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Uranium comminution ages: Sediment transport and deposition time scales

Âges de comminution de l'uranium : échelles de temps de transport et de dépôt de sédiment

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A B S T R A C T

The uranium isotope comminution age is determined from the $^{234}U/^{238}U$ ratio and reflects the timescale associated with the transformation of bedrock to sediment. The comminution age is applicable to Late Pleistocene sediments and measures the amount of time elapsed since sediment generation by mechanical weathering and erosion. The age significance of the $^{234}U/^{238}U$ ratios is based on physical disruption of the ^{238}U-decay series by recoil loss of ^{234}Th that occurs in mineral grains smaller than 50 μm. Results from study of fine-grained deep sea sediments in the North Atlantic Ocean, alluvial sediments in California and Australia, and modern glacial outwash are encouraging, but critical aspects of the method require further investigation. Particular issues are the effects of laboratory chemical leaching treatment on sediment samples and estimation of ^{234}U loss rates as a function of grain size. In the North Atlantic marine environment the U isotope variations are inferred to reflect differences in the transport time of the sediment–the time elapsed between the generation of the small sediment particles by glacial action in Iceland and Fennoscandian source areas, and the time of deposition on the seafloor in the North Atlantic Ocean at a drift site south of Iceland. Calculated transport times vary from less than 10 kyr to about 400 kyr, and correlate with provenance and glacial cycles. Application to alluvial sediments in California and Australia suggests that where sediments are glacially-derived and transported short distances, the U comminution age may approximate the sedimentation age, but in larger basins that are not glaciated the sediments retain information about residence/transport times that can extend to ca. 400 kyr. To verify that initial $^{234}U/^{238}U$ ratios for glacial sediments are close to the secular equilibrium ratio, outwash from several major glaciers around the world was measured and found to be within ± 1% of the accepted equilibrium $^{234}U/^{238}U$ value.

R É S U M É

L'âge de comminution de l'isotope de l'uranium est déterminé à partir du rapport $^{234}U/^{238}U$ et reflète l'échelle de temps associée à la transformation de la roche mûre en sédiment. L'âge de comminution est applicable aux sédiments du Pléistocène supérieur et mesure la quantité de temps qui s'est écoulée entre la production de sédiment par altération et érosion. La signification des rapports $^{234}U/^{238}U$ est fondée sur la rupture

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physique de la série de désintégration de ^{238}U par perte recul de ^{234}Th qui se produit dans des grains minéraux inférieurs à 50 μm. Les résultats de l'étude de sédiments océaniques fins de profondeur dans l'Atlantique Nord, de sédiments alluviaux en Californie et en Australie et de dépôts glaciaires actuels sont encourageants, mais les aspects critiques de la méthode requièrent des investigations plus poussées. Celles-ci pourraient être les effets du lessivage chimique en laboratoire sur des échantillons de sédiment et l'estimation des taux de perte de ^{234}U en fonction de la taille des grains. Dans l'environnement océanique de l'Atlantique Nord, les variations isotopiques de U sont supposées refléter les différences dans le temps de transport du sédiment – le temps écoulé entre la production de particules de petite taille par action glaciaire à partir de zones sources en Islande et en Scandinavie et le temps de dépôt sur le plancher océanique de l'Atlantique Nord sur un site de drift au sud de l'Islande. Les temps de transport calculés varient entre moins de 10 ans et environ 400 000 ans, selon la provenance et les cycles glaciaires. Une application aux sédiments alluviaux de Californie et d'Australie suggère que là où les sédiments ont une origine glaciaire et sont transportés sur de courtes distances, l'âge de comminution de l'U correspond approximativement à l'âge de sédimentation, mais que dans de plus grands bassins qui ne sont pas englacés, l'information que retiennent les sédiments à propos du rapport temps de transport/résidence peut atteindre ca. 400 kans. Pour vérifier que les rapports initiaux $^{234}U/^{238}U$ sont proches du rapport d'équilibre séculaire, des dépôts glaciaires en provenance de plusieurs importants glaciers à travers le monde ont été analysés et se situent à ± 1 % de la valeur d'équilibre $^{234}U/^{238}U$ admise.

1. Introduction

There are now a large number of approaches to isotopic geochronology – the use of radioactive decay or other natural nuclear processes to measure the ages of geologic rock formations and features. When applied to sediments and sedimentary rocks, however, isotopic geochronology is typically ineffective, or at least challenging (e.g., Dickin, 1995, Rasmussen, 2005). The more successful approaches to dating sedimentary formations depend on the presence of intercalated volcanic ash layers that are more amenable to common geochronologic methods, or correlation between fossil assemblages that have been dated using volcanic materials. Sedimentary formations that contain neither fossils nor volcanic interbeds are usually not dateable. One of the difficulties with dating clastic sediments is that the rock and mineral grains that comprise them had a prior existence, potentially for a long time, as parts of other rock formations before they were broken down by erosion, transported, and deposited as a sedimentary formation. The challenge for dating is in finding a physical or chemical change that happens at or near the time of sediment deposition, and that expresses itself as a disruption to a radioactive decay system.

Recent attempts at dating clastic sedimentary rocks involve the uranium and thorium radioactive decay series or cosmogenic nuclides. In both cases, there are difficulties in establishing when the isotopic clocks are set, and this difficulty, as well as analytical limitations, translates into considerable uncertainty in the determined age. For the use of U-Th isotopic disequilibrium (e.g. Chabaux and Riotte, 2003; Dosseto et al., 2008; Granet et al., 2007, 2010; Vigier et al., 2001), the assumption is that U and Th are chemically separated (fractionated) during weathering in soils where the sediment originates. For cosmogenic nuclides, which are sensitive to exposure of rock material to the cosmic ray-produced neutrons at the Earth's surface, the exposure age measured in sediments is a combination of the time since deposition and time spent close to the Earth's surface in a soil or regolith before or during transport (Phillips et al., 1997; Bierman and Nichols, 2004).

