Considerations for U-series dating of sediments: insights from the Flinders Ranges, South Australia

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Keywords

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Considerations for U-series dating of sediments: insights from the Flinders Ranges, South Australia

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Abstract

Uranium isotope ratios have been determined for the fine-grained detrital fraction of Pleistocene Wilkawillina valley-fill sediments, four local Proterozoic bedrock samples and fine-grained aeolian material from a sand dune deposit of the Flinders Ranges, South Australia. The aim was to quantify the comminution age, i.e. the time elapsed since physical weathering of the bedrock, and residence time of the valley-fill sediments and to place tighter constraints on input parameters for the comminution age calculation. Despite using two independent approaches for determination of the recoil lost fraction of ^{234}U from the sediment (weighted geometric and surface area estimates), samples fail to produce realistic comminution ages and hence, residence times. The issues involved in the ability to determine sediment comminution ages are discussed. The $(^{234}U/^{238}U)$ activity ratio of the local bedrock is not in secular equilibrium, despite the bedrock being much older than 1 Ma, i.e. the timeframe for ^{234}U and ^{238}U to reach secular equilibrium in a closed system. Using the average Flinders Ranges bedrock $(^{234}U/^{238}U)$ ratio instead of an assumed $(^{234}U/^{238}U)$ activity ratio of unity for the source would significantly reduce calculated residence times. This result warrants concern for future studies using the comminution approach for which a secular equilibrium source $(^{234}U/^{238}U)$ activity ratio is assumed. Significant input of aeolian material may modify the measured $(^{234}U/^{238}U)$ activity ratios. Such input may be more tightly constrained in future studies using rare earth element and radiogenic isotopic data. Future comminution studies would benefit from further consideration of the importance of 1) leaching lost ^{234}U from source rock and bulk sediment samples, 2) wind deposition of fine-grained material and 3) the appropriateness and robustness of sample pre-treatment procedures.

Keywords: uranium isotopes; timescale; sediment transport; Flinders Ranges

1. Introduction

In order to quantify how fast a landscape responds to tectonic, climatic and human factors, accurate weathering rates and soil and/or sediment ages are required. The uranium-series (U-series) isotopes are a valuable tool for deriving the timescales of weathering and erosion processes (e.g., Plater et al., 1992; Scott et al., 1992; Vigier et al., 2001; Dequincey et al., 2002; Chabaux et al., 2003; Granet et al., 2007; Dosseto et al., 2008a; Dosseto et al., 2008b; Chabaux et al., 2008; Vigier and Bourdon, 2011). Recently, DePaolo et al. (2006) developed a method for dating the formation age of fine-grained sediments, in other words, the time elapsed to present day since physical weathering of source rock to a threshold grain size (≤ ~50 μm), termed the '*comminution age*' (DePaolo et al., 2006; Lee et al., 2010; Dosseto et al., 2010; Handley et al., in press). The comminution dating approach utilises ^{234}U-^{238}U disequilibrium in fine-grained sediments attributed to recoil loss of ^{234}U

(see Section 2 for details). U-series recoil-loss dating has yielded reasonable timescale estimates when compared to independently constrained ages (e.g., Aciego et al., 2011), but can be offset by several 100 ka (Lee et al., 2010). Therefore, further testing and consideration of the methodology is required to improve the accuracy of ages produced and prove its value as a dating technique.

Here we present a comminution study on Pleistocene alluvial deposits in the Flinders Ranges, South Australia. The uranium isotopes of local Proterozoic bedrock samples have also been determined to test whether the source material is in (^{234}U/^{238}U) secular equilibrium prior to the onset of physical weathering. We also constrain the potential (^{234}U/^{238}U) activity ratio of local aeolian material to examine the influence of external inputs on sediment residence time. We show that the bedrock samples have significant ^{234}U-^{238}U disequilibria. This has major implications for the comminution approach and the general assumption that the comminution chronometer does not start until the commencement of physical weathering of bedrock. We suggest that this is due to the preferential removal of ^{234}U from the source material via leaching from recoil-damaged sites.

2. Comminution age theory

The energy associated with the alpha decay of ^{238}U (half-life, $t_{1/2}$, = 4.5 Ga) to ^{234}Th ($t_{1/2}$ = 24 days) results in the recoil (physical displacement) of the daughter ^{234}Th nuclide from the initial parent location within a mineral. This recoil distance varies depending on mineralogy but is estimated to range between 20 and 50 nm in common silicate minerals (see Maher et al., 2006 and references therein). ^{234}Th then decays to ^{234}U ($t_{1/2}$ = 245 ka) via the intermediate ^{234}Pa nuclide ($t_{1/2}$ = 7 hours). If recoil takes place within recoil-length distance of the grain edge then ^{234}Th may be physically ejected from the grain. In large grains (sand-size and larger) the recoil loss of ^{234}Th (hence ^{234}U) is insignificant due to the large volume to surface ratio of the grains. However in fine-grained material (~ 50 µm or less) the recoil loss of ^{234}Th creates a measurable disequilibrium between the parent, ^{238}U, and 'great-granddaughter', ^{234}U, nuclides, i.e. (^{234}U/^{238}U) ratios < 1 (where the parenthesis denotes an activity ratio). In comminution age theory, the magnitude of ^{238}U-^{234}U disequilibrium in fine-grained sediment is therefore related to the timescale of radioactive decay and proportion of recoil loss of ^{234}Th. A detailed description of the U-series comminution theory and methodology can be found in DePaolo et al. (2006) and Lee et al. (2010). The calculated comminution age of sediment is defined as the period of time elapsed since weathering of bedrock into fine-grained material to present day (Fig. 1). This includes the time a grain has spent in temporary storage e.g., in soils and floodplains and in transport prior to final deposition. To quantify the length of time that the sediment has resided in the catchment since mechanical weathering, prior to final deposition (T_{res}) (Fig. 1), the U-series comminution equation of DePaolo et al. (2006) can be utilised:

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

where λ_{234} is the ^{234}U decay constant (2.82629 x 10^{-6} a^{-1}; using $t_{1/2(234U)}$ of 245,250 a, Bourdon et al., 2003), A_{meas} is the measured (^{234}U/^{238}U) 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 from the grain, and A_0 is the initial (^{234}U/^{238}U) of the source rock. The sediment residence, or transport time (T_{res}), can then be calculated if the deposition age (t_{dep}) of the sediment is known, by simply subtracting the deposition age from the comminution age (Fig. 1).

Previous authors (DePaolo et al., 2006, Lee et al., 2010, Handley et al., in press) have shown that comminution ages are highly dependant on the value used for the recoil lost fraction (f_α). Estimates of f_α can be produced using a number of different methods (see Maher et al., 2006 and Lee et al., 2010 for summaries of the different approaches). The most commonly employed methods are at present based upon either a weighted geometric estimation (DePaolo et al., 2006) using sample grain size distributions and assumptions for surface roughness and grain aspect ratio, or measurements of specific surface area (e.g., Brunauer-Emmett-Teller (BET) gas adsorption measurements) with an incorporated fractal correction (Semkow, 1991; Bourdon et al., 2009; Aciego et al., 2011) to account for the significant difference between the size of the adsorbed gas molecule (commonly N_2: 0.354 nm) and the recoil length scale (~20-50 nm; Hashimoto et al., 1985; Ziegler, 1996) (see the appendix for f_α calculation equations and input parameter details). As pointed out by previous authors of the few comminution studies undertaken so far (e.g., DePaolo et al., 2006; Lee et al., 2010; Handley et al., in press) the technique holds significant potential, but much more work is required before it can be considered as an accurate dating tool.

