

Sediment Transport Time
Measured with U-series Isotopes:
Results from ODP North Atlantic Drift Site 984

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Abstract: High precision uranium isotope measurements of marine clastic sediments are used to measure the transport and storage time of sediment from source to site of deposition. The approach is demonstrated on fine-grained, late Pleistocene deep-sea sediments from Ocean Drilling Program Site 984A on the Bjorn Drift in the North Atlantic. The sediments are siliciclastic with up to 30 percent carbonate, and dated by $\delta^{18}\text{O}$ of benthic foraminifera. Nd and Sr isotopes indicate that provenance has oscillated between a proximal source during the last three interglacial periods – volcanic rocks from Iceland – and a distal continental source during glacial periods. An unexpected finding is that the $^{234}\text{U}/^{238}\text{U}$ ratios of the silicate portion of the sediment, isolated by leaching with hydrochloric acid, are significantly less than the secular equilibrium value and show large and systematic variations that are correlated with glacial cycles and sediment provenance. The ^{234}U depletions are inferred to be due to α -recoil loss of ^{234}Th , and are used to calculate “comminution ages” of the sediment - the time elapsed between the generation of the small ($\leq 50 \mu\text{m}$) sediment grains in the source areas by comminution of bedrock, and the time of deposition on the seafloor. Transport times, the difference between comminution ages and depositional ages, vary from less than 10 ky to about 300 to 400 ky for the Site 984A sediments. Long transport times may reflect prior storage in soils, on continental shelves, or elsewhere on the seafloor. Transport time may also be a measure of bottom current strength. During the most recent interglacial periods the detritus from distal continental sources is diluted with sediment from Iceland that is rapidly transported to the site of deposition. The comminution age approach could be used to date Quaternary non-marine sediments, soils, and atmospheric dust, and may be enhanced by concomitant measurement of $^{226}\text{Ra}/^{230}\text{Th}$, $^{230}\text{Th}/^{234}\text{U}$, and cosmogenic nuclides.

Keywords: Isotope geochemistry, sediment transport, U-series isotopes, geochronology, North Atlantic, glacial cycles

1. Introduction

The timescales of sedimentary processes are important for understanding the relationships between tectonics, climate, and landscape evolution. However, the most important sedimentary timescales are difficult to determine despite recent advances in geochronology [1-3]. Here we present evidence that U-series isotope measurements of clastic silicate sediment provide a means of determining the time required to transport detritus from its site of generation by weathering and erosion to the site of deposition. The “transport time,” as defined here and illustrated with data from deep marine sediments, includes storage time, such as in soils, floodplains, and continental shelf environments. The approach used emphasizes the role of α -recoil, rather than chemical leaching, in determining the extent of disruption of U-series radioactive equilibrium.

The general conclusions of this paper derive from a study of U, O, Nd and Sr isotopes in fine-grained deep sea sediments, aged 10 to 365 ka, cored in the North Atlantic Ocean at Ocean Drilling Program Site 984A [4]. The drill site is located on the Bjorn Drift, where bottom currents have reworked the detritus and the sedimentation rates are high [5]. The sediments are largely siliciclastic, but have a significant carbonate component. A detailed late Quaternary climate record is available based on the $\delta^{18}\text{O}$ of foraminifera and magnetic susceptibility. The measured $^{234}\text{U}/^{238}\text{U}$ ratios of the silicate portion of the sediments change systematically through glacial cycles. These variations can be understood in terms of α -recoil effects in fine-grained detritus [6, 7]. Below we review the expected behavior of $^{234}\text{U}/^{238}\text{U}$ ratios in fine sediment grains, which leads to the definition of a “comminution age” for sediment, and then evaluate the extent to which data for Site 984A fit the expected behavior. The emphasis here on α -recoil needs justification, as many other authors have assumed that chemical leaching of solids is the primary mechanism for producing disruption to the U-series radioactive decay series.

This study is one of the first to apply high precision mass spectrometric measurements to U-series isotopes in silicate sediments. In the earliest U-series isotopic studies, $^{234}\text{U}/^{238}\text{U}$ ratios were measured by alpha counting techniques, where the precision of about $\pm 5\%$ to $\pm 10\%$ [e.g. 8, 9] was too poor to see the details of solid phase ^{234}U distributions. The $^{234}\text{U}/^{238}\text{U}$ ratio can now be measured with an accuracy of ca. $\pm 0.1\%$ by TIMS and multi-collector ICPMS [3, 10-14]. The greatly improved measurement precision makes it possible to clarify the ^{234}U loss characteristics of solids, and how they relate to grain size, mineralogy, surface area, and chemical environment.

2. U isotopes in sediment grains

2.1 General model for α -recoil effects

Our interpretation of variations in the $^{234}\text{U}/^{238}\text{U}$ ratios in sediments is based on a model for the disruption of the ^{238}U decay series due to the loss of the decay product ^{234}Th by recoil associated with the alpha decay of ^{238}U [15-21] (Figure 1). The recoil ^{234}Th atoms (24.1 days) rapidly β -decay to ^{234}Pa (6.7 hours) and then to ^{234}U . In “normal” rock material, it is expected that the $^{234}\text{U}/^{238}\text{U}$ ratio will be the “secular equilibrium” ratio – the inverse of the ratio of the decay constants of the two nuclides:

$$\frac{^{234}\text{U}}{^{238}\text{U}_{SE}} = \frac{\lambda_{238}}{\lambda_{234}} = 0.00005489 \quad \text{or} \quad \left(\frac{^{234}\text{U}}{^{238}\text{U}} \right)_{SE} = 1 \quad (1)$$

The parentheses in the second equation denote the activity ratio. In general, $^{234}\text{U}/^{238}\text{U}$ ratios are discussed in terms of the activity ratio even though the isotope ratio is now the measured quantity [10, 22, 23]. A fragment of rock or mineral that is “normal” in this context is large enough that there is no loss of intermediate decay products in the U decay series, and undisturbed for a sufficiently long time to establish secular equilibrium (roughly 1 million years for the ^{238}U decay series). In most studies of U-series isotopes in silicate rocks, ($^{234}\text{U}/^{238}\text{U}$) is either not measured or not reported, because it is assumed that the ratio is very close to the secular equilibrium value. In studies where it is reported [e.g. 24, 25], which are studies of young volcanic rocks for the most part, the activity ratios average 1.000 ± 0.005 , and are unity within the analytical uncertainty. The conclusion that most rocks have the secular equilibrium ($^{234}\text{U}/^{238}\text{U}$) values probably

applies to crystalline rocks, but may not be an accurate description of some sedimentary rocks and volcanic tuffs, depending on porosity, grain size, and degree of lithification.

In rock fragments or mineral grains that are sand size or smaller, a measurable fraction of the ^{234}Th atoms produced from alpha decay of ^{238}U is ejected from the solid grains into the surrounding medium (Figure 1). One result of this effect is that surface water and groundwaters have ($^{234}\text{U}/^{238}\text{U}$) up to 20 times higher than the secular equilibrium ratio [3, 26 and others, 27-38]. As groundwater acquires a high ($^{234}\text{U}/^{238}\text{U}$), the solid phase ($^{234}\text{U}/^{238}\text{U}$) becomes less than 1, although for many materials the depletion is negligible. Depletion in the ($^{234}\text{U}/^{238}\text{U}$) of solids becomes significant only when the grain size is sufficiently small or the surface area in contact with percolating fluids is large. The ($^{234}\text{U}/^{238}\text{U}$) enrichment in pore waters is much larger than the ($^{234}\text{U}/^{238}\text{U}$) depletion in the associated solids because the U concentration in waters is typically 1000 times smaller than in solids.

The lowering of ($^{234}\text{U}/^{238}\text{U}$) in fine-grained sediment, originally described by Ku [8], is easily measurable with modern mass spectrometric methods [3, 6], although it has not received much attention by comparison to ($^{234}\text{U}/^{238}\text{U}$) in natural waters. The ^{234}Th recoil distance is in the range 30 to 40 nanometers in silicates [15, 16, 39]. The original estimate by Kigoshi [15] was 55 nm in zircon (which would imply a range of about 70 nm in feldspar), but more recent measurements, as well as calculations using the quantum-mechanical SRIM model [40], suggest that the value is closer to 30 nm for most silicate minerals [7]. For an ideal spherical mineral grain, the fraction of ^{238}U decays that should result in the immediate ejection of the daughter ^{234}Th atom from the grain (denoted here as f_α) is [15]:

$$f_\alpha = \frac{3}{4} \left(\frac{L}{r} - \frac{L^3}{12r^3} \right) \quad (2)$$

where L is the recoil distance and r is the grain radius. Measurements of $^{234}\text{U}/^{238}\text{U}$ ratios in fine-grained sediments suggest that the fraction of ^{234}U atoms lost as a result of ^{234}Th recoil is typically much greater than that predicted by the spherical grain model and the

mean grain size. In deep-sea sediments with average grain size of about 10 μm , fractional depletions of 20 to 30 % in ($^{234}\text{U}/^{238}\text{U}$) are observed [6, 8, 9], whereas equation 2 would predict 0.5% for spheres of 10 μm diameter. This discrepancy may be one reason that preferential leaching of ^{234}U from lattice-damaged sites is thought to be important. However, detailed consideration of grain geometry suggests that there is in fact little or no discrepancy.