This article summarizes recent research using the U radioactive decay series, but with a specific approach referred to as the "U comminution age". The comminution age method (DePaolo et al., 2006) is designed to measure the time that elapses subsequent to bedrock being reduced by *physical* weathering to small grains–small being defined functionally as less than about 50 μm in diameter. The U radioactive decay series is sensitive to the size of the particles in which the U is contained, as described below. The term comminution refers to any process that accomplishes the reduction of rock material to silty-sand, silt, or clay-sized mineral grains. A key conceptual problem is to determine (or define) when sand and silt-size particles are produced from bedrock. Glacial erosion represents one geologic situation where this time may be well defined.

2. Comminution age model

The decay of ^{238}U to ^{206}Pb occurs in several steps (cf. Dickin, 1995; Ku, 2000). The first few steps in the sequence produce ^{234}U via an intermediate daughter isotope ^{234}Th. In most rocks and minerals that are older than a million years, and even in many that are younger, the $^{234}U/^{238}U$ ratio is almost exactly equal to the inverse ratio of the decay constants (λ) for these two U isotopes. This condition is referred to as radioactive equilibrium, and implies that the rate of production of ^{234}U by the decay of ^{238}U is equal to the rate of decay of ^{234}U, so that the ratio of $^{234}U/^{238}U$ is constant and equal to $\lambda_{238}/\lambda_{234}$. The equilibrium condition can also be described in terms of the activity ratio $(^{234}U/^{238}U)_{AR}$ being equal to unity.

In a small sediment grain with diameter of order 10 μm or less, it is impossible for the $^{234}U/^{238}U$ ratio to be maintained at the equilibrium ratio. The failure to maintain equilibrium is due to the fact that in the process

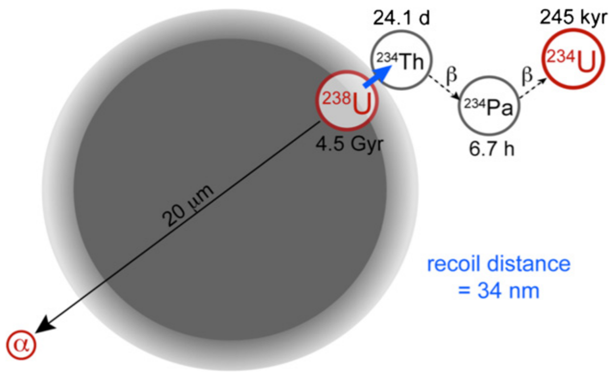

Fig. 1. Conceptual model of recoil effects associated with the alpha decay of ^{238}U contained in a spherical mineral grain having a diameter of about 15 μm. The emission of the alpha particle during ^{238}U-decay causes the ^{234}Th daughter nucleus to recoil a distance of about 34 nanometers (0.034 μm). If the ^{238}U atom resides close enough to the grain boundary it can be ejected from the grain. The subsequent β decay to ^{234}Pa and ^{234}U occurs outside the grain, usually in pore fluids, which tend to be enriched in ^{234}U relative to ^{238}U because of this process. The net effect on the grain is that the bulk ^{234}U/^{238}U ratio tends toward a value less than the radioactive equilibrium value due to the ^{234}U loss near the grain boundaries. The fractional loss rate of ^{234}U is a function of the surface/volume ratio of the mineral grain. This loss is negligible for large grains (≥ 100 μm diameter), but can be 10 to 30% for grains less than 10 μm in diameter.

Fig. 1. Modèle conceptuel d'effets recul associés à la désintégration alpha de l'^{238}U contenu dans un grain minéral sphérique de diamètre d'environ 15 μm. L'émission de la particule alpha pendant la désintégration de l'^{238}U provoque le recul du noyau fils ^{238}U d'une distance d'environ 34 nanomètres (0,034 μm). Si l'atome d'^{238} U est suffisamment proche de la limite du grain, il peut être éjecté du grain. La désintégration ultérieure β en ^{234}Pa et ^{234}U se produit en dehors du grain, en général dans les fluides des pores, qui tendent à être enrichis en ^{234}U par rapport à ^{238}U en raison de ce processus.

of radioactive decay of ^{238}U, during which a high-energy alpha particle is ejected from the ^{238}U nucleus, the radioactive decay product nucleus ^{234}Th is propelled through the mineral crystal lattice a distance of about 0.034 μm as a result of "recoil" from the ejection of the alpha particle (Fig. 1; cf. Maher et al., 2006a). Consequently, the outermost 0.034 μm layer of the mineral grain will accumulate ^{234}U at a slower rate because some of the ^{238}U-decays will result in the ^{234}Th (eventually to become ^{234}U), being ejected from the mineral grain entirely. The smaller the grain radius, the larger will be the fraction of "missing" ^{234}U.

If one imagines a U-bearing mineral grain with radius large compared to 0.034 μm and having the equilibrium ^{234}U/^{238}U ratio, and then breaking this large grain into much smaller grains of a few μm diameter each, these small grains will at first still have the equilibrium ^{234}U/^{238}U ratio. As the "comminuted" grains age, the decay of ^{234}U will be faster than the accumulation of ^{234}U from ^{238}U-decay because of the recoil losses from the grains. Hence, the ^{234}U/^{238}U ratio of the small grains will decrease with time until a steady state ratio of ^{234}U/^{238}U is reached, with this steady state ratio being substantially lower than the equilibrium ratio. The time required to reach this steady state ratio is > 500,000 years, and therefore, during this time, the ^{234}U/^{238}U ratio is acting as a clock, measuring the time since the original large grain was crushed (or comminuted) to much smaller grains.

The evolution of the ^{234}U/^{238}U activity ratio with time is described by the following equation (graphed in Fig. 2):

$$A_{meas} = (1 - f_{\alpha}) + [A_0 - (1 - f_a)]e^{-\lambda_{234} t_{comm}} \quad (1)$$

where f_α is the fraction of ^{238}U-decays that result in the daughter isotope being lost from the grains, A_O represents the original activity ratio (typically expected to be 1.000), λ_{234} is the decay constant of ^{234}U, and t_{comm}, is the time since crushing or comminution.

This model, although simple, could be a reasonably good representation of the formation of fine-grained sediment, especially by glacial erosion. The implication is that recently-produced fine sediment grains contain, in their ^{234}U/^{238}U ratios, a measure of how long they have been in existence as small grains. In the case of glacial sediment, the ^{234}U/^{238}U ratio could measure the time elapsed since the production of the grains by glacial grinding of bedrock.

