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SELECTION OF SUITABLE DATA SETS IMPROVES ^{230}Th/U DATES OF DIRTY MATERIAL

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Abstract: ^{230}Th/U dating of dirty material such as fen peat and secondary carbonates depends on the ability to select suitable and to discard unsuitable data sets before the calculation of ^{230}Th/U ages. This means that open system conditions with respect to uranium during ageing are excluded and solely one source of detrital contamination was present in the samples. Three kinds of selection approaches of suitable data sets were applied: (1) isotope ratio plots, (2) the isotope-ratio evolution plot and the iterative determination of the decay-corrected initial detrital ^{230}Th/^{232}Th activity ratio (AR) as well as (3) depth profiles of the uranium concentration and the ^{234}U/^{238}U AR and the ash content. For reliable ^{230}Th/U age dating of dirty material all selection procedures have to be commonly applied because none of them works perfectly.

Keywords: uranium series dating, dirty material, peat, secondary carbonate.

1. PROBLEMS OF ^{230}Th/U DATING OF DIRTY MATERIAL

Terrestrial Upper and Middle Quaternary interglacial and interstadial organic (e.g. fen peat, lignite) and inorganic deposits (calcareous tufa and speleothems) can be dated by the ^{230}Th/U method within the age range of up to 500 ka. Several conditions have to be fulfilled and the raw analytical data have to undergo a rigorous and comprehensive reliability check. ^{230}Th/U dating is well proven for most materials that accumulate uranium during their formation. As for any numerical dating method it has to be presupposed that the system to be dated has not been affected by post-sedimentary processes such as mobilization of uranium. That means that the sampled material behaved as a closed system with respect to uranium during ageing (Ivanovich and Harmon, 1992).

Post-genetic leaching and accumulation of uranium might have occurred in secondary carbonates and fen peat. Moreover, more than one source of detrital contamination – local and regional mud in groundwater and surface water as well as aeolian dust – might have been involved. Under such circumstances, isotope ratios of uranium and thorium may not yield reliable ^{230}Th/U ages.

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In order to identify samples affected by the mentioned problems suitable data sets have to be effectively selected and the unsuitable ones discarded before the calculation of ^{230}Th/U ages. A common but not or very successful way has been to exclude all data sets from samples with an exaggerated uranium concentration. Such material is often present in the upper and lower rim layers of fen peat. The paper describes the steps to get reliable ^{230}Th/U ages from dirty material.

2. PRINCIPLE OF ^{230}Th/U DATING OF PURE MATERIAL

The ^{230}Th/U dating method is based on the radioactive decay series of ^{238}U. The daughter isotope ^{234}U ($\tau = 2.4525\times10^5$ a; Chen *et al.*, 2000) decays into the daughter isotope ^{230}Th ($\tau = 75.69$ ka; Chen *et al.*, 2000) with the emission of an alpha particle. The half-life τ of ^{238}U ($\tau = 4.468\times10^9$ a) is considerably longer than that of ^{234}U and ^{230}Th. As a consequence, radioactive equilibrium is almost approached after about one million years in most geologically old rocks and sediments (**Fig. 1**). A characteristics of radioactive equilibrium is that all members of the decay series have the same specific activity (which is the decay rate per mass unit). Thus, the activity ratios of any two of the series is equal to one.

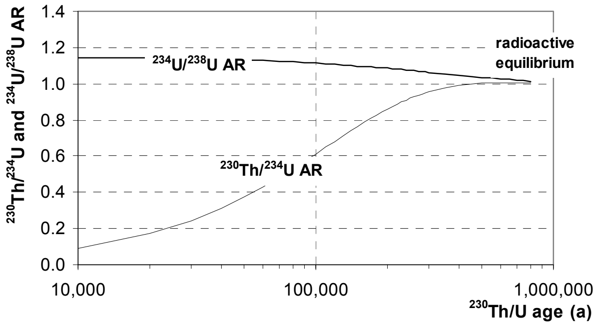

Fig. 1. *Change in the ^{230}Th/^{234}U and ^{234}U/^{238}U activity ratios with increasing age for an initial ^{234}U/^{238}U AR of 1.15 (mean in ocean water).*

The radioactive equilibrium can be disturbed by geochemical processes if the members of the radioactive series have certain geochemical properties, for example, uranium VI ions are soluble in oxygenated water while thorium is practically insoluble. During weathering, uranium tends to be dissolved in water and thorium bound by clay minerals. During this process, uranium 234 is preferentially mobilized from rocks, which is why the ^{234}U/^{238}U activity ratio in groundwater usually is greater that that in the source rock.

The uranium dissolved in groundwater may be incorporated into a new system. The most simple ^{230}Th/U dating model presupposes that the new system contains solely uranium. Then, the numerical ^{230}Th/U clock starts at zero and a ^{230}Th/^{234}U AR = 0. The radioactive disequilibrium between ^{230}Th and ^{234}U maintains during ageing until the radioactive equilibrium is approached after about 350-500 ka. This process is described by **Eq. 2.1** which has to be solved iteratively. Activity ratios are given in square brackets and $\lambda = \ln 2/\tau$:

$$\left[\frac{^{230}Th}{^{234}U}\right] = \left[\frac{^{238}U}{^{234}U}\right] \cdot \left(1 - e^{-\lambda_{230} \cdot t}\right) + \left(1 - \left[\frac{^{238}U}{^{234}U}\right]\right) \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \left(1 - e^{-(\lambda_{230} - \lambda_{234}) \cdot t}\right) \quad (2.1)$$

The change in the ^{230}Th/^{234}U and the ^{234}U/^{238}U ARs with the age t is shown in **Fig. 1** assuming an initial ^{234}U/^{238}U AR of 1.15. In nature, the ^{234}U/^{238}U AR of terrestrial samples has a wide range of between 1 and 20. The most rapid change in the ^{230}Th/^{234}U AR takes place between 50,000 and about 200,000 years.