2.2. Geometrical estimation of ^{234}U loss

Sediments have larger f_α values than calculated with equation 2 for several reasons. Mineral grains are not typically spherical and they have surface roughness. If a grain has a plate shape (or oblate spheroidal shape) with an aspect ratio of β and a surface roughness factor of λ_s , then f_α will be larger than predicted by equation 2 by a factor of $\lambda_s(1+\beta)/3$ for disk-shaped grains, and approximately $\lambda_s(3+\beta)/2$ for oblate spheroids with $\beta > 5$. In addition, because sediments have a distribution of grain sizes, and the recoil loss factor is a function of grain surface area rather than volume, the finest fractions of the sediment make a contribution to the bulk sediment f_α that is much larger than their mass- or volume fraction would imply. A more accurate formulation for the bulk sediment fractional loss factor is therefore:

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

where $X(r)$ is the volume fraction of grains with major radius r . Figure 2 shows a comparison of the f_α value calculated for spherical grains with a specific radius, for disk- and oblate-spheroid-shaped grains with the same large dimension as the spheres, and with additional effects due to surface roughness and grain size distribution. For the example distribution, the enhancement of f_α due to the presence of smaller grains is a factor of about 3. Also shown is an estimate of f_α for Site 984 sediment using a measured grain size distribution from Carter and Raymo [41] and typical values of β (1 for the largest grains to 10 for the smallest), and λ_s (2 for the larger grains to 1 for the smaller grains). This figure shows that it is possible to account for the observed range of f_α values in the

Site 984 sediments (about 0.135 to 0.19 as discussed below) entirely by α -recoil with reasonable values of β and λ_s , and without additional leaching effects.

Another way to estimate f_α is to use measurements of specific surface area [15, 29]. If the surface roughness is of the same scale as, or larger than the recoil range, then the following should apply:

$$f_\alpha = \frac{1}{4} L \cdot S \cdot \rho_s \quad (4)$$

where S (m^2/g) refers to the specific surface area and ρ_s is bulk density. Unfortunately, f_α can be much smaller than one might predict from standard measures of surface area. For example, the BET method is sensitive to surface roughness at the scale of the adsorbed gas molecules, which is about 0.3 nm. Since the recoil length is about 30 nm, or 100 times larger than the gas molecules, the BET measurements can grossly overestimate the recoil loss factor.

There are other potential complications of the geometric analysis of recoil. The geometric models will not provide an accurate description of preferential ^{234}U loss from sediment grains if the grains are subject to preferential leaching of ^{234}U [42-46], if the grains are undergoing active dissolution, or if there is ^{234}Th implantation between grains [47]. Dissolution is expected to limit the amount of ^{234}U depletion because the most ^{234}U -depleted parts of the grain – the near-surface regions – should also be the first to dissolve. The effects of preferential leaching, mineral dissolution, and implantation are discussed further below in the light of data presented here.

3. The ^{234}U comminution age

According to the model presented above, when a small mineral grain is produced by erosion, it begins to leak ^{234}Th to its surroundings and the bulk ($^{234}\text{U}/^{238}\text{U}$) starts to decrease. If the grain size does not change substantially over time, the $^{234}\text{U}/^{238}\text{U}$ ratio will eventually reach a steady state value that is a function of the grain size (or surface-to-volume ratio) and the ^{234}Th recoil distance. The time required to reach the steady state ($^{234}\text{U}/^{238}\text{U}$) appropriate to a particular grain population is about 1 million years (Figure 3).

The decrease in ($^{234}\text{U}/^{238}\text{U}$) measures the time since the small grain was produced, which is referred to here as the "comminution age." In the case of glacial sediment, the rock flour produced by glacial abrasion is produced directly from bedrock, and hence the time of "comminution" (literally "to reduce to powder") is well defined in a geological context. For mechanical weathering by other processes, the production of sub-50 μm grains may be more extended in time. Regardless of the mechanism, once a particle reaches sufficiently small size, its ($^{234}\text{U}/^{238}\text{U}$) will begin to decrease, and the ratio will therefore be monitoring its "age." If the time between production of the small grains and deposition on the sea floor is relatively short (10,000 years or less; which is much smaller than the 354,000 year mean life of ^{234}U), then the particles will still have ($^{234}\text{U}/^{238}\text{U}$) close to the secular equilibrium value (or the bedrock source value) when they are deposited. If the timescale for transport to the site of deposition is much longer (greater than 50,000 years), then the grains will be deposited with ($^{234}\text{U}/^{238}\text{U}$) that is significantly less than the source rock value.

The ($^{234}\text{U}/^{238}\text{U}$) ratios of sediment grains continue to decrease after sedimentation and burial. Consequently, the comminution age of a sediment grain is the sum of the depositional age (time elapsed since deposition) and the "transport time," or the time that elapsed between the formation of the grain and its deposition. The ($^{234}\text{U}/^{238}\text{U}$) of bulk sediment (Figure 3) depends on its fractional loss rate (f_α), and its comminution age. Measurements of sediment size fraction ($^{234}\text{U}/^{238}\text{U}$) as a function of depth below the seafloor (or versus age where it is known independently) potentially allow retrieval of both the effective fractional loss rate, and the comminution age at the time of deposition, using a graphical construct as illustrated in Figure 3b. As described below, it may also be possible to estimate f_α for a particular grain population by measuring the shorter-lived U-series isotopes ^{230}Th and ^{226}Ra . The comminution age at the time of deposition can be considered to be the "sediment transport time." Because of the timescale set by the mean life of ^{234}U , this approach is applicable only to sediments that are younger than about 1 million years.

The mathematical expression for the comminution age is derived from the equation that describes the activity ratio of the comminuted solid:

$$A_{meas} = (1 - f_{\alpha}) + [A_o - (1 - f_{\alpha})]e^{-\lambda_{234}t_{com}} \quad (5)$$

where A_{meas} is the measured activity ratio of the sediment, t_{com} is the comminution age, and A_o is the activity ratio of the provenance rock. Equation 5 incorporates the approximation $\lambda_{234} - \lambda_{238} = \lambda_{234}$, and the assumption that f_{α} is constant. Rearranging yields this expression for the comminution age:

$$t_{com} = -\frac{1}{\lambda_{234}} \ln \left[\frac{A_{meas} - (1 - f_{\alpha})}{A_o - (1 - f_{\alpha})} \right] \quad (6)$$

The uncertainty in the calculated comminution age is largely due to uncertainty in the estimate of f_{α} , and partly to any uncertainty in A_o .

4. Samples and Analytical Procedures

The samples analyzed are from North Atlantic Ocean ODP Site 984A (61°25.507'N, 24°04.939'W) drilled during Leg 162 [4]. Site 984 is located on the Bjorn Drift on the southeastern flank of the Reykjanes Ridge (southwest of Iceland) at about 1650 m water depth (Fig. 4). The accumulation rate of the sediment is between 11 and 22 cm/kyr, which is high enough that the Quaternary sediment record is well displayed. The sediment is mainly composed of well-sorted terrigenous silt [48] containing biogenic carbonate, basaltic material derived from Iceland, and a fine amorphous component that may be biogenic silica [41, 49]. Although it has been inferred that most of the detritus deposited at Site 984A is derived from Iceland, the results presented below, as well as those reported previously by Revel et al. [50, 51] for a nearby locality, clearly show that much of it has a continental source. Foraminiferal abundance and calcium carbonate contents are generally low. Calcium carbonate contents were not measured directly on samples from Hole 984A, but were found to be between 3% and 30%, with an average of

7% in the equivalent depth interval of Hole 984. The mineralogy of the sediment is dominated by plagioclase, smectite, and quartz, with lesser amounts of illite, kaolinite and chlorite, in order of decreasing abundance [41]. The bottom current, which supplies sediment to the drift site (Figure 4), acts to select particles according to their hydraulic dimensions resulting in a condensed grain size distribution. The average grain size, based on relatively few samples that have been measured is about 15 μm [41]. The Site 984 location is fed sediment mainly by currents produced from Iceland Sill overflow water (ISOW), which are likely to carry sediment originally derived from the European continent as well as sediment derived from Iceland. Ice-rafted debris is also present, but the expected deposition rate during glacial times (ca. 150 $\text{mg}/\text{cm}^2/\text{ky}$) constitutes less than 1% of the total sediment flux [52].

Details of the analytical procedures as well as U isotopic data from the pore fluid are given in Maher et al. [6], who leached the sediment samples according to the sequential extraction procedure of Tessier et al. [53] with some modification. The sodium acetate leaching procedure did not remove all of the carbonate. To completely remove carbonate as well as authigenic phases, the samples for this study were leached in 1.5 N HCl for 30 minutes in an ultrasonic shaker. After removal of the leachate and subsequent distilled water rinses, the residues were completely digested using concentrated HF-HClO₄.

The HCl residues were analyzed for $^{234}\text{U}/^{238}\text{U}$ with the Lawrence Berkeley National Laboratory Isoprobe (Table 1). The analysis procedure incorporates an instrumental mass discrimination correction based on the $^{235}\text{U}/^{238}\text{U}$ ratio, and a Faraday-Daly intercalibration using an in-house secular equilibrium U standard [14]. The analytical precision is estimated to be $\pm 0.15\%$ of the activity ratio (2 sigma). The samples were measured for Sr and Nd isotopes using standard chemical separation methods and the U.C. Berkeley ThermoFinnigan Triton multicollector thermal ionization mass spectrometer. The analytical uncertainties in the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are small (roughly 10 ppm of the ratio) and entirely negligible for the purposes of this study.

Oxygen isotope data were obtained at WHOI using standard techniques. The sediment ages (Table 1) are determined from the foraminifer $\delta^{18}\text{O}$ data by correlation to the timescale of Shackleton et al. [54], plus additional statistical treatment described in Raymo et al.[5]. The data are available from the supplement to Raymo et al.[5].

