-sized clay pellets disaggregate during wet-sieving and sample pre-treatment? Flume experiments show that the pellets are durable during transport and relatively resistant to disaggregation (Maroulis and Nanson, 1996). Therefore, if silt-sized clay pellets persist at the clay removal step, a percentage of secondary clay material (mineralogically speaking), is unlikely to be removed during centrifugation to remove the 0–2 μm fraction. This material may have unrepresentatively high ($^{234}\text{U}/^{238}\text{U}$) ratios relative to its amalgamated pellet grain size, and if present in abundance, will then perturb calculations of f_{α} based on grain geometry or surface area. The use of sodium hexametaphosphate during sample pre-treatment is anticipated to deflocculate clays and help to alleviate this issue.

2.3.4. Sample mineralogy

The α -recoil length, L , varies for different minerals (see Section 6.2.1) and therefore, bulk sample α -recoil length is dependant on sample mineralogy. Any uncertainty in sample mineralogy will consequently add extra uncertainty to the estimation of the recoil loss factor. This is probably the case for the present study in which sample mineralogy was not determined. Furthermore, the dominance of a mineral that is highly non-spherical/oblate (e.g., mica) may lead to additional uncertainty to the weighted geometric estimation of recoil loss factor, as this model assumes a linear relationship in grain aspect ratio between the largest and smallest grains.

The presence of zircon (or other high U concentration accessory minerals) is another factor that could potentially complicate the interpretations of palaeochannel sediment U-series disequilibria. The SEM image of GT2 in Fig. 3 clearly shows that zircon is present in the $<53\text{ }\mu\text{m}$ sieved and leached fraction of Cooper Creek sediments, and over 25 grains were observed in the GT2 SEM sample stub. Zircon has a high affinity for the nuclides of interest, particularly compared to other silicate minerals such as quartz and feldspar (Blundy and Wood, 2003). Therefore, if digested along with the bulk rock sample, even minor amounts of zircon are expected to dominate U-series budget. The higher U–Th concentration and different recoil length, of zircon (22.7 nm, (theoretical) Ziegler et al., 1996, or 55 nm, (observed) Kigoshi, 1971), relative to that of feldspar (30 nm; (theoretical) Ziegler et al., 1996), may result in zircon dominance of bulk sample ($^{234}\text{U}/^{238}\text{U}$) ratios and control

Fig. 4. (a) Location of the Cooper Creek palaeochannel study area in relation to Lake Eyre and major settlements. (b) Location of the internally draining Lake Eyre Basin within Australia. The Innamincka Dome (ID) and location of the Murrumbidgee palaeochannel (MPC) study in southeast Australia carried out by Dosseto et al. (2010) are also shown. (c) Stratigraphy of the floodplain trenches of the Gidgealpa palaeochannel off the southern branch of Cooper Creek (modified from Cohen et al., 2010). Deposition ages of the sandy units determined by OSL (Cohen et al., 2010) and the location of samples used in this study (GT#) are shown. Samples GT4 and GT5 consist of several amalgamated samples from higher in their respective profiles than the OSL dated horizon and were therefore, likely to be deposited more recently than the OSL age. GD = Gidgealpa dune.

on estimated f_x values. Whether the zircon is fluvially or aeolian derived may then be of great significance to the measured bulk sample ^{234}U – ^{238}U disequilibria and any calculated comminution age of the sediment. We note that the sample digestion method used in this study (Section 5) is

not expected to digest zircon. However, this issue needs to be considered further in future comminution studies. The impact of zircon could be tested by separation of the zircon fraction (silt-sized range) from a bulk sample, and subsequent processing of the zircon fraction as a separate

digestion (in a pressure bomb) for U-series analysis. However, separation of fine-grained zircon from a sample of only a few grams may be challenging, and require micro-heavy liquid techniques.

3. REGIONAL CONTEXT OF THE STUDY AREA: THE LAKE EYRE BASIN

The Cooper Creek, together with the Diamantina and Georgina Rivers, form the major sediment transport pathways within the Lake Eyre Basin, one of the world's largest ($\sim 1.2 \times 10^6 \text{ km}^2$), internally draining, semi-arid catchment areas (Fig. 4a and b). The Cooper Creek originates in Queensland at the confluence of the Thomson and Barco rivers and flows $\sim 1500 \text{ km}$ southwest towards Lake Eyre salt playa (depocentre 15 m below mean sea level) in arid South Australia (Fig. 4b). The catchment drains approximately one-seventh of the Australian continent and is characterised by relatively flat relief, stream gradients of 0.1–0.2 m/km and a series of anabranching ephemeral channels known as the 'Channel Country'. The catchment is geologically hosted by a series of Early Palaeozoic to Cainozoic nested, gently warped basins and associated near-horizontal sedimentary sequences. A detailed geological background of the region can be found in Nanson et al. (2008).

Local sediment may be supplied to the study area via the erosion of the Innamincka Dome and its associated low-gradient fan, which splays out into the Strzelecki Desert west of Innamincka (Fig. 4). Cainozoic crustal warping produced the topographic high and the entire flow of the Cooper Creek presently passes through the Dome in a confined channel. The exposed surface of the Dome consists mainly of the Winton Formation (shales and sandstones in a kaolinitic matrix, with minor limestone with leaf impressions) and the Mt Howie Sandstone (kaolinitic pebbly-sandstone, pebbles of the Winton Formation) of Late Cretaceous age and the Tertiary Eyre Formation (fluvial kaolinitic cross bedded sandstone and minor shales) and silcrete (silicified palaeosol of Mid Tertiary age) (Geological Survey of South Australia, 1975).

A compilation of new and previously published alluvium thermoluminescence (TL) ages of the Lake Eyre Basin is presented by Nanson et al. (2008). The alluvial evidence suggests that more pronounced fluvial activity, relative to today, extended back to at least oxygen isotope stages (OIS) 8 and 7 (up to 280 ka) and peaked ~ 120 –90 ka during OIS 5. A smaller peak is observed (65–60 ka) in late OIS 4 and a smaller still (45–40 ka) in mid OIS 3 (Nanson et al., 2008). An overall picture is envisaged of a significantly oscillatory wet-dry climate, superimposed upon a gradual trend of increasing aridity (which is noted Australia-wide) and a general decline in the magnitude of the wet episodes throughout the mid to late Quaternary (Nanson et al., 2008). The significant sandy fluvial deposits observed within Cooper Creek palaeochannels (e.g., Fig. 4c) suggests that larger more competent rivers than today delivered coarse sand to the Cooper Creek Fan over approximately the last 100 ka (Cohen et al., 2010). Due to high evaporation and low relief only significant monsoon rains produce enough water to reach Lake Eyre at present times, usually on a decadal timescale and which most recently occurred in 2010. The present day Cooper Creek floodplain is dominated by clay and sand-sized mud aggregates with sporadic sand dunes (Nanson et al., 1986; Maroulis and Nanson, 1996).