The absolute dating error increases with age. The relative dating error is quite large for small ^{230}Th/U ages when the ^{230}Th activity is low. It approaches a minimum around 100-120 ka and then rises rapidly with increasing ^{230}Th/U age. The maximum age that can be determined by any numerical dating method is the minimum age of the sample. The maximum ^{230}Th/U age of a sample that can be determined by radiometric dating is about 350 ka, that by mass spectrometric dating is about 500 ka (Geyh and Müller, 2005).

3. INTERFERING FACTORS OF THE ^{230}Th/U METHOD

There are two main factors which complicate the ^{230}Th/U age determination or even make it impossible: open-system conditions with respect to uranium and detrital contamination with allochthonous ^{230}Th. Thorium is considered as non-soluble in water and allochthonous uranium has not yet been identified in fen-peat samples.

Open systems with respect to uranium

Kaufman and Broecker (1965) developed an isotope-ratio evolution plot for the ^{238}U decay series in which the ^{234}U/^{238}U AR is plotted versus the ^{230}Th/^{238}U AR. It shows the variation of the two ARs with increasing age. Each initial ^{234}U/^{238}U AR yields a separate evolution line. All the lines meet the point (1,1) at radioactive equilibrium or at infinite age. The ARs of coeval samples fit more or less straight lines of their corresponding ages, which are termed "isochrones" (**Fig. 2**).

ARs of samples which accumulated or lost uranium during ageing (open system with respect to uranium) deviate from the evolution lines and from isochrons. Two cases have to be distinguished – rapid and slow loss or accumulation of uranium (**Fig. 3**). In the first case, ^{234}U and ^{238}U are not fractionated by U mobilization. The data points are shifted horizontally from the modeled evolution curve. In the second case of slow uranium mobilization, ^{234}U and ^{238}U are fractionated. Both activity ratios are affected and the data points move away from the evolution lines without regard to direction (Osmond and Ivanovich, 1992). Up to now there is now way to correct ^{230}Th/U ages for effects resulting from open system conditions with respect to uranium.

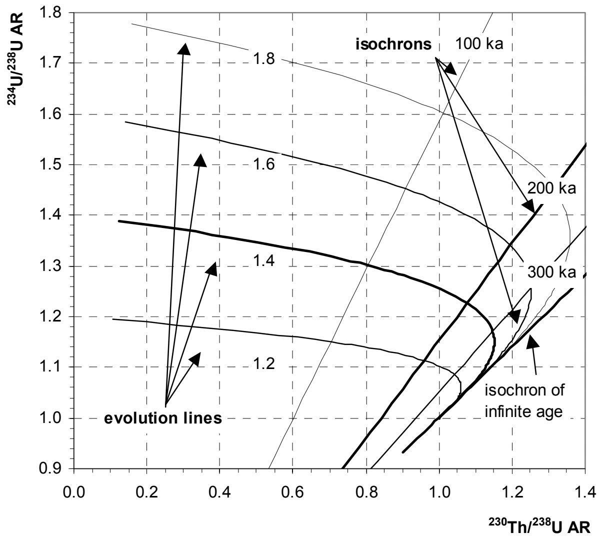

Fig. 2. *Isotope-ratio evolution plot of the ^{234}U/^{238}U AR and the ^{230}Th/^{238}U AR as function of the age. Any initial ^{234}U/^{238}U AR yields an individual evolution line. All of them meet the point (1,1) at infinite age, i.e. at radioactive equilibrium with respect to uranium. The ARs of coeval samples plot on more or less straight lines known as isochrons (Kaufman and Broecker, 1965).*

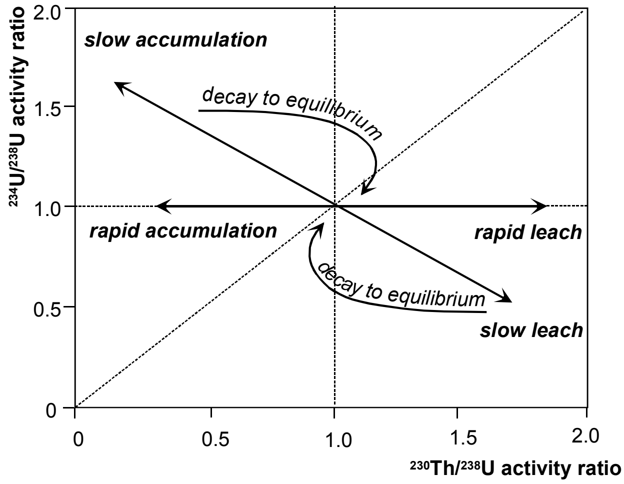

Fig. 3. *Isotope-ratio evolution plot of the $^{234}U/^{238}U$ AR versus the $^{230}Th/^{238}U$ AR showing the effect of rapid and slow uranium mobilization on the modeled evolution lines (Osmond and Ivanovich, 1992).*

Detrital contamination and the correction for it

During the formation of a new uranium system (e.g. calcareous tufa or fen peat), airborne dust or water-borne mineral mud are usually incorporated. These contaminants usually contain thorium which is bound to detrital clay. In the case of secondary carbonates (calcareous tufa, speleothem), also the dripping water may be contaminated. The presence of allochthonous (detrital) ^{230}Th in the original detrital material means that the ^{230}Th/U clock shows ^{230}Th/U ages that are too old. The age error caused by an initial ^{230}Th content may amount to 1000 years up to 100,000 years.

The detrital ^{230}Th decays during ageing while the activity of the radiogenic ^{230}Th increases as a result of the decay of ^{234}U. Hence the ^{230}Th/U age error due to detrital contamination decreases with increasing age. The two or more sources of ^{230}Th (one radiogenic and at least one detrital) have to be distinguished and quantified to enable a correction of the ^{230}Th/U age.

