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## Improved determination of marine sedimentation rates using $^{230}\text{Th}_{xs}$

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[1] Measurements of excess  $^{230}\text{Th}$  ( $^{230}\text{Th}_{xs}$ ) have proved to be a useful tool in constraining changes in sedimentation rate, and improving our understanding of the fluxes of other components into marine sediments. To obtain the initial activity of  $^{230}\text{Th}_{xs}$  ( $^{230}\text{Th}_{xs}^0$ ) in sediment: the total measured  $^{230}\text{Th}$  must be corrected for the presence of  $^{230}\text{Th}$  associated with detrital minerals, for ingrowth from uranium-bearing authigenic phases and then also corrected for the decay of  $^{230}\text{Th}_{xs}$  since deposition. We describe a number of improvements in the way these corrections are applied to obtain more accurate determinations of  $^{230}\text{Th}_{xs}^0$ . We present a new method for the determination of a local estimate for the detrital  $^{238}\text{U}/^{232}\text{Th}$  activity ratio; suggest more appropriate values for the isotopic composition of authigenic uranium; and question the assumption of secular equilibrium in detrital material. We also present a new, freely-available MATLAB<sup>®</sup> script called 'XSage' that can calculate  $^{230}\text{Th}_{xs}^0$  from user-supplied datasets of uranium and thorium isotope activities from sedimentary samples following the theoretical approach described. 'XSage' can determine variations in sedimentation rate between stratigraphic horizons of known age and thus produce high-resolution age models. Using a Monte Carlo approach, the program calculates uncertainties for these age models and on the durations of intervals between tie-points. An example of the application of the XSage program using a previously published record is provided.

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### 1. Introduction

[2] The utility of sedimentary archives in understanding Earth history is dependent upon accurate temporal constraints. One approach that has been used in marine cores to improve mass flux and age models derived from stratigraphic dating methods, such as oxygen isotope stratigraphy or dated ash

layers, is the use of  $^{230}\text{Th}_{xs}$  as a constant-flux proxy [Francois *et al.*, 2004; Henderson and Anderson, 2003].  $^{230}\text{Th}_{xs}$  has been used, for instance, to assess sediment focusing in the central equatorial Pacific Ocean [Marcantonio *et al.*, 2001]; to assess the changing fluxes of windblown dust from the Sahara during the Holocene [Adkins *et al.*, 2006]; and to assess possible changes in sedimentation rate

during Heinrich events in the North Atlantic [McManus *et al.*, 1998].

[3]  $^{230}\text{Th}_{xs}$  is produced by the decay of dissolved  $^{234}\text{U}$  in the water column. The rate of production is dependent on the inventory of uranium in the water column and on its isotopic composition, both of which are thought to have remained constant over the past few thousand years [Henderson, 2002]. This highly insoluble  $^{230}\text{Th}$ , produced at a constant rate, is efficiently scavenged from the water column and transported to the underlying sediment by sinking particles [Bacon and Anderson, 1982] such that the vertical flux of  $^{230}\text{Th}$  to the sea-floor is assumed to be equal to production in the overlying water column [Bacon *et al.*, 1985]. This component of  $^{230}\text{Th}$  in the sediment is termed ‘excess’ thorium ( $^{230}\text{Th}_{xs}$ ) as it is not supported by the decay of sedimentary uranium. Typically, concentrations of both uranium and thorium isotopes are measured from samples taken downcore.

## 2. Approach and Assumptions of $^{230}\text{Th}_{xs}$ Normalization

[4] To calculate the  $^{230}\text{Th}_{xs}$  contribution to the measured total  $^{230}\text{Th}$  concentration in deep-sea sediment, corrections for other sources of  $^{230}\text{Th}$  must be made. These comprise  $^{230}\text{Th}$  associated with detrital material and that produced in the sediment by the decay of authigenic uranium, added to the sediments shortly after sedimentation in reducing environments [e.g., Henderson and Anderson, 2003]. Corrections for detrital and authigenic sources of  $^{230}\text{Th}$  rely on a number of assumptions. The  $^{232}\text{Th}$  content of the sediment is assumed to come entirely from detrital material in the sediment and the activity of uranium associated with this detrital component is calculated using an assumed  $^{238}\text{U}/^{232}\text{Th}$  for the detrital material,  $(^{238}\text{U}/^{232}\text{Th})_{det}$ . An assumption is then made that detrital  $^{230}\text{Th}$  is in secular equilibrium with this uranium such that  $^{238}\text{U}_{det} = ^{230}\text{Th}_{det}$ . Here and throughout this article, all references to isotopic values and ratios are given as activities. Any  $^{238}\text{U}$  not accounted for by the detrital component is assumed to be authigenic uranium. Calculation of the  $^{230}\text{Th}$  derived from this authigenic uranium assumes that the incorporation of authigenic uranium occurs at the time of sediment deposition, at a ‘known’  $^{234}\text{U}/^{238}\text{U}$  ratio,  $(^{234}\text{U}/^{238}\text{U})_{init}$ , assumed to be that of seawater (=1.147) and that the authigenic uranium has not subsequently been lost from the sediment (e.g. via oxidation and subsequent dissolution). Because  $^{230}\text{Th}$  is radioactive, the calculated  $^{230}\text{Th}_{xs}$  must also be corrected for its own

decay to give the  $^{230}\text{Th}_{xs}$  at the time of deposition ( $^{230}\text{Th}_{xs}^0$ ).