For any sediment, the age of the grains must be equal to the age of the sediment (the elapsed time since the sediment was deposited), plus the time that elapsed while the sediment was being transported from the site of its glacial origin to the site of deposition. So the "comminution age" is the sum of the transport time and the sediment age. Consequently, in situations where the sediment age is known, the comminution age and the sediment age can be used to estimate the transport time (e.g., Dosseto et al., 2010). In situations where the transport time is known, or known to be very short, the comminution age can be interpreted as the age of sediment deposition. The comminution age clock is useful for a little more than 500,000 years, so this method is mainly for study of relatively recent (Late Pleistocene) sedimentary systems.

3. Issues and complications

3.1. The recoil loss factor

The model described above and encompassed in Eq. (1) is dependent on obtaining knowledge of the value of the

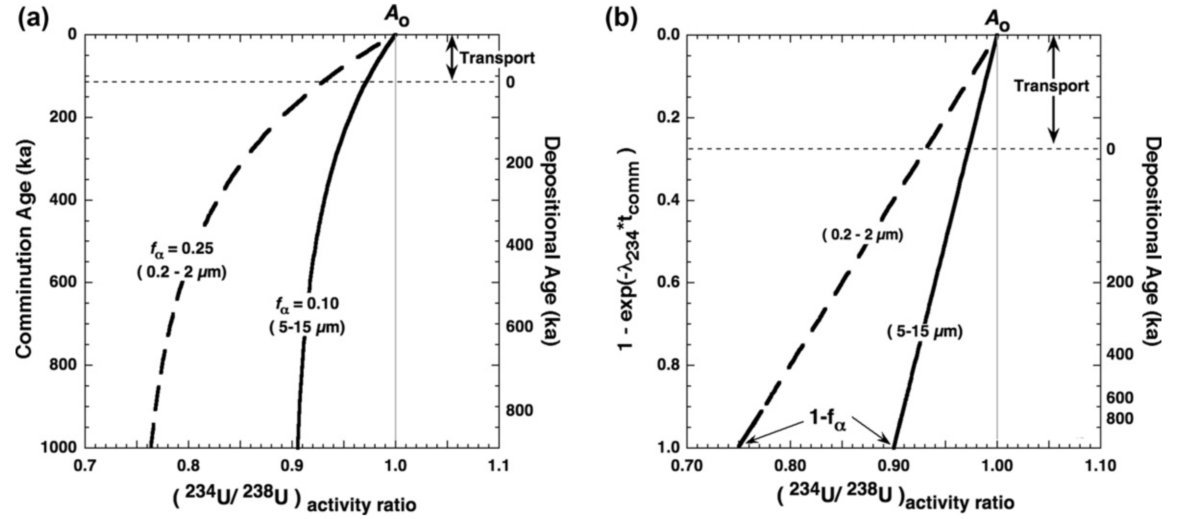

Fig. 2. Model isotope ratio evolution curves for small sediment grains comminuted from larger rock fragments at time zero. (a) $^{234}U/^{238}U$ activity ratio versus age, showing hypothetical transport time of about 110,000 years followed by deposition and burial. The curves are based on the f_α value shown, and the correspondence with grain size follows approximately from the data in Fig. 3. (b) Equivalent to 2a but with age plotted so that the isotopic ratio changes linearly (see Eq. (1)). If sediment ages are known, this plot can be used to extrapolate data from a continuous sedimentary section to estimate both the transport time and the recoil loss factors (cf. DePaolo et al., 2006).

Fig. 2. Modèle de courbes d'évolution du rapport isotopique de grains de sédiment de petite taille, comminutés à partir de plus grands fragments de roche au temps zéro. (a) rapport d'activité $^{234}U/^{238}U$ en fonction de l'âge; (b) équivalent à (a), mais avec les chiffres d'âge reportés de manière à ce que la valeur isotopique change linéairement (voir Éq. (1)).

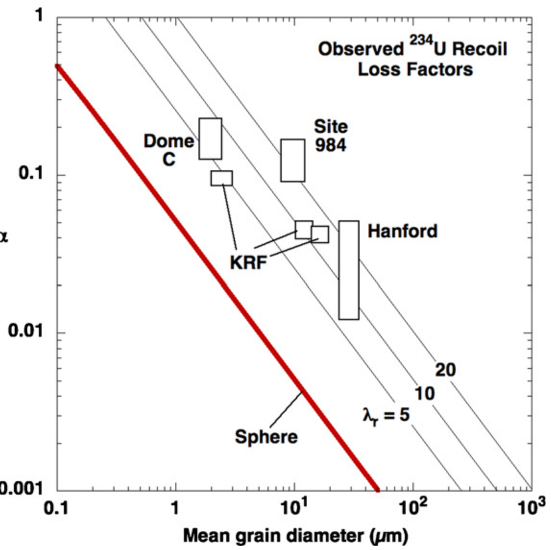

Fig. 3. Measured or estimated f_α values for samples of sand, silt and clay. Hanford data are from Maher et al. (2006a). Site 984 data from DePaolo et al. (2006). Dome C dust data from Aciego et al. (2011). King's River Fan (KRF) data are from Lee et al. (2010). The parameter λ_r is a roughness factor that accounts for both grain shape and surface roughness relative to a spherical grain.