Kaufman and Broecker (1965) introduced the concept of a binary mixture of radiogenic and detrital ^{232}Th. If the latter has only one source, the proportion of detrital ^{230}Th can be estimated via the thorium concentration or the ^{232}Th activity. As the half-life of ^{232}Th is very large ($\tau = 14.05\times10^9$ a), it behaves like a stable isotope. Hence, its activity may allow to estimate the initial detrital ^{230}Th activity of a sample of any age. If the initial ^{230}Th/^{232}Th AR is determined or known, the ^{230}Th/U age can be corrected to approximate the absolute age of the sample. Ku and Liang (1984), Schwarcz and Latham (1989) and Luo and Ku (1991) refined this concept.

According to the Kaufman-Broecker concept (1965), the initial ^{230}Th/^{232}Th AR = f_o (or f as decay-corrected f_o) is the correction parameter to be used to calculate the radiogenic ^{230}Th activity ([^{230}Th]*) from the measured activity [^{230}Th] as follows:

$$\left[{}^{230}Th\right]^* = \left[{}^{230}Th\right] - \left[{}^{232}Th\right]\cdot f_o \cdot e^{-\lambda_{230}\cdot t} = \left[{}^{230}Th\right] - f \times \left[{}^{232}Th\right] \tag{3.1}$$

If f >20, the detrital ^{230}Th activity is so low that any correction for detrital ^{230}Th of radiometrically determined ^{230}Th/U ages is negligible.

If f_o or f has not been determined, the effect of the detrital correction for a ^{230}Th/U age may be estimated by assuming $f = 1$, i.e. when the detrital contamination is finite and $f = 0$ when detrital contamination is missing (**Eqs 2.1** and **3.1**). A correction for detrital ^{230}Th is, however, required in any case if the corrected and uncorrected ^{230}Th/U ages differ by more than 10 %. **Table 1** shows the corrected ^{230}Th/U ages of four coeval samples from the Eemian section at Dierkshausen, Germany. The uncorrected ^{230}Th/U ages ($f = 0$) range from 99 to 133 ka, the corrected ages ($f = 1$) from 91 to 115 ka. The actual f value of 0.49±0.20 yields ^{230}Th/U ages ranging from 99 to 116 ka associated with the minimum scatter of the individual corrected ^{230}Th/U ages of ±3.7 ka.

An analogous correction exists for detrital uranium using the initial ^{234}U/^{232}Th AR = g_o as correction factor. The radiogenic ^{234}U activity ([^{234}U]*) is obtained using **Eq. 3.2**, also assuming only one source of contamination:

$$\left[{}^{234}U\right]^* = \left[{}^{234}U\right] - \left[{}^{232}Th\right]\cdot g_o \cdot e^{-\lambda_{234}\cdot t} = \left[{}^{234}U\right] - g \cdot \left[{}^{232}U\right] \tag{3.2}$$

In order to determine the initial f = ^{230}Th/^{232}Th, Osmond *et al.* (1970) adopted the binary mixing concept of Kaufman-Broecker (1965) and introduced a mixing plot (**Fig. 4**). It is called Rosholt I plot, but is usually incorrectly referred to as "isochron" plot. It yields a least-squares-fitted straight line for the ^{230}Th/^{232}Th versus ^{234}U/^{232}Th activity ratios of coeval samples. Its slope equals the present ^{230}Th*/^{234}U AR of the radiogenic ^{230}Th* and its intercept on the y-axis equals the present f = ^{230}Th/^{232}Th AR. Both ARs are required to correct the ^{230}Th activity (**Eq. 3.1**) and to calculate the ^{230}Th/U age (**Eq. 2.1**). A slope = 0 corresponds to a ^{230}Th/U age of zero. The "infinite" age has a slope of 1 (radioactive equilibrium).

The correlation coefficient of this plot is usually larger than 99 %. This unusually high value is due to the close correlation between ^{230}Th and ^{234}U in samples with low detrital contamination. In addition, the correlation

Table 1. *Radiometric ^{230}Th/U ages (ka) of four coeval fen-peat samples from the Eemian section at Dierkshausen. The corrected ^{230}Th/U ages (BP) are compiled for f = 0, f = 1 and the actual f = 0.49±0.20. The standard deviations of the first weighted means were calculated with the standard deviations of the individual ^{230}Th/U ages, those of the second weighted means reflect the actual scatter of the individual ^{230}Th/U ages. It is obvious that the theoretical and actual scatter of the weighted means are only comparable if the actual detrital correction of the raw ^{230}Th/U ages is applied.*

Sample	*f* = 0	*f* = 1	*f* = 0.49±0.2
Uh 9	99.2±7.5	98.5±7.4	98.9±7.4
Uh 43	132.8±8.7	90.8±6.1	111.0±12.0
Uh 22	115.9±7.9	109.6±7.5	112.9±7.8
Uh 44	117.2±6.0	114.7±4.8	116.0±4.9
Mean	116.3±6.9	103.4±5.4	109.7±3.7
Weighted mean	115.4±3.7	105.0±3.1	111.2±3.5
	115.4±6.2	112.4±5.8	111.2±3.9

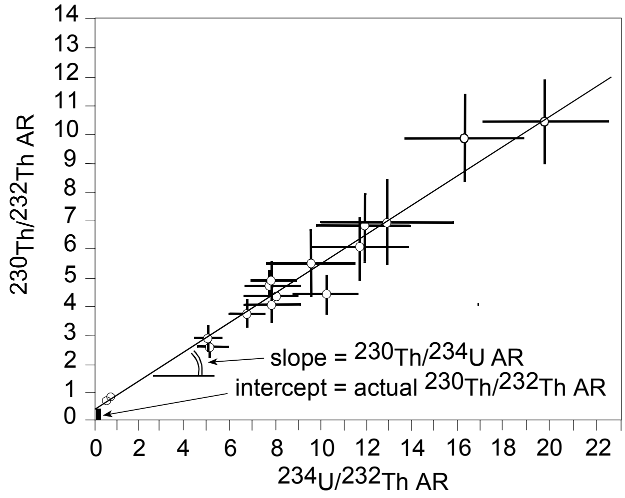

Fig. 4. *Rosholt I plot or "isochron" plot (^{230}Th/^{232}Th AR versus ^{234}U/^{232}Th AR): The slope of the mixing line corresponds to the ^{230}Th*/^{238}U AR (Eq. 1). The intercept on the y-axis gives the decay-corrected ^{230}Th/^{232}Th AR required for the detrital correction of the individual ^{230}Th/U ages (Eq. 2).*

between isotope ARs with a common denominator has a "zero-correlation" coefficient of non-correlated values of at least 70 % (Chayes, 1949 and 1971; Geyh, 1994 and 2001).