4. PALAEOCHANNEL SAMPLE DETAILS

The Cooper Creek palaeochannel samples were collected from six trench pits dug across the Gidgealpa palaeochannel (Fig. 4c), extending south from the Gidgealpa dune (GD, Fig. 4c). Field sampling procedures and the stratigraphy of the fluvial deposits are described in detail in Cohen et al. (2010). The Gidgealpa palaeochannel lies within the Strzelecki desert close to the 'South branch' of the Cooper Creek and is still inundated during significant floods. The adjacent alluvium was found, by Cohen et al. (2010), to be the source for transverse and linear dunes, demonstrating an important inter-relationship between dune and floodplain. OSL depositional ages of the fluvial sand units, underlying the muddy floodplain deposits, range from $119 \pm 12 \text{ ka}$ to $22 \pm 5 \text{ ka}$ (Fig. 4c and Table 1). To obtain

Table 1
Uranium concentrations and isotopic compositions of Cooper Creek palaeochannel sediments.

Sample	Sample depth from surface (m)	Deposition age ^a OSL (ka)	Clay-included				Clay-excluded			
			U (ppm)	2SE	$(^{234}\text{U}/^{238}\text{U})$	2SE	U (ppm)	2SE	$(^{234}\text{U}/^{238}\text{U})$	2SE
GT1	4.75	118 ± 13	1.185	0.003	0.950	0.005	1.909	0.003	0.978	0.003
GT2	4.65–4.2	119 ± 11	1.479	0.002	1.017	0.005	2.142	0.003	0.996	0.003
GT3	4.7	102 ± 19	1.503	0.004	0.977	0.005	1.796	0.003	0.979	0.003
GT4	3.7–2.7	$<35 \pm 5$	1.575	0.005	0.965	0.006	1.965	0.004	0.983	0.003
GT5	2.6–2.35	$<22 \pm 5$	1.390	0.003	0.957	0.004	1.277	0.003	0.974	0.004
GT6	3.0	$<85 \pm 5$	3.288	0.011	1.058	0.006	2.454	0.005	1.019	0.003
GT6*	3.0	$<85 \pm 5$					3.191	0.003	1.021	0.002
TML	Rock standard		10.073	0.025	1.002	0.003				

The TML rock standard was digested and processed alongside the Cooper Creek samples.

^a The deposition ages of the sediments were determined by OSL dating by Cohen et al. (2010).

* repeat sample (of full sequential extraction procedure, removal of the clay-sized fraction and U-series analysis).

sediment residence times for palaeochannel sediments calculated from comminution ages it is necessary to know the deposition age of the sediment. Therefore, this study focuses on the sandy units already dated by Cohen et al. (2010). Due to the lack of fine material in some of the dated units it was necessary to combine the dated samples with neighbouring sand-rich samples in order to obtain sufficient silt-sized material. This may add some additional uncertainty to the calculated residence times. The exact stratigraphic location of the samples used in this study is given in Table 1 and Fig. 4c.

5. ANALYTICAL TECHNIQUES

The $<50\ \mu\text{m}$ fraction, typically 2–3 g of material per bulk sample (from ~ 200 to 300 g of predominantly sandy material), was obtained by wet-sieving ($53\ \mu\text{m}$ mesh size) using deionised water. Approximately 2 g of the retained fine material underwent a sequential extraction procedure to remove organic and exchangeable material, carbonate and Fe-, Mn-oxide secondary minerals following a methodology modified from Schultz et al. (1998). Stage 1: removal of exchangeable/adsorbed/organics. The sample was first heated at $98\ ^\circ\text{C}$ for 30 min in 30 mL of NaOCl (pH 7.5). After cooling, the sample was centrifuged and the NaOCl supernatant discarded. This stage was repeated again and afterwards the sample was rinsed (rinse stage) by adding 10 mL of $18.2\ \text{M}\ \Omega$ water, centrifuging at 7000 rpm for 15 min and then discarding the supernatant. The rinse stage was carried out twice. Note that all supernatants (including $18.2\ \text{M}\ \Omega$ water) were removed carefully via pipette after each centrifuge step. Stage 2: removal of carbonates. Twenty millilitres of 1 M NaAc in HAc at pH 4 was added to the residue from Stage 1. The sample was continually agitated using a rotary mixer at 30 rpm for 2 h at room temperature. After centrifugation the supernatant was discarded. The rinse stage was then repeated twice. Stage 3: removal of amorphous and crystalline Fe-, Mn-oxides. 20 mL of $0.04\ \text{M}\ \text{NH}_2\text{OH}\cdot\text{HCl}$ was added to the residue of Stage 2. The sample was continually agitated using a rotary mixer at 30 rpm for 5 h. After centrifugation the supernatant was discarded. The rinse stage was then repeated twice. Stage 4: removal of clay-sized material. The clay-sized $0\text{--}2\ \mu\text{m}$ fraction of the samples was removed by controlled centrifugation, following the United States Geological Survey centrifugation method (Open-File Report 01-041). Prior to centrifugation, approximately 50 mL of filtered 5% sodium hexametaphosphate solution was added to the sample to disperse the particles. The mixture was then sonicated with an ultrasonic probe for 20 s at 140 W and agitated overnight at 30 rpm using a rotary mixer. The centrifugation step was undertaken an additional three times beyond when the sample was considered clear of suspended matter to try to ensure complete removal of the clay-sized material. The potential fractionation of $^{234}\text{U}\text{--}^{238}\text{U}$ caused by the sequential leaching procedure in steps 1–3 was not determined in this study but this should be investigated in future studies to assess the reliability of the pre-treatment approach.

Uranium concentrations and $^{234}\text{U}\text{--}^{238}\text{U}$ isotopic ratios were determined on the post-leached residue at the Macquarie University U-series Research Laboratory. Approximately 0.1 g of sediment was spiked with a $^{236}\text{U}\text{--}^{229}\text{Th}$ tracer and digested in a mixture of concentrated acids ($\text{HClO}_4\text{--HF--HNO}_3\text{--HCl}$). Separation of U followed standard anionic resin chromatography detailed in Turner et al. (2011). Uranium concentrations, determined by isotope dilution, and U isotope ratios were measured on a Nu Instruments Multi-Collector ICP-MS at Macquarie University following the approach described by Turner et al. (2011). Internal accuracy ($<0.3\%$) and precision ($<0.1\%$) were assessed by regular analyses of the U010 and U005A solution standards. TML-3, a secular equilibrium rock standard, digested alongside the samples yielded ($^{234}\text{U}/^{238}\text{U}$) within error of secular equilibrium (Table 1). A replicate analysis of GT6 (that underwent sequential extraction steps 1–4, acid digestion and column processing in a separate sample batch) yielded ($^{234}\text{U}/^{238}\text{U}$) within 2% (and analytical error) of the initial GT6 analysis (Table 1). Noting that the reagents in the sequential extraction procedure are discarded at the end of each step and the sample is then rinsed with Milli-Q water, the total procedural blank for the phase extraction, digestion and column separation procedure is $<60\ \text{pg}$.