3. Study area

The Flinders Ranges of South Australia (Fig. 2a) are a series of north-south striking ridges of folded, uplifted and dissected, largely sedimentary, Proterozoic and Cambrian rocks (Preiss, 1987). The relatively softer siltstones and shales have been eroded to form valleys and lower elevation rounded hills, while the more weathering-resistant quartzites and sandstones form prominent ridges and peaks as well as a small number of largely enclosed draining basins such as Wilpena Pound and Wilson's Pound (Fig. 2a). The ranges are flanked by several low elevation, internally draining playa lakes such as Lake Torrens, Lake Frome and Lake Callabona (e.g., Fig. 2a) that act as sediment sinks for eroded, fluvial material from the Flinders Ranges. The ranges are one of the most tectonically active regions of Australia and a significant proportion of the present day relief above the piedmont surface (up to 600-1000 m) is attributed to late Miocene to Recent tectonic uplift (e.g., Sandiford, 2003; Quigley et al., 2006). ^{10}Be cosmogenic isotope studies at sites in the Flinders

Ranges suggest that the present relief between valley floors and range summits may have been generated in as little as approximately 4 Ma (Quigley, et al. 2007a). The present day climate is arid to semi-arid with mean annual precipitation between < 200 mm (east and far north) to > 400 mm (range ridges) and annual evaporation exceeding 2000 mm.

Significant (up to 18 m thick) Late Pleistocene silt- and clay-rich valley fill deposits, now heavily incised, are documented in both the western and eastern draining catchments of the Flinders Ranges (e.g., Williams et al., 2001; Williams and Nitschke, 2005; Haberlah et al., 2010a; 2010b). Such fine-grained fluvial deposits are not accumulating today. The deposits were initially considered to be lake sediments (Cock et al., 1999) but are more recently described as slope wash deposits, dominated by aeolian sourced-material accumulated in either a 'fluvial wetland' or resulting from flood events (Williams et al., 2001; Haberlah et al., 2010a; 2010b; Haberlah and McTainsh, 2011). Some individual beds, only a few centimetres thick, can be traced for over a 100 m (Williams et al., 2001). The aeolian material is thought to be sourced predominantly from Lake Torrens to the west of the Flinders Ranges (Fig. 2a; Williams and Nitschke, 2005). This lake remained dry to ephemeral during the Quaternary and has accumulated more than 300 m of sediment since the Eocene (Williams and Nitschke, 2005). Based on the prominence of a dated travertine structure, which lies above the present playa surface, the floor of Lake Torrens is inferred to have been lowered by ~ 2.5 m by wind erosion during the last glacial (Schmid, 1990). The elevated Flinders Ranges act as a dust trap for wind-blown sediment travelling eastwards across the continent (Bowler, 1976; Hesse and McTainsh, 2003). Discontinuous shallow mantles of red-brown very fine sandy or silty clay, that outcrop on the summits and ridges of the Flinders Ranges (irrespective of the underlying lithology), are remnants of past dust activity (Nitschke, 2002; Williams and Nitschke, 2005). The Flinders Ranges themselves are a major source of sediment for Lake Torrens (Williams and Nitschke, 2005). The upper 75 m of the lake comprise sediments of Quaternary age (Schmid, 1985; 1989). The dominance of young, Flinders Rangers derived sediment in Lake Torrens is supported by moderate to high [10]Be *in situ* bedrock erosion rate estimates (5-123 m Ma[-1]) determined by Quigley et al. (2007b) for summit surfaces, hill slope crests, hill slopes and stream bottoms in the central Flinders Ranges. Slightly further north, around the gorges of Brachina and Parachilna Creeks, *in situ* [10]Be measurements on quartzite and sandstone bedrock indicate erosion rates of 2-11 m Ma[-1] and 7-22 m Ma[-1], respectively (Heimsath et al., 2010).

4. Sample details

Valley-fill sediments (samples WL07-FPa-f), within the Wilkawillina catchment on the eastern side of the Flinders Ranges (Fig. 2b), were collected at the same sampling points as samples taken by Haberlah et al. (2010a), for which optically stimulated luminescence (OSL) and accelerator mass

spectrometer (AMS) charcoal deposition ages have been previously determined (profile WL07-FP of Haberlah et al., 2010a). The deposition ages of these sediments range from 17.1 ± 1.6 ka to 45.5 ± 3.9 ka (Fig. 1b). The ~15 m WL07-FP section is located at the downstream end of the largest interfluve of the Wilkawillina floodplain and is fully described in Haberlah et al. (2010a). Fine-grained silts with intermittent gravel bands/lenses and infrequent sand sheets dominate the section.

In order to be able to place tighter constraints on the $(^{234}U/^{238}U)$ activity ratio of the source rocks, four Proterozoic Flinders Ranges bedrock samples were collected (Fig. 1a): two fine-grained sedimentary rocks (BRA-SS1 and GS-S1) and two quartzites (HK-Q1 and WP-Q1). WP-Q1 was taken from the prominent quartzite ridge of Wilson's Pound (Fig. 1a), a relatively enclosed drainage basin featuring a small, dry lakebed. A sand dune sample from within Wilson's Pound (WP-DS1), just to northeast of the dry lakebed was also sampled on the premise that the fine material within the sand dune deposit may represent the in-blown dust component, which is distinguishable from the weathering products of quartzite.

5. Methods and analytical techniques

Prior to sampling the valley-fill deposits, approximately 5-10 cm of the exposed profile surface was scraped away to ensure that 'fresh' material was collected. Half of the sediment collected (~500 g to 1 kg in total per sample) was dry sieved at 500 μm and 200 μm and then wet-sieved at 53 μm using deionised water. Approximately 4 g of the retained and dried < 53 μm fraction then 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). Removal of the clay-sized (< 2 μm) fraction was then carried out by controlled centrifugation, following the United States Geological Survey centrifugation method (Open-File Report 01-041). Full details of the extraction procedure are given in the appendix. 56-64 % of initial pre-sequentially processed sample weight was lost during the procedure, most visibly during removal of the < 2 μm size fraction.

The sand dune (aeolian) sample was dry sieved at 500 μm and 200 μm and then wet-sieved at 53 μm using deionised water. Approximately 4 g of the retained and dried 0-53 μm fraction was ashed at 550 °C for 8 hours to remove organic material prior to sample digestion.

The bedrock samples (~1.5 kg of material per sample) were sawn to remove any visibly weathered edges and then approximately a third of the sample was crushed and then milled to a fine powder using an agate rotary ball mill.

Uranium elemental concentrations and $(^{234}U/^{238}U)$ activity ratios were determined on the post-leached valley-fill 2-53 μm fraction, ashed 'aeolian' sample and bedrock samples using the procedure employed at the Macquarie University U-series Research Laboratory for sedimentary

samples. Approximately 0.1 g of sample was spiked with a ^{236}U-^{229}Th tracer and digested in a mixture of concentrated acids (HClO$_4$-HF-HNO$_3$-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). The New Brunswick Laboratory (NBL) U010 synthetic standard was used to carry out linear drift correction and normalisation of samples for U isotopes, using the certified atomic ratios of 5.47 x 10^{-5}, 1.01 x 10^{-2} and 6.88 x 10^{-5} for ^{234}U/^{238}U, ^{235}U/^{238}U and ^{236}U/^{238}U, respectively. The NBL synthetic standard U005-A was run as an unknown at regular intervals throughout the analytical session to assess the robustness of instrumental corrections. The average corrected U005-A ^{234}U/^{238}U, ^{235}U/^{238}U and ^{236}U/^{238}U ratios (n = 6) were 3.43 ± 0.01 x 10^{-5} (2SD), 5.093 ± 0.004 x 10^{-3} (2 standard deviations (SD)) and 1.19 ± 0.02 x 10^{-5} (2SD), which are within error of the NBL published values of 3.42 x 10^{-5}, 5.09 x 10^{-3} and 1.19 x 10^{-5}, respectively. BHVO-2 and TML-3, secular equilibrium rock standards, digested alongside the samples gave (^{234}U/^{238}U) very close to or within error (2 standard errors (SE)) of secular equilibrium (Table 1). The U total procedural blank for the phase extraction, digestion and column separation procedure is < 60 pg. Note that the reagents in the sequential extraction procedure are discarded at the end of each step and that the sample is then rinsed with Milli-Q water.