Fig. 3. Valeurs $f_?$ mesurées ou estimées pour des échantillons de sable, de silt et d'argile. Données sur Hanford (Maher et al., 2006a), sur le site 984 (DePaolo et al., 2006), sur le Dome C (Aciego et al., 2011), sur King's River Fan (KRF) (Lee et al., 2010). Le paramètre λ_r est un facteur de rugosité qui tient compte à la fois de la forme du grain et de la rugosité de surface relatives à un grain sphérique.

recoil loss parameter f_α. Although this is a geometric factor, it is difficult to estimate accurately for natural mineral grains because the shapes and surfaces of such grains are complex (Anbeek, 1992; Brantley and Mellott, 2000). Relative to a simple sphere of radius r, the effective surface area of mineral grains for recoil loss exceeds $4\pi r^2$ by a factor of between about 2 and 20 based on recent measurements (Fig. 3). This excess loss factor can be expressed crudely as "roughness" of the mineral surface. The data in Fig. 3 show that the roughness factor tends to be larger for larger grain sizes (Lee et al., 2010). Furthermore, the surface area measured for minerals is dependent on the method used for the measurement. Gas adsorption techniques (such as BET), sense roughness at the scale of a few Angströms (10^{-10} m) and hence tend to overestimate the surface area that applies to recoil loss, which is only sensitive to roughness at the larger scale of the recoil length (L), about 3×10^{-8} m. Methods have been devised to scale BET measurements to provide useful surface area measurements for recoil (Bourdon et al., 2009), according to the following equation:

$$f_\alpha = \frac{1}{4} \left\lfloor \frac{2^{D-1}}{4-D} \left(\frac{a}{L}\right)^{D-2} \right\rfloor L \cdot S_{BET} \cdot \rho \qquad (2)$$

where D is the fractal dimension of the grain surface, S_{BET} is the measured BET surface area and a is the adsorbate molecule diameter (0.35 nm for N_2). The fractal dimension can be measured independently. This approach was applied successfully to estimating recoil loss from dust grains embedded in Antarctic ice (Aciego et al., 2011) and in soils (Oster et al., 2012).

A promising approach to measuring f_α by geochemical means, but one that has not yet been adequately tested, is the use of measurements of ^{226}Ra and ^{230}Th. The ratio of these two isotopes, if measured on the same population of sediment grains measured for $^{234}U/^{238}U$, should theoretically give the value of f_α that is applicable to the $^{234}U/^{238}U$ ratios according to:

$$f_\alpha = \frac{34}{37}\left(1 - \frac{^{226}Ra}{^{230}Th}\right) \quad (3)$$

where the factor preceding the parentheses accounts for the difference in recoil distance between ^{238}U-decay and ^{230}Th decay (DePaolo et al., 2006; Lee et al., 2010). The rationale for this approach is that the short mean life of ^{226}Ra (2300 yr), means that in grains older than several thousand years, but still young in comparison to the 354,000 year mean life of ^{234}U, the $^{226}Ra/^{230}Th$ should have reached the steady state value and hence represent a direct measure of f_α. A potential limitation is that any chemical leaching of the sediment grains could separate uranium from thorium and result in significant complications for this approach. Data reported in Vigier et al. (2001), however, suggest that the Ra-Th method merits further testing.

Dosseto et al. (2010) used an efficient approach to the problem of estimating f_α. Instead of using grain size separates they used bulk < 50 μm fractions and then determined the particle size distribution. This information was used in concert with a geometric model with estimates of grain aspect ratios and surface roughness to arrive at a value of f_α.

3.2. Weathering, partial dissolution, or coating of mineral grains

The U isotope ratio of small mineral grains measures age only if the surfaces of the mineral grains do not change significantly with time as a result of dissolution into pore fluids, or by acquiring coatings of secondary minerals. Dissolution could cause removal of the outer ^{234}U-depleted region of the grains, which would cause the grains to appear younger, but could also increase surface roughness and enhance recoil loss, making the grains appear older.

The effect of dissolution on the $^{234}U/^{238}U$ of sediment grains can be evaluated by comparing the time necessary to achieve ^{234}U depletion in the outer rind of a mineral grain as a result of recoil effects (the mean life of ^{234}U = 354 kyr), to the time scale for removing a layer of thickness L from the surface of a grain by dissolution. This ratio is (DePaolo et al., 2006):

$$\frac{\tau_{recoil}}{\tau_{dissolution}} = \frac{R}{^{234}\lambda L \rho} \quad (4)$$

The parameter R is the specific mineral dissolution rate, which has been estimated for silicate soils and some sediments to be of order 2.5×10^{-18} mol/m^2/sec (2×10^{-11} kg/m^2/yr, assuming that the primary dissolving mineral is plagioclase feldspar; cf. Maher et al., 2006b). Using $L = 3 \times 10^{-8}$ m and $\rho = 2700$ kg/m^3 yields a value for this dimensionless number of about 0.1, which suggests that dissolution is a second order effect in many cases. However, there are complications because the dissolution rate of the U-bearing minerals determines the size of the effect, and those rates could be larger or smaller than the value used above. In addition, dissolution rates also vary with environment (Maher, 2010) and time (e.g. Maher et al., 2004; White and Brantley, 2003).

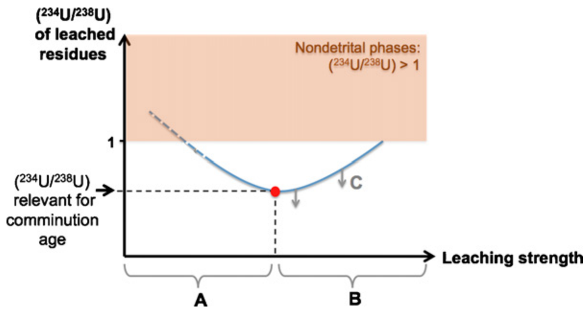

Fig. 4. Schematic of the expected effects of leaching treatments on the $^{234}U/^{238}U$ activity ratio of sediment samples. If samples are not leached, they tend to include secondary (non-detrital) phases that precipitated from pore fluids and have $(^{234}U/^{238})_{AR} > 1$. Leaching should initially remove these secondary minerals resulting in lowering of $(^{234}U/^{238})_{AR}$ as depicted for line segment "A." If leaching treatments are too strong ("B"), however, the outer ^{234}U-depleted parts of the grains could be dissolved, causing $(^{234}U/^{238})_{AR}$ to increase. The optimal leaching procedure should presumably give the minimum value for $(^{234}U/^{238})_{AR}$.

Fig. 4. Schéma des effets attendus des traitements de lessivage sur le rapport d'activité $^{234}U/^{238}U$ d'échantillons de sédiment, sachant que, si les échantillons ne sont pas lessivés, ils tendent à inclure les phases secondaires (non détritiques) formées à partir des fluides poreux, et que s'ils sont lessivés, les minéraux secondaires sont alors évacués.