Scanning Electron Microscope (SEM) BSE images of gold-coated samples were acquired using a Zeiss EVO MA15 at the GAU (Geochemical Analytical Unit) at Macquarie University operating under 10 kV acceleration. The scanning electron microprobe images of GT2 in Fig. 3 show the clean nature of the processed samples after sieving to $<53\ \mu\text{m}$, sequential leaching and clay removal.

BET surface areas were measured by N_2 gas adsorption for sequentially leached and clay removed samples GT1 and GT6 (which were the only samples with sufficient fine-grained material for analysis). Measurements were carried out using a Micromeritics ASAP 2020 at Stanford University and using a Micromeritics Gemini VII 2390 at the Particle and Surface Sciences laboratory in Gosford, Australia to determine inter-laboratory variations in surface area measurements. The measurements produced by each laboratory are presented in the footnote to Table 2. The BET measurements made at each of the two laboratories were carried out on the same sample aliquot and therefore any variation in the result is likely due to measurement variation rather than sample heterogeneity.

Particle size distributions of the $<53\ \mu\text{m}$ bulk sediments (clay-included) were obtained using a Micromeritics Sedi-Graph III 5120 at Macquarie University. The clay-excluded particle size distributions were calculated by excluding the $<2\ \mu\text{m}$ measurements and re-normalising the data.

6. RESULTS AND DISCUSSION

6.1. ($^{234}\text{U}/^{238}\text{U}$) activity ratios

Sample pre-treatment was carried out to remove organic material and secondary minerals including carbonate from the $<53\ \mu\text{m}$ sieved fraction. Secondary minerals such as

Table 2

Calculated recoil loss factors (f_α values) for Cooper Creek palaeochannel sediments.

f_α	Sample	Minimum ($1-A_{\text{meas}}$)	Geometric (λ_s 1–2)	Geometric (λ_s 1–17)	BET ^a	BET _{fract} ^a	BET ^b	BET _{fract} ^b	λ_s needed for min f_α
Clay-included	GT1	0.050	0.012	0.025					1–48
	GT2	n.p.	0.012	0.024					n.p.
	GT3	0.023	0.012	0.030					1–12
	GT4	0.035	0.011	0.041					1–15
	GT5	0.043	0.011	0.035					1–22
	GT6	n.p.	0.012	0.029					n.p.
Clay-excluded	GT1	0.022	0.011	0.041	0.092	0.008	0.130	0.019	1–8
	GT2	0.004	0.011	0.042					
	GT3	0.021	0.012	0.041					1–7
	GT4	0.017	0.011	0.048					1–5
	GT5	0.026	0.011	0.041					1–9
	GT6	n.p.	0.012	0.039	0.029	0.003	0.063	0.014	n.p.

$1-A_{\text{meas}}$ is the minimum value for f_α required to satisfy the comminution equation, as defined in Section 6.2.

f_α geometric is the weighted geometric estimation of f_α calculated using Eq. (3) given in the text, measured particle size data, λ_s as shown, β from 1 to 10 and $L = 30$ nm.

f_α BET and f_α BET_{fract} are calculated using Eqs. (4) and (5) given in the text.

n.p., it is not possible to solve the equation for f_α as the measured ($^{234}\text{U}/^{238}\text{U}$) activity ratio is greater than the corresponding A_0 ($^{234}\text{U}/^{238}\text{U}$) ratio.

Particle size distribution data for the clay-excluded samples are recalculated from the clay-included data, restricting the grain size to the 2–53 micron fraction.

λ_s surface roughness; β , aspect ratio.

An assumed bulk density of 2670 kg/m³ was used in the surface area estimations of f_α . λ_s needed for minimum f_α is the range in surface roughness required to reach the minimum value of f_α able to solve the comminution equation (assuming all other input parameter values remain the same).

^a Using BET surface area and isotherm linear plot data for GT1 and GT6 from Standford (surface area = 4.6103 ± 0.1215 m²/g and 1.4264 ± 0.0184 m²/g, respectively; calculated fractal dimension (D) = 2.77 and 2.68, respectively).

^b Using BET surface area and isotherm linear plot data for GT1 and GT6 from Gosford (surface area = 6.4910 ± 0.0155 m²/g and 3.1253 ± 0.0077 m²/g, respectively; calculated fractal dimension (D) = 2.60 and 2.47, respectively).

Fe-, Mn-oxides, carbonates and clays are likely to incorporate U having the ($^{234}\text{U}/^{238}\text{U}$) ratio of the fluid they precipitate from and so most likely possess a ($^{234}\text{U}/^{238}\text{U}$) > 1. Therefore, secondary minerals are not representative of the primary detrital ($^{234}\text{U}/^{238}\text{U}$) activity ratio and any calculated comminution age would be erroneous. However, as the local sedimentary basement exposed on the Innaminka Dome is clay (kaolinite) rich, clay-sized, clay compositional material, that would usually considered as a secondary mineral, may be incorporated as primary source material in the palaeochannel deposits. U-series isotopic compositions were subsequently determined for both the clay-included (after sequential leaching Stage 3) and clay-excluded fractions (after phase extraction Stage 4) described in the analytical techniques.

U concentrations and ($^{234}\text{U}/^{238}\text{U}$) activity ratios of the Cooper Creek palaeochannel sediments are listed in Table 1 and presented on Fig. 5. The majority of clay-included and clay-excluded samples have ($^{234}\text{U}/^{238}\text{U}$) < 1, as expected for detrital fine-grained sediments that have lost ^{234}U due to the recoil loss of its parent ^{234}Th (Fig. 2). GT6 has ($^{234}\text{U}/^{238}\text{U}$) > 1 for both the clay-included and clay-excluded samples, suggesting either incomplete removal of secondary phases, which is supported by the higher U concentration of this sample, or significant implantation of ^{234}Th (Table 1 and Fig. 5b). If the clay-sized component of the sample was formed secondary to the detrital grains,

it is expected to have ($^{234}\text{U}/^{238}\text{U}$) > 1 (Maher et al., 2006). Removal of that component is, therefore, expected to lower the ($^{234}\text{U}/^{238}\text{U}$) ratio of the bulk sample, and such is observed for samples GT2 and GT6. However, the ($^{234}\text{U}/^{238}\text{U}$) ratios of GT1, GT4 and GT5 increased after removal of the clay-sized fraction, suggesting that the clay material lost may have been primary and had low ($^{234}\text{U}/^{238}\text{U}$) due to high recoil efficiency in small, old, grains. Overall, removal of the clay fraction has shifted the clay-excluded data closer to secular equilibrium. ($^{234}\text{U}/^{238}\text{U}$) activity ratio broadly correlates with U concentration in both sets of differentially phase-extracted samples ($R^2 = 0.74$; Fig. 5b). The inclusion or exclusion of the clay-sized fraction is important to consider in future studies, as the estimated α -recoil loss factor of a bulk sediment sample will clearly be significantly controlled by the presence or absence of this size-fraction.

