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^{230}Th/U dating of interglacial and interstadial fen peat and lignite: Potential and limits

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Abstract: The state-of-the-art and potential of the ^{230}Th/U disequilibrium method are discussed for the dating of fen peat and lignite. Recommendations are given for the collection of suitable samples. The numerous interfering factors in ^{230}Th/U dating of fen peat show that a rigorous examination of the reliability of the measured data sets is required if reliable ^{230}Th/U ages are to be obtained. The accuracy of such ^{230}Th/U ages allows a reliable correlation of interglacial and interstadial deposits to the warm periods documented in the SPECMAP timescale but does not yet allow detailed temporal resolution.

[^{230}Th/U-Altersbestimmung interglazialer und interstadialer Niedermoortorfe und Ligniten: Potential und Grenzen]

Kurzfassung: Der Stand und die Zukunft der Altersbestimmung von Niedermoortorf und Lignit mit der ^{230}Th/U-Ungleichgewichtsmethode werden diskutiert. Empfehlungen zur Auswahl der Probeentnahmestellen und zur Entnahme von geeigneten Proben werden gegeben. Aufgrund der zahlreichen negativen Einflussmöglichkeiten ist eine gründliche Eignungsprüfung der gemessenen Aktivitätsverhältnisse von Uran und Thorium solcher Proben notwendig, um zuverlässige Alter bestimmen zu können. Die Datierungsgenauigkeit ist ausreichend, um interglaziale und interstadiale Ablagerungen sicher den Warmperioden der SPECMAP-Zeitskala zuzuordnen, noch nicht aber, um sie zeitlich auflösen zu können.

Keywords: ^{230}Th/U dating, fen peat, lignite, minimum age

1 Basic principles of ^{230}Th/U dating

Peat deposits are important archives of Pleistocene climate change but correlation of individual records with long-term archives such as marine oxygen isotope records (SPECMAP; Martinson et al. 1987) remains tentative. Correlations based on palynological and stratigraphic studies are usually based on certain pre-assumptions and can hence not provide any independent age constrains. Sound numerical dating methods seem to be suitable tools to achieve a reliable correlation between the marine and terrestrial climatic records. One of them is the ^{230}Th/U dating method. It is suitable for all materials that accumulated uranium during their formation and have not been affected by post-sedimentary processes that would mobilise uranium and thorium. When this is the case, the sampled material can be expected to have behaved as a closed system with respect to uranium and/or thorium during ageing. Moreover, it should not be older than 350-500 ka (Ivanovich & Harmon 1992; Bourdon et al. 2000).

The ^{230}Th/U dating method is based on the radioactive decay series of ^{238}U. The first long-lived daughter isotope ^{234}U (τ = 2.4525×10^2 ka, Cheng et al. 2000) decays into the isotope ^{230}Th (τ = 75.69 ka, Cheng et al. 2000) with the

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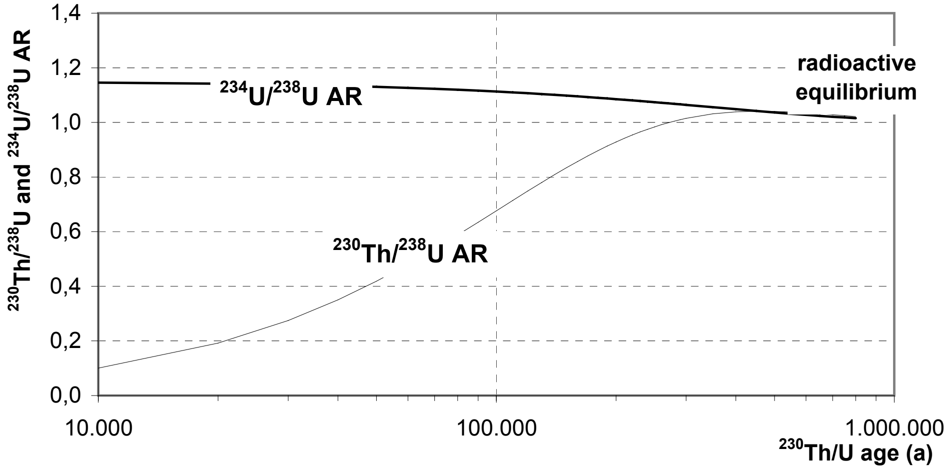