5. Results

The ($^{234}\text{U}/^{238}\text{U}$) measured for pore fluid and bulk sediment from Site 984A [from 6], and the HCl-leached residues used in this study are shown in Figures 5 and 6. The pore fluids have elevated ($^{234}\text{U}/^{238}\text{U}$) as expected due to preferential release of ^{234}U from the solids due to recoil, but not as high as they might be if it were not for concomitant dissolution (weathering) of silicate minerals and recrystallization of carbonate [6, 55]. Both silicate weathering and carbonate recrystallization add U with low $^{234}\text{U}/^{238}\text{U}$ to the pore fluid. Primary marine carbonate is deposited with the seawater activity ratio of 1.146 [56] and its presence affects the ($^{234}\text{U}/^{238}\text{U}$) of the bulk solids. The HCl leaching procedure attacks mainly authigenic minerals and carbonate, both of which tend to have ($^{234}\text{U}/^{238}\text{U}$) greater than unity. The residues from HCl leaching are assumed here to represent the detrital silicate fraction essentially free of carbonate and authigenic components.

The measured ($^{234}\text{U}/^{238}\text{U}$) of the HCl-leached residues vary between 0.83 and 0.96 (Figure 6). There is pronounced cyclicity as a function of depth, which by comparison to the O isotope record appears to correspond to glacial cycles. For the past three 100-kyr glacial cycles, the sediments deposited at Site 984A during interglacial periods have had relatively high ($^{234}\text{U}/^{238}\text{U}$), whereas during the prolonged glacial periods the $^{234}\text{U}/^{238}\text{U}$ ratios are relatively low. This pattern does not apply to the sediments that are older than 300 ka (i.e. deeper than about 45 meters mean composite depth (mcd)).

Figure 7 shows the HCl-residue data plotted using the sediment age data so that the time evolution curves are straight lines as in Figure 3b. A simple interpretation of the pattern is that there is a bimodal distribution of initial ($^{234}\text{U}/^{238}\text{U}$). One component of the sediments was deposited with an initial ($^{234}\text{U}/^{238}\text{U}$) near 1.00 and has a recoil loss factor

of 0.135. The other component was deposited with an initial ($^{234}\text{U}/^{238}\text{U}$) near 0.88 and has a recoil loss factor of 0.19.

The Nd and Sr isotope parameters (ϵ_{Nd} and $^{87}\text{Sr}/^{86}\text{Sr}$) are well correlated (Figure 8). This correlation is consistent with the sediments being composed of two components. A similar correlation is observed for samples from the Gardar drift [50, 51]. The high $-\epsilon_{\text{Nd}}$ component is likely to be Icelandic volcanic rocks. The most extreme sample, from a depth of 49.84 m in the Site 984A core (mcd = 54.18 m) is taken from an ash layer and is an example of a pure volcanic component from Iceland. Icelandic volcanic rocks vary in isotopic composition to some degree, but the values of $\epsilon_{\text{Nd}} = +6.4$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.70355$, which characterize the ash layer and the inferred sediment component, are typical and close to the overall Iceland average values. The range of values for Iceland tholeiitic basalt is roughly $\epsilon_{\text{Nd}} = +5$ to $+8$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7033$ to 0.7037 [57]. The other sediment component must have $\epsilon_{\text{Nd}} \leq -10$ and $^{87}\text{Sr}/^{86}\text{Sr} \geq 0.715$. This low- ϵ_{Nd} component is clearly derived from continental sources, and the isotopic ratios are a good match to typical European basement rocks [51, 58] and in particular, to glacial sediments of the southern margin of the Norwegian-Greenland Sea [59].

The comminution ages for the Site 984A samples are calculated assuming that the sediments are 2-component mixtures and that f_a correlates with the initial ($^{234}\text{U}/^{238}\text{U}$). The uncertainty in f_a is estimated to be about $\pm 10\%$ to $\pm 20\%$, which yields an uncertainty in t_{com} of about the same relative magnitude. Since the comminution ages are mostly in the range of 400 to 600 kyr, the uncertainties in t_{com} and in the inferred transport times are about ± 40 to ± 100 kyr. Hence the transport times are not highly precise.

The inferred bulk sediment transport time, Nd isotopic composition, $\delta^{18}\text{O}$ data, and sedimentation rates derived from the $\delta^{18}\text{O}$ data, are compiled and plotted against age in Figure 9. The Nd isotopic composition and $^{234}\text{U}/^{238}\text{U}$ transport time are plotted against one another in Figure 10. The transport time changes systematically between glacial times and interglacial times for the past three glacial cycles. The transport time varies

from less than 10 kyr (± 50 kyr) up to 400 kyr (± 100 kyr) and is generally long during glacial times. The Nd isotope measurements also show corresponding, although not perfectly correlated, changes in provenance between glacial and interglacial times. During interglacial times the sediment is typically dominated by material derived from Iceland and transported rapidly to the site of deposition (Figure 10). During glacial times, the sediment is generally from a continental source and has a long transport time. However, there are examples where detritus that is mostly from the volcanic source has a long transport time, and where detritus with a large continental component has a short transport time. The breakdown of the correlation between glacial cycles and transport time is clearest for the deepest three samples (ages 350 – 365 ka; Figure 9). One of these is an ash sample and would not be expected to conform to the pattern. The other two samples are also largely from the volcanic source, but appear to have been transported quickly to the site of deposition even though they were deposited during a glacial period.

6. Discussion

6.1. Recoil loss factor, grain size and surface area

The comminution age calculated from sediment ($^{234}\text{U}/^{238}\text{U}$) is dependent on the recoil loss factor, f_α , which should be a function of grain size or specific surface area. The data presented here on dated sediments are used to estimate f_α (Figure 5) but it would be desirable to understand in more detail the relationship between grain size and recoil loss rates of ^{234}U , and to be able to estimate f_α from a measurable property of the sediment. Specific surface area has been measured by the BET method on some Site 984 bulk samples [55] and is found to be about $55 \text{ m}^2/\text{g}$, which corresponds to $f_\alpha \approx 1$. This high value is probably a reflection of the extremely high surface area of the clay mineral fraction. The measured f_α values suggest specific surface area of about 3 to $8 \text{ m}^2/\text{g}$, which is close to that measured for feldspar with a grain size similar to that of the sediment at Site 984 [6, 60].

A direct measure of the recoil loss rate could potentially be derived from measurements of other U-series isotopes. Both ^{230}Th ($\lambda^{-1} = 109$ kyr) and ^{226}Ra ($\lambda^{-1} = 2.3$ kyr) might be useful for this purpose. These isotopes will reach steady state much faster than ^{234}U ($\lambda^{-1} = 354$ kyr), and the relevant recoil ranges are similar to that of ^{234}Th . For example, our calculations using the online program SRIM [40], indicate that the recoil distances associated with ^{238}U , ^{234}U , ^{230}Th decay in feldspar (density = 2.7 g/cm^3) are 30, 32, and 32 nm respectively. With small corrections for the difference of recoil range, measurements of these isotopes in conjunction with measurements of ^{234}U could yield direct estimates of f_α . For example, assuming that $f_\alpha = (30/32)[1-(^{226}\text{Ra}/^{230}\text{Th})]$, the comminution age is given by:

$$t_{com} = -\frac{1}{\lambda_{234}} \ln \left\{ \frac{(A_{meas} - 1) - 0.94[(^{226}\text{Ra}/^{230}\text{Th}) - 1]}{(A_o - 1) - 0.94[(^{226}\text{Ra}/^{230}\text{Th}) - 1]} \right\} \quad (7)$$

Measurements reported in the literature on suspended stream sediment are relevant to the idea of using ^{226}Ra to estimate f_α , and more generally to our interpretations of the deep-sea sediment U isotope ratios at Site 984. Vigier et al [3] measured suspended sediment in the Mackenzie River of Northwestern Canada and found that the particles have ($^{234}\text{U}/^{238}\text{U}$) in the range 0.897 to 0.992. The grain size distribution of the samples was not measured, but the samples represent material retained by a $0.2 \mu\text{m}$ filter. The maximum grain size is probably less than about $20 \mu\text{m}$. Considering the fine grain size, it is likely that the f_α values are greater than 0.1, based on our measurements of Site 984 sediments. If the mean grain size is in the range $1 - 10 \mu\text{m}$, then the f_α values are likely to be in the range 0.1 to 0.5. The Vigier et al [3] measurements of ($^{226}\text{Ra}/^{230}\text{Th}$) confirm this inference; the measured values are 0.596 to 0.918, and in all cases ($^{226}\text{Ra}/^{230}\text{Th}$) is smaller than ($^{234}\text{U}/^{238}\text{U}$). Vigier et al [3] did not consider the geometric aspects of recoil loss despite the fine grain size of their samples, and used instead a chemical leaching model and ($^{238}\text{U}/^{230}\text{Th}$) to estimate that the “age” of the suspended load is in the range 5 to 25 kyr. They note that the ages inferred with their approach are low in comparison to soil residence times that should approach 100 kyr. The calculated $^{234}\text{U}/^{238}\text{U}$ comminution ages using equation 7 are 102 to 387 kyr for the samples where t_{com} is relatively well

constrained by the data. Four of the six samples have t_{com} between 102 and 151 ka. These ages accord better with estimates of soil residence times, and are also similar in magnitude to those estimated for the Site 984A sediments from the continental source. Thus the Vigier et al [3] data are consistent with our estimates of f_{α} , the idea that ($^{226}\text{Ra}/^{230}\text{Th}$) can be used to estimate f_{α} , and our overall model for comminution ages. Vigier et al [3] did not leach their sediment samples before dissolution, so it is possible that adsorbed Ra, Th or U affects to some extent their reported activity ratios, and hence also the inferred comminution ages.