Secondary mineral precipitation generally is a concern, and necessitates leaching natural samples before analysis (Dosseto et al., 2010; Lee et al., 2010; Maher et al., 2004). Leaching can be difficult and there is not yet an established best practice for the U comminution age method. In general, if leaching is too weak, high $^{234}U/^{238}U$ authigenic phases are likely to be included in the analysis, which will bias the results to young or even negative ages (Fig. 4). If leaching is too strong, it could possibly preferentially remove the ^{234}U-depleted surface layer of the grains, which would also bias the results toward high $^{234}U/^{238}U$ and younger ages. In preliminary tests of multiple leaching procedures, Lee et al. (2010) determined that sequential leaching approaches similar to that of Tessier et al. (1979) yield the most useful results. However, DePaolo et al. (2006) used only a single weak HCl leach and also achieved consistent results on deep-sea sediments. Dosseto et al. (2010) used a procedure that starts with ashing of the samples to remove organic material followed by leaching with 1.5 N HCl while monitoring the Ca, Fe, U and Th concentrations in the leachate. This procedure is followed with a second leaching step to remove residual Fe-oxides.

3.3. Initial $^{234}U/^{238}U$ ratio

It is expected that comminuted glacially-derived sediment of near-zero age will have a $^{234}U/^{238}U$ activity ratio close to unity. However, there are data in the

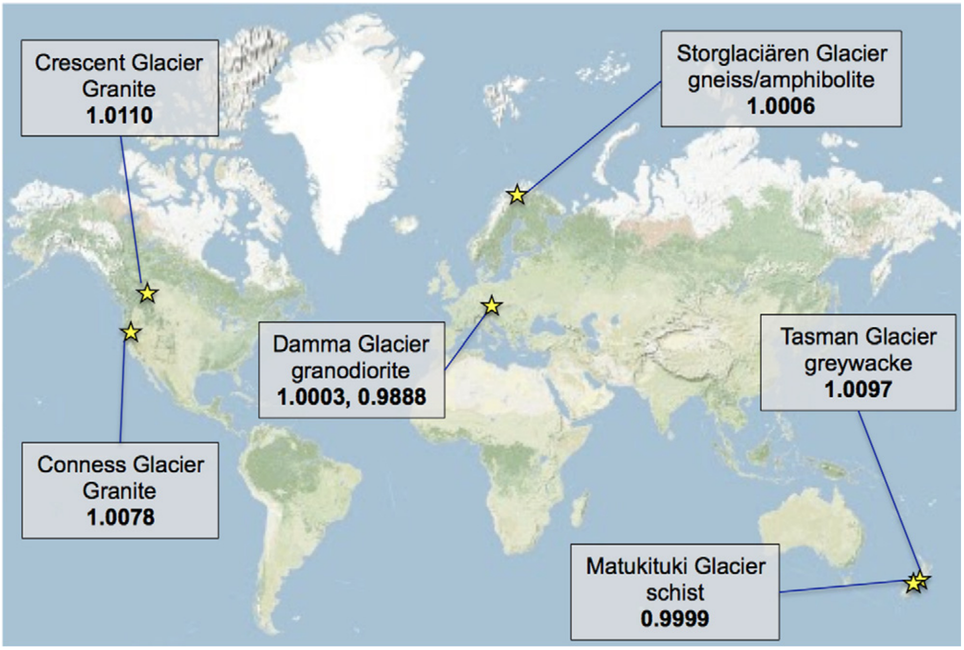

Fig. 5. Measured $^{234}U/^{238}U$ activity ratio for silt and sand from glacial outwash. Glacier name and bedrock lithology is indicated. Locations and samples are: Crescent Glacier, British Columbia, outwash at glacier toe, silt; Conness Glacier Sierra Nevada, California, Little Ice Age moraine, sand/gravel; Damma Glacier, Switzerland, bedrock (1st number) and steam sediment 1km below glacier, sand plus fines (2nd number); Storglaciaren, Sweden, subglacial till, very fine silt; Tasman glacier, New Zealand Alps, stream suspended load, fine silt; Matukituki Glacier, New Zealand Fiordland, clayey stream sediment. Uncertainty on measured ratios is generally $\pm$ 0.0017; analytical procedures including leaching methods are described in Lee et al. (2010).

Fig. 5. Rapport d'activité $^{234}U/^{238}U$ mesuré sur des silts et des sables provenant de dépôts glaciaires. Le nom des glaciers, leur localisation et la lithologie de la roche mère sont indiqués.

literature that suggest that bedrock samples do not always conform to this expectation (Gascoyne et al., 2002). To further address the issue, which is critical to interpretation of U comminution ages, we analyzed samples of glacial outwash from several alpine glaciers around the world to assess the variability of the initial $^{234}U/^{238}U$ activity ratio. The results are summarized in Fig. 5. These data, which will be more completely described in a separate publication, suggest that glacial outwash generally has $(^{234}U/^{238}U)_{AR}$ of 1.00 $\pm$0.01. This result appears to be independent of bedrock lithology; the metasedimentary rocks of the New Zealand Alps are not significantly different from the granitic rocks of the Swiss Alps. It is possible that the values that are slightly greater than unity are significant, but additional work would need to be done to confirm this observation.

4. Sediment age versus transport time

The application of U comminution ages to sedimentary sections is best done using multiple measurements on a continuous stratigraphic section or independently dated samples so that self-consistency can be evaluated. Available data for isotopic ratio and comminution age versus stratigraphic position or age are illustrated in Figs. 6 and 7, with two examples showing variable and relatively long transport time and one showing a section where transport time is most likely small.

Site 984A in the North Atlantic Ocean is a drift site; the sediments are deposited from ocean bottom currents and hence are transported several hundred kilometers along the ocean floor after first being deposited into the oceans by streams (DePaolo et al., 2006). These sediments represent a case where transport times could be relatively long. The second example is from the Kings River Fan (KRF), a large Pleistocene age alluvial fan in central California. The sediments in the Kings River Fan are glacially-derived from the neighboring Sierra Nevada, transported a relatively short distance by streams and deposited in a non-marine environment (Weissmann et al., 2002). This alluvial fan environment is one in which it might be inferred that transport times are small enough that the comminution age should correspond to the depositional age of the sediment. The third example is from a moderately large drainage basin in Southeast Australia (900 km long, 10^6 km^2; Dosseto et al., 2010) that was not glaciated in the Pleistocene and which gives indications of a wide variation in sediment transport time through the basin (or residence time in the basin) over the past 100,000 years.