[5] The approach is outlined below.

$$^{230}\text{Th}_{xs}^0 = e^{\lambda_{230}t} \times [^{230}\text{Th}_{meas} - ^{230}\text{Th}_{det} - ^{230}\text{Th}_{auth}] \quad (1)$$

where  $\lambda_{230}$  is the decay constant of  $^{230}\text{Th}$ ,  $t$  is the age of the sediment and:

$$^{230}\text{Th}_{det} = ^{238}\text{U}_{det} = (^{238}\text{U}/^{232}\text{Th})_{det} \times ^{232}\text{Th}_{meas} \quad (2)$$

and:

$$\begin{aligned} ^{230}\text{Th}_{auth} = & (^{238}\text{U}_{meas} - ^{238}\text{U}_{det}) \\ & \times \left[ (1 - e^{-\lambda_{230}t}) + \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \left( \left( \frac{^{234}\text{U}}{^{238}\text{U}} \right)_{init} - 1 \right) \right. \\ & \left. \cdot (e^{-\lambda_{234}t} - e^{-\lambda_{230}t}) \right] \quad (3) \end{aligned}$$

[6] The calculated  $^{230}\text{Th}_{xs}^0$  may be used in two, subtly different, ways. The first uses the measured  $^{230}\text{Th}_{xs}^0$  values as a vertical flux proxy. The flux of other components from the water column into marine sediments can be assessed by measuring their concentration relative to that of  $^{230}\text{Th}_{xs}^0$  and by assuming that the measured  $^{230}\text{Th}_{xs}^0$  is equal to its production in the overlying water column. This approach gives an estimate for the instantaneous flux for that component at the time that the measured sediment was laid down. It has been used, for example, to assess changing fluxes of ice-rafted debris into North Atlantic sediments during Heinrich events [McManus *et al.*, 1998] and to assess the changing fluxes of windblown dust from the Sahara during the Holocene [Adkins *et al.*, 2006].

[7] A critical assumption of the above is that there is minimal lateral movement of  $^{230}\text{Th}$  in the water column. This appears reasonable based on sediment trap [Yu *et al.*, 2001] and modeling [Henderson *et al.*, 1999] studies, although it has been questioned recently based on sediment thicknesses observed from seismic data [Lyle *et al.*, 2005]. Furthermore, at some locations, lateral movement of  $^{230}\text{Th}$  in the water column can be more than 30% of a water column’s production [Henderson *et al.*, 1999].

[8] The second, alternative approach is to use the concentration of  $^{230}\text{Th}_{xs}^0$  in the sediment to determine relative variations in total sedimentation rate between tie-points. In the ideal case, the concentration of  $^{230}\text{Th}_{xs}^0$  in the sediment is expected to be

inversely proportional to the sedimentation rate: the higher the sedimentation rate, the lower the concentration of  $^{230}\text{Th}_{xs}^0$ , the sediment effectively ‘diluting’ the  $^{230}\text{Th}_{xs}^0$ , supplied at a constant rate from the overlying water column. The relative variation in sedimentation rate is calculated using relative variations in concentration of  $^{230}\text{Th}_{xs}^0$  to modify an average sedimentation rate determined between stratigraphic tie-points of known age. In this approach, the sedimentation rate for each depth interval is calculated using the following expression:

$$F_n = F_a \times \frac{\overline{\text{Th}}}{\text{Th}_n} \quad (4)$$

where  $F_n$  is the sedimentation rate for the sample interval;  $\text{Th}_n$  is the concentration of  $^{230}\text{Th}_{xs}^0$  in that sample interval;  $F_a$  is the average sedimentation rate in  $\text{cm kyr}^{-1}$  between the tie-points; and  $\overline{\text{Th}}$  is the depth-interval-weighted average concentration of  $^{230}\text{Th}_{xs}^0$  between the tie-points. In practice, the dated tie-points will also have associated uncertainties, potentially in both depth and age. This approach has been used to determine the durations of short geomagnetic events [Knudsen *et al.*, 2007; Bourne *et al.*, 2012].

[9] Using  $^{230}\text{Th}_{xs}^0$  in this second way, to constrain relative sedimentation rates, requires an additional assumption that sediment focusing throughout the interval of interest is constant. It is therefore important that the sedimentary environment remained broadly constant between the tie-points used by the  $^{230}\text{Th}_{xs}$  normalization. Independent methods must be used to check that potential variation in focusing is minimal relative to changes in sedimentation rate, such that the uncertainty introduced by focusing does not obscure any variation in the sedimentation rate. Such independent methods might include: sortable silt analysis to assess changes in sediment transport [e.g., McCave *et al.*, 1995; McCave and Hall, 2006]; measuring the magnetic properties of the sediment to investigate potential variations in grain size [e.g., Banerjee *et al.*, 1981; Stanford *et al.*, 2011]; or physical inspection of core material to assess changes in sediment type. The use of intermediate tie-points or stratigraphic analysis, whereby variation in focusing can be constrained between multiple dated stratigraphic intervals, may also provide some indication of whether focusing is variable at a site with time or changes in climate.

[10] In summary, either approach using  $^{230}\text{Th}_{xs}$  relies on five principal assumptions:

[11] 1. An assumed  $(^{238}\text{U}/^{232}\text{Th})_{det}$  in detrital material.

[12] 2. Detrital material is in secular equilibrium  $^{238}\text{U}_{det} = ^{230}\text{Th}_{det}$ .

[13] 3. Authigenic U has an initial  $^{234}\text{U}/^{238}\text{U}$  of seawater (=1.147), forms at time of sediment deposition, and does not dissolve or mobilize in the sediment column.