Fig. 1: Change in the ^{230}Th/^{238}U and ^{234}U/^{238}U activity ratios with increasing age for an initial ^{234}U/^{238}U AR of 1.15 (corresponding to the mean of marine sediments).

Abb. 1: Änderung der ^{230}Th/^{238}U- und ^{234}U/^{238}U-Aktivitätsverhältnisse mit der Alterung für ein initiales ^{234}U/^{238}U-Aktivitätsverhältnis von 1,15 (entsprechend dem Mittelwert mariner Sedimente).

emission of an alpha particle. The half-life of ^{238}U (τ = 4.468×10^{9} a) is considerably longer than that of ^{234}U. As a consequence, radioactive equilibrium is established after about one million years in most geologically old rocks and sediments. At radioactive equilibrium, all members of the decay series have the same specific activity (which is the decay rate per mass unit), i.e., the activity ratios of any two of the series members are equal to one.

Radioactive equilibrium can be disturbed by geochemical processes if the members of the radioactive series have certain geochemical properties. An example is the uranium and thorium isotopes of the uranium-238 decay series. U(VI) ions are soluble in oxygenated water while thorium is practically insoluble. Hence, during weathering, uranium tends to be dissolved in water and thorium bound by clay minerals.

Uranium dissolved in groundwater can be incorporated into new systems. Examples are speleothems, foraminifera and fen peat. The most simple ^{230}Th/U dating model assumes that the new system initially contains only uranium. Radioactive disequilibrium exists between ^{238}U and ^{230}Th during ageing. The numerical ^{230}Th/U clock starts at zero and a ^{230}Th/^{238}U activity ratio (AR) = 0. The radioactive disequilibrium between ^{230}Th and ^{238}U continues and evolves during ageing. A new radioactive equilibrium is approached after 350-500 ka. This process can be used to date sample material and is described by Equation 1, which has to be solved iteratively. Activity ratios are given in square brackets and λ = ln 2/τ:

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

The change in the ^{230}Th/^{238}U AR with age t is shown in Figure 1 assuming an initial ^{234}U/^{238}U AR of 1.15, which is characteristic for most marine carbonates. The ^{234}U/^{238}U AR of samples from terrestrial environments covers a wide range between 1 and 20. The most rapid change in the ^{230}Th/^{238}U AR takes place between 50,000 and about 200,000 years. The maximum age that can be measured by any dating method is the minimum age of the sample. For the radiometric and mass spectrometric ^{230}Th/U dating methods, this maximum age is about 350 ka and about 500 ka, respectively (Chapter 7).