For the Site 984A deep-sea sediments, the samples that suggest long transport times also tend to have low $^{143}Nd/^{144}Nd$ and high $^{87}Sr/^{86}Sr$ (DePaolo et al., 2006). These sediments are derived from the Fennoscandian Shield and then transported by bottom currents westward in the North Atlantic south of Iceland. The samples with higher $^{234}U/^{238}U$ and corresponding short transport times have high $^{143}Nd/^{144}Nd$ and low $^{87}Sr/^{86}Sr$ and are presumably derived from Iceland and transported a short distance to the site of deposition. The record of transport time,

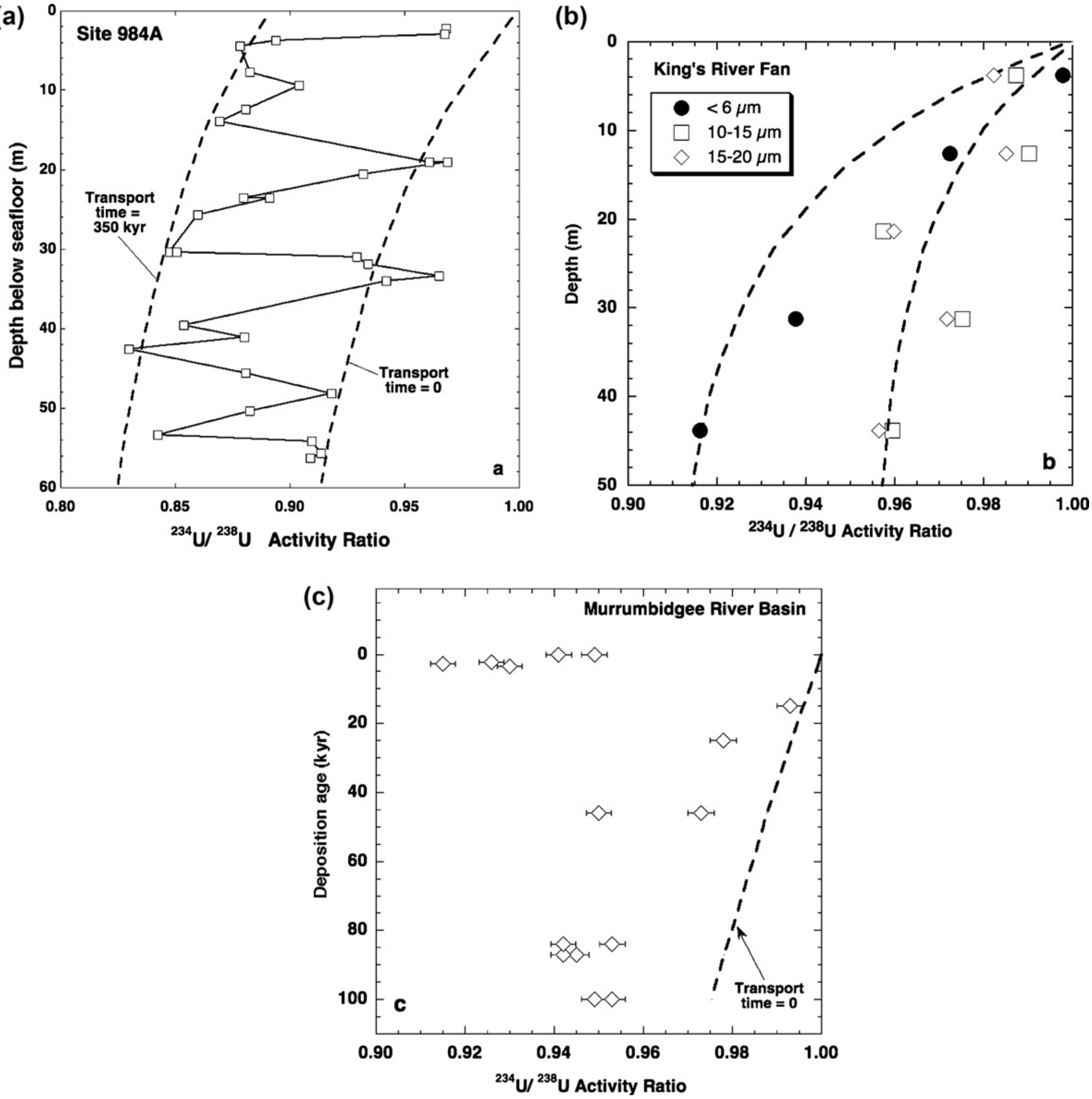

Fig. 6. Measured $^{234}U/^{238}U$ on leached bulk sediment samples from Site 984A (DePaolo et al., 2006), grain size separates from the King's River Fan (Lee et al., 2010), and < 50 μm sediment fractions from the Murrumbidgee River basin (Dosseto et al., 2010). In (a) and (b), the dashed lines represent model curves that would correspond to a constant sedimentation rate. (a) Site 984 has cyclical variation in $^{234}U/^{238}U$. The data are approximately bounded by the two curves shown, both assuming initial $^{234}U/^{238}U$ = 1.000, one for pre-deposition transport of about 350,000 years and the other for a transport time of zero. The variations in transport time correlate roughly with glacial cycles and with changes in sediment provenance. (b) King's River Fan data show relatively systematic changes in $^{234}U/^{238}U$ with depth. The dashed curves are fit through the deepest samples from the core, which are almost 800,000 years old and hence should be close to steady state with respect to $^{234}U/^{238}U$. The $^{234}U/^{238}U$ of the ≤ 6 μm fraction decreases monotonically with depth, but imply an increasing sedimentation rate with decreasing age. The 10 to 15 μm and 15 to 20 μm fractions are nearly identical in U isotopes. The complications in $^{234}U/^{238}U$ could be expected for an alluvial fan due to changes in transport time correlated with Pleistocene glaciation cycles, redistribution of older fan sediment at younger times, and admixtures of aeolian sediment. In the uppermost sample the 10 to 20 μm fractions have lower $^{234}U/^{238}U$ than the < 6 μm fraction. This could be an indication that coarser material has a different transport time than finer materials, or that the fine fraction is more affected by weathering. (c) Sediment samples (< 50 μm fraction) from paleochannels in the Murrumbidgee River basin show systematically increasing $^{234}U/^{238}U$ during the latest Pleistocene glacial period and then a shift to lower values in the Holocene.