[14] 4. No lateral transport of  $^{230}\text{Th}$  in the water column.

[15] 5. A known age model with accurately dated tie-points.

[16] If relative variation in  $^{230}\text{Th}_{xs}^0$  is to be used to constrain relative variations in sedimentation rate then this requires a further assumption that:

[17] 6. Sediment focusing is constant between tie-points.

[18] Note also that because the variation in sedimentation rate is derived from relative variation in  $^{230}\text{Th}_{xs}^0$ , assumption 4 may be modified to ‘no change in lateral transport of  $^{230}\text{Th}$  in the water column’ when assessing relative sedimentation rate changes.

[19] In this study, we discuss uncertainties in the first three of these assumptions, and describe a piece of new, freely-available MATLAB® software, ‘XSage’, that enables the user to insert appropriate uncertainties into a self-consistent calculation of  $^{230}\text{Th}_{xs}^0$  and sedimentation-rate histories from Th and U measurements, also taking into account uncertainties in the input linear age model. The XSage model is designed principally to improve the use of  $^{230}\text{Th}_{xs}$  data to refine changes in sedimentation rates between tie-points, but it also has potential to improve the use of  $^{230}\text{Th}_{xs}$  as a constant-flux proxy.

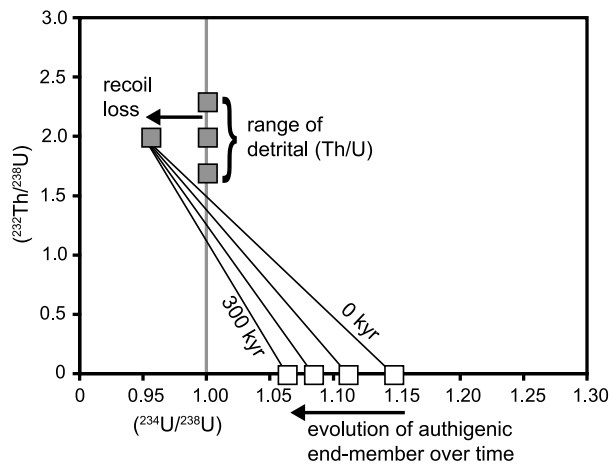
### 3. Addressing the Assumptions of $^{230}\text{Th}_{xs}$ -Normalization

#### 3.1. $(^{238}\text{U}/^{232}\text{Th})_{det}$ in Detrital Material

[20] The assumption of known  $(^{238}\text{U}/^{232}\text{Th})_{det}$  often involves the use of ‘appropriate’ basin wide ratios [e.g., Henderson and Anderson, 2003], which may lead to systematic inaccuracies where the local sediment differs from the assumed value.

[21] A more localized estimate of  $(^{238}\text{U}/^{232}\text{Th})_{det}$  may be achieved if the absence of authigenic uranium can be identified at some depths in the





**Figure 1.** Detrital components (grey squares) shown schematically with uranium isotopes at secular equilibrium (grey line) and after recoil loss, with a  $^{234}\text{U}/^{238}\text{U}$  ratio of 0.96. The authigenic component (white squares), consisting of uranium only, initially has a seawater  $^{234}\text{U}/^{238}\text{U}$  of 1.147 (at 0 kyr) but evolves over time after deposition as the excess  $^{234}\text{U}$  decays. Multiple mixing lines show the expected evolution through time of the relationship between the detrital component and the evolving authigenic component.

measured core. Measured  $^{238}\text{U}/^{232}\text{Th}$  at these depths can then be assumed to represent the detrital end member. Identification of sediment with no authigenic uranium can be made if the  $^{234}\text{U}/^{238}\text{U}$  of the sediment is measured, as is commonly the case. Incorporation of authigenic uranium into sediment will elevate the  $^{234}\text{U}/^{238}\text{U}$  above 1, due to the excess  $^{234}\text{U}$  in seawater and sediment porewater [Robinson *et al.*, 2004; Ku, 1965]. The  $^{238}\text{U}/^{232}\text{Th}$  of samples with  $^{234}\text{U}/^{238}\text{U}$  less than 1 may therefore be used to provide a better constraint on the local  $(^{238}\text{U}/^{232}\text{Th})_{det}$ . XSage follows this new approach by allowing the user the option to identify sediment samples without an authigenic uranium component. These samples are then used to estimate the local  $(^{238}\text{U}/^{232}\text{Th})_{det}$  based on their  $^{234}\text{U}/^{238}\text{U}$  ratios and determine an appropriate uncertainty.

### 3.2. Is Detrital Material in Secular Equilibrium?

[22] Some deep-sea sediments have  $^{234}\text{U}/^{238}\text{U}$  below 1 [Ku, 1965]. This observation indicates that the assumption that the detrital component is in secular equilibrium (i.e.  $(^{234}\text{U}/^{238}\text{U})_{det} = 1$ ) is invalid.  $^{234}\text{U}/^{238}\text{U}$  measured in marine sediments can be as low as  $\sim 0.96$  due to the loss of roughly 4% of the daughter  $^{234}\text{U}$  from the sediment grains by alpha-recoil [Ku, 1965; DePaolo *et al.*, 2006]. The