It is notable that the grain size range for the Site 984 sediments is close to ideal for observing systematic U isotope effects. The Site 984 sediments have both an appropriate mean grain size and a relatively compressed grain size distribution due to sorting during bottom current transport. The grain size distribution also does not vary drastically with time. In other sedimentary settings, the grain size distribution may not be as uniform or consistent over time, and the U isotope measurements would need to be done on only the appropriate size fractions. Separating the finest size fractions may also be a means to isolate eolian input where that is an issue. If U isotope data are obtained only on the fine-grained fraction, it is possible that its transport history is different from that of the coarser fractions. This issue could be addressed by combining U isotope measurements of the fine fractions with cosmogenic nuclide measurements of the coarser fractions.

6.2. Natural preferential leaching and mineral dissolution

As noted above, the interpretation of ($^{234}\text{U}/^{238}\text{U}$) values in solids may be affected by preferential leaching of ^{234}U from sites within mineral grains in the interior regions (i.e. > 30 nm depth from the surface). If the ^{234}U is leached only from sites within a few recoil distances of the grain surface, the net effect would be to increase the effective value of the recoil range. This would not change the approach used here significantly, since the recoil loss rate cannot be directly estimated from the recoil range anyway. Data from a sequence of Pleistocene fluvial sediments cored at the Hanford site in south central Washington [7, 61] are relevant to this issue. The Hanford sediments have a granitic

provenance and were deposited mainly by catastrophic flood events associated with deglaciation pulses during the Pleistocene [62]. The sediments vary in age from about 15,000 years up to more than 1 million years [63]. The HCl-leached sand size fractions (>65 μm) have ($^{234}\text{U}/^{238}\text{U}$) close to the secular equilibrium value (0.988 to 1.006) whereas the fractions that are silt size and smaller (<45 μm) have activity ratios that are significantly lower (0.947 to 0.967) but higher than those measured for the Site 984A sediments. The Hanford data provide little evidence that natural leaching by groundwater is lowering the $^{234}\text{U}/^{238}\text{U}$ ratios significantly, because the grains that are sufficiently large that they should not be affected by recoil (Figure 2), also show virtually no lowering of ($^{234}\text{U}/^{238}\text{U}$). Any leaching that is occurring must be affecting only a thin region near the grain surface, to a depth that is not much greater in magnitude than the recoil range.

The effect of dissolution on the ($^{234}\text{U}/^{238}\text{U}$) of sediment grains can be roughly 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, which is $\lambda_{234}^{-1} = 354$ kyr, to the time scale for removing a layer of thickness L from the surface of a grain by dissolution. This ratio:

$$\frac{\tau_{recoil}}{\tau_{diss}} = \frac{R}{\lambda_{234}^{-1} L \rho} \quad (8)$$

depends on the specific mineral dissolution rate, R , which has been estimated for the Site 984A sediments by Maher et al. [55] to be 2.5×10^{-18} mol/m²/sec (2.1×10^{-12} g/cm²/yr), assuming that the primary dissolving mineral is plagioclase feldspar or any material with approximately the same Ca concentration. Using $L = 30$ nm and $\rho = 2.7$ g/cm³ yields a value for this dimensionless number of 0.1, which suggests that the ^{234}U depletion structure of the grains at Site 984 is only slightly affected by dissolution. If the depletion rind in the grains is actually thicker than L as a result of preferential leaching, then the effect of dissolution is proportionally smaller. On the other hand, if the dissolution rate were significantly higher, then mineral dissolution would limit the amount of ^{234}U depletion and tend to make the calculated transport times shorter.

6.3. *Effects of leaching during analysis and ^{234}Th implantation*

An essential component of the analytical procedure used in this study is the leaching of the sediment samples in weak HCl. The details of the leaching procedure may affect the results, and thus far we have not experimented extensively with different leaching procedures. For deep-sea sediments like those of Site 984, which contain both primary and authigenic carbonate, it is necessary for the samples to be leached to remove carbonate. Our results suggest strongly that leaching with acetic acid is insufficient to quantitatively remove carbonate [6]. Clay minerals, with their small grain size and large surface area, are likely to contain a significant amount of adsorbed U, Th and Ra, and hence leaching is also necessary to remove these adsorbed components. Leaching may also affect the measured magnitude of recoil effects by removing some easily dissolved surface irregularities on silicate grains, and by leaching some ^{234}U out of lattice-damaged sites beneath the grain surface. The net effect of the HCl-leaching procedure we used does not appear to generate spurious ($^{234}\text{U}/^{238}\text{U}$) ratios, insofar as the ^{234}U depletions we measure are reasonable, consistent in magnitude, and compatible with the grain size and likely surface roughness of the samples. It is noteworthy that the ash sample at mcd = 54.18 m, which should have started with the secular equilibrium ($^{234}\text{U}/^{238}\text{U}$) and was instantaneously transported to the ocean floor, has almost exactly the ($^{234}\text{U}/^{238}\text{U}$) ratio expected for the inferred age and estimated f_{α} value. In the study of Hanford sediments referred to above, we have shown that much stronger leaching does not yield the desired results. Leaching of Hanford sediment with concentrated HNO_3 apparently dissolves the ^{234}U -depleted surface regions of the grains, yielding residues with increased ($^{234}\text{U}/^{238}\text{U}$) [7].

Another potential complication is that recoil ^{234}Th from mineral grains with high U concentration could be implanted into neighboring grains, either in the source rock or in the sediment [64]. This effect, which would tend to lower the communitation ages, is probably insignificant in our data for two reasons. The small recoil range of ^{234}Th would restrict implantation to a small percentage of grain surfaces, and experiments suggest that

the ^{234}U resulting from this implantation is rapidly leached away [19]. It is also possible that our HCl leaching procedure removes any implanted ^{234}U .

6.4. Transport times for sediment

An unexpected result of this study is that sediment transport times are as long as 300 to 400 kyr. Prevailing models suggest that fine-grained sediment is transported through stream systems rapidly; probably “instantaneously” (i.e. in less than 10 kyr) in terms of the resolution of our comminution ages. Soil residence times are thought to be in the range 10 kyr to 100 kyr, although they must vary with climate and terrain. More data are needed from other sedimentary environments to determine the generality of our results. Until now, sediment transport time has not been measured directly, but rather has been inferred from material balance in watersheds [e.g. 65].

For the case of the drift sediments of Site 984A, the sediment may have a long transport time because it is redistributed from somewhere else on the ocean floor. During both interglacial and glacial times, sediment derived mainly from Iceland, which is close to Site 984, is transported to the site rapidly. Almost all of the sediment with long transport times is derived from the continental source. It is therefore likely that this sediment was either stored on the continent or continental shelf areas for a relatively long time, or is older Pleistocene sediment that was reworked by the bottom currents. If soil residence time is 100 kyr or more, and the sediment is reworked material deposited in earlier glacial cycles, then it might be reasonable to get total transport times of greater than 200 kyr as observed. It is also possible that the comminution ages we calculate are too high due because the source rock activity ratio is less than one.

6.5. Glacial-interglacial sedimentation changes

Both the cyclical variation in sediment provenance and the variations in transport time are significant for the oceanographic and sedimentary evolution of the North Atlantic. The Bjorn Drift is one of several regions of the North Atlantic Ocean bottom in

which sedimentation rates are abnormally high (ca. 10-20 cm/kyr; Figure 9d). The strong currents generated by southwestwardly flowing high-density waters of the Norwegian-Greenland Sea flow over the shallow sills formed by the Iceland-Faeroe Ridge and deposit large amounts of reworked sediment along the Bjorn Drift [66, 67]. The fact that the sediments at Site 984A are reworked adds some complications to the temporal correlation of their properties with the benthic $\delta^{18}\text{O}$ -record. The data indicate that there are relatively rapid changes in sediment provenance that occur over time periods as short as 5000 years (Figure 11). The lower time limit for provenance shifts is limited by sampling frequency for this study; it could be shorter than 5000 years. The data for the transition to the present interglacial suggest that both the provenance and transport time track the global ice volume record within a few thousand years. Similar changes in provenance were observed for North Atlantic drift sediments by Revel et al. [50]. However, the older sediments in our record do not show such a good correlation between transport time and ice volume, and only during the most recent glacial period was the sediment supply strongly dominated by the continental source (Figure 9b).

The changes in sediment properties measured here could potentially be explained either by changes in the overall sediment sources for the North Atlantic, or by changes in the strength of the bottom currents [cf. 50]. The sedimentation rates vary by about a factor of two, but are not consistently correlated with either the changes in provenance or the transport times (Figure 9d). Recent studies suggest that deep-water formation was sharply reduced and possibly even ceased during glacial conditions [68]. In the absence of a strong bottom current it might be expected that sedimentation at Site 984A would be dominated by detritus from Iceland. The Nd and Sr data, as well as the U isotope data, do not support this idea because the glacial time periods are the time of greatest contribution from foreign, presumably current-transported, detritus. The data presented here are more consistent with weaker bottom currents, or weaker continental sediment supply, during interglacial times. An alternative explanation is that the glacial- to-interglacial changes mainly reflect the extent of glaciation of Iceland. During the last glacial maximum, Iceland was entirely covered with continental glaciers [69] and surrounded by sea ice much of the year (Figure 4). The sediment supply from Iceland to

Site 984 may have been low under these conditions. The margins of Western and Northern Europe were largely south of the sea ice, and the shelf areas were above sea level (Figure 4, [70]), so glaciers may have been scouring and transporting older Pleistocene shelf sediment to the Norwegian-Greenland Sea and the eastern margin of the Atlantic, from where it was then transported to the Bjorn Drift by bottom currents. Such sediment might arrive at Site 984 with a relatively large comminution age.