6.2. Calculated comminution ages and residence times of Cooper Creek sediments based on ‘reasonable’ assumptions for input parameters

As described in Section 2, determination of a meaningful calculated comminution age, and therefore sediment residence timescale, principally depends on uncertainty in the estimation of the recoil loss factor (f_α) and any uncertainty in the ($^{234}\text{U}/^{238}\text{U}$) of the starting material (A_0) (DePaolo

et al., 2006). Subtle variations in estimated f_α values have been shown to greatly affect inferences about physical weathering rates (Maher et al., 2006). Following the comminution methodology and numerical bounds of Eq. (2), with a set ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the source (A_0) and using the measured sample ($^{234}\text{U}/^{238}\text{U}$) ratios (A_{meas}), a minimum value for f_α is required to satisfy the comminution equation, which is defined as: $1 - A_{\text{meas}}$. Note that, for measured samples with ($^{234}\text{U}/^{238}\text{U}$) > 1 (GT2 and GT6 clay-included and GT6 clay-excluded samples), it is not possible to determine the minimum f_α theoretically, as the measured sample is required to have ($^{234}\text{U}/^{238}\text{U}$) < A_0 . The theoretical minimum f_α values for the Cooper Creek sediments are shown in Table 2 and Fig. 6a and b. In the following two sections, sample f_α values are calculated using input assumptions reflecting those in the present U isotope comminution literature.

6.2.1. Geometric calculation of f_α for Cooper Creek palaeochannel sediments

Table 2 shows the f_α values determined for Cooper Creek palaeochannel sediments using both the geometric weighted mean method (Eq. (3)) and surface area methods (Eqs. (4) and (5)) discussed above. For the geometric model, particle size distribution data is utilised but assumptions are required for the surface roughness factor (λ_s) and aspect ratio (β). The weighted geometric recoil loss factor was calculated for Cooper Creek palaeochannel sediments using two models, (a) assuming λ_s between 1 and 2, following DePaolo et al. (2006) and Dosseto et al. (2010) and (b) where λ_s varies between 1 and 17, the inferred range in surface roughness for the Kings River Fan sediments investigated by Lee et al. (2010). The surface roughness factor is taken to increase linearly with increasing grain diameter in both cases. The aspect ratio of grains, β , is also likely to vary in natural sediment samples, as demonstrated by the largely spherical to elongated grains in the SEM image of GT2 (Fig. 3). Linearly varying β values ranging from 1 to 10 were used in the geometric calculations of α -recoil loss factor, following DePaolo et al. (2006) and Dosseto et al. (2010), where a spherical grain represents $\beta = 1$ (largest grain) and an oblate spheroidal grain has $\beta > 1$ (smallest grain).

The α -recoil length, L , varies depending on grain mineralogy and is relatively poorly constrained at present. Current estimates lie between 20 and 40 nm in silicate minerals (see Maher et al., 2006 and references therein). The mineralogy of the Cooper Creek palaeochannel sediments has not been specifically determined and so an intermediate, theoretical value for feldspar (30 nm) (Ziegler et al., 1996) is used in this study following Maher et al. (2006), DePaolo et al. (2006) and Dosseto et al. (2010) and is similar to that used by Lee et al. (2010) ($L = 34$ nm).

As expected, the geometric calculations of f_α for both the clay-included and clay-excluded samples show that if a greater surface roughness is assumed (i.e., λ_s from 1 to 17 compared to 1–2), a larger amount of recoil loss is predicted (at least double) due to the increased surface area available (Table 2 and Fig. 6a and b). Using similar parameter range assumptions to previous authors (except for sample GT2

clay-excluded), the recoil factors produced using λ_s from 1 to 2 are lower than the minimum f_α required to solve the comminution equation. Weighted geometric model estimations of f_α produce values within the typical parameter range of f_α (0.01–0.1) given by Bourdon et al. (2009) but lie below the range of published f_α values for palaeochannel deposits from temperate Australia (grey stipple, y-axis Fig. 6) even for the clay-included samples.

6.2.2. Surface area measurement estimations of f_α for Cooper Creek palaeochannel sediments

Bulk sample surface area measurements by BET can also be used to calculate the α -recoil loss factors. However, BET gas adsorption based estimates can greatly overestimate f_α due to the significant difference between the size of adsorbant gas molecule and the α -recoil length (e.g., Maher et al., 2006). As discussed above, in principle it is possible to overcome this issue by considering a fractal recoil model (e.g., Semkow, 1991; Bourdon et al., 2009). Table 2 and Fig. 6b display the calculated α -recoil loss fraction for two samples (clay-excluded GT1 and GT6) for which there was sufficient post-leaching material available for BET surface area analysis. BET measurements were carried out on the same sample aliquots at two different laboratories (see analytical techniques and Table 2 footnote for details and results) to investigate the effect of inter-laboratory surface area variations on calculated f_α values. In agreement with previous findings (e.g., Bourdon et al., 2009), the data demonstrate clearly that if the BET data are used without the fractal amendment then much higher f_α values are obtained (e.g., $f_\alpha = 0.092$ and 0.008 for BET^a and BET_{fract}^a, respectively; Table 2). The observed inter-laboratory variations in BET measurements (Table 2 footnote) produce relatively variable f_α values (compare BET_{fract}^a with BET_{fract}^b). In comparison to the weighted geometric method, the BET_{fract} f_α values are closest in magnitude to those of the geometric (λ_s 1–2) model. However, the BET_{fract} values of f_α are also lower than the minimum f_α required to solve the comminution age equation (Fig. 6b).

In summary, it is shown that f_α of a sample can vary significantly depending on whether or not the clay fraction is removed, which model of f_α estimation is used and the input values assumed. Sample GT1, which has both weighted geometric and fractal corrected surface area estimations of f_α , shows that only the weighted geometric model (using 17 as the upper limit for surface roughness) lies above the minimum f_α value necessary to solve Eq. (2). This might suggest that, either the maximum assumed values of surface roughness for the Cooper sediments are too low, or alternatively, if we assume that the estimated recoil loss factor values are largely correct for each sample (e.g., for the BET_{fract} method), the inconsistencies between the f_α values and the theory of the comminution methodology (minimum f_α) may be explained by preferential loss of ^{234}U via leaching. In the latter case, preferential leaching of ^{234}U would lead to lower ($^{234}\text{U}/^{238}\text{U}$) ratios and therefore, higher minimum f_α values. Regarding the former scenario, it is indeed plausible that the surface roughness is larger than that assumed here, based on previous studies (up to a maximum of 17). White et al. (1996) calculated the surface roughness of the