$^{230}\text{Th}/^{238}\text{U}$  in such sediment,  $(^{230}\text{Th}/^{238}\text{U})_{det}$ , is therefore likely to be even lower. Assuming that a further 4% of daughter  $^{230}\text{Th}$  is lost because of the second alpha decay involved in the formation of  $^{230}\text{Th}$ ,  $(^{230}\text{Th}/^{238}\text{U})_{det}$  could be as low as 0.92 (i.e.  $1 \times 0.96^2$ ). We therefore propose a modification to the detrital correction, where  $\sim 0.96 \pm 0.04$  (i.e. the range 0.92–1.00) is the value for  $(^{230}\text{Th}/^{238}\text{U})_{det}$ :

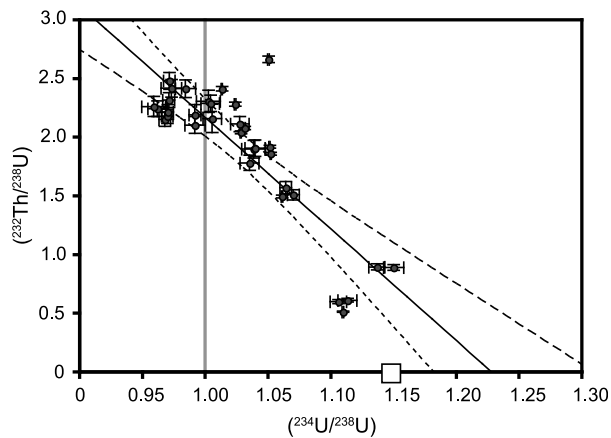
$$^{230}\text{Th}_{det} = (\sim 0.96 \pm 0.04) \times (^{238}\text{U}/^{232}\text{Th})_{det} \times ^{232}\text{Th}_{meas} \quad (5)$$

[23] This modification to the calculation of  $^{230}\text{Th}_{det}$  assumes that the disequilibrium of  $(^{230}\text{Th}/^{238}\text{U})_{det}$  is maintained through time and does not evolve either towards secular equilibrium, or to lower values by additional recoil loss. That the authigenic component may have  $^{234}\text{U}/^{238}\text{U}$  elevated above that of seawater (see below) indicates that recoil products may well be lost from detrital phases and hence that return to secular equilibrium is unlikely, although further disequilibrium cannot be ruled out. Therefore, the potential for bias on  $^{230}\text{Th}_{xs}$  normalization between age tie points will be limited but accumulation rates calculated independently of tie-points and comparisons between sites may be affected. XSage allows the user to specify the degree of disequilibrium with an associated uncertainty but uses a default value of  $0.96 \pm 0.04$  for  $(^{238}\text{U}/^{232}\text{Th})_{det}$ .

### 3.3. Authigenic $^{234}\text{U}/^{238}\text{U}$

[24] Addition of authigenic uranium to a detrital end-member should follow a simple mixing relationship (Figure 1). Typically the authigenic end-member is assumed to have a  $(^{234}\text{U}/^{238}\text{U})_{init}$  ratio equal to that of seawater ( $=1.147$ ) [Robinson *et al.*, 2004; Andersen *et al.*, 2010]. To investigate this assumption, we revisit a down-core  $^{230}\text{Th}$  record that was measured from the south-western Indian Ocean to reconstruct the history of deep water flow into that basin over the last 140 kyr [Thomas *et al.*, 2007]. This core, WIND 28K, was collected during RRS Charles Darwin cruise CD129 at  $51^\circ 46' \text{E}$   $10^\circ 9' \text{S}$ , in 4157 m water depth.

[25] Down-core data from WIND 28K are not well described by mixing lines based on assumed  $^{234}\text{U}/^{238}\text{U}$  at seawater values (Figure 2). Better agreement to the data is possible if the authigenic component has  $^{234}\text{U}/^{238}\text{U}$  higher than seawater. This additional excess  $^{234}\text{U}$  could be due to the maintenance of a  $^{234}\text{U}/^{238}\text{U}$  deficit in the detrital phase and thus higher  $^{234}\text{U}/^{238}\text{U}$  in sediment pore waters than in seawater. This is supported by



**Figure 2.** Down core data from the 140 ka WIND 28K record from the Indian Ocean [Thomas *et al.*, 2007] (dark grey circles). Best-fit mixing line (black line with dashed lines indicating  $2\sigma$  uncertainty) suggests that an authigenic component with  $^{234}\text{U}/^{238}\text{U}$  equal to that of seawater ( $=1.147$ , white square) is inappropriate and that the  $^{234}\text{U}/^{238}\text{U}$  of the authigenic component is likely to be greater than that of seawater.

$^{234}\text{U}/^{238}\text{U}$  activity ratios of pore water from ODP Site 984A in the North Atlantic, which have higher than seawater values, in the range 1.2–1.6 [Maher *et al.*, 2004]. The observation of  $^{234}\text{U}/^{238}\text{U}$  greater than 1.147 in the authigenic phase in WIND 28K and in pore waters from ODP Site 984A raises the possibility that this feature may occur more generally. It may therefore be appropriate to use a  $(^{234}\text{U}/^{238}\text{Th})_{\text{init}}$  value greater than 1.147 in equation (3).

[26] The impact of a higher  $(^{234}\text{U}/^{238}\text{U})_{\text{init}}$  on the  $^{230}\text{Th}_{\text{xs}}^0$  correction will be to increase the apparent  $^{230}\text{Th}_{\text{auth}}$  component for samples which have a significant authigenic uranium content. This correction will become increasingly important as sample age increases. For samples where the relative  $^{230}\text{Th}_{\text{xs}}^0$  content is lower (shallower core depths, higher authigenic uranium) these additional corrections may become significant. XSage provides an opportunity to choose an appropriate value for  $(^{234}\text{U}/^{238}\text{U})_{\text{init}}$  with an associated uncertainty.