Fig. 6. Rapports $^{234}U/^{238}U$ mesurés sur des échantillons de sédiment grossier lessivés, en provenance du site 984A (DePaolo et al., 2006), des fractions granulométriques variées du King's River Fan (Lee et al., 2010) et des fractions < 50 μm du bassin de la rivière Murrumbidgee (Dosseto et al., 2010), respectivement, Fig. 6a, b et c. En a et b, les lignes tiretées représentent les courbes du modèle qui correspondraient à un taux de sédimentation constant.

combined with the provenance information, yield information that probably relates to extent of sea ice in the North Atlantic over the last 400,000 years. When Iceland is ice-locked, there is likely to be little sediment input from Iceland to Site 984A area, whereas when the surrounding sea is ice-free there is a larger flux of Icelandic volcanic sediment.

Fig. 6c shows data from the Murrumbidgee River basin in southeastern Australia (Dosseto et al., 2010). In this case

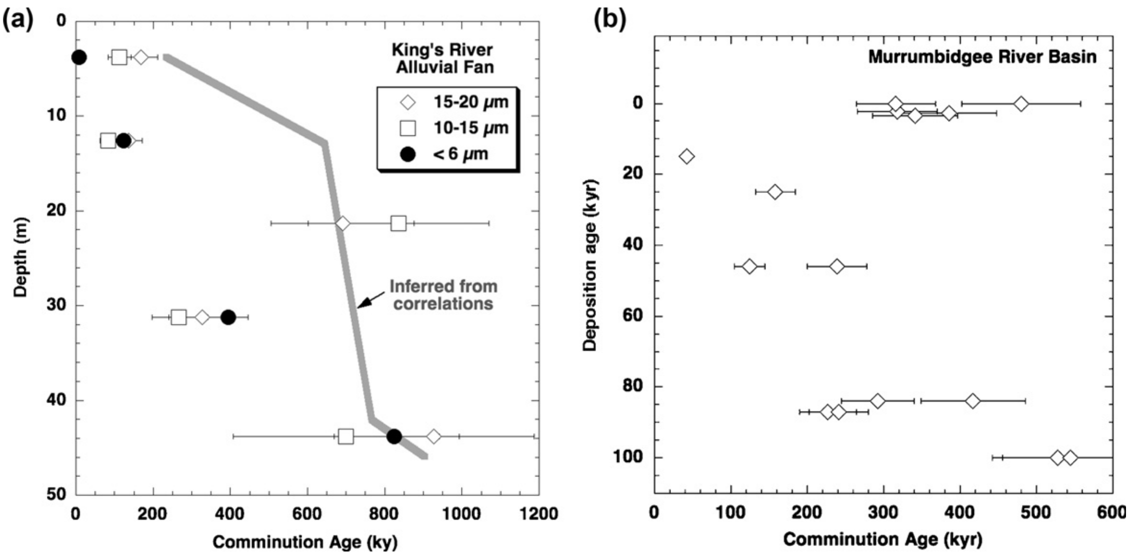

Fig. 7. Calculated U comminution ages and estimated uncertainties for King's River Fan samples reported in Lee et al. (2010) and Murrumbidgee River basin samples reported in Dosseto et al. (2010). For the King's River Fan, uncertainties are estimated as twice the analytical uncertainty on the measured $(^{234}U/^{238}U)_{AR}$ plus an additional uncertainty of ± 0.01 in f_{α} (see Lee et al., 2010 for additional details). An average value of f_{α} of 0.047 was used for both the 10 to 15 μm and the 15 to 20 μm size fractions (see Fig. 6b). For the Murrumbidgee River samples, uncertainty estimates are described in the original reference and attempt to capture all aspects of the analysis, although the uncertainty in f_{α} that is due to leaching is still likely to be approximate.

Fig. 7. Ages de comminution d'uranium calculés et incertitudes estimées pour les échantillons de King's River Fan (Lee et al., 2010) et du bassin de la rivière Murrumbidgee (Dosseto et al., 2010), respectivement Fig. 7a et 7b.

the sediments, which were collected from paleochannels in the middle and lower part of the basin, have been dated independently using luminescence methods. The measured $^{234}U/^{238}U$ ratios, even without consideration of the f_{α} values, show a substantial variation. Shown for reference in the figure is a curve corresponding to $f_{\alpha} = 0.1$ (close to the average measured) and for zero transport time. The data suggest that sediment residence time in the basin became systematically shorter through the last Pleistocene glacial cycle, was near zero at the last glacial maximum, and then became long again during the present interglacial. Fig. 7b shows the calculated comminution ages, which mirror the measured $^{234}U/^{238}U$ ratios because the measured $f\alpha$ values are not highly variable. For the zero age samples, the comminution age equals the residence time (300 kyr to almost 500 kyr), whereas for the older samples the residence time is the comminution age minus the depositional age. This case shows that quite long sediment residence times are possible in continental basins.

The Site 984A and the Murrumbidgee River basin data are an indication of the type of information that can be derived from sediment $^{234}U/^{238}U$ using the comminution age approach. The sediments in these cases can be independently dated, so the $^{234}U/^{238}U$ can be used to infer transport or residence time. In both cases the transport time is large enough that it can be determined with useful precision. The Kings River Fan data are significant because the U comminution age approach could be useful for absolute dating of continental sediments, which generally do not contain index fossils and hence are difficult to date. The KRF $^{234}U/^{238}U$ data show some of the expected character required for age determinations, but also some complications. One important issue is that the age cannot be estimated without a reliable value for f_{α}. The simplest model for f_{α}, uses the fact that the deepest samples are known to have reversed magnetic polarity (older than 780,000 years), and hence must be close to steady state with respect to $^{234}U/^{238}U$. The KRF core has not been independently dated, but there are inferred approximate ages for the units represented in the shallower portions of the core, derived from correlations with other nearby alluvial deposits and ultimately based on K-Ar ages that are not especially reliable (Lee et al., 2010). Using the oldest measured sample to estimate f_{α}, Fig. 7a shows the calculated U comminution ages for the size-separated samples shown in Fig. 6b, and a comparison curve that represents the inferred age profile based on geologic correlations. The comminution ages suggest that the sediments are considerably younger than has been inferred from stratigraphic inferences, and that there may in addition be variations in residence time that could relate to glacial cycles as in the Murrumbidgee basin.