Fig. 5. (a) $(^{234}\text{U}/^{238}\text{U})$ activity ratio versus deposition age and (b) U concentration (ppm) versus $(^{234}\text{U}/^{238}\text{U})$ activity ratio for Cooper Creek palaeochannel sediments. Clay Inc. is the 0–53 μm sequentially leached sediment fraction. Clay exc. is the clay removed, 2–53 μm sequentially leached sediment fraction. Grey arrows highlight the increase or decrease in $(^{234}\text{U}/^{238}\text{U})$ after removal of the clay fraction from the same sample.

silicate fraction of Californian soils and show surface roughness factors of up to >600 maybe appropriate. Table 2 shows the minimum surface roughness required (5–48) using the weighted geometric estimation of f_α to reach the theoretical minimum f_α value (assuming that the other parameters remain fixed as before). For the Cooper Creek sediments, and the presently available data, it is not possible to determine the relative importance of each option but clearly the role of chemical erosion versus physical erosion on the final $(^{234}\text{U}/^{238}\text{U})$ of a given particle requires further consideration, and tighter constraints on surface roughness are needed for each sample. White et al. (1996) also show that the surface roughness for the primary silicate component of the soil increases with soil age, a factor not presently

considered by the comminution methodology (i.e., changes in surface roughness with soil or deposit age).

6.2.3. Comminution age and sediment residence times of Cooper Creek palaeochannel sediments

Based on the ‘reasonable’ assumptions used for f_α estimation detailed above, the residence times of Cooper Creek palaeochannel sediments for clay-excluded and clay-included samples have been calculated using Eq. (2) and are presented in Table 3 and Fig. 7. Few realistic comminution ages (and sediment residence times) were produced from the clay-included samples (Table 3). α -Recoil factors constrained by BET surface area measurements (assuming $A_0 = 1$) produce either negative residence times or do not give a solution to the comminution age equation. However, arithmetically valid residence times for the clay-included sediments (geometric model with $\lambda_s = 1$ –17) lie between 423 and 620 ka. For the clay-excluded samples, more solutions were possible (Fig. 7) and sediment residence times range between 122 and 342 ka. Due to the wide range in age produced for the same sample depending on whether the clay-sized fraction is included or excluded (e.g., GT3 and GT4, Fig. 7), and also different relative patterns i.e., a decrease (clay-excluded) or increase (clay-included) in residence age for sediments deposited between ~100 and 35 ka, it is not possible to infer links between residence ages and geomorphologic processes in semi-arid Australia at this stage.

Within the context of the preceding discussion and due to the range of sample pre-treatment procedures, potential lab-dependent variations for surface area measurements (Table 2), the use of variable equipment to measure particle size distribution (e.g., sedigraph versus mastersizer) and variations in the assumptions involved to estimate sediment residence time, at present it is difficult to compare data sets produced by different research groups. Subsequently, in order to be able to directly compare the Cooper Creek palaeochannel sediment residence times with those for the Murrumbidgee River palaeochannel sediments in south-eastern Australia (the only other data set produced using the U-series comminution approach in Australia), the samples and data should be processed in the same way and comminution ages calculated using the same assumptions. The Murrumbidgee samples were sequentially leached using the same methodology as that described here and were analysed with the clay fraction included. The recoil loss fraction was calculated using the weighted geometric model with the assumption that $\lambda_s = 1$ –2, $\beta = 1$ –10. A_0 was assumed to be in secular equilibrium (i.e., equal to 1). However, the corresponding model for the Cooper Creek failed to produce comminution ages (Table 3) and therefore, it is not possible to make comparisons between residence times of temperate and semi-arid Australia.

6.3. Numerical estimation of comminution age uncertainties: Monte Carlo simulations

The comminution age error shown in Table 3 for the Cooper Creek sediments was calculated by propagating the error on the measured $(^{234}\text{U}/^{238}\text{U})$ ratio and including

Fig. 6. Geometric and surface area estimations of recoil loss factors (f_α) for (a) clay-included (0–53 μm fraction), and (b) clay-excluded (2–53 μm fraction) Cooper Creek palaeochannel sediments following methodologies described in the text and notation used in Table 2. 1–2 and 1–17 refer to the range in surface roughness used in the weighted geometric estimation of f_α . $1-A_{\text{meas}}$ represents the minimum value of f_α required for the comminution age equation to be solved (see Section 6.2). Bars on the y-axis exemplify published ranges in recoil loss factor for: Murrumbidgee River palaeochannel sediments, southeast Australia (0–53 μm fraction) of Dosseto et al. (2010) (light grey stippled bar) and the unleached coarse silt 45–60 μm fraction of fluvial sediments from Hanford, Washington, USA (Maher et al., 2006; DePaolo et al., 2006) (dark grey solid bar).

a 16% uncertainty estimation for f_α (Table 3 footnote, after Dosseto et al., 2010). However, the true uncertainty on the comminution age, based on reasonable ranges of assumed input parameters, has yet to be fully constrained and is likely to be larger than that quoted for the Cooper Creek samples. In the following section, we present the results

from a series of Monte Carlo simulations, carried out to estimate the uncertainty upon comminution age related to each individual input parameter in the calculation of f_α (weighted geometric and BET surface area measurement with fractal correction methods). The combined uncertainties for each f_α calculation method were then estimated, along with a total combined estimation of comminution age uncertainty based on the combined uncertainties of f_α , A_0 and A_{meas} .

6.3.1. Uncertainties associated with the weighted geometric determination of f_α

Due to the limitations of the Cooper Creek sediment samples in producing f_α values high enough to solve the comminution equation, uncertainty estimations were carried out using a synthetic sample for which a grain size distribution and reference comminution age (572 ka) were generated. The considered ranges of input parameters used in the Monte Carlo simulations are given in Table 4. Uncertainties were then estimated based on the probability distributions obtained from the Monte Carlo simulations. We adopt the 95% confidence limit of these distributions as a measure of total uncertainty. Full details of this procedure are given in Appendix A.

In the first set of simulations, the input parameters of surface roughness (λ_s), aspect ratio (β) and α -recoil length (L) were assigned small individual uncertainties of 1% (i.e., $\pm 0.5\%$ of the values used to generate the reference age), keeping A_0 and A_{meas} fixed at 1 and 0.975, respectively (Appendix A). The results show that if the input parameters L , λ_s and β are known within 1% of their true values, the uncertainty on the calculated comminution reference age of 572 ka is ± 14 ka (at the 95% confidence limit; Fig. 8). It is highly likely that the uncertainty on each assumed input parameter is presently greater than 1%. Therefore, the uncertainty on the reference comminution age has also been calculated for each individual parameter based on what we consider to be a feasible uncertainty (or range) for each parameter. All other parameters in the simulation were fixed at the initial values (Appendix A).