In order to obtain a well defined mixing line ("isochron"), at least four (Ludwig and Titterington, 1994), but preferably many more coeval samples containing widely differing detrital ^{232}Th contents have to be analyzed. The reliability and precision of the ^{230}Th/U age usually increases with the number of Th and U isotope analyses and the extent of detrital contamination. If in contrast the coeval samples all have a similar level of detrital contamination, a data cluster is obtained in the Rosholt I plot, which excludes a reliable determination of the slope of the mixing line and of the intercept on the y-axis f. $f = {}^{230}$Th/^{232}Th AR must be positive. Negative ^{230}Th contamination is theoretically excluded and usually yields erroneous ^{230}Th/U ages.

Samples can be taken as coeval if the individual ^{230}Th/U ages plot within the confidence interval of the mean ^{230}Th/U age. This is usually the case if the samples were collected from the same interglacial or interstadial deposit.

The plot of ^{234}U/^{232}Th AR versus the ^{238}U/^{232}Th AR yields the actual ^{234}U/^{238}U AR and the decay-corrected present ^{234}U/^{232}Th AR at the intercept on the y-axis (Rosholt II plot). The correlation coefficient is even larger (> 99.9 %) for similar reasons already described for the Rosholt I plot.

4. IDENTIFICATION OF NON-SUITABLE DATA SETS

The reliability of ^{230}Th/U ages determined on detritus contaminated material, depends on the possibility to identify and discard data obtained from material that is unsuitable for ^{230}Th/U dating. There are the two already mentioned main causes of complications:

1. The material behaved as an open system with respect to uranium during ageing. Uranium accumulated or was leached after sedimentation, with the result that ^{230}Th/^{234}U AR and ^{230}Th/U ages are too low or too high, respectively. Post-sedimentary mobilisation of thorium is not considered a problem owing to its negligible solubility in water.
2. The detrital ^{230}Th has more than one source. In the case of fen peat, airborne dust and fluviatile mud might have become incorporated during growth of the peat; similarly, lacustrine carbonate may have been contaminated by mud during accumulation.

There are three principal approaches to identify analytical data that is unreliable owing to one or both of these two causes:

- isotope-ratio plots by Rosholt (1976) and Osmond *et al.* (1970),
- the isotope-ratio evolution plot (Kaufman and Broecker, 1965) and the iterative determination of the f value (Geyh, 2001), and uranium or ^{234}U/^{238}U depth profiles as well as U-^{234}U/^{238}U or U-ash correlations.

On the basis of 222 sets of data obtained from the ^{230}Th/U dating of 33 peat sections in Europe and Siberia using different analytical protocols and measurement techniques, it was found that a rigorous examination is required in order to reject those data sets that are unsuitable for ^{230}Th/U age calculation. Routine application of all known reliability tests is indispensable because none of them works perfectly.

One case study of the Wentegole site in the present arid Gobi Desert, China, is chosen to demonstrate the usefulness of the first and second principal approaches to select suitable data sets. This section contains two overlain lake marl layers separated by a clay layer from each other. Six samples were analyzed using the total dissolution technique (Luo and Ku, 1991). The Nizhnaja Boyarshina site of fen peat situated in the Smolensk Province, Russian Plain, delivered ^{230}Th/U data sets using the L/L method (Schwarcz and Latham, 1989) at the St. Petersburg Laboratory in Russia (Arslanov, 2005). These data sets are used to demonstrate the limited applicability of the third principal selection approach.

Isotope-ratio plots

The principal feature of binary mixing is that any two properties of the components of a mixture show a linear correlation. The Kaufman and Broecker concept (1965) is based on this and states that a plot of any two isotope ratios must yield a straight line. If this premise is not fulfilled, the ^{230}Th/U ages are not reliable.

Rosholt (1976) introduced the currently most frequently used Rosholt I and Rosholt II plots (top of **Fig. 5**). Correlation coefficients > 99.0 % and > 99.9 %, respectively, reflect the strong correlation of ^{230}Th and ^{234}U activities as well as those of ^{234}U and ^{238}U in samples with a low level of detrital contamination. Hence, these two plots are often not very sensitive for detecting samples that do not fulfil the two main requirements for ^{230}Th/U dating.

Osmond *et al.* (1970) developed two additional plots: ^{230}Th/^{238}U AR versus ^{232}Th/^{238}U AR (Osmond I plot) and ^{234}U/^{238}U AR versus ^{232}Th/^{238}U AR (Osmond II plot)