Sr-Nd isotope cuts (from the same sample digestion as for U isotopes) were prepared and analysed for the Wilson's Pound quartzite and dune sediment at the Geochemical Analytical Unit (GAU) at Macquarie University following the methods described in Handley et al. (2008). The Sr and Nd fractions were loaded onto degassed single Re filaments and analyzed in static mode on a ThermoFinnigan Triton TIMS. Mass fractionation was corrected by normalising Sr to ^{86}Sr/^{88}Sr = 0.1194 and Nd to ^{146}Nd/^{144}Nd = 0.7219. NIST SRM-987 and BHVO2 gave ^{87}Sr/^{86}Sr ratios of 0.710241 ± 8 (2SE) and 0.703438 ± 7 (2SE), respectively. BHVO2 gave a ^{144}Nd/^{143}Nd ratio of 0.512975 ± 6 (2SE). Total analytical blanks for Sr and Nd are < 100 pg.

BET surface area measurements of the valley-fill samples, including a replicate analysis of WL07-FPa (same leached sample, different aliquot), determined by N$_2$ gas adsorption on sequentially leached and clay-removed samples, were carried out at the Particle and Surface Sciences laboratory in Gosford, Australia using a Micromeritics Gemini VII 2390. A replicate analysis of WL07-FPa carried out using a Micromeritics ASAP 2020 at Stanford University (on one of the same sample aliquots as that carried out at Gosford) lies within the range of surface area given by the two WL07-FPa Gosford measurements (Table 2).

Particle size distributions of the 2-53 μm processed bulk sediments were obtained using a Micromeritics SediGraph III 5120 at Macquarie University.

6. Results

U concentrations and $(^{234}U/^{238}U)$ activity ratios of the Wilkawillina valley-fill sediments, quartzite and fine-grained bedrock samples and a representative dust sample are listed in Table 1 and presented on Fig. 3. The uppermost Wilkawillina sample (WL07-FPa) has a $(^{234}U/^{238}U)$ ratio > 1 (Fig. 3). The remaining valley-fill sediments (WL07-FPb-f) possess $(^{234}U/^{238}U)$ ratios < 1, consistent with alpha-recoil loss of ^{234}Th (parent of ^{234}U) in fine-grained primary detrital grains (DePaolo et al., 2006). They also display a general decrease in $(^{234}U/^{238}U)$ with decreasing depositional age and sample depth (Table 1, Fig. 3a). The Wilkawillina samples show greater U isotopic disequilibria than (clay-free) semi-arid Australian palaeochannel sediments from the Cooper Creek, which have $(^{234}U/^{238}U)$ ratios between 1.019 and 0.974 (Handley et al., in press).

The $(^{234}U/^{238}U)$ activity ratios of the Proterozoic quartzites and fine-grained sedimentary bedrock samples are not in secular equilibrium, as would typically be assumed (see later discussion), but have $(^{234}U/^{238}U)$ ratios that range from 0.912 to 0.971 (Fig. 3b). In fact, the fine-grained bedrock samples show a similar degree of depletion in ^{234}U relative to ^{238}U and similar U concentration to the Quaternary Wilkawillina valley-fill sediments. Both quartzite samples display slightly less $^{234}U-^{238}U$ disequilibria relative to the Wilkawillina sediments and lower U concentrations. The dust sample is also out of secular equilibrium and possesses a higher U concentration, slighter lower $(^{234}U/^{238}U)$ ratio (Fig. 3b), less radiogenic $^{87}Sr/^{86}Sr$ ratio and higher $^{144}Nd/^{143}Nd$ ratio than the quartzite bedrock basin it was enclosed within (see footnote to Table 1).

7. Discussion

As we now discuss, an unexpected outcome of this study was the inability of the method to produce comminution ages and hence, sediment residence times using reasonable input parameter values.

7.1. Comminution age and sediment residence time

One issue with the comminution approach is the ability to adequately constrain the key inputs to the age equation. Below we first summarise the qualitative implications of the data before exploring some of the key issues with comminution assumptions in detail.

7.1.1. Wilkawillina sediment $^{234}U-^{238}U$ disequilibria

Sample WL07-FPa cannot be used in the comminution calculation because it has a higher $(^{234}U/^{238}U)$ than secular equilibrium (i.e. the assumed maximum starting ratio). This elevated ratio, in the stratigraphically uppermost sample, may be a result of the uptake of U from ^{234}U enriched surficial pore water or significant ^{234}Th adsorption (e.g. Plater et al., 1992; Osmond and Ivanovich, 1992; Vigier et al., 2005). Another possibility is the incomplete removal of secondary clay or other

secondary minerals during sample processing. However, as WL07-FPa was processed in the same manner as the other clay-rich samples (see section 5 and the appendix) and a similar percentage of material was removed (62 %) compared to the other samples (56-64 %), it is unlikely that the latter explanation can account for the significantly elevated (^{234}U/^{238}U) ratio.

For the remaining samples, the general trend of decreasing (^{234}U/^{238}U), i.e. increasing disequilibria, with decreasing deposition age of the Wilkawillina sediments (Fig. 3a) suggests, on face value, that the comminution age of the sediments increases, and therefore, the sediment residence time increases up section from 45 ka towards the time of the last glacial maximum (LGM) (17-20 ka, Barrows et al., 2002). Before attempting to calculate absolute comminution ages and hence residence times of the Wilkawillina sediments using the comminution approach, it is first important to consider the assumptions inherent in the method.

7.1.2. Recoil loss factor

As stated in the introduction, the recoil loss factor, f_α, has been identified as a major factor of uncertainty in the U-series comminution methodology (e.g., DePaolo et al., 2006; Handley et al., in press) therefore, recoil loss factors for the Wilkawillina valley-fill sediments have been determined by two independent methods: 1) the weighted geometric method based on grain size distribution data; assuming surface roughness and aspect ratio vary between 1-2 and 10-1, respectively, following a similar assumption by DePaolo et al. (2006) and Dosseto et al. (2010), and 2) using BET surface area data, with and without an applied fractal correction (Bourdon et al., 2009). Full details of the calculations for each of these methods are given in the appendix.

By setting A_{meas} to the measured (^{234}U/^{238}U) of the sample and A_0, the (^{234}U/^{238}U) ratio of the source, equal to 1 (or 0.95), in order to satisfy the comminution equation a minimum value of f_α is defined by 1-A_{meas} (Table 3). The minimum value of f_α is the lowest possible value that will yield a positive comminution age upon solving the equation. Note it is not possible to determine the theoretical minimum value for WL07-FPa because the measured (^{234}U/^{238}U) ratio is greater than unity. The calculated recoil loss values are displayed on Fig. 4 and listed in Table 3. Recoil loss factors estimated by both the weighted geometric method and BET surface area data with an applied fractal correction yield f_α values that lie between 0.009-0.010 and 0.040-0.082, respectively. Unfortunately, all these f_α values are lower than the minimum permissible f_α required to solve the comminution equation (dashed line in Fig. 4; Table 3). As a result, comminution ages or residence times cannot be attained for the Wilkawillina samples using reasonable parameterisations for surface roughness, aspect ratio and recoil length scale (DePaolo et al. 2006; Handley et al., in press). The BET surface area estimations of f_α without the applied fractal correction lie above the minimum value of f_α (Table 3) and produce sediment residence ages. However, this method of

calculation is believed to grossly overestimate the true f_α due to the large difference in size between the adhering gas molecule and the length of α-recoil as noted in section 2. Therefore, these ages are likely to be younger than the true ages.