#### 4. The XSage Model Approach

[27] The uncertainty on the  $^{230}\text{Th}_{\text{xs}}$  activity in any one sample is dependent upon the uncertainty of the measured uranium and thorium activities as well as upon the assumptions used to determine the proportion of the total sample  $^{230}\text{Th}$  accounted for by  $^{230}\text{Th}_{\text{det}}$  and  $^{230}\text{Th}_{\text{auth}}$ .

[28] 1. The uncertainty on  $^{230}\text{Th}_{\text{det}}$  is controlled by the uncertainties associated with the assumed  $(^{238}\text{U}/^{232}\text{Th})_{\text{det}}$  activity ratios and the degree to which the detrital material is thought to be in secular equilibrium.

[29] 2. The uncertainty on any authigenic component,  $^{230}\text{Th}_{\text{auth}}$ , is dependent upon the detrital component  $^{238}\text{U}_{\text{det}}$ ; on the assumed value for  $(^{234}\text{U}/^{238}\text{U})_{\text{init}}$ ; and the time since sediment deposition.

[30] 3. In all cases, corrections for decay of  $^{230}\text{Th}_{\text{xs}}$  since deposition mean that the uncertainty on the age of the sample (which is dependent upon the ages and depths, and associated uncertainties, of the tie-points) plays a role in the final uncertainty on the  $^{230}\text{Th}_{\text{xs}}^0$  activity of the sample.

[31] In each case the relative importance of each input uncertainty is not only dependent upon the size of the input uncertainties themselves but also on the relative proportions of the three thorium components in the sample's total  $^{230}\text{Th}$ . Furthermore, if the  $^{230}\text{Th}_{\text{xs}}^0$  activity is used as a modifier on the average sedimentation rate, to obtain variations in sedimentation rate between tie-points, and hence on the age model, each calculated sedimentation rate from a single sample is dependent upon the  $^{230}\text{Th}_{\text{xs}}^0$  activities of all the samples, as well as the average linear sedimentation rate determined from the ages and depths of the tie-points.

[32] The complexity and inter-dependence of the various equations therefore makes the use of classical error propagation difficult when attempting to determine the uncertainty on calculated sedimentation rates, age models and interval durations. Instead, the XSage MATLAB® script uses a Monte Carlo iterative approach to calculate a range of possible answers and subsequently determine average values for the final  $^{230}\text{Th}_{\text{xs}}^0$  activities, sedimentation rates, and ages, with estimates of all their associated uncertainties.

#### 4.1. Description of Program

[33] When using XSage, the user supplies measured  $^{238}\text{U}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$  (and optionally  $^{234}\text{U}$ ) activities for samples from the interval of interest. Using tie-points of known depth and age and user-defined ratios of  $(^{238}\text{U}/^{230}\text{Th})_{\text{det}}$  and  $(^{238}\text{U}/^{232}\text{Th})_{\text{det}}$  and  $(^{234}\text{U}/^{238}\text{U})_{\text{init}}$  (see equations (3) and (5)), the script can then calculate for each sample depth: the detrital component,  $^{230}\text{Th}_{\text{det}}$ ; the component formed by the decay of authigenic uranium (if present),  $^{230}\text{Th}_{\text{auth}}$ ; and the initial excess component,  $^{230}\text{Th}_{\text{xs}}^0$ .

[34] Using the relative variation in the calculated  $^{230}\text{Th}_{xs}^0$  between samples, the script then calculates the variations in sedimentation rate through the core relative to the average sedimentation rate (calculated from the tie-points). The normalized sedimentation rates are then also used to determine an age-depth relationship for the core section.  $^{230}\text{Th}_{xs}^0$  is subsequently iteratively recalculated using the new age-model in the time-dependent corrections for decay.

## 4.2. Monte Carlo Method to Calculate Uncertainties

[35] The Monte Carlo simulation models the inputs as probability distributions. For each iteration the script randomly samples appropriate values from the probability distributions for the measured  $^{238}\text{U}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$  activities of the samples, the ages and depths of the tie-points, and the user-defined values of the  $(^{234}\text{U}/^{238}\text{U})_{init}$ ,  $(^{238}\text{U}/^{230}\text{Th})_{det}$  and  $(^{238}\text{U}/^{232}\text{Th})_{det}$  activity ratios (see equations (3) and (5)). The measured activity ratios and user-defined ratios are modeled as Gaussian probability distributions using standard deviations provided by the user. The Monte Carlo simulation can optionally model the age and depths of the tie-points as ‘top-hat’ distributions whereby the uncertainties provided set the minima and maxima for the ages and depths and the probability of any value between the bounds is equally likely. Alternatively the ages and depths can be modeled as independent Gaussian probability distributions. When running the script, the user can specify the size of the uncertainties and which of the above may vary between each iteration (in order to better understand the error ‘budget’ of the final uncertainty). It should be recognized that any uncertainties calculated by the XSage script only capture the uncertainties in the calculations and supplied data and not the potential for unrecognized sedimentation rate variation due to under-sampling or the potential for variations in lateral redistribution of sediment and/or  $^{230}\text{Th}$ . Thus uncertainty in focusing must be accounted for independently following the XSage calculation of the uncertainties associated with the measurements, tie-points and assumed ratios.