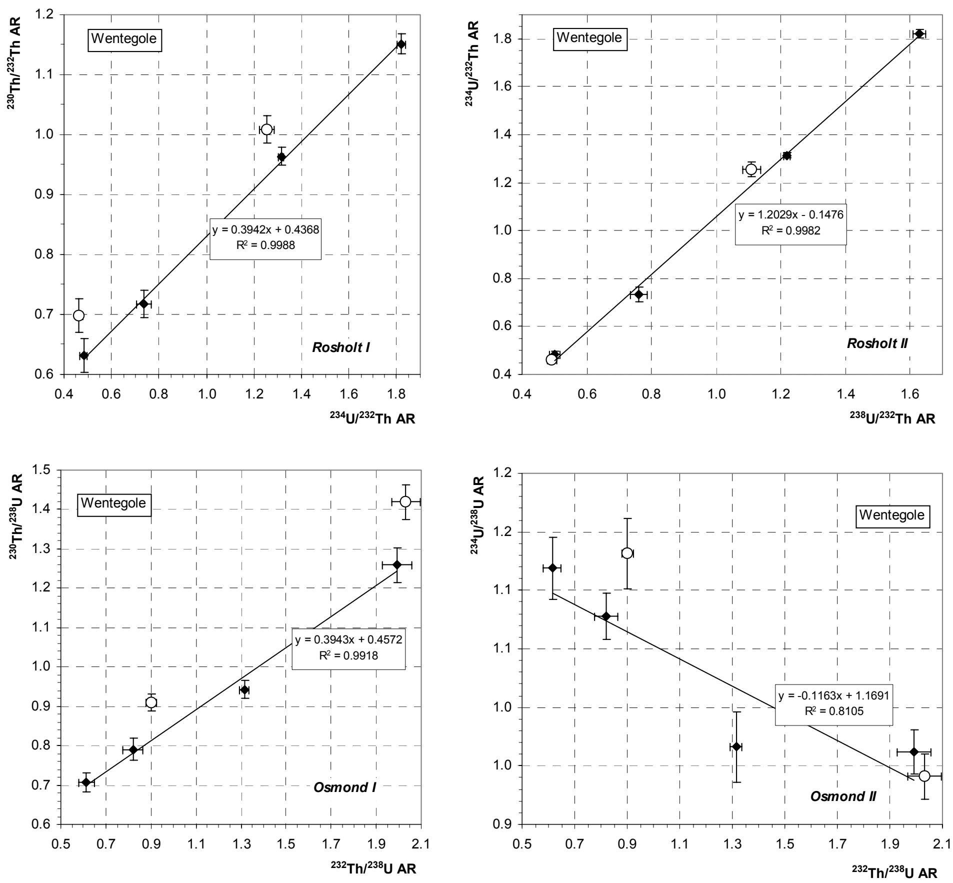

Fig. 5. *top: Rosholt I and Rosholt II plots (Rosholt et al., 1976) of the Wentegole data sets: The slopes of the mixing line equals the ^{230}Th/^{234}U AR and the ^{234}U/^{238}U AR and the y-intercepts give the ^{230}Th/^{232}Th AR and ^{234}U/^{232}Th AR. The data sets represented by open dots do not fit the mixing line and were discarded from the ^{230}Th/U age determination.*

bottom: Osmond I und Osmond II plots (Osmond, 1970) of the Wentegole data sets: The slopes of the mixing lines give the ^{230}Th/^{232}Th AR and the ^{234}U/^{232}Th AR and the y-intercepts provide the ^{230}Th/^{238}U AR and ^{234}U/^{238}U AR. The data sets represented by open dots do not fit the mixing line in the Osmond plots and were be discarded from the ^{230}Th/U age determination.

(bottom of **Fig. 5**). In impure and old samples, the ^{232}Th and ^{230}Th activities normally do not correlate with each other. This is because most of the ^{230}Th was produced by radioactive decay of ^{234}U. Therefore, the correlation coefficient of the Osmond I plot sometimes only approximates the minimum "zero-correlation" coefficient of 70 % for pairs of isotope ratios with a common denominator. Then, several data points with their error ellipses do not fit the straight lines of any of the Osmond plots. The Osmond I plot is the most sensitive one for identifying analytical data that should be discarded from the final calculation of the ^{230}Th/U age.

At least three isotope ratio plots allowed to identify the two non-suitable data sets for ^{230}Th/U dating of the two lake marl layers at Wentegole. The data sets of all six samples yielded a ^{230}Th/U age of 56.3±3.6 ka (χ^2 = 14.8) and a decay-corrected initial ^{230}Th/^{232}Th AR f = 0.449±0.006. The corresponding iterative determination of f yielded 0.512 and a deviating ^{230}Th/U age of 45±10 ka.

The ^{230}Th/U age of 54.1±2.1 ka (χ^2 = 2.0) of the four suitable data sets is more precise; f = 0.438±0.006. The iteratively determined decay-corrected initial ^{230}Th/^{232}Th AR is f = 0.443 and the ^{230}Th/U age 53.0±1.6 ka. Both ^{230}Th/U ages fit in the Pleistocene interstadial period MIS 3.3 (Imbrie *et al.*, 1984).

The evaluation of all of the other data sets for the 33 sections has confirmed that the Rosholt I and Rosholt II plots usually provide only a poor indication of which data should be rejected. The most sensitive is the Osmond I plot. In a few cases, even with as many as ten data sets, it has not been possible to obtain a reliable and unambiguous final ^{230}Th/U age. It could not be decided which data sets have to be rejected and differing final ^{230}Th/U ages were obtained.

It was initially expected that a numerical evaluation of the four plots yields additional information. The slopes of the straight lines and their intercepts on the y-axis yield pairs of initial isotope ratios (**Table 2**). However, the corresponding evaluation of all 222 data sets of the studied 33 sections has provided evidence that the numerical results do not give any indication by which unsuitable data sets can be identified. This is true for the correlation coefficient r as well as for the activity ratios given by the slope of the mixing lines of one of the plots, which is the same as the activity ratio given by the intercept on the y-axis of one of the other plots (see the compilation below). The reason is that the determination of regression lines refer to all data and the effect of outliers is suppressed while the plot sensitively allow to identify single outliers.

The results obtained from the Wentegole Site are

Table 2. *Isotope ratios for the ^{230}Th/U age determination to be determined by the Osmond-Rosholt isotope ratio plots.*

Isotope ratio	Slope	Intercept
^{234}U/^{238}U	Rosholt II	Osmond II
^{230}Th/^{232}Th	Osmond I	Rosholt I
^{230}Th/^{238}U	Rosholt I	Osmond I
^{234}U/^{232}Th	Osmond II	Rosholt II

compiled below and confirm this statement. The evaluation of the four suitable data sets and of all including the two non-suitable data sets do not show helpful deviations. This is shown in **Table 3**.