7.1.3. Activity ratio of the source, A_0

The $(^{234}U/^{238}U)$ activity ratio of the source material, i.e. bedrock, is also a source of uncertainty within the comminution equation. Most studies (e.g., DePaolo et al., 2006; Lee et al., 2010; Dosseto et al., 2010) assume that prior to physical weathering, fractionation of ^{234}U-^{238}U is negligible and therefore, the $(^{234}U/^{238}U)$ ratio of the source will be in secular equilibrium (equal to 1). However, it has been shown in a detailed U-series isotope study of crystalline rocks by Rosholt (1983) that recoil loss of ^{234}U, and preferential leaching of ^{234}U relative to ^{238}U, can occur in surface and near-surface crystalline rocks and also in some un-fractured crystalline rocks from drill cores. Also, U assimilation and ^{234}U recoil gain were measured in fractured rocks from some drill cores. Therefore, tighter constraints on the $(^{234}U/^{238}U)$ variability of the source rock are required to improve the accuracy of the comminution age. Allowances for chemical weathering and preferential leaching of ^{234}U from the source rock prior to physical weathering are not presently incorporated into the comminution equation. Unfortunately, placing tighter constraints on the $(^{234}U/^{238}U)$ of the source will prove challenging if sediment provenance is unknown or the sediment deposits of interest are located within large catchment areas that drain a wide variety of lithology (e.g., Lake Eyre Basin, Australia).

To help reduce the uncertainty on the $(^{234}U/^{238}U)$ ratio of the source for this study, four local, Proterozoic bedrock samples (two quartzites and two fine-grained sedimentary rocks) were analysed (Table 1). All bedrock samples show moderate to significant disequilibrium between ^{234}U and ^{238}U, with $(^{234}U/^{238}U) < 1$ and with an average value of 0.95 (Fig. 3b). The $(^{234}U/^{238}U)$ ratio of the fine-grained sedimentary rocks (shale and siltstone) lie within the range observed for the Wilkawillina valley-fill sediments themselves, necessitating minimal residence time if they are the predominant bedrock source. Despite being unable to obtain residence times for the Wilkawillina sediments it is possible to illustrate the effect such non-secular equilibrium source rocks have on calculated residence times using the BET (non-fractal corrected) timescale results (Fig. 4) for which f_α was sufficiently high to satisfy the comminution equation (noting that these f_α values are likely to be overestimates of the true values). Using the average value of the four local bedrock sediments (0.95), instead of an assumed value of 1, reduces the apparent residence time of the samples by up to an order of magnitude (Table 4). The implications of non-secular equilibrium bedrock $(^{234}U/^{238}U)$ activity ratios are discussed in more detail below.

7.2. Limitations of the comminution approach

For the Wilkawillina samples, the inability to produce residence timescales using a reasonable range of input parameter values for f_α and A_0 may reflect: 1) analytical issues during sample preparation, 2) the inability to produce suitable f_α values, or 3) that the source rocks were not in secular equilibrium and the appropriate $(^{234}U/^{238}U)$ values are unknown. Interpretation of measured $(^{234}U/^{238}U)$ ratios may also be hindered by the complex nature of the samples i.e., that they are not simply the product of physical weathering within the catchment. Further considerations and improvements are therefore required before the comminution method can be applied to all fluvial systems. All three hypotheses and sample complexity are discussed below.

7.2.1. Analytical issues and f_α values

The Wilkawillina sediments were processed in the same way to those of previous comminution studies (Dosseto et al., 2010; Handley et al., in press), noting that Dosseto et al. did not remove the clay-sized fraction. Therefore, it seems unlikely that sample processing issues are responsible for the inability to produce comminution ages. However, significantly more material was lost during the sequential extraction procedure (56-64% of the initial starting material) than is usual (~20%) due to the high abundance of clay-sized material in the deposits. If primary minerals were removed along with secondary clay material during the extraction of the < 2 μm fraction, this may explain the lower f_α values obtained (due to the higher surface to volume ratio in finer grains, which enables greater loss of ^{234}Th via α-recoil). The question of whether the clay-sized fraction should be removed or not needs to be considered further in future studies as this component likely contains a mixture of undesired secondary clay material but also desired, clay-sized detrital grains. Furthermore, the disparate leaching methodologies presently employed by each author/research group need to be tested thoroughly to ensure that they do not fractionate $(^{234}U/^{238}U)$ ratios. Standardisation of an accepted leaching protocol for comminution studies would help to circumvent this issue. Nevertheless, the calculated f_α values of the Wilkawillina sediments produce similar f_α values when compared to f_α estimates for other Australian fine-grained samples (< 53 μm fraction) shown on the y-axis of Fig. 4. The Wilkawillina weighted geometric and surface area (fractal corrected) f_α values also lie within the typical parameter range of f_α (0.01-0.1) given by Bourdon et al. (2009). Noting that the study of Bourdon et al. (2009) focused mainly on carbonates/carbonate rich rocks as opposed to silicates.

7.2.2. Non-secular equilibrium source rocks

Of greatest pertinence to this, and other studies using the comminution methodology to calculate sediment residence times, is that the source rocks (A_0) may be out of secular equilibrium and

therefore (^{234}U/^{238}U) cannot be assumed to be '1' within the comminution age equation. Changing this input parameter from unity to a measured average of 0.95 for the Wilkawillina catchment results in a reduction of the calculated apparent residence time by an order of magnitude (section 7.1.3). The non-secular equilibrium of (^{234}U/^{238}U) in bedrock identified in this study is corroborated and supported by a previous U-series study of crystalline bedrock from surface, near surface and drill core sites in the USA (Rosholt, 1983). Rosholt identified both ^{234}U gain and loss within the sample suites analysed, which translates to a wide range of potential (^{234}U/^{238}U) starting activity ratios; both less than and greater than unity depending on the degree of U mobility and the nuclide redistribution process involved. The three different bedrock lithologies sampled in the Flinders Ranges in this study all show (^{234}U/^{238}U) activity ratios less than one, suggesting that the rocks have experienced *in situ* depletion of ^{234}U relative to ^{238}U. Recoil loss of ^{234}U and/or preferential leaching of ^{234}U from bedrock during incipient chemical weathering can explain such loss (Rosholt, 1983; Andersen et al., 2009). The fractured and jointed nature of much of the Flinders Ranges bedrock (e.g. Quigley et al., 2007a) enhances the opportunity for recoil loss and leaching of ^{234}U. The greatest ^{234}U-^{238}U disequilibria was observed in the more friable shale and siltstones compared to the quartzites, supporting such a theory (Fig. 3b). The moderate to high ^{10}Be erosion rates published for the Flinders ranges (Quigley et al., 2007b; Heimsath et al., 2010) detailed in section 3 suggest that disequilibrium persists to some depth within the bedrock. The inference is that users of the comminution method cannot assume (as is common at present) that the source (A_0) (^{234}U/^{238}U) ratio is 1. This assumption probably needs to be assessed for each catchment studied. The degree of ^{234}U-^{238}U disequilibria of the source may be dependant on the lithology, extent of chemical weathering/leaching loss of ^{234}U from recoil damage tracks and tectonic history (e.g., the degree of rock micro-fracturing) of the bedrock of interest, as young, fresh volcanic rocks typically show (^{234}U/^{238}U) ratios within error of secular equilibrium (e.g., Sims et al., 2002; Handley et al., 2011; Turner et al., 2012).