During the last glacial period, sediment derived from the European continent and transported by bottom currents appears to have been the main contributor to sedimentation at Site 984. In the next two earlier glacial periods, the sediment deposited at Site 984 was more typically a sub-equal mixture of volcanic and continental detritus. Although it is unlikely that ice-rafted detritus contributed significantly to the sedimentation, it is nevertheless the case that the IRD flux was highest in the last two glacial periods, and much lower in the next earlier two glacial periods [71]. In the earliest glacial period represented in our data (Marine Isotope Stage (MIS) 10; 339-362 ka) the sediment was mainly derived from Iceland and there is little contribution from the continental source until peak glacial conditions just before the transition to the interglacial. The results suggest that sedimentation patterns during glacial periods, and even within individual glacial periods, have varied substantially over the past 365 ky.

7. Conclusions and implications

The data presented here document systematic lowering of ($^{234}\text{U}/^{238}\text{U}$) in marine silicate sediments with grain size in the range of clay to medium silt and fine sand (0.1 to 50 μm). It is argued that the depletions in ^{234}U are mainly due to α -recoil effects associated with the decay of ^{238}U , rather than chemical leaching. The ($^{234}\text{U}/^{238}\text{U}$) ratios can in many cases be converted to a model “comminution age,” the time since the rock material constituting the particle was first reduced to a small size by erosion and weathering processes.

Calculation of U isotope comminution ages requires information on the ^{234}U (or ^{234}Th) α -recoil loss rate from mineral grains. This loss rate can be inferred by measurements of samples from a stratigraphic sequence of known age or sedimentation rate. Because the depositional age is known and the comminution age is the sum of the depositional age and the “transport time,” both the sediment transport time and the recoil loss rate can be obtained. An alternative method for determining the α -recoil ^{234}U loss rate is through measurements of other U series nuclides, in particular the ($^{226}\text{Ra}/^{230}\text{Th}$) ratio. It is possible that with concurrent measurement of cosmogenic nuclides, the soil residence time and the transport time could be separated.

Sediments from a North Atlantic drift site (ODP Site 984A) just south of Iceland were measured for U, Sr, Nd and O isotopes. The $^{234}\text{U}/^{238}\text{U}$ ratios show large and systematic variations with depth in sediments that range in age from 10 ka to 365 ka. The U isotope variations correlate with glacial cycles and with sediment provenance as determined by Nd and Sr isotopes. During the last three interglacial times, the sediment at Site 984 was mainly derived from Iceland and transported rapidly (within about 10 kyr) to the site of deposition. During the last glacial period the sediment is derived largely from a continental source, probably Northern Europe, and has a comminution age at the time of deposition of 300 to 400 kyr. The long transport time measured for the glacial sediment is surprising, and suggests that the sediment is reworked from exposed shelf areas. Site 984 sediments may have yielded especially clear results because they are reworked by bottom currents, have at least two strongly contrasting sources, and have a relatively compressed grain size distribution. Further work will need to address the effects of leaching during analysis, and the relationships between α -recoil, grain size and mineralogy.

An implication of the data and models described here is that ($^{234}\text{U}/^{238}\text{U}$) measurements could be useful for determining the depositional ages of fluvial and lacustrine sediments. In areas of rapid erosion, it may be possible to assume that transport (and storage) times are short, and therefore that the comminution age equals the depositional age. U isotope

measurements may also be useful for dating glacial deposits and atmospheric mineral dust, including that recovered from ice cores, and for measuring the age or production rates of soils.

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Captions:

Figure 1: Schematic diagram of recoil ejection of ^{234}Th from a spherical grain as a result of the alpha decay of ^{234}U , followed by beta decay of ^{234}Th to ^{234}U . The net effect is depletion in ^{234}U relative to ^{238}U in the surface layer of the grain, and an enrichment of ^{234}U relative to ^{238}U in pore water surrounding the grain. Because ^{234}Th is insoluble and particle reactive, ejected ^{234}Th should adsorb to grain surfaces. When it decays to ^{234}Pa and ^{234}U , the recoil from beta-decay is too small to re-implant ^{234}Th back into the grains (and any implanted ^{234}U is likely to be easily leached and returned to the pore fluid). Similar recoil effects are associated with the α -decay of ^{234}U , ^{230}Th and ^{226}Ra .

Figure 2: Calculated and measured ^{234}U recoil loss factors (f_α) as a function of grain size. The solid line is a plot of equation 2, which applies to a single spherical grain, or a hypothetical sediment composed of spherical grains with a single grain size. Also shown are lines for plate- and oblate spheroid-shaped grains. The line labeled “Roughness=2” shows the effect of a surface roughness factor (λ_s) of 2 on oblate spheroidal grains. The uppermost line adds the effects of a grain size distribution where 50% of the grains have the mean grain size, 25% are 10 times smaller, and 25% are 10 times larger than the mean grain size. The mean grain size (15 μm) and inferred range of the recoil loss factor for sediment from ODP Site 984A is indicated. The measured range of f_α (the observed $^{234}\text{U}/^{238}\text{U}$ depletion factor) of Hanford coarse silt (45 – 60 μm) is also shown. In general, the observed f_α values can be accounted for by α -recoil effects and do not require preferential leaching of ^{234}U .

Figure 3: Evolution of the ($^{234}\text{U}/^{238}\text{U}$) in sediment grains as a function of time. For large grains (>65 μm), the loss of ^{234}U is small and they show no aging effects. For silt and clay sized grains, the fractional loss rate of ^{234}U is between a few percent and 50%. Small grains produced by mechanical erosion initially should have the secular equilibrium isotope ratio, but eventually evolve an isotope ratio that is commensurate with their size. The time scale for this evolution is $1/\lambda_{234}$, which is 354 kyr. After about a million years

the grains reach a steady state ($^{234}\text{U}/^{238}\text{U}$) that depends only on their size, but between the time of formation and 1 Myr after, the isotopic ratio depends on both size and age.

Figure 4: Map of the North Atlantic region showing the location of ODP Site 984 on the southeast side of Reykjanes Ridge. Also shown are estimated locations of the shorelines at the last glacial maximum [LGM, 70] and the location and direction of flow of modern bottom currents in the northernmost Atlantic Ocean [5]. The heavy stippled line is the southern extent of winter sea ice at the last glacial maximum [70]. The southern margin of summer sea ice at the LGM was much farther north, close to the upper boundary of the figure. The southern extent of continental glaciers in Europe is also shown; all of the other land shown (Iceland, Greenland, Eastern Canada) was completely ice-covered at the LGM.

Figure 5: U isotope ratio data for Site 984A sediments and pore fluids. Measurements by TIMS have uncertainties of about $\pm 1\%$ to $\pm 3\%$. Measurements using multi-collector ICPMS (Isoprobe) have uncertainties of $\pm 0.1\%$ or slightly better depending on sample size. Data from Maher et al. [6]

Figure 6: (a) The $^{234}\text{U}/^{238}\text{U}$ activity ratio of HCl-leached residues of bulk Site 984 samples plotted against mean composite depth. (b) Foraminifer $\delta^{18}\text{O}$ values versus depth from Raymo et al. [5].

Figure 7: Residue $^{234}\text{U}/^{238}\text{U}$ activity ratio versus exponential age factor. The Site 984 sediments appear to have variations in specific surface area that are correlated with the U isotopic ratio, which is likely to be common, but the range of the recoil loss factor is not large ($f_{\alpha} = 0.135$ to 0.19 in this case). With the initial ($^{234}\text{U}/^{238}\text{U}$) value and f_{α} , the “comminution age” can be calculated. The sediment age is known independently from the O isotope data and correlations, so the sediment age can be subtracted from the comminution age, leaving the “transport time” for the sediment – the time between comminution and deposition.

Figure 8: Sr and Nd isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd}) of HCl-leached bulk sediment from Site 984. The data are consistent with sediments being two component mixtures. One component has high ϵ_{Nd} and low $^{87}\text{Sr}/^{86}\text{Sr}$ and is most likely sediment derived from Iceland volcanic rocks. The other component has low ϵ_{Nd} and high $^{87}\text{Sr}/^{86}\text{Sr}$ and is similar to European basement rocks [50, 51, 59].

Figure 9: (a) Calculated sediment transport time for the Site 984 sediments, (b) measured ϵ_{Nd} value of Site 984 sediments, (c) foraminifer $\delta^{18}\text{O}$ values plotted versus age, and (d) estimated sedimentation rate based on O-isotope chronology. The dashed lines are provided to enable comparison between the graphs; they do not correspond to stage boundaries.

Figure 10: Initial (at time of deposition) U isotope ratio and calculated transport time versus Nd isotope ratio, which indicates provenance. The sediments appear to be mostly mixtures of detritus from Iceland, which gets transported quickly to the site, and continental detritus that has transport times of 300 to 400 kyr. There are also many samples with similar mixed provenance but a range of calculated transport times.