Isotope-ratio evolution plot and iterative correction for detrital ^{230}Th

Two simple approaches were developed by Geyh (1994, 2001) to identify unsuitable data sets. In the first case the factor *f* is determined by the Rosholt I plot and applied to correct the raw ^{230}Th/^{234}U AR (**Eq. 3.2**). In the isotope-ratio evolution plot (Kaufman and Broecker, 1965; **Fig. 6**) the scatter of the dots representing the corrected data sets is smaller than that of the raw data. Outliers are easily identified.

The isotope-ratio evolution plot of the six data sets of the Wentegole Site is shown in **Fig. 6**. Two already identified detritus-corrected data sets do not fit to the isochrons between 50 and 60 ka and have to be discarded for the final calculation of the ^{230}Th/U age.

The second approach bypasses the error-evaluation problems associated with the "isochron" approach (Rosholt I plot). The ^{230}Th/^{232}Th AR and ^{234}U/^{232}Th AR of coeval samples with different contamination show a wide scatter (**Fig. 6**). Application of the detrital correction with iteratively increasing the *f* value causes the points to move to the left (Kaufman and Broecker, 1965). The higher the detrital contamination the further the points move to the left. The optimum detrital correction factor *f* is found when the points of the cluster are the closest together (**Fig. 7**). The points in the cluster become further apart again when the *f* value is more increased. The elliptical shape of the cluster results from differences in the initial ^{234}U/^{238}U AR of the analysed samples and the absence of a correction for detrital uranium.

The width of the dot cluster of the four suitable data sets approaches its minimum at *f* = 0.443 and a detritus-corrected ^{230}Th/U age of 53.0±1.6 ka. The "Rosholt-I" or "isochron" plot delivered *f* = 0.438±0.006 and 54.1±2.1 ka. The change of the iteratively corrected ^{230}Th/U ages as a function of *f* (**Fig. 8**) allows to identify the suitable data sets (in bold) at the principal intersection point (thick ring). The two non-suitable data sets yield two separate intersection points (thin rings).

The iterative determination of the decay-corrected initial ^{230}Th/^{232}Th AR of the detrital contamination has the advantage that the approach is simple and not bothered with the problem of error correlation of activity ratios with a common denominator. The single detritus-corrected ^{230}Th/U ages can easily be checked for statistical consistency. This method has not yet been extended to detrital uranium contamination. Until now fen peat has not yet shown such kind of contamination.

Table 3. *Isotope ratios for ^{230}Th/U age dating of four selected suitable and six determined raw data sets from the Wentegole site determined by the Osmond-Rosholt isotope ratio plots compiled in Table 2. It is obvious that neither the correlation coefficient r nor the comparison of the two independently determined isotope ratios allow a decision that the four selected data sets are more suited for dating than the all determined six ones.*

	4 suitable data sets			All 6 data sets		
	r	isotope ratio		*r*	isotope ratio	
^{234}U/^{238}U	-0.95	1.169	1.149	-0.98	1.182	1.189
^{230}Th/^{232}Th	+0.99	0.398	0.389	+0.95	0.407	0.407
^{230}Th/^{238}U	+1.00	0.465	0.453	+0.97	0.474	0.478
^{234}U/^{232}Th	+1.00	-0.100	-0.108	+1.00	-0.121	-0.119

Profiling and correlation

It is an often mentioned opinion that open systems for uranium are clearly identifiable on the basis of elevated uranium concentration or ^{234}U/^{238}U AR with respect to the plateau value of the central part of any peat profile. It is presupposed that the top and base rim layers of at least 10 cm thickness have continuously absorbed uranium dissolved in the seeping groundwater during the entire

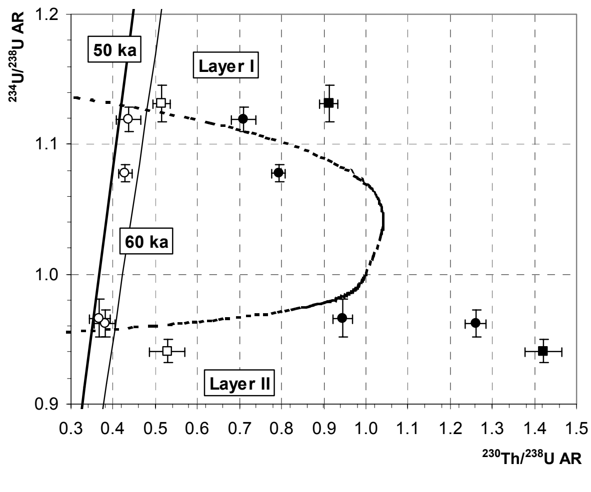

Fig. 6. *Isotope-ratio evolution plot: Scatter of data for two layers of lake marl at Wentegole in the Gobi Desert, China. From each layer three analyses were carried out. The width of scatter of the data in the ^{230}Th/ ^{232}Th- ^{234}U/ ^{232}Th diagram decreases with increasing thorium index. Open symbols represent corrected activity ratios, filled uncorrected ones and diamonds belong to outliers.*

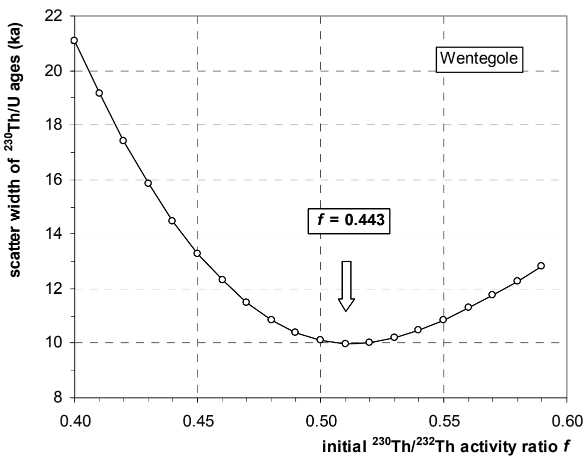

Fig. 7. *The scatter of the iteratively corrected ^{230}Th/U ages of two lake-marl layers at Wentegole in the Gobi Desert, China, approaches a minimum at f = 0.443. The Rosholt I plot yields 0.438±0.006 for the decay-corrected initial ^{230}Th*/ ^{232}Th AR of the detrital contamination.*