## 4.3. Output of Durations (Correlated Errors)

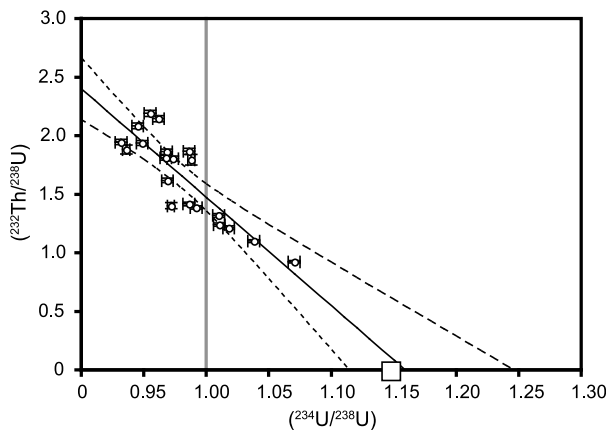
[36]  $^{230}\text{Th}_{xs}^0$ -normalization is particularly useful for determining accurate ages and durations of events that have durations much shorter (i.e. thousand-year

durations) than the resolution afforded by standard stratigraphical and chronological techniques such as oxygen isotope stratigraphy. XSage allows the user to specify intervals of particular interest. This is important as the uncertainty on the duration of any such interval of interest is not necessarily as large as that implied by the uncertainties on the ages of its two bounding depths. This is because the ages of the two depths are strongly correlated such that, for example, if one increases, it is likely that the other does too whilst the duration may not change significantly. If intervals of interest are specified then, to estimate the uncertainty on their duration, the duration of each interval is calculated during each iteration and the resulting answers are used to directly determine average durations and their uncertainty.

## 4.4. Example Calculations

[37] Here we present an example, using measured uranium and thorium isotope activities in a marine core from a published article to demonstrate the utility of the XSage programme. *Bourne et al.* [2012] used measurements of  $^{230}\text{Th}_{xs}^0$  to determine relative sedimentation rates in a marine core from the Blake-Bahama Ridge (Ocean Drilling Program, Leg 172, Core 1062E). They determined a record of thorium-normalized sedimentation rate throughout Marine Isotope Stage (MIS) 5. Using the thorium-normalized sedimentation rates allowed the determination of the duration of a short (less than 10 kyr) geomagnetic excursion, the Blake excursion, that occurred during MIS 5e. Within the studied interval, focusing is thought to have been relatively constant (varying within  $\sim 15\%$  of the average) [*Bourne et al.*, 2012]. In the following, we will use this data to demonstrate how XSage may be used to calculate normalized sedimentation rates and an age model with associated uncertainties.

[38] Using XSage, we can compare the normalized sedimentation rates calculated firstly by the commonly applied approach, as described in Section 2, and then, secondly, using the modifications proposed in this paper in Section 3. In both cases, the linear age model is constrained by the same two dated boundaries obtained from oxygen isotope stratigraphy: the younger marks the transition from MIS 5 to MIS 4 at  $13.64 \pm 0.35$  mbsf, which is assigned an age of  $72.0 \pm 1.5$  ka; and the older age constraint, at  $20.20 \pm 0.40$  mbsf marks the transition from MIS 6 to MIS 5 and is assigned an age of  $135.0 \pm 1.5$  ka [*Bourne et al.*, 2012].



**Figure 3.** Down core data from ODP Core 1062E from the Atlantic Ocean [Bourne *et al.*, 2012] (white circles). The best-fit mixing line (black line with dashed lines indicating 95% confidence intervals) suggests that an authigenic component with  $^{234}\text{U}/^{238}\text{U}$  equal to that of seawater (=1.147, white square) is appropriate in this case, in contrast to that shown in Figure 2.

[39] For our first calculation, we follow the standard approach and assume that the  $(^{238}\text{U}/^{232}\text{Th})_{det}$  ratio is equal to a basin-wide estimate of Atlantic detrital material of  $0.6 \pm 0.1$  [Henderson and Anderson, 2003] and that the detrital material is in secular equilibrium such that  $^{238}\text{U}_{det} = ^{230}\text{Th}_{det}$ . Lastly, we assume that  $(^{234}\text{U}/^{238}\text{U})_{init}$ , the  $^{234}\text{U}/^{238}\text{U}$  of any authigenic end-member, is equal to that of sea-water (1.147). Any corrections for decay use the linear time scale derived from the average sedimentation rate between the two tie-points.

[40] For the second calculation, following the adjusted protocol of this paper, we use the mean  $^{238}\text{U}/^{232}\text{Th}$  of samples with  $(^{234}\text{U}/^{238}\text{U})$  less than 1 to provide a better constraint on the local  $(^{238}\text{U}/^{232}\text{Th})_{det}$  and its uncertainty. These suggest  $0.55 \pm 0.16$  to be a better estimate of the local  $(^{238}\text{U}/^{232}\text{Th})_{det}$ . Alpha-recoil from detrital material is accounted for, as in equation (5). In this case, a seawater value for  $(^{234}\text{U}/^{238}\text{U})_{init}$  of 1.147 appears to be a reasonable assumption for the authigenic end-member (Figure 3). Corrections for decay are made iteratively by XSage using thorium-normalized age models.