7.2.3. Complex sedimentary systems

Of additional consideration for the Wilkawillina samples is the complex nature of the sediments themselves. Williams and Nitschke (2005) suggest that the fine-grained late-Pleistocene valley-fill sediments in the central Flinders Ranges contain a mixture of locally weathered argillite material and reworked aeolian material that was blown in as dust, predominantly from the adjacent Lake Torrens. Therefore, the sediment residence time of Flinders Ranges valley-fill sediments is likely to encompass sediment recycling between the Flinders Ranges and Lake Torrens whereby products of the erosion of the Flinders Ranges (at least during the Quaternary) are transported to, and temporarily stored within Lake Torrens, before being blown back to Flinders. Additional aeolian

input to the Ranges from further west (e.g., Arcoona Plateau) could not be ruled out by Williams and Nitschke (2005). In such a scenario, the measured (^{234}U/^{238}U) ratios of the valley-fill deposits would reflect a mixture between higher (^{234}U/^{238}U), 'shorter' comminution age fluvial material and lower (^{234}U/^{238}U), 'longer' comminution age recycled sediment. The trend of increasing disequilibria with decreasing depositional age is consistent with an increasing contribution of 'older' recycled aeolian sediment in the younger deposits and would be expected if relative aridity and dust flux increased towards the LGM (e.g., Bowler, 1976; Hesse et al., 2004). Furthermore, if the floor of Lake Torrens has been lowered by ~ 2.5 m during the last glacial period due to wind erosion, the most recent contribution of dust from the lake bed would be of greater depositional age and therefore, potentially of older comminution age, amplifying the effect of lower (^{234}U/^{238}U) in the more recently deposited Wilkawillina valley-fill deposits. This hypothesis is conditional on minimal etching and chipping of grain edges during aeolian transport, which would remove the greatest (^{234}U/^{238}U) disequilibria edges, during the relatively short transport of material between Lake Torrens and the Flinders Ranges (40-100 km). If the Wilkawillina valley-fill deposits are composed of a mixture of fluvial sediment and increasing amounts of dust with decreasing age of the deposits, a mixing relationship may be expected between 'fluvial sediment' and 'dust'. However, no clear mixing trend is observed (i.e. straight line) on a plot of 1/U concentration versus (^{234}U/^{238}U) (not shown). Further analysis of the U isotopic ratio of present day and past aeolian material is required to place greater constraints on the effect of such inputs and on the implication for calculated timescales. Rare earth element and Sr-Nd isotopic data of both sediment samples and potential source inputs (local bedrock and dust) would help to further constrain sediment provenance and the contribution of aeolian material. The radiogenic isotope data of the dust and quartzite bedrock (Table 1 footnote) are distinct from one another, suggesting that the fine-grained fraction of the sand dune deposit is of different provenance to the bedrock and is likely to be aeolian derived but the Sr-Nd isotopic ratios of the valley-fill sediments were not determined in this study.

The preferential loss of ^{234}U relative to ^{238}U via leaching of loosely bound, recoiled ^{234}U from damaged lattice sites (e.g., Fleischer, 1980; Andersen et al., 2009) is not considered in the comminution method and it has been argued that recoil alone account for observed sediment sample ^{234}U-^{238}U disequilibria (DePaolo et al., 2006; Maher et al., 2006). However this effect needs to be considered in further studies as it could lead to overestimation of calculated ages.

8. Summary and conclusions

Fine-grained detrital sediments from Pleistocene valley-fill deposits from the Wilkawillina catchment within the Flinders Ranges have (^{234}U/^{238}U) activity ratios less than unity (except for the uppermost sample in the profile). Local Proterozoic bedrock and a 'dust' sample also display

(^{234}U/^{238}U) ratios < 1. The Wilkawillina U isotope data, combined with estimates of recoil loss factor for each sample (the latter of which were determined by two independent methods), are unable to produce residence ages using the comminution equation. This suggests that the comminution approach is not amenable to all sediments. In the case of the Wilkawilina valley-fill sediments, interpretation of the measured (^{234}U/^{238}U) ratios is complicated by the potential mixed provenance of the sediments. If the samples are a mixture of local Flinders Rangers argillite material and aeolian material sourced from Lake Torrens (Nitschke, 2002; Williams and Nitschke, 2005), the measured (^{234}U/^{238}U) ratios do not simply represent the time the sediment has resided within the Wilkawillina catchment. The general decrease in (^{234}U/^{238}U) with decreasing deposition age (from 44 ka to 22 ka) may be explained by the increasing involvement of an aeolian component as aridity and dust flux expectedly increase towards the LGM - providing that the aeolian component has larger ^{234}U-^{238}U disequilibria than the local bedrock, as is the case for the quartzite, but not the fine-grained bedrock, investigated here. U-series analysis of true aeolian material is required to advance our understanding of the impact the dust on the measured (^{234}U/^{238}U) ratios of Flinders Ranges valley-fill deposits. Most importantly, the Proterozoic bedrock samples show that the (^{234}U/^{238}U) ratio of the source, or starting ratio (A_0), within the comminution equation, cannot be assumed to be unity. Using a (^{234}U/^{238}U) ratio of 0.95 (the average of the four bedrock samples analysed) rather than 1, would translate to a reduction in calculated residence times on the scale of an order of magnitude. The bedrock U isotope data indicate that fractionation of ^{234}U from ^{238}U occurs prior to physical weathering, most likely due to preferential leaching of ^{234}U from recoil-damaged lattice sites within minerals. Considering the erosion rates constrained by ^{10}Be (Quigley et al., 2007b; Heimsath et al., 2010) and the half-life of ^{234}U, we propose that U isotope disequilibrium persists to some depth in the bedrock in the Flinders Ranges. The implication of this for the comminution approach is that the comminution 'clock' may start much earlier than is consistent with the theory of this method, i.e. the clock will begin before grains are mechanically weathered to the critical threshold size of ~50 μm, such that the magnitude of disequilibria measured in sediments (relative to secular equilibrium) does not correlate simply to sediment residence time. Further constraints on bedrock (^{234}U/^{238}U) ratios for different lithologies and tectonic settings (e.g. active ranges versus stable plateaus) may help to address this issue. At present, the comminution method appears to yield relatively trustworthy absolute ages where sediment provenance is relatively simple, fine-grained sediment is formed rapidly and where sediment transport and storage are limited (e.g., glacially produced sediment deposited in the Kings River Fan, California; Lee et al., 2010) or where the sediments are subject to minimal post-depositional weathering (e.g., dust trapped in ice sheets; Aciego et al., 2011). However, this study suggests that the comminution approach has, at present, limited applicability and accuracy for sediment deposited within

catchments involving of multiple sediment sources and proven non-secular equilibrium source material. Further tests of the methodology are required on sediments for which independent age constraints are able to be obtained.

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Figure Captions

Fig. 1. Schematic diagram showing the relationship between comminution age, deposition age and sediment residence time. Modified from Dosseto et al. (2010). OSL, optically stimulated luminescence.

Fig. 2. a) Map showing the locations of samples and sampling sites within the Flinders Ranges, South Australia. Inset shows the location of the study area within Australia (modified from Haberlah et al., 2010a). b) Stratigraphic profile of the Wilkawillina valley-fill deposits (section WL07-FP of Haberlah et al., 2010a). Samples WL07-FPa-f were collected at the same localities for which the sediment deposition ages are indicated on the profile (see Table 1 for the specific depths at which samples were taken relative to present day surface and corresponding deposition ages). See Haberlah et al. (2010a) for a detailed section description.