Surface roughness (λ_s) is assumed to vary linearly with grain diameter. However, there is significant uncertainty on the appropriate limits of surface roughness (Sections 6.2.1 and 6.2.2). While a value of 1 (smooth surface) is commonly assigned to the smallest grains, values for the largest grains vary between 2 and 17 in the U-series comminution literature (Dosseto et al., 2010 and Lee et al., 2010, respectively). Here we explored a range of 7–30 for the largest grains; this range is considered to represent a reasonable uncertainty on this parameter considering silicate surface roughness values of up to 600 may be possible (White et al., 1996; Section 6.2.2). Monte Carlo simulations ran with this choice of λ_s produced a large range in t_{com} , between 169 and 801 ka, resulting in a significant uncertainty of ± 316 ka. It was not possible to use a range of 1–2 as the lower limit of λ_s in our model (cf. DePaolo et al., 2006; Dosseto et al., 2010) as this produced f_α values below the minimum f_α limits of the equation and therefore, could not produce solutions based on the chosen combination of other input parameters values and ($^{234}\text{U}/^{238}\text{U}$) ratios used.

As for surface roughness, the aspect ratio (β) is typically modelled as a linear function of grain diameter, with the largest value (ellipsoidal grains) assigned to the smallest grains and a value of 1 (spherical grains) assigned to the largest grains in the sample. Based on previous studies that assume a value of 10 for the smallest grains (e.g., Dosseto et al., 2010), we allowed β of the smallest grains to vary between 9 and 12 in our Monte Carlo analysis. Results from these simulations produced t_{com} ages of 393–733 ka at the 95% confidence level and therefore, an uncertainty of ± 170 ka in the comminution age.

As noted in Section 6.2.1, the α -recoil lengths for individual minerals are relatively poorly constrained at present (Maher et al., 2006). Assumed values lie in the range of 30 nm (Maher et al., 2006; DePaolo et al., 2006; Dosseto et al., 2010) to 34 nm (Lee et al., 2010). Therefore an uncertainty of 30 ± 2 nm was used in the Monte Carlo simulations. This produced a range of t_{com} between 492 and 678 ka and an uncertainty of ± 93 ka (Table 4).

Using the combined uncertainties of λ_s , β , and L in a Monte Carlo simulation, a significant uncertainty of ± 283 ka (at a confidence level of 95%) is obtained for the comminution age. The corresponding f_α values produced for the total combined uncertainty range from 0.025 to 0.083 (Table 4).

6.3.2. Uncertainties associated with the BET and fractal dimension determination of f_α

Similarly, in order to explore the uncertainty associated with the BET surface area with fractal correction f_α method, it is necessary to first generate a model comminution age. The input assumptions used in the determination of a synthetic age are detailed in Appendix A (Step 2). Using

Fig. 7. Sediment residence time versus deposition age for clay-included and clay-excluded Cooper Creek palaeochannel sediments. Comminution age was calculated using Eq. (2) for the f_α values given in Table 2. 1–2 and 1–17 refer to the range in surface roughness used in the weighted geometric estimation of f_α . The residence time of the sediment (T_{res}) within the Lake Eyre Basin, prior to final deposition, was determined by subtracting the depositional age (t_{dep}) (given by the OSL data of Cohen et al., 2010) from the comminution age (Fig. 1; Eq. (1)). The deposition age error is taken from Cohen et al. (2010). Errors on sediment residence times are analytical uncertainties at the 2σ level calculated by propagation of the error on the measured sample ($^{234}\text{U}/^{238}\text{U}$) and an assumed relative error of 16% on the recoil loss fraction (following Dosseto et al., 2010).

Table 3

Calculated Cooper Creek palaeochannel sediment comminution ages and corresponding residence timescales, T_{res} (ka) using f_α values from Table 2.

	Sample	t_{com}				T_{res}			
		Geometric (λ_s 1–2)	Error	Geometric (λ_s 1–17)	Error	Geometric (λ_s 1–2)	Error	Geometric (λ_s 1–17)	Error
Clay-included	GT1	Fail		Fail		Fail		Fail	
	GT2	n.p.		n.p.		n.p.		n.p.	
	GT3	Fail		525	85.3	Fail		423	68.8
	GT4	Fail		655	107	Fail		620	101
	GT5	Fail		Fail		Fail		Fail	
	GT6	n.p.		n.p.		n.p.		n.p.	
Clay-excluded	GT1	Fail		279	45.1	Fail		161	26.0
	GT2	138	22.3	31.3	5.05	19.1	3.09	–88	14.2
	GT3	Fail		253	40.9	Fail		151	24.4
	GT4	Fail		157	25.4	Fail		122	19.7
	GT5	Fail		364	59.0	Fail		342	55.4
	GT6	n.p.		n.p.		n.p.		n.p.	

T_{res} (sediment residence time) is calculated using the f_α values given in Table 2 and Eqs. (1) and (2) in the text.

n.p. It is not possible to derive T_{res} as the measured ($^{234}\text{U}/^{238}\text{U}$) activity ratio is greater than the corresponding A_0 ($^{234}\text{U}/^{238}\text{U}$) ratio.

Fail, model failed to solve the comminution age equation due to the associated f_α value being less than $1-A_{\text{meas}}$ (see Section 6.2).

All T_{res} calculated using BET surface area estimations of f_α gave either negative sediment residence timescales or were not solvable (therefore, they are not shown).

Errors are the analytical uncertainties at the 2σ level calculated by propagation of the error on ($^{234}\text{U}/^{238}\text{U}$) and the recoil fraction (16%) following Dosseto et al. (2010).

the input parameter values given, a reference comminution age of 404 ka was obtained. This age is not identical to that generated by the weighted geometric method due to the different input parameters involved (e.g., bulk density, fractal dimension and the diameter of the adsorbant gas molecule in the BET surface area (fractal) method as opposed to surface roughness and aspect ratio as input parameters in the weighted geometric method). The combination and range of input parameter values required therefore resulted in slightly different initial ages being generated.

Using the same approach as above, the assumed input parameters of the method (Eq. (5)): total surface area (BET_{tot}), fractal dimension (D), density (ρ) and α -recoil length scale (L) were varied by 1% in a Monte Carlo simulation, i.e., $\pm 0.5\%$ of the initial values used to generate the reference age (Appendix A). This resulted in a small range in comminution age of 401–407 ka and therefore, a small uncertainty of ± 3 ka. The uncertainty of each individual parameter was then assessed in turn using the parameter ranges specified in Table 4.

Inter-laboratory variations in BET surface area measurements for the same Cooper Creek sample are highlighted in Table 2 (footnote); therefore, an uncertainty of ± 2 m²/g was assigned to the initial surface area of 8 m²/g. This yielded a maximum uncertainty of ± 118 ka associated with the reference model age of 404 ka. If a more conservative uncertainty of ± 0.7 –1 is considered (e.g., the uncertainty given by Bourdon et al., 2009 for BET soil and rock surface area measurements between 8 and 12 m²/g), the associated t_{com} uncertainty decreases to $\sim \pm 80$ ka (not shown).

The uncertainty explored for D , the fractal dimension, was determined using a conservative estimate based on the inter-laboratory variation observed in this parameter for the Cooper Creek samples (Table 2, footnote). Using a range in D from 2.45 to 2.55 (± 0.05 of the initial value), the simulations produced a t_{com} ranging from 310 to 540 ka, equivalent to an associated uncertainty of ± 115 ka.