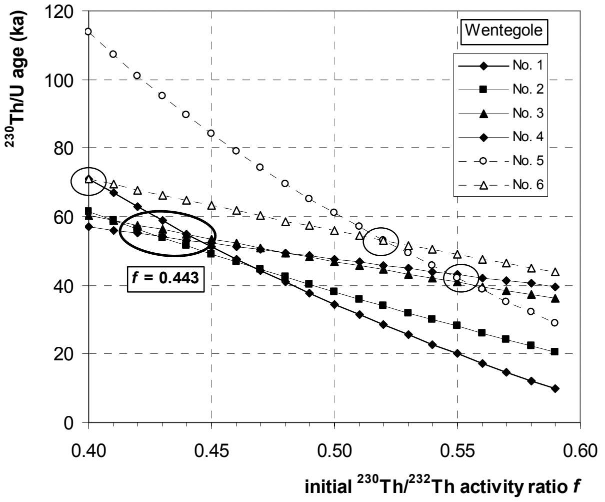

Fig. 8. *Change of the detritus corrected ^{230}Th/U ages of two lake-marl layers from the Gobi Desert, China, with increasing f value. The lines of the four selected data sets suitable for ^{230}Th/U dating have an intersection point at f = 0.443 (thick ring). The Rosholt I plot yields 0.438±0.006. The lines of the samples No. 5 and 6 do not fit in this picture and were rejected from the final evaluation. The intersections (thin rings) are far from that of the samples that are suitable for dating.*

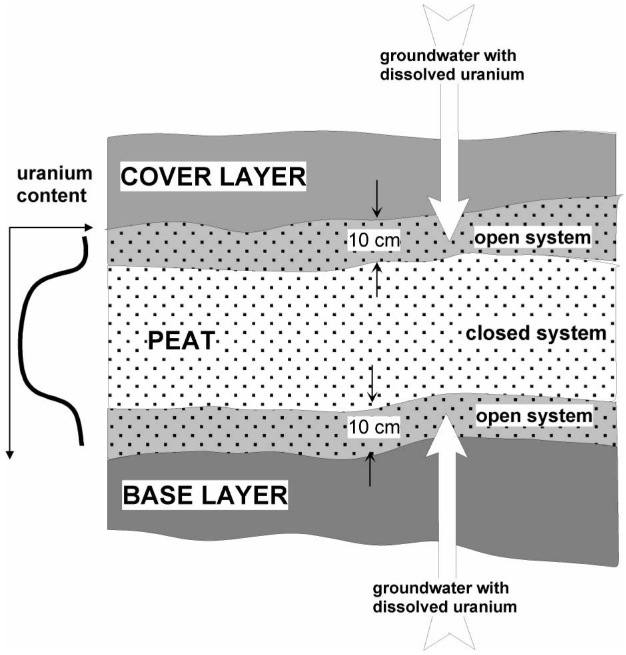

Fig. 9. *Scheme of a model interglacial fen peat section: Samples suitable for ^{230}Th/U dating may only be found in the central part. The top and base rim layers might have behaved as open system with respect to uranium during ageing and are therefore not suitable for ^{230}Th/U dating. It is assumed that in these parts of the section uranium dissolved in the continuously entering groundwater is post-genetically accumulated and increases the uranium concentration.*

period of ageing (**Fig. 9**).

This would be a very simple reliability test to identify those data sets of samples that do not yield reliable ^{230}Th/U ages. However, the situation is more complex, as shown by the example of the Nizhnaja Boyarshina site in the Smolensk Province in the Russian Plain (**Fig. 10**). The corresponding tests on all 222 data sets of the 33 fen peat sections evidence that many outliers surprisingly show either depleted uranium concentrations and ^{234}U/^{238}U AR in the marginal layers or belong to samples from the central part. Hence, it is obvious that these kinds of plot do not allow a definite decision which data sets have to be discarded and whether the requirements of ^{230}Th/U dating are met.

The Nizhnaja Boyarshina Site contains a fen-peat section which was palynologically classified as Eemian (Mikulino interglacial). The isotope data sets are shown in **Figs 10** and **11**. Arslanov (2005) rejected not only the five data sets from the rim samples with elevated uranium concentration but also six others from the central part without any explanation. He calculated a ^{230}Th/U age of 105.9±5.4 ka which cannot be verified neither by the "isochron" nor the "iteration" approach. The data sets of the upper part of the Nizhnaya Boyarshchina Site consisting of moss peat yielded an ^{230}Th/U age of 126^{+108}_{-52} and a f = 0.47±0.32. If the data set of the base sample is discarded a considerably deviating but more precise ^{230}Th/U age of 46±12 ka and f = 0.86±0.19 is obtained.

The lower part of this section consists of fen peat. All data sets yield a non-acceptable ^{230}Th/U age of 18±16 ka. Discarding two of them identified by the isotope plots a ^{230}Th/U age of 230^{+77}_{-44} ka is obtained. In an alternative evaluation three data sets were discarded and yielded an ^{230}Th/U ages of 68.4±8.0 ka. Combining both layers the four isotope ratio plots identified five suitable data sets from the central part which yielded a reasonable ^{230}Th/U age of 118±15 ka (χ^2 = 1.6) and f = 0.55±0.13. Surprisingly, the sample with the exaggerated ^{234}U/^{238}U AR is also identified as suitable for ^{230}Th/U dating. Due to the highly deviating ^{230}Th/U ages of the different selections of data sets the peat of the Nizhnaja Boyarshina site cannot be dated.