Fig. 3. $(^{234}U/^{238}U)$ versus a) deposition age and b) U concentration (determined by isotope dilution) for Wilkawillina valley-fill sediments, local bedrock and Flinders Ranges 'dust'. 2SE for U concentration and $(^{234}U/^{238}U)$ are smaller than or equal to symbol size. Errors on deposition ages are from Haberlah et al. (2010a).

Fig. 4. Calculated recoil loss factors (f_α) for Wilkawillina valley-fill sediments by weighted geometric and surface area measurements with (f_α BET$_{fract}$) and without (f_α BET) an applied fractal correction (see the appendix for equation and input parameter details). The weighted geometric model uses sample grain size data, an alpha-recoil length of 30 nm, surface roughness values ranging from 1-2 (increasing with increasing grain diameter) and aspect ratio ranging between 1 for the largest grain and 10 for smallest grain (Appendix Table A1). Symbols on the y-axis exemplify published ranges in recoil loss factor for Australian palaeochannel sediments: Murrumbidgee River palaeochannel sediments, southeast Australia (0-53μm fraction) (Dosseto et al., 2010); Cooper Creek palaeochannel sediments for both clay-included and clay-excluded samples using weighted geometric and surface area (BET$_{fract}$) estimations (Handley et al., in press). It is not possible to calculate the theoretical range of f_α or T_{res} for samples where measured sample (^{234}U/^{238}U) ratios are greater than that assumed for A_0 (Tables 3 and 4).

T = present day

Comminution Age, t_{com}
(U-series isotopes)

Deposition Age, t_{dep}
(OSL/radiocarbon)

Sediment Residence Time, T_{res}

$(T_{res} = t_{com} - t_{dep})$

T = 0 (physical weathering of bedrock to threshold grainsize)

a)

Lake Torrens

Flinders Ranges

• Blinman

Brachina Gorge

BRA-SS1

GS-S1

WL07-FPa-f

Wilkawillina Study site

Wilpena Pound

HK-Q1

WP-DS1

Wilson's Pound

• Hawker

WP-Q1

Study Area
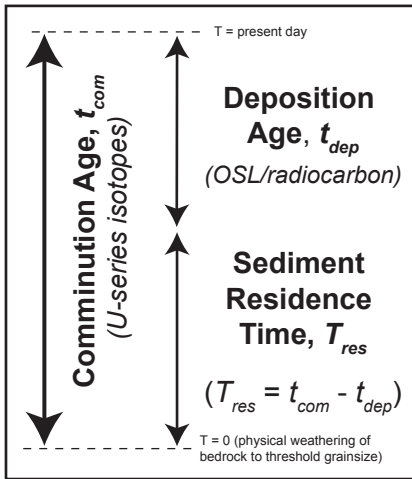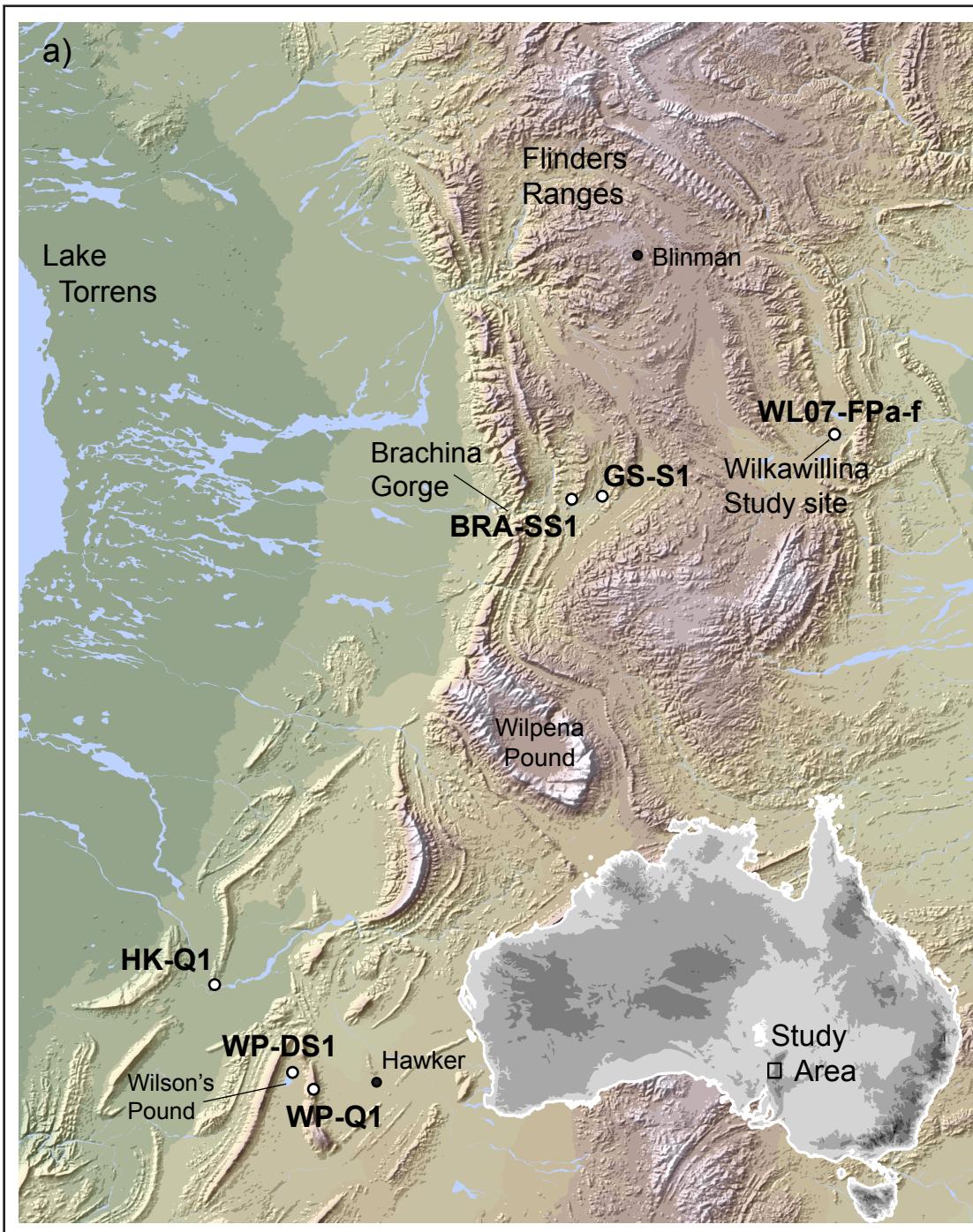
b) Wilkawillina valley-fill stratigraphic section

ENE   WSW

Top (m)

17.1 ± 1.6/
17.4 ± 1.7   WL07-FPa

22.4 ± 0.1   WL07-FPb
24.9 ± 1.4

29.3 ± 0.4   WL07-FPc
27.5 ± 0.4

NNE

N

NE

36.7 ± 0.9   WL07-FPd

38.9 ± 2.9   WL07-FPe
41.7 ± 0.4

NE

NE

NE

45.5 ± 3.9   WL07-FPf

OSL samples   AMS samples
● single grains   ⬟ charcoal
○ small aliquots   ☆ shell

a)

older comminution age, longer residence time?

more disequilibria

secular equilibrium

less disequi-libria

younger comminution age, shorter residence time?

Deposition age (ka)

$(^{234}U/^{238}U)$

b)

- ● Wilkawillina
- ▪ Fine-grained bedrock
- △ Quartzite bedrock
- ◆ Flinders 'dust'

secular equilibrium

$(^{234}U/^{238}U)$

[U] ppm

recoil loss factor (f_α)

- ● f_α geometric
- ◆ f_α BET
- ■ f_α BET$_{fract}$
- ✕ f_α Cooper clay-exc.
- ▲ f_α Cooper clay-inc.
- ○ f_α Murrumbidgee clay-inc.