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

2 Fen peat and lignite for ^{230}Th/U dating

The history of ^{230}Th/U dating of fen peat began with a study by Titayeva (1966). Her efforts failed as the analyzed Holocene peat was too young for ^{230}Th/U dating. But Titayeva recognised that "excess" (detrital) thorium and uranium have to be taken into account for ^{230}Th/U dating of fen peat. The first ^{230}Th/U ages of this material were published by Vogel & Kronfeld (1980). Because the ages were not corrected for detrital thorium and uranium, as suggested by Titayeva (1966), their results were not acceptable by Quaternary geologists. The first chronostratigraphically satisfactory ^{230}Th/U ages of fen peat were determined by van der Wijk et al. (1986) and Heinjes & van der Plicht (1992).
Fen peat and lignite have a potential for ^{230}Th/U dating because the fulvic and humic acids they contain have an extremely large capacity for forming complexes with uranium dissolved in groundwater. Moreover, in the reducing milieu of peat, soluble U(VI) is reduced to U(IV) and bound in very stable, immobile uranyl organic complexes. As a result fen peat may have uranium concentrations of up to 100 ppm.
The following scenario of fen peat formation is the basis for ^{230}Th/U dating of fen peat and lignite. Figure 3 shows a schematic section of a growing fen moss in a shallow lake. During its growth, uranium dissolved in groundwater enters the moss and is tightly bound to fulvic and humic acids. Before the peat has been compacted, groundwater can enter even deeper parts of the moss. In the terminal stage, organic material fills the entire volume of the lake. In the succeeding glacial period, the organic deposits are covered by mineral soil and compacted.
Figure 4 shows a section of interglacial fen peat sandwiched between detrital material above and below. The uranium dissolved in the groundwater seeping through the bottom and top mineral cover layers during the period of ageing is continuously absorbed in the bottom and top parts of the peat. It has been empirically found that the corresponding rim layers are seldom thicker than 10 cm. The organic material in the rim layers behaves as an open system with respect to uranium and is not datable. As a

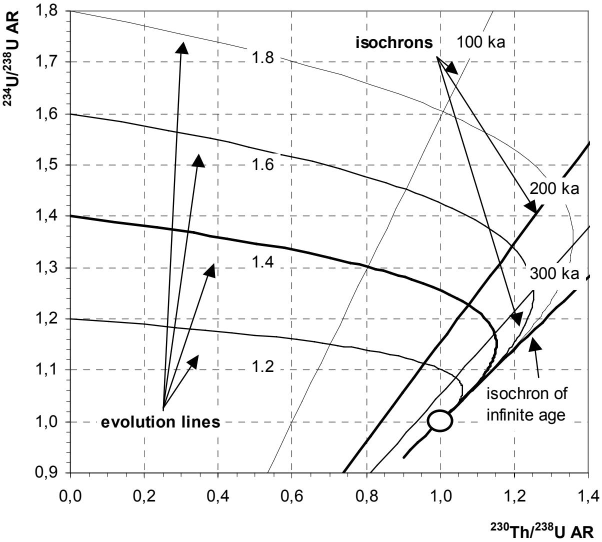

Fig. 2: Variation of the ^{234}U/^{238}U AR and the ^{230}Th/^{238}U AR with increasing age. Every initial ^{234}U/^{238}U AR yields an evolution line. All of them meet at the point (circle at 1,1) at infinite age, i.e. at radioactive equilibrium. The ARs of coeval samples plot on straight lines called isochrons (Kaufman & Broecker 1965).

Abb. 2: Entwicklung der ^{234}U/^{238}U- und ^{230}Th/^{238}U-Aktivitätsverhältnisse mit wachsenden Alter. Jedes ^{234}U/ ^{238}U AR liefert eine eigene Entwicklungslinie, die wie alle anderen bei unendlichem Alter im Punkt 1,1 (Kreis) enden. Die Aktivitätsverhältnisse gleich alter Proben liegen auf Geraden, den Isochronen (Kaufman & Broecker 1965).

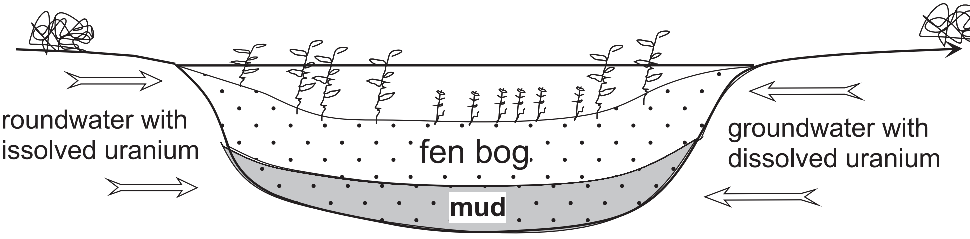

Fig. 3: Accumulation of uranium bound to fulvic and humic acids in fen peat during the peat formation in a shallow lake.