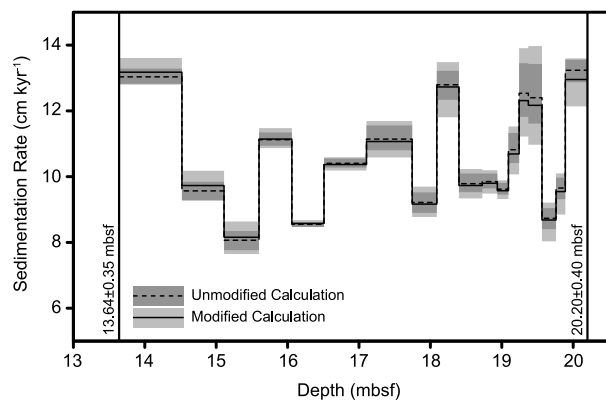
[41] For both calculations, XSage calculates each of the components that comprise the total  $^{230}\text{Th}$ , including  $^{230}\text{Th}_{xs}^0$ , as well as an age model determined using thorium-normalized sedimentation rates. For this core, the calculated  $^{230}\text{Th}_{xs}^0$  activities for each sample are similar in both calculations. The  $^{230}\text{Th}_{xs}^0$  activities differ by no more than

5% between the two approaches. The differences between the two sets of sedimentation rates are therefore also limited ( $\sim 2\%$ ) (Figure 4). As a result, the age models for the two calculations are similar.

[42] This similarity is principally due to the fact that, in this case, the concentration of  $^{230}\text{Th}_{xs}^0$  varies relatively little such that the thorium-normalized sedimentation rate does not vary significantly about the average sedimentation rate between the tie-points. Using the linear decay correction in the first calculation is therefore a reasonable approximation of the iterative calculation.

[43] Previous published measurements have tended to avoid sediments where the authigenic or detrital corrections amount to a significant proportion of the total  $^{230}\text{Th}$ , because their associated uncertainties are poorly constrained. Therefore, the corrections are relatively minor. However, our revised approach, with better estimation of uncertainties, opens the possibility of using sites in the future where the authigenic correction is larger (where the age of the sediment is greater) or at sites with a larger detrital input.

[44] XSage also provides uncertainties on all calculated values. This allows us to examine how the input uncertainties in our calculations propagate to the final answer. Compared to the traditional approach of the first calculation, the modified thorium excess approach takes into account more of the uncertainties associated with the thorium normalization method, in particular that associated with



**Figure 4.** Thorium-normalized sedimentation rates calculated using XSage for ODP Core 1062E [Bourne *et al.*, 2012]. Results given, with 95% confidence intervals, for rates calculated using the unmodified approach (dashed line, dark grey band) and using the modified approach suggested in this paper (solid line, light grey band).



the potential for alpha-recoil from detrital material. As a result, the uncertainties on the sedimentation rates are increased by at least 50%, more accurately reflecting the uncertainties inherent in the calculation and its assumptions.

[45] Thus, in any case, the revised approach does more accurately reflect the uncertainties in the method whether or not the absolute value for the  $^{230}\text{Th}_{\text{xs}}^0$  changes significantly between the two calculations.

[46] XSage is available for download at <http://climotop.earth.ox.ac.uk/research/xsage>, along with additional documentation. XSage is also available in the auxiliary material for this paper.<sup>1</sup>

## 5. Summary

[47] Normalization using  $^{230}\text{Th}_{\text{xs}}^0$  presents investigators with an opportunity to more accurately determine sediment fluxes and to better constrain age models. We suggest a number of improvements to the corrections applied to the total measured  $^{230}\text{Th}$  used to obtain  $^{230}\text{Th}_{\text{xs}}^0$  activities:

[48] 1. The determination of a localized estimate of  $(^{238}\text{U}/^{232}\text{Th})_{\text{det}}$  by identifying samples that are unlikely to contain authigenically derived uranium (those in which  $^{234}\text{U}/^{238}\text{U}$  is greater than 1) and taking the mean of their  $^{238}\text{U}/^{232}\text{Th}$ .

[49] 2. The assumption that the detrital component is in secular equilibrium is invalid. We propose that the detrital correction should be modified by a factor of  $0.96 \pm 0.04$  to account for the recoil of two alpha decays between  $^{238}\text{U}$  and  $^{230}\text{Th}$ .

[50] 3. The value for  $(^{234}\text{U}/^{238}\text{U})_{\text{init}}$  used in the correction for  $^{230}\text{Th}$  derived from authigenic uranium may be higher than the 1.147 of seawater as evidenced by mixing lines from core data. This excess  $^{234}\text{U}$  potentially arises from the maintenance of a  $(^{234}\text{U}/^{238}\text{U})$  deficit in the detrital phase.

[51] Finally, our MATLAB routine ‘XSage’ allows the rapid calculation of  $^{230}\text{Th}_{\text{xs}}^0$  activities using measured total uranium and thorium isotopic activities. It allows the calculation of sedimentation rates, age models and can produce an estimate and uncertainty on the duration of an individual horizon using a Monte Carlo approach. Furthermore it allows flexible and quick comparison between different approaches and assumptions.

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2012GC004295.