Varying the average bulk density, ρ , from 2700 kg/m³ (Bourdon et al., 2009; Dosseto et al., 2010) to 2670 kg/m³ (a value typically assumed for upper crust materials in Bouguer gravity corrections) produced little uncertainty on the modelled comminution age (± 4 ka, Table 4). Therefore, while a representative sample density should be used, reasonable variation in the assumed value has little impact upon the comminution age uncertainty relative to the other input assumptions.

The length scale of α -recoil, L , was assigned the same uncertainty to that used in the weighted geometric model (28–32 nm, see above). This produced an uncertainty of ± 24 ka in the computed t_{com} , significantly smaller than that obtained for the geometric model (± 93 ka; Table 4). This is not surprising, however, given the larger uncertainties associated with the individual parameters in the weighted geometric model.

6.3.3. Uncertainties associated with variations in the source rock U isotope ratio

The majority of the bedrock exposed within the Lake Eyre Basin is significantly older 1 Ma and therefore, it

should be safe to assume that, prior to the onset of physical weathering, the ($^{234}\text{U}/^{238}\text{U}$) of the source rock (A_0) is in secular equilibrium. However, as noted in Section 2.2.1, fine-grained sediments within sedimentary rocks may be held in a steady state of ^{238}U – ^{234}U disequilibrium (Fig. 2a) or the source rock may have experienced preferential loss of ^{234}U prior to physical erosion (e.g., by leaching of ^{234}U from recoil damaged sites), in which case, the ($^{234}\text{U}/^{238}\text{U}$) of the source rock may be less than unity. If, for example, the ($^{234}\text{U}/^{238}\text{U}$) ratio of the source is unknown, but lies between 0.98 and secular equilibrium (1.00), this produces an uncertainty of ± 178 ka (Table 4) using the weighted geometric model. In the situation that source activity ratios of greater than 1 are also possible (e.g., due to the implantation of ^{234}Th without subsequent leaching of ^{234}U from the damaged site), for example, up to 1.02, this translates to greater relative uncertainty of ± 265 ka (not shown). For the surface area method if A_0 is unconstrained and lies between 0.98 and 1, this produces an expected similar uncertainty of ± 136 ka (Table 4) in comminution age.

6.3.4. Total combined uncertainties in comminution age

To calculate a total combined uncertainty, which includes not only the uncertainty associated with f_α estimation, but also the uncertainty associated with the source (A_0) and measured sample (A_{meas}) ($^{234}\text{U}/^{238}\text{U}$) activity ratios, Monte Carlo simulations were performed for both the weighted geometric and BET surface measurement (with fractal correction) approaches using the ranges of input variables detailed in Table 4. In both simulations, A_0 was taken to range from 0.98 to 1 (as above) and the uncertainty assigned to A_{meas} was $\pm 3\%$ (0.972–0.978) on the synthetic measured ($^{234}\text{U}/^{238}\text{U}$) ratio (0.975). For the weighted geometric model, the simulation produced a combined uncertainty of ± 278 ka and the surface area measurement method produced an uncertainty of ± 224 ka. These uncertainties of approximately $\pm 50\%$ of the true ages are clearly non-trivial and while it may be argued that some of the parameters have smaller uncertainties than those used here (e.g., BET surface area measurements), the majority of input assumptions remain relatively poorly constrained at present (e.g., sample dependent L value) and in some cases our ranges may be perceived as conservative.

6.4. Approach for the comparison of comminution ages from different studies

With a wide variety of pre-treatment procedures and recoil loss factor estimation methods (including discrepancies between studies in assumed input parameter values) already published in the relatively limited U-series comminution dating literature, it is desirable to standardise procedures for future studies to be able to directly compare estimated comminution ages from different studies or research groups.

First of all, a consensus is required on the best pre-treatment procedure for the removal of unwanted secondary phases and on whether the clay-sized fraction should or should not be removed as part of the pre-treatment procedure. Our study clearly shows the significant differences in

Table 4

The input parameter values and uncertainty estimations of Monte Carlo simulations.

Parameter	Range considered		Range in t_{com} (ka)		Uncertainty on t_{com} ($\pm$ ka)	Associated f_{α} range		Solutions (out of 25,000)
	Low	High	Low	High		Lowest	Highest	
<i>Weighted geometric method</i>								
Surface roughness, λ_{s}	1–7	1–30	169	801	316	0.026	0.066	All
Aspect ratio, β	1–9	1–12	393	733	170	0.028	0.037	All
Length of α -recoil, L (nm)	28	32	492	678	93	0.029	0.033	All
Source rock ($^{234}\text{U}/^{238}\text{U}$), A_0	0.98	1	209	564	178	0.031	0.031	All
1% uncertainty (λ_{s} , β , L)			555	582	14	0.031	0.032	All
Combined f_{α} uncertainty			126	692	283	0.025	0.083	24,843
Combined t_{com} uncertainty			17	572	278	0.023	0.083	24,754
<i>Surface area (fract.) method</i>								
Fractal dimension, D	2.45	2.55	310	540	115	0.031	0.043	All
Total surface area, BET_{tot}	8	12	253	488	118	0.033	0.049	All
Density, ρ (kg/m ³)	2670	2700	396	404	4	0.037	0.037	All
Length of α -recoil, L (nm)	28	32	381	429	24	0.034	0.040	All
Source rock ($^{234}\text{U}/^{238}\text{U}$), A_0	0.98	1	126	397	136	0.037	0.037	All
1% uncertainty (D , BET_{tot} , ρ , L)			401	407	3	0.037	0.037	All
Combined f_{α} uncertainty			197	554	179	0.028	0.059	All
Combined t_{com} uncertainty			25	472	224	0.028	0.059	All

Parameter ranges shown are those used in the estimation of the individual parameter uncertainties in comminution age (see Section 6.3 and Appendix A for more details).

Quoted t_{com} ranges show the t_{com} distribution produced by the simulation at 95% confidence limit.

The uncertainty in t_{com} equates to half of the calculated range in t_{com} .

For the surface area models, the diameter of the adsorbant nitrogen gas molecule (a) for BET analysis (0.35 nm) and the ^{234}U decay constant (λ_{234} : 2.82629×10^{-6} , Bourdon et al., 2003) are considered constant.

1% uncertainty models were carried out by varying the input parameters shown in parenthesis by $\pm 0.5\%$ of the initial value used in the calculation of the reference model ages (572 ka and 404 ka for the weighted geometric and surface area estimations of f_{α} , respectively).

Models for the estimation of combined f_{α} uncertainties in t_{com} use the individual parameter ranges given in the table.

Models for the estimation of combined t_{com} uncertainties use the individual parameter ranges given in the table, including that given for A_0 and an assumed uncertainty of $\pm 3\%$ in A_{meas} (0.972–0.978). See Appendix A and Section 6.3 for further details.