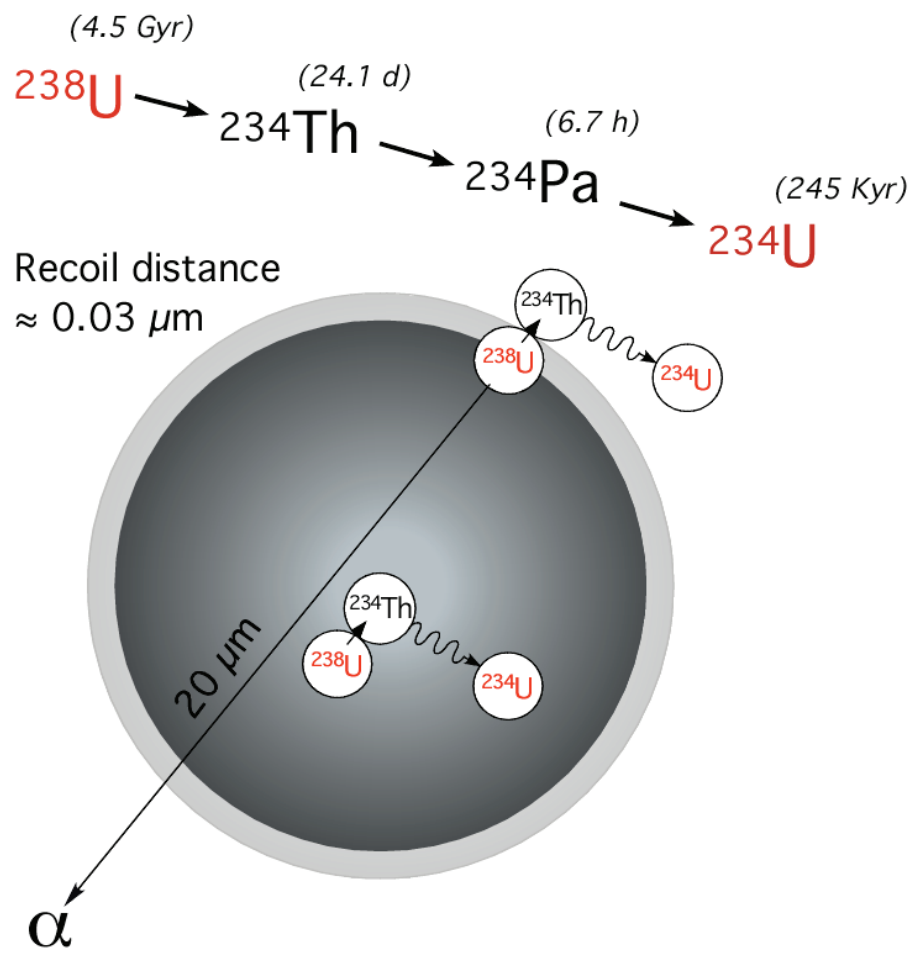


Figure 1

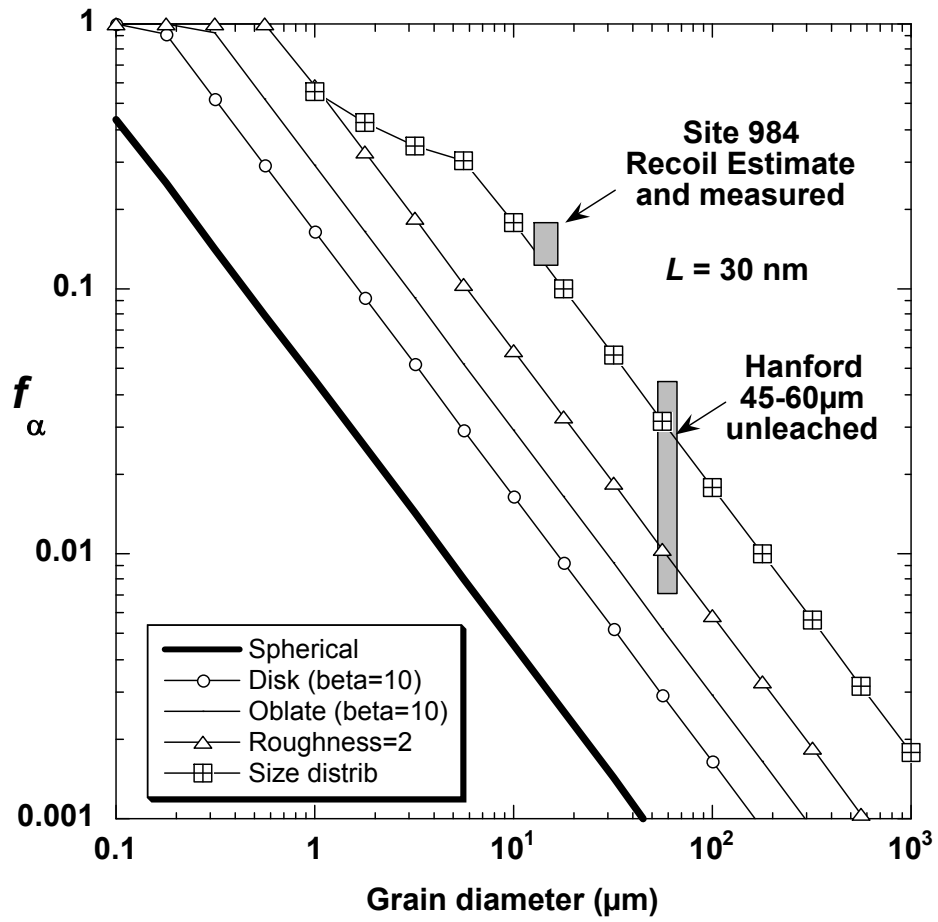


Figure 2

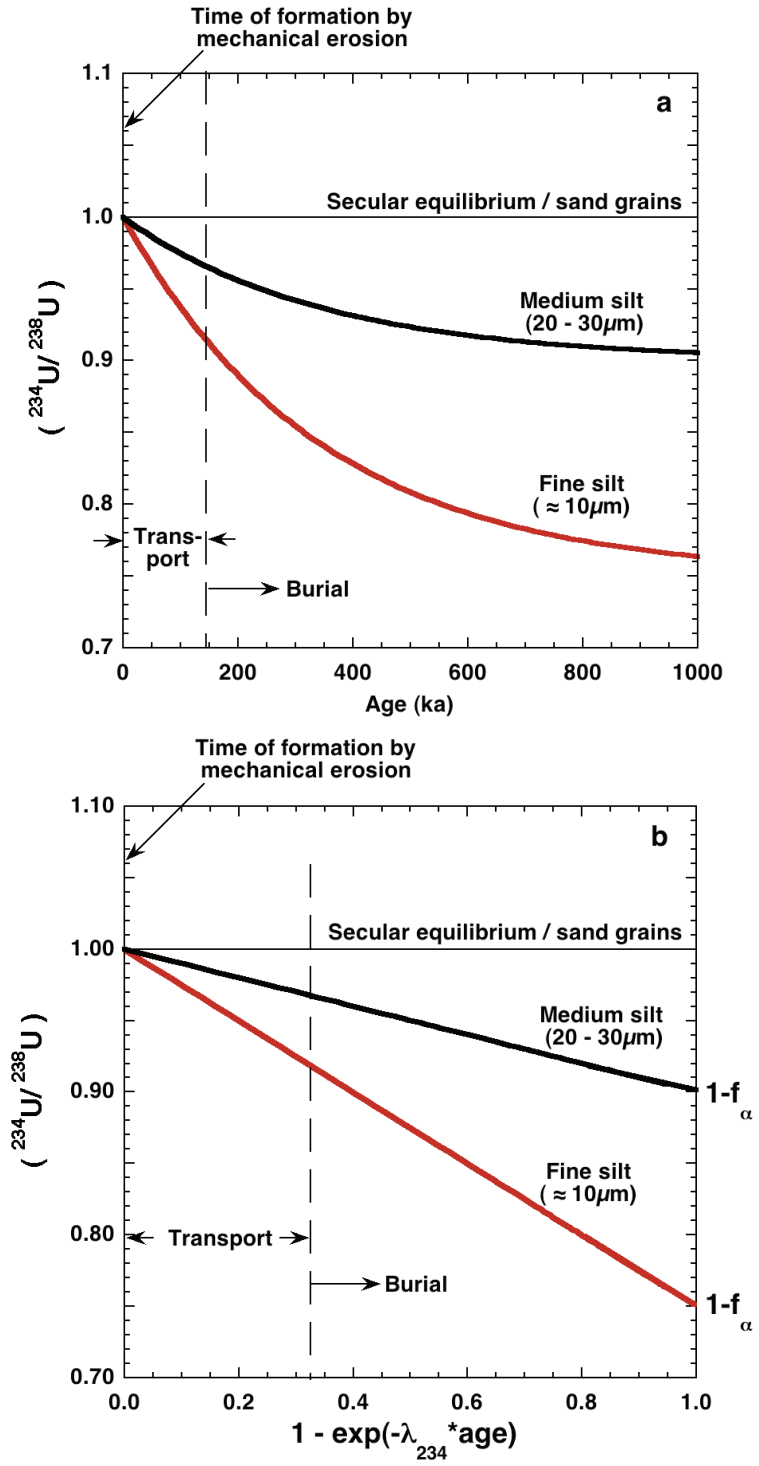


Figure 3