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## References

- Adkins, J., P. deMenocal, and G. Eshel (2006), The “African humid period” and the record of marine upwelling from excess  $^{230}\text{Th}$  in Ocean Drilling Program Hole 658C, *Paleoceanography*, *21*, PA4203, doi:10.1029/2005PA001200.
- Andersen, M. B., C. H. Stirling, B. Zimmermann, and A. N. Halliday (2010), Precise determination of the open ocean  $^{234}\text{U}/^{238}\text{U}$  composition, *Geochem. Geophys. Geosyst.*, *11*, Q12003, doi:10.1029/2010GC003318.
- Bacon, M. P., and R. F. Anderson (1982), Distribution of thorium isotopes between dissolved and particulate forms in the deep sea, *J. Geophys. Res.*, *87*, 2045–2056.
- Bacon, M. P., C. A. Huh, A. P. Fleer, and W. G. Deuser (1985), Seasonality in the flux of natural radionuclides and plutonium in the deep Sargasso Sea, *Deep Sea Res., Part A*, *32*, 273–286.
- Banerjee, S. K., J. King, and J. Marvin (1981), A rapid method for magnetic granulometry with applications to environmental studies, *Geophys. Res. Lett.*, *8*, 333–336.
- Bourne, M., C. Mac Niocaill, A. L. Thomas, M. F. Knudsen, and G. M. Henderson (2012), Rapid directional changes associated with a 6.5kyr-long Blake geomagnetic excursion at the Blake–Bahama Outer Ridge, *Earth Planet. Sci. Lett.*, *333–334*, 21–34.
- DePaolo, D. J., K. Maher, J. N. Christensen, and J. McManus (2006), Sediment transport time measured with U-series isotopes: Results from ODP North Atlantic drift site 984, *Earth Planet. Sci. Lett.*, *248*, 394–410.
- Francois, R., M. Frank, M. M. Rutgers van der Loeff, and M. P. Bacon (2004),  $^{230}\text{Th}$  normalization: An essential tool for interpreting sedimentary fluxes during the late Quaternary, *Paleoceanography*, *19*, PA1018, doi:10.1029/2003PA000939.
- Henderson, G. M. (2002), Seawater ( $^{234}\text{U}/^{238}\text{U}$ ) during the last 800 thousand years, *Earth Planet. Sci. Lett.*, *199*, 97–110.
- Henderson, G. M., and R. F. Anderson (2003), The U-series toolbox for paleoceanography, *Rev. Mineral. Geochem.*, *52*, 493–531.
- Henderson, G., C. Heinze, R. Anderson, and A. Winguth (1999), Global distribution of the  $^{230}\text{Th}$  flux to ocean sediments constrained by GCM modelling, *Deep Sea Res., Part I*, *46*, 1861–1893.
- Knudsen, M. F., G. M. Henderson, C. Mac Niocaill, and A. J. West (2007), Seven thousand year duration for a geomagnetic excursion constrained by  $^{230}\text{Th}_{\text{xs}}$ , *Geophys. Res. Lett.*, *34*, L22302, doi:10.1029/2007GL031090.
- Ku, T. L. (1965), An evaluation of the  $\text{U}^{234}/\text{U}^{238}$  method as a tool for dating pelagic sediments, *J. Geophys. Res.*, *70*, 3457–3474.

- Lyle, M., N. Mitchell, N. Piasias, A. Mix, J. I. Martinez, and A. Paytan (2005), Do geochemical estimates of sediment focusing pass the sediment test in the equatorial Pacific?, *Paleoceanography*, *20*, PA1005, doi:10.1029/2004PA001019.
- Maher, K., D. J. DePaolo, and J. C. F. Lin (2004), Rates of silicate dissolution in deep-sea sediment: In situ measurement using  $^{234}\text{U}/^{238}\text{U}$  of pore fluids, *Geochim. Cosmochim. Acta*, *68*, 4629–4648.
- Marcantonio, F., R. F. Anderson, S. Higgins, M. Stute, P. Schlosser, and P. Kubik (2001), Sediment focusing in the central equatorial Pacific Ocean, *Paleoceanography*, *16*(3), 260–267, doi:10.1029/2000PA000540.
- McCave, I. N., and I. R. Hall (2006), Size sorting in marine muds: Processes, pitfalls, and prospects for paleoflow-speed proxies, *Geochem. Geophys. Geosyst.*, *7*, Q10N05, doi:10.1029/2006GC001284.
- McCave, I. N., B. Manighetti, and S. G. Robinson (1995), Sortable silt and fine sediment size/composition slicing: Parameters for palaeocurrent speed and palaeoceanography, *Paleoceanography*, *10*(3), 593–610, doi:10.1029/94PA03039.
- McManus, J. F., R. F. Anderson, W. S. Broecker, M. Q. Fleisher, and S. M. Higgins (1998), Radiometrically determined sedimentary fluxes in the sub-polar North Atlantic during the last 140,000 years, *Earth Planet. Sci. Lett.*, *155*, 29–43.
- Robinson, L. F., N. S. Belshaw, and G. M. Henderson (2004), U and Th concentrations and isotope ratios in modern carbonates and waters from the Bahamas, *Geochim. Cosmochim. Acta*, *68*, 1777–1789.
- Stanford, J., E. Rohling, S. Bacon, A. P. Roberts, F. Grousset, M. Bolshaw (2011), A new concept for the paleoceanographic evolution of Heinrich event 1 in the North Atlantic, *Quat. Sci. Rev.*, *30*, 1047–1066.
- Thomas, A. L., G. M. Henderson, and I. N. McCave (2007), Constant bottom water flow into the Indian Ocean for the past 140 ka indicated by sediment  $^{231}\text{Pa}/^{230}\text{Th}$  ratios, *Paleoceanography*, *22*, PA4210, doi:10.1029/2007PA001415.
- Yu, E. F., R. Francois, M. P. Bacon, and A. P. Fleer (2001), Fluxes of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  to the deep sea: Implications for the interpretation of excess  $^{230}\text{Th}$  and  $^{231}\text{Pa}/^{230}\text{Th}$  profiles in sediments, *Earth Planet. Sci. Lett.*, *191*, 219–230.