Where the number of accepted simulations are less than the total ran (25,000) some of the random models produced f_{α} values below the minimum f_{α} required to arithmetically solve the comminution equation (see the text for further details).

comminution age produced depending on whether the clay-sized grain fraction is removed or not. To determine the most suitable sequential extraction method a detailed study is required to compare presently published sequential phase extraction methods, their efficiency of unwanted phase removal and to assess any modification to U concentration and, in particular, ($^{234}\text{U}/^{238}\text{U}$) activity ratio for a range of sediment types (glacial, fluvial and aeolian origin) which may have different secondary phase coatings. The sediment size-fraction(s) for which U-series studies are carried out on should also be standardised to assist comparison between data sets.

The next step required is to use the same estimation method for the recoil loss factor. In the comparison of the weighted geometric and BET surface area (fractal) methods in this study (1% uncertainty model, Table 4), the BET surface area (fractal) method carries slightly less uncertainty and therefore, we recommend this option as the preferred method of recoil loss factor determination. However, it would be useful to extend the Monte Carlo approach taken here to include an assessment of the uncertainty in alternative recoil loss factor calculation methods (see Maher et al., 2006; Lee et al., 2010 for summaries of potential f_{α} estimation models). The same assumptions

(between studies) for any unknown input parameter values and their ranges are also required. Our suggested assumptions for unknown input parameter values are given in Table 5. We do not imply that the input values given and the surface area (fractal) model for f_{α} estimation provide the least uncertain approach, but rather that it will facilitate comparison of data from separate studies, which is not the case at present.

7. SUMMARY AND CONCLUSIONS

The comminution approach for the calculation of sediment residence timescales was investigated using U isotope measurements of the fine-grained fraction of sandy palaeo-channel sediments from semi-arid Australia. The comminution age is shown to be highly dependent on the estimated fraction of ^{234}Th lost from the grain via α -recoil, which is in turn dependent on the chosen method of f_{α} estimation and the inherent parameter assumptions (e.g., surface roughness factor and grain aspect ratio). In several cases, the selected parameter values (based upon similar assumptions used in the literature) failed to produce high enough recoil loss factors for Cooper Creek sediments to allow valid solutions to the comminution equation.

Fig. 8. Example output from a Monte Carlo simulation (see Section 6.3 and Appendix A for further details on the model details). (a) Histogram of the comminution ages (valid comminution ages allowed by the assigned ranges in input parameters) obtained from 25,000 random models. (b) Cumulative frequency of comminution age in (a). The age range within the 95% confidence limit can be taken as a first-order measure of the uncertainty in the computed comminution age. The solution shown is for an uncertainty of $\pm 0.5\%$ in the initial input parameters used in the calculation of the reference model age (572 ka) for: surface roughness (λ_s) aspect ratio (β) and α -recoil length (L), using the weighted geometric model (with fixed source and sample $^{234}\text{U}/^{238}\text{U}$ ratios). The results show that if the input parameters L , λ_s and β are known within 1% of their true values, the uncertainty on the calculated comminution reference age of 572 ka is ± 14 ka, or $\pm 2.4\%$ (at the 95% confidence limit).

Monte Carlo simulations were carried out using a synthetic sample to investigate the uncertainty in comminution age attached to each individual input parameter, as well as to determine a combined uncertainty estimation for each recoil loss estimation model, incorporating uncertainties in the source rock and measured sample ($^{234}\text{U}/^{238}\text{U}$) ratios. Using realistic ranges of input values, the total combined uncertainty in comminution age can amount to

± 220 – 280 ka. Much smaller uncertainties for the weighted geometric and surface area measurement (with fractal correction) methods are attained (± 14 and ± 3 ka, respectively) if the input parameters incorporated in the recoil loss factor models are known within 1% and there is no associated uncertainty in the source rock and measured sample ($^{234}\text{U}/^{238}\text{U}$) ratios. However, attaining such low uncertainties in the characterisation of the input parameters will be challenging. The BET surface area (fractal) estimation carries slightly less uncertainty in the determination of recoil loss factor (based upon a 1% uncertainty input parameter model), compared to the weighted geometric estimation of recoil loss factor.

Standardisation of pre-treatment procedures and f_α estimation method is required before the comminution ages and sediment residence times yielded in separate studies can be compared. A suggestion for generic assumed input parameter values for such a comparison are given here. The potential for preferential leaching of ^{234}U (relative to ^{238}U) during the pre-treatment leaching procedure should also be examined in future studies to assess the reliability of the leaching approach.

Clearly, the comminution technique affords great potential to determine the formation age of sediments providing that the present uncertainty of input parameters can be reduced, which should be a major goal for researchers in this field. Future directions include the measurement of U isotopes in catchment-representative source rocks, particularly where fine-grained sedimentary rocks (e.g., mudstones and siltstones) or fractured rocks dominate. This is required to confirm the assumed secular equilibrium value of this input parameter and place tighter constraint on the ($^{234}\text{U}/^{238}\text{U}$) variability of the source. Additional consideration of complicating factors such as whether the clay-sized fraction should be included or removed during sample pre-treatment, the effects of pre-treatment leaching on sample ($^{234}\text{U}/^{238}\text{U}$) activity ratios, the addition of dust and control of zircon are also required before the absolute comminution ages can be considered meaningful.

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Table 5

Suggested input parameter values to permit comparison between U-series comminution age studies.

Parameter	Suggested value	Comment
<i>Weighted geometric method (Eq. (3))</i>		
Surface roughness, λ_s	1–10	Assuming a linear increase from the smallest to the largest grain
Aspect ratio, β	10–1	Assuming a linear decrease from the smallest to the largest grain
Length of α -recoil, L (nm)	30	Theoretical value for feldspar (Ziegler et al., 1996)
^{234}U decay constant, λ_{234}	$2.82629 \times 10^{-6} \text{ yr}^{-1}$	After Bourdon et al. (2003)
Source rock ($^{234}\text{U}/^{238}\text{U}$), A_0	1	Assuming no source rock disequilibrium
Measured ($^{234}\text{U}/^{238}\text{U}$), A_{meas}	As measured	
<i>Surface area (fract.) method (Eq. (5))</i>		
Fractal dimension, D	As determined	Following Bourdon et al. (2009)
Total surface area, BET_{tot}	As measured	
Density, ρ (kg/m^3)	2670	Upper crust value used for Bouguer gravity corrections
N_2 adsorbate gas molecule diameter (nm)	0.35	
Length of α -recoil, L (nm)	30	Theoretical value for feldspar (Ziegler et al., 1996)
λ_{234}	$2.82629 \times 10^{-6} \text{ yr}^{-1}$	After Bourdon et al. (2003)
Source rock ($^{234}\text{U}/^{238}\text{U}$), A_0	1	Assuming no source rock disequilibrium
Measured ($^{234}\text{U}/^{238}\text{U}$), A_{meas}	As measured	

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2012.10.047>.

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