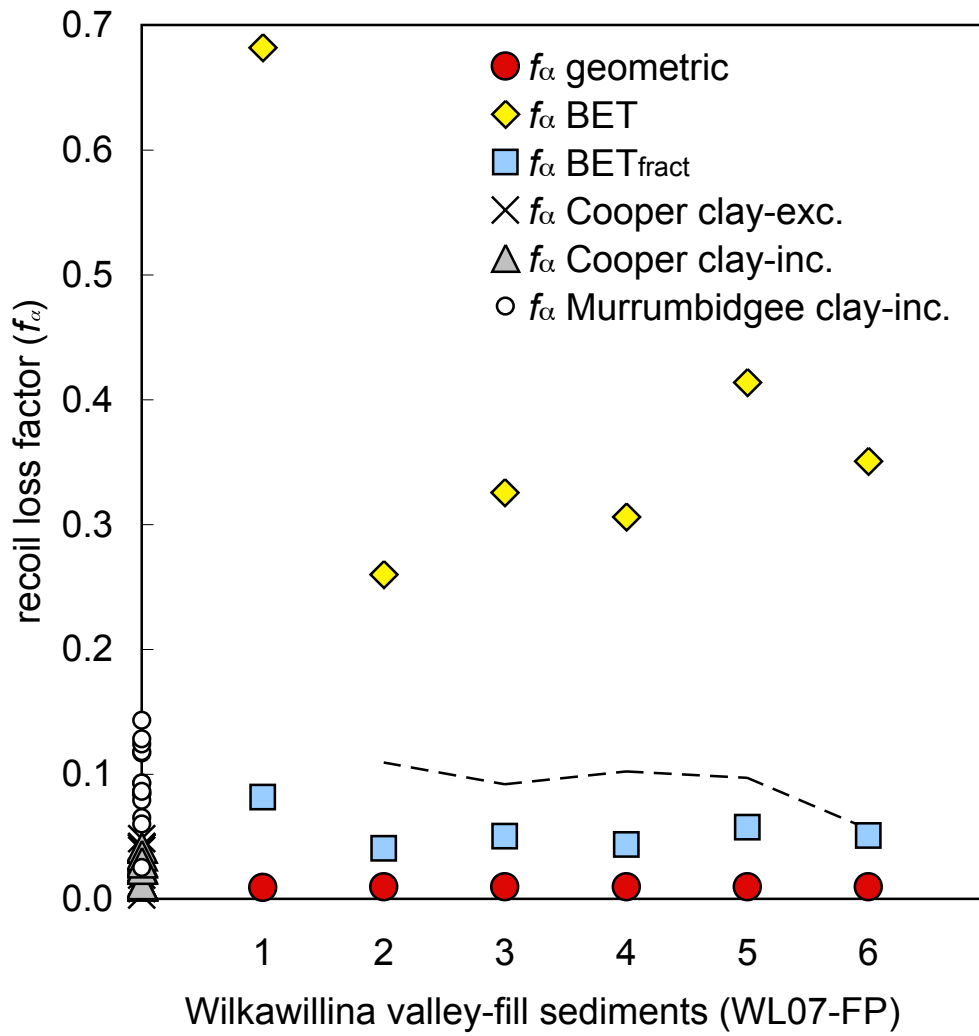Wilkawillina valley-fill sediments (WL07-FP)

Table 1. Sample details, U-isotope composition and U concentration of Wilkawillina valley-fill sediments, local bedrock and Flinders Ranges 'dust'

Sample	Location	Grid Reference S	E	Depth (cm)	Sample type	Deposition age (ka)/rock age	$(^{234}U/^{238}U)$	2SE	[U] ppm	2SE
WL07-FPa	Wilkawillina floodplain	31°16'10.56"	138°52'4.19"	85	valley-fill	17.1±1.6[a]	1.069	0.002	2.203	0.002
WL07-FPb	Wilkawillina floodplain	31°16'10.56"	138°52'4.19"	255	valley-fill	24.9±1.4[b]	0.891	0.002	2.129	0.003
WL07-FPc	Wilkawillina floodplain	31°16'10.56"	138°52'4.19"	465	valley-fill	29.3±0.4[c]	0.908	0.003	2.442	0.004
WL07-FPd	Wilkawillina floodplain	31°16'10.56"	138°52'4.19"	750	valley-fill	36.7±0.9[c]	0.899	0.002	2.654	0.004
WL07-FPe	Wilkawillina floodplain	31°16'10.56"	138°52'4.19"	855	valley-fill	38.9±2.9[b]	0.903	0.002	2.550	0.004
WL07-FPf	Wilkawillina floodplain	31°16'10.4"	138°52'03.9	1320	valley-fill	45.5±3.9[b]	0.944	0.003	2.815	0.005
WP-DS1	Wilson's Pound	31°52'58.3"	138°20'35.0"	< 15	dune (0-53μm)	unknown	0.956	0.002	2.096	0.002
WP-Q1	Wilson's Pound	31°54'24.9"	138°21'49.1"		quartzite	*Proterozoic*	0.971	0.003	0.220	0.000
HK-Q1	Hookina Creek	31°47'52.9"	138°15'47.8"		quartzite	*Proterozoic*	0.966	0.002	0.493	0.000
GS-S1	Brachina Catchment	31°19'54.7"	138°37'56.0"		shale	*Proterozoic*	0.940	0.002	3.363	0.005
BRA-SS1	Brachina Catchment	31°20'17.6"	138°36'23.9"		siltstone	*Proterozoic*	0.912	0.002	2.303	0.003
BHVO-2					rock standard		1.003	0.003	0.363	0.001
TML					rock standard		1.005	0.003	10.897	0.021

Wilkawillina valley-fill sediments (WL07-FPa-f) from locality WL07-FP of Haberlah et al. (2010a).

Deposition ages determined by Haberlah et al. (2010a): [a]OSL (single grain), [b]OSL (smalll aliquot), [c]AMS (charcoal).

Depth in cm from present day surface.

Dune deposit taken from upper 15 cm of a vegetated dune in centre of Wilson's Pound (< 53 μm fraction analysed).

$^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios of WP-Q1 and WP-DS1 are 0.738311 ± 9 (2SE) and 0.511737 ± 7 (2SE) and 0.724147 ± 6 (2SE) and 0.512013 ± 10 (2SE), respectively.

Table 2. BET surface area measurements of Wilkwillina valley-fill sediments

Sample	Lab	BET surface area m²/g	Error m²/g
WL07-FPa	Gosford	33.67	0.25
WL07-FPa[a]	*Stanford*	*30.25*	*0.61*
WL07-FPa[b]	*Gosford*	*28.55*	*0.15*
WL07-FPb	Gosford	12.83	0.02
WL07-FPc	Gosford	16.08	0.04
WL07-FPd	Gosford	15.11	0.06
WL07-FPe	Gosford	20.43	0.10
WL07-FPf	Gosford	17.31	0.05

[a] repeated BET analysis on same sample aliquot at a different laboratory
[b] repeated BET analysis same sequentially processed sample, different aliquot