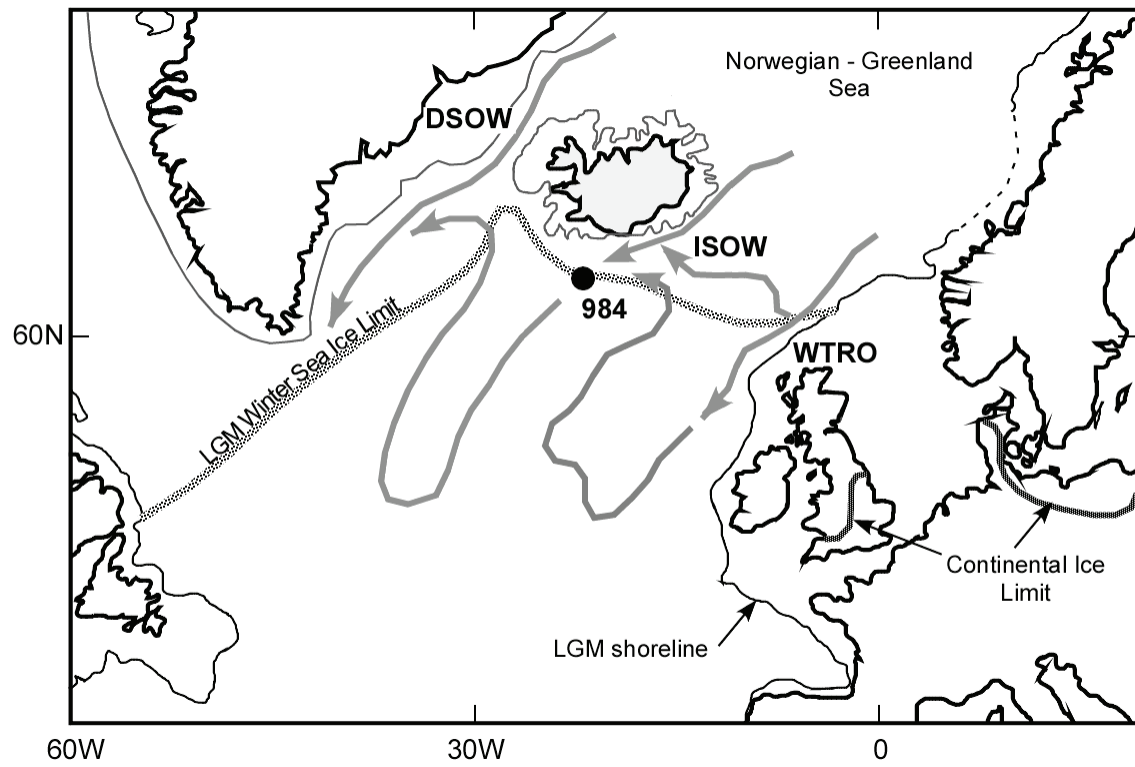


Figure 4

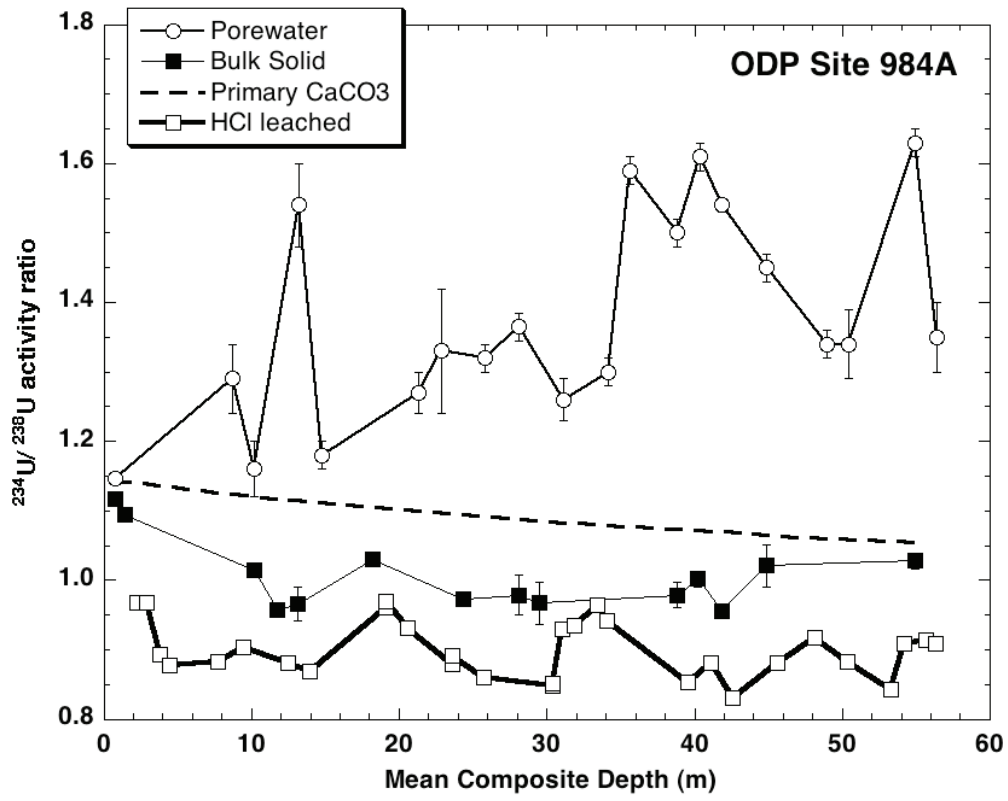


Figure 5

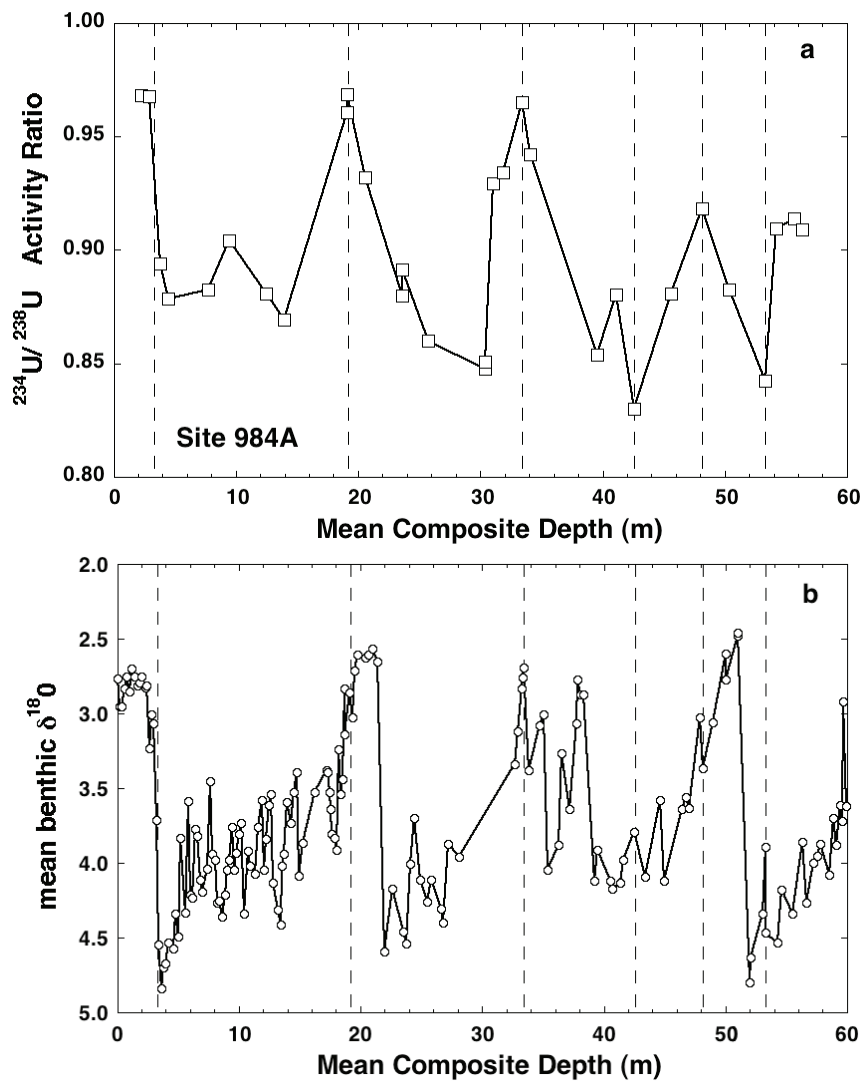


Figure 6

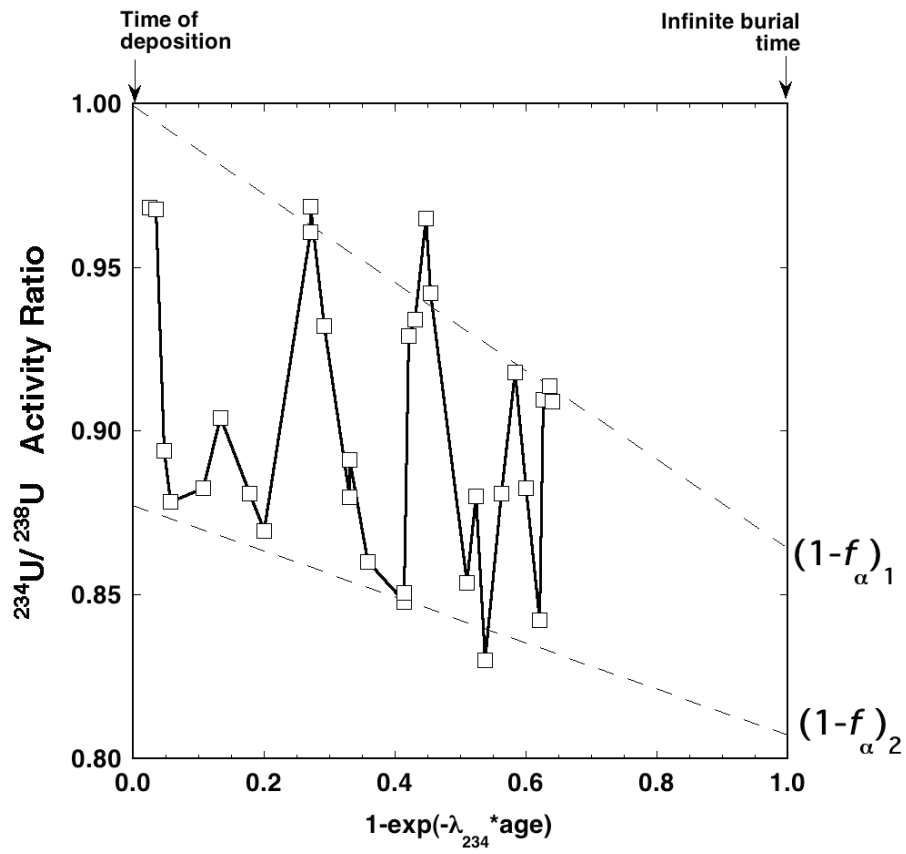