This example provides evidence that the central part of thick peat deposits might not always have behaved as closed system for uranium or may contain more than one source of detrital contamination. Suitable and unsuitable samples cannot be distinguished neither by their uranium concentration nor the ^{234}U/^{238}U AR. This statement holds also true for the correlation between the ^{234}U/^{238}U AR and the ^{238}U activity as well as between the ^{238}U activity (or ^{234}U/^{238}U AR) and the ash content (**Fig. 11**). Only in some cases these plots partly confirm what was already found with the isotope ratio plots by the Osmond and Rosholt.

In conclusion, only the common application of all known selection procedures permit a trusty identification of those data sets which are suitable for ^{230}Th/U dating.

5. CONCLUSION

The determination of reliable ^{230}Th/U ages from impure material requires a comprehensive and rigorous identification of suitable and unsuitable data sets. The samples which are not suitable for ^{230}Th/U dating may have behaved as open system for uranium or might have contained more than one detrital component. The total sample dissolution technique seems to be superior in

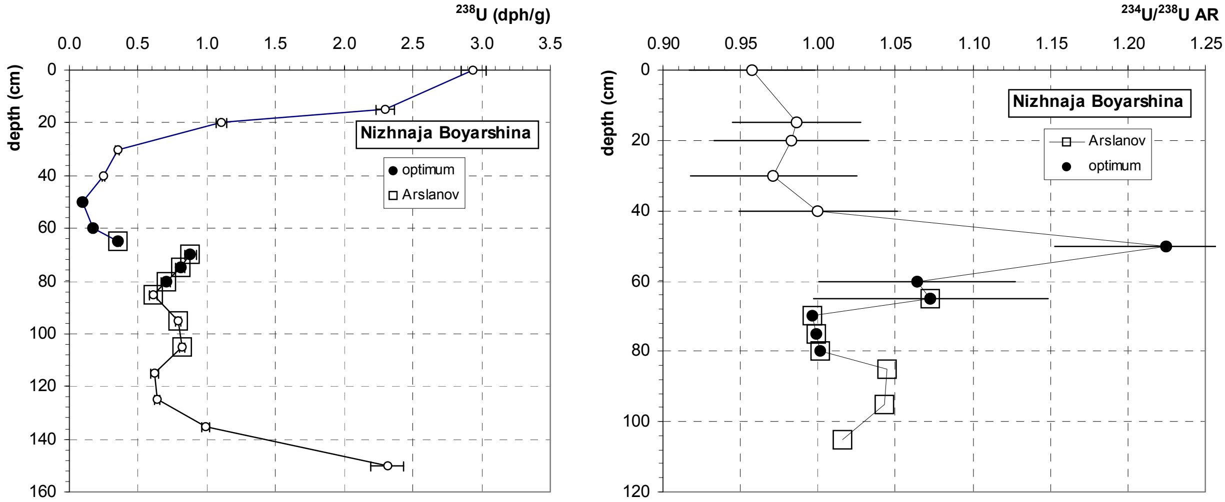

Fig. 10. *The data shown as open squares from the fen peat at the Nizhnaja Boyarshina site, Russian Plain were used for the evaluation of the ^{230}Th/U ages (Arslanov, 2005). The best suitable data sets (black dots) were identified by the isotope-ratio plots by Rosholt and Osmond. Left: ^{238}U activity versus depth. Right: ^{234}U/^{238}U AR versus depth.*

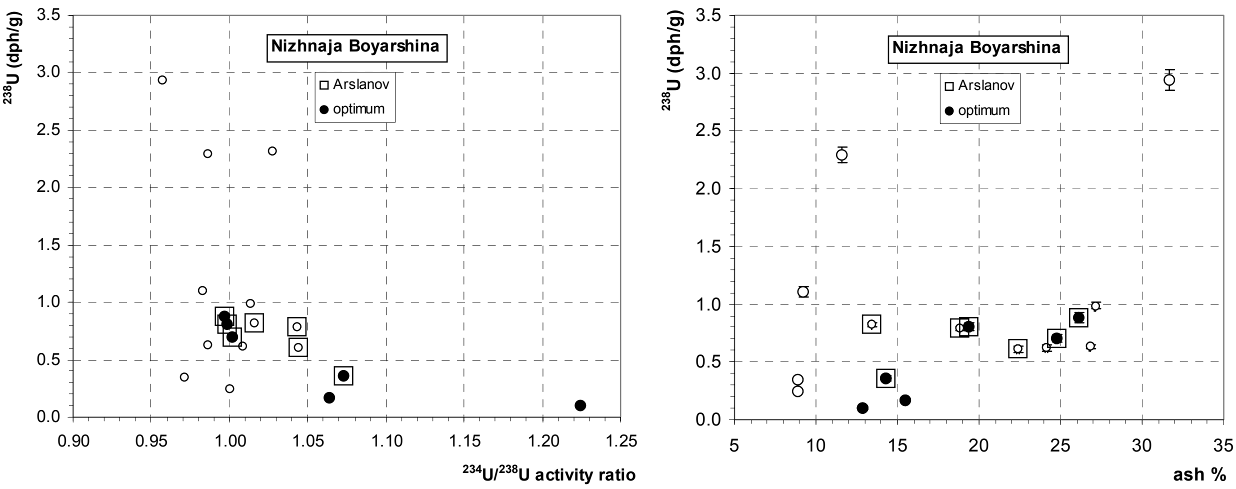

Fig. 11. *The dots represent the data sets from the Nizhnaja Boyarshina site in the Russian Plain. The dots used for the evaluation of the ^{230}Th/U ages are surrounded by open squares (Arslanov, 2005). The most suitable data sets (black dots) were identified by the Rosholt et al. (1976) and Osmond (1970) isotope plots. Left: ^{234}U/^{238}U AR versus ^{238}U activity. Right: ^{238}U activity versus ash content.*

respect to the L/L technique avoiding isotope fractionation between the uranium isotopes or loss of ^{230}Th during the chemical treatment. Single uranium and thorium isotope analyses only yield reliable ^{230}Th/U ages if the material was free of any of the described interferences.

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