Table 3. Calculated recoil loss factors for Wilkawillina valley-fill sediments

f_α	sample	minimum $(1-A_{meas})$	geometric $A_0 = 1$	geometric $A_0 = 0.95$	BET $A_0 = 1$	BET $A_0 = 0.95$	BETfract $A_0 = 1$	BETfract $A_0 = 0.95$
	WL07-FPa	n.s.	0.009	0.009	0.682	0.682	0.082	0.082
	WL07-FPa[a]				*0.613*	*0.613*	*0.074*	*0.074*
	WL07-FPa[b]				*0.578*	*0.578*	*0.077*	*0.077*
	WL07-FPb	0.109	0.010	0.010	0.260	0.260	0.040	0.040
	WL07-FPc	0.092	0.010	0.010	0.326	0.326	0.050	0.050
	WL07-FPd	0.102	0.010	0.010	0.306	0.306	0.044	0.044
	WL07-FPe	0.097	0.010	0.010	0.414	0.414	0.058	0.058
	WL07-FPf	0.056	0.010	0.010	0.351	0.351	0.051	0.051

[a] repeated BET analysis on same sample aliquot at a different laboratory (see Table 2).
[b] repeated BET analysis same sequentially processed sample, different aliquot (see Table 2).
n.s. = not solveable due to measured $(^{234}U/^{238}U) > 1$.
$1-A_{meas}$ is the minimum value for f_α required to satisfy the comminution equation, as defined in section 7.1.2.
f_α geometric is the weighted geometric estimation of f_α calculated using equation 1 given in the appendix.
f_α BET and f_α BET$_{fract}$ are calculated using equations 2 and 3 given in the appendix.
See the appendix for further equation details and the input parameter values used.

Table 4. Calculated residence times of Wilkawillina valley-fill sediments

	sample	geometric (psd) $A_0 = 1$	geometric (psd) $A_0 = 0.95$	BET $A_0 = 1$	BET $A_0 = 0.95$	BETfract $A_0 = 1$	BETfract $A_0 = 0.95$
T_{res}	WL07-FPa	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
(ka)	WL07-FPb	n.s.	n.s.	167±26.9	91±15	n.s.	n.s.
	WL07-FPc	n.s.	n.s.	88±14	29±4.6	n.s.	n.s.
	WL07-FPd	n.s.	n.s.	106±17.0	42±6.8	n.s.	n.s.
	WL07-FPe	n.s.	n.s.	55±9.0	10±1.6	n.s.	n.s.
	WL07-FPf	n.s.	n.s.	16±2.6	n.s.	n.s.	n.s.

T_{res} is calculated by subtracting the sediment deposition age from the comminution age as detailed in the text.

The comminution age was calculated using the equation given in text using the $f\alpha$ values given in Table 3

The input parameter values used are given in Table A1 in the appendix.

n.s. = not solveable: either due to measured $(^{234}U/^{238}U) > 1$ (as for WL07-FPa) or f_a being too low

to produce a solution or positive comminution age.

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Appendix

Sequential phase extraction procedure

Secondary minerals such as carbonates, Fe-, Mn-oxides and clays are likely to incorporate U with a (^{234}U/^{238}U) ratio of the fluid they precipitate from, characterised by (^{234}U/^{238}U) activity ratios > 1. Therefore, secondary minerals are undesired materials in U-series isotope comminution age studies as they are not representative of the primary detrital (^{234}U/^{238}U) bulk activity ratio.

Approximately 4 g of the post-sieved < 53μm 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) which is presented in Handley et al. (in press) and given below.

Stage 1: removal of exchangeable/adsorbed/organics.
The sample was first heated at 98°C for 30 minutes in 30 mL of NaOCl (pH 7.5). Once cool, the sample was centrifuged and the NaOCl supernatant discarded. This stage was then repeated. Afterwards the sample was rinsed (rinse stage) via the addition of 10 mL of 18.2 MΩ water, centrifugation at 7000 rpm for 15 minutes and then the supernatant was discarded. The rinse stage was carried out twice. Note that all supernatants (including 18.2 MΩ water) were removed carefully via pipette after each centrifuge step.

Stage 2: removal of carbonates.
20 mL of 1M 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 hours 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 0.04M NH$_2$OH.HCl was added to the residue of Stage 2. The sample was continually agitated using a rotary mixer at 30 rpm for 5 hours. After centrifugation the supernatant was discarded. The rinse stage was then repeated twice.

Stage 4: removal of clay-sized material.

The clay-sized 0-2 μm fraction of the samples was removal 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 seconds at 140 W and agitated overnight at 30 rpm using a rotary mixer. The centrifugation step was undertaken an additional 3 times beyond when the sample was considered clear of suspended matter to try to ensure complete removal of the clay-sized material.

The question of whether the clay-sized fraction should be removed or not requires further consideration in future studies. Secondary clay material, as stated above, will incorporate the $(^{234}\text{U}/^{238}\text{U})$ ratio of the fluid it precipitates from and is therefore undesirable sample material. However, by removing the clay-sized fraction, the clay-sized primary detrital component will also be removed from the sample. This fraction is likely to contain significant disequilibria due to its fine grain size and therefore, would have contributed significantly to the bulk sample measured $(^{234}\text{U}/^{238}\text{U})$ ratio. Whether or not this fraction should be removed may depend upon sample source area and sample mineralogy.

To ensure that the leaching method used here does not induce any unwanted isotopic fractionation, thorough leaching tests are required. A future study whereby leachate and residual component U element concentration and $(^{234}\text{U}/^{238}\text{U})$ activity ratio is determined at each step of the phase extraction procedure is required to confirm the robustness of the pre-treatment procedure.

Recoil loss factor (f_α) calculation

Geometric estimation

In the geometric estimation of f_α, the amount of recoil is related to the size, surface area (roughness) and sphericity of the grain. Consequently, a weighted geometric model is preferred to yield reasonable estimations of f_α (DePaolo et al., 2006):

$$f_\alpha = \int_{\frac{L}{2}}^{r_{max}} X(r)\beta(r)\lambda_s(r)\frac{3}{4}\left(\frac{L}{r} - \frac{L^3}{12r^3}\right)dr \qquad (1)$$

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). The parameter values used in this study are given in Table A1.

Surface area estimation

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

$$f_\alpha = \frac{1}{4} L \cdot S_{BET} \cdot \rho \tag{2}$$

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 size between the length of α-recoil ($\sim$ 30 nm) and the adhering gas molecule ($\sim$ 0.35 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:

$$f_\alpha = \frac{1}{4} \left[\frac{2^{D-1}}{4-D} \left[a/L \right]^{D-2} \right] L \cdot S_{BET} \cdot \rho \tag{3}$$

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).

The weighted geometric and BET surface area methods described above were used to estimate and compare values of f_α, employing the assumed input parameter values given in Table A1.

Table A1. Input parameter values used in recoil loss factor and comminution age equations

Parameter	Value
weighted geometric method	
surface roughness, λ_s	1 to 2
aspect ratio, β	10 to 1
length of α-recoil, L (nm)	30
Source rock ($^{234}U/^{238}U$), A_0	1 or 0.95
Sample ($^{234}U/^{238}U$), A_{meas}	as measured
^{234}U decay constant, λ_{234}	2.82629×10^{-6}
Surface area (fract.) method	
fractal dimension, D	as calculated[a]
total surface area, BET_{tot}	as measured
density, ρ (kg/m^3)	2670
length of α-recoil, L (nm)	30
Source rock ($^{234}U/^{238}U$), A_0	1 or 0.95
diameter adsorbant gas, a (nm)	0.35
^{234}U decay constant, λ_{234}	2.82629×10^{-6}

[a]calculated using BET isotherm linear plot data following Bourdon et al. (2009).

^{234}U decay constant (λ_{234}) from Bourdon et al. (2003).

The surface area calculation without fractal correction (BET, Table 3 in the main text, Equation 2 in the appendix) uses the input parameter values (for L and ρ) as those given for the surface area (fract.) method given here (BETfract, Table 3 in the main text).

λ_s varies from 1-10 assuming a linear increase from the smallest to largest grains.

β varies from 10-1 assuming a linear decrease from the smallest to largest grains.

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