Figure 7

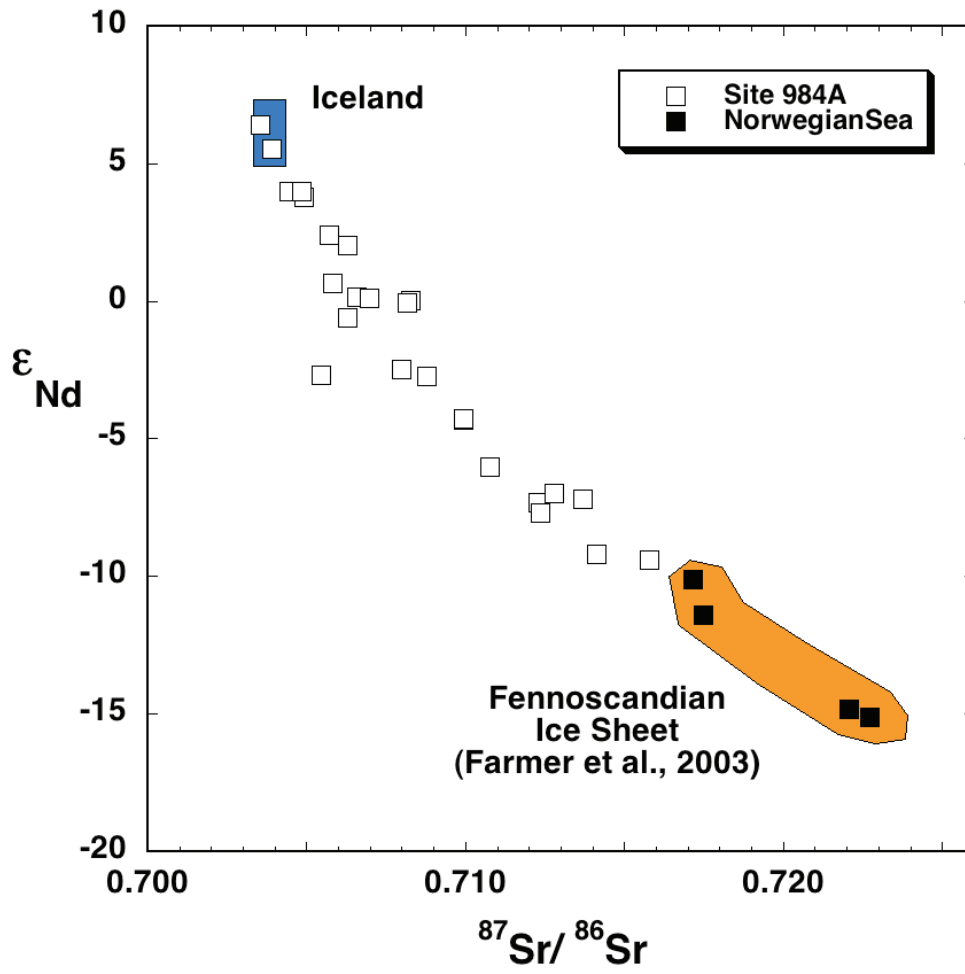


Figure 8

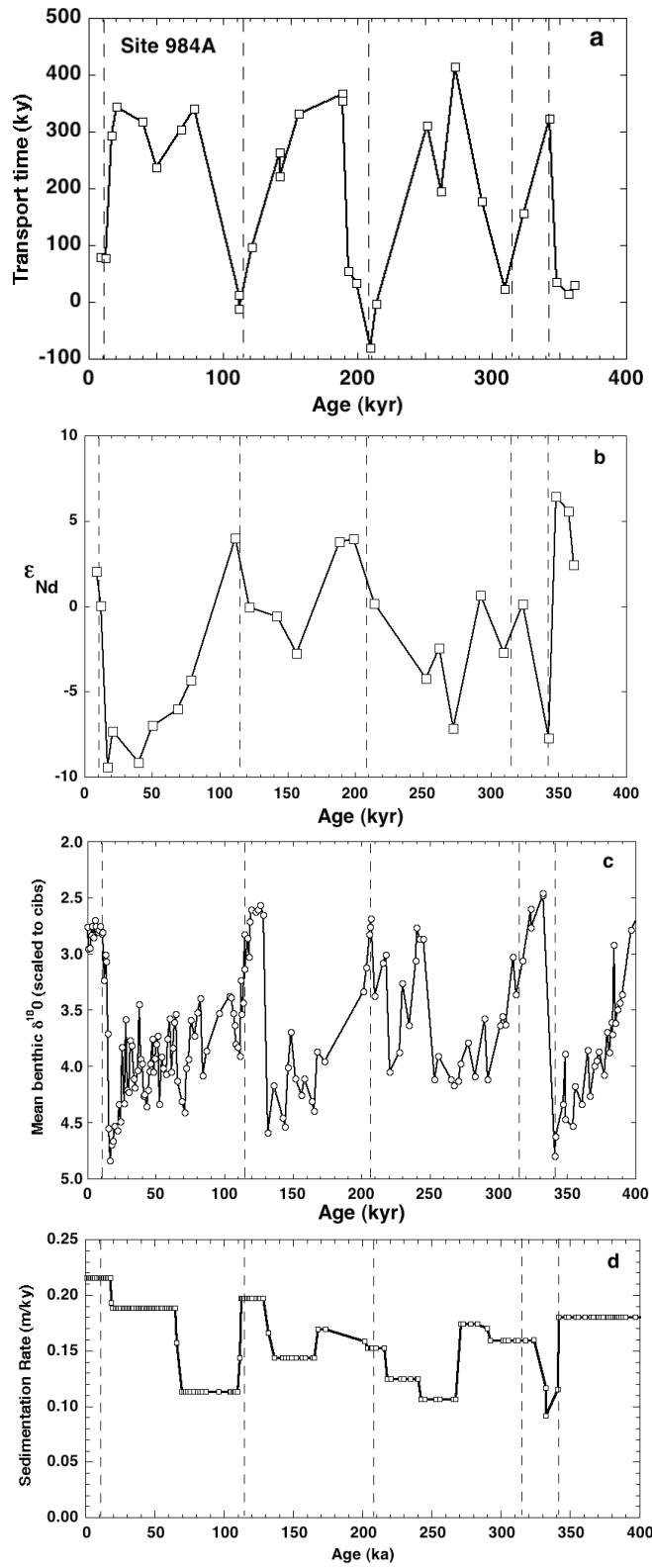


Figure 9

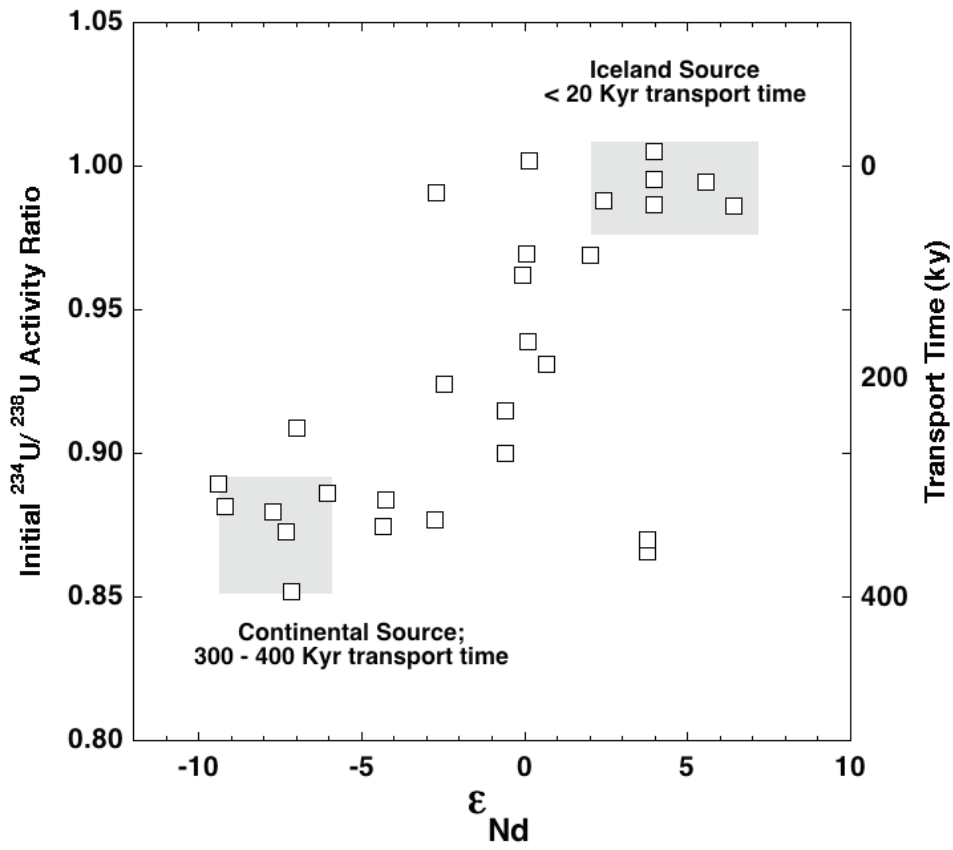


Figure 10