5. Relationship to cosmogenic nuclide- and U,Th-series methods

Cosmogenic radionuclide (CRN), concentrations in sediments (such as ^{10}Be and ^{26}Al; Bierman et al., 1995; Phillips et al., 1997; Gosse and Phillips, 2001) are also used in the study of sediment transport and age, and this approach has some similarities and interesting differences relative to the U isotope comminution age approach. For CRN's, the isotopes accumulate in the sediment grains and in bedrock (no dependence on grain size) due to cosmic ray neutron bombardment, and only when the grains are situated within about 1 meter of the Earth's surface, not when they are more deeply buried. After burial, the radionuclides decay and the concentrations decrease. The CRN signal in sediments therefore reflects the time of residence of the grains in soils, the erosion rate of the bedrock, the transport time, and the burial time (related to the time since deposition). CRN production rates also depend on the elevation and latitude at which the sediment originated and was deposited. The concentration of cosmogenic nuclides in freshly eroded sediment has been shown to be inversely proportional to the erosion rate, and independent of grain size (Heimsath et al., 1999). The U comminution clock starts only when the grains become quite small. The CRN method generally requires quartz, or quartz-rich sediment; the U isotope technique by contrast is insensitive to the presence of quartz, because of the low U content of quartz, and instead relates to the history of the grains that are composed of minerals other than quartz.

The differences between the CRN methods and U comminution ages make the two approaches complementary and potentially powerful probes of sediment generation and transport processes. The in situ produced cosmogenic nuclide content of fresh sediment should be a direct indicator of the rate at which the catchment containing the sediment is eroding (e.g., Bierman and Nichols, 2004; Matmon et al., 2012), and this information could be valuable for interpreting the U isotope effects. Once incorporated into a sedimentary deposit, such as a floodplain, fan, or terrace, and buried by more than 1 meter, the ^{10}Be and ^{26}Al concentrations decrease as the result of radioactive decay. During transport it is not clear whether or to what extent the grains get more cosmic ray irradiation. However, the U isotope effects continually accumulate during soil residence, transport, storage and after final deposition. By measuring two CRNs, correction can be made for the effects of erosion on absolute production rates, and sediment ages can be determined if the pre-deposition irradiation is sufficient. Comparison of U isotope and CRNs could be an exciting new approach, leading to new insights about U isotopes and CRNs, as well as erosion and sediment transport.

Other applications of U series isotopes to sediment transport processes involve the combined U and Th decay series (Dosseto et al., 2008; Granet et al., 2007, 2010). The U-Th approach relies on the likelihood that during soil formation, there is chemical separation of U from Th, since U is generally more soluble than Th. The U-Th method is also potentially complementary to the U comminution age approach. The U-Th method is inferred to be independent of grain size, so in general measurements made with the U-Th method have not been done on grain size characterized samples, which impedes direct comparison of the two methods. Concurrent application of the U-Th chemical fractionation method and the comminution age method, employing grain size separated fractions of the sediment involved, could be a fruitful way to improve confidence in the interpretations of sediment transport history.

6. Summary and conclusions

The time scales of U-series isotopes, which are in the range of a few thousand to a few hundred thousand years, are applicable to study of sediment transport and deposition processes. These isotope systems can be applied to Late Pleistocene or active sedimentary systems to help estimate the rates at which sediment is generated by weathering and erosion and transported to the sites of deposition. In many circumstances the U comminution ages can yield the time since deposition, i.e. depositional age of the sediment. The specific approach of using the U comminution age, which involves measuring the depletion of ^{234}U relative to ^{238}U, is not dependent on chemical fractionation as in the case of the U-Th isotopic disequilibrium approach, but rather on the physical shape and size of sand grains. The U comminution age method is complementary to the U-Th approach, as well as to cosmogenic nuclide methods.

The primary source of uncertainty in the application of U comminution ages is in determining the effective ^{234}U loss rate due to recoil effects in small sediment grains (fraction of ^{238}U-decays leading to loss of ^{234}U is denoted as f_α). The ^{234}U loss rate is related to the surface/volume ratio of the grains, which is difficult to estimate precisely due to uncertainty in the surface area stemming from roughness of natural mineral grain surfaces. Multiple approaches have been proposed for estimating surface area of mineral grains, the most promising results have come from combining gas adsorption methods with estimates of the fractal dimension of the grain surfaces (Bourdon et al., 2009; Oster et al., 2012). It may also be possible to use measurements of $^{226}Ra/^{230}Th$ to directly measure f_α, but this approach has not been tested. In situations where a continuous sediment section can be measured, it is possible to use the data to infer both the transport time and f_α.

Recent studies of the $(^{234}U/^{238}U)_{AR}$ of modern glacial outwash and stream sediments suggest that the initial $(^{234}U/^{238}U)_{AR}$ of silt and fine silt-sized sediment grains is typically equal to the radioactive equilibrium ratio (activity ratio = 1.00 ± 0.01). There is no obvious correlation of this ratio with bedrock lithology, although there are small deviations from the equilibrium value that are larger than the analytical uncertainties. The effects of mineral grain dissolution on the U comminution age systematics can be small, but no study has specifically addressed this issue. Secondary authigenic minerals can disturb the U isotope systematics, and need to be leached away prior to analysis. Leaching procedures can affect the results and more robust protocols for sample preparation need to be established.

The available data suggest that the U comminution age method has substantial potential to aid in quantifying sediment transport times, especially for ocean sediments that are redistributed on the ocean floor by bottom currents, and for dating alluvial and other types of terrestrial sediments that are up to or slightly more than 500,000 years old. The comminution age method may also be useful for understanding the formation of cataclastic material such as fault gouge in active fault zones.

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