Abb. 3: Akkumulation von im Grundwasser gelöstem Uran an Fulvo- und Huminsäuren des Niedermoortorfs während der Entwicklung eines Niedermoores im flachen See.

consequence, groundwater entering the central part of fen peat more than 20-cm-thick should be free of uranium and the central part remains a closed system with respect to uranium. It is suitable for ^{230}Th/U dating.

The uranium and thorium data determined in a chronological study of the Netiesos interglacial site in Lithuania by GAIGALAS et al. (2005) is used in the following as a case study to illustrate the ^{230}Th/U dating of fen peat and lignite. The authors determined an ESR age on freshwater mollusc shells of 101.5 ± 11.5 ka. Six samples were collected between 30 and 55 cm depth. All were analyzed using the L/L (leachate/leachate) method (SCHWARCZ & LATHAM 1989; KAUFMAN 1993); the two outer samples (from 30 and 55 cm depth) were not analyzed with the total sample dissolution (TSD) method (BISCHOFF & FITZPATRICK 1991; LUO & KU 1991). The U and Th isotope ratios were measured radiometrically at St. Petersburg University and summarized with 2σ standard deviations in a research report (Table 1). The standard deviations of these results deviate slightly from those published by GAIGALAS et al. (2005). The reason is unknown.

3 Factors that interfere with ^{230}Th/U dating of fen peat and lignite

There are two main factors which render ^{230}Th/U age determination difficult or even impossible:

1. Open-system conditions with respect to uranium and thorium, as well as

Tab. 1: Isotopenergebnisse der Niedermoorproben von Netiesos in Litauen (GAIGALAS et al. 2005).

No.	name	depth (cm)	ash (%)	^{238}U ± 2σ (dpm/g)	^{230}Th/^{238}U ± 2σ	^{234}U/^{238}U ± 2σ	^{230}Th/^{232}Th ± 2σ
5133	L-1	30-35	50.4	0.537 ± 0.011	0.655 ± 0.032	1.194 ± 0.068	1.824 ± 0.081
5134	L-2	35-40	51.9	0.572 ± 0.018	0.617 ± 0.022	1.079 ± 0.047	1.555 ± 0.043
5135	L-3	40-45	49.7	0.494 ± 0.017	0.666 ± 0.029	1.119 ± 0.053	1.437 ± 0.059
5136	L-4	45-50	49.3	0.728 ± 0.022	0.657 ± 0.030	1.088 ± 0.046	1.790 ± 0.100
5137	L-5	50-55	47.3	0.640 ± 0.018	0.672 ± 0.031	1.136 ± 0.044	1.748 ± 0.107
5138	L-6	55-60	45.8	0.477 ± 0.008	0.755 ± 0.021	1.105 ± 0.026	1.545 ± 0.053
5129	T-2	35-40	51.9	1.582 ± 0.049	0.825 ± 0.032	1.001 ± 0.044	1.584 ± 0.075
5130	T-3	40-45	49.7	1.446 ± 0.034	0.900 ± 0.025	1.014 ± 0.033	1.240 ± 0.026
5131	T-4	45-50	49.3	2.009 ± 0.052	0.833 ± 0.025	1.030 ± 0.038	1.448 ± 0.036
5132	T-5	50-55	47.3	1.786 ± 0.039	0.843 ± 0.026	1.029 ± 0.032	1.352 ± 0.043

2. Detrital contamination with allochthonous ^{230}Th.

Open system conditions: Fen peat and lignite theoretically offers a chemically ideal milieu for closed-system conditions with respect to uranium. In contrast to carbonates (e.g., corals, foraminifera, speleothem), the reducing milieu of the peat means that any uranium present is reduced to insoluble U(IV), which form stable complexes with inorganic and organic ligands, such as humic and fulvic acids. Moreover, movement of humic acids over large distances and, therefore, post-depositional displacement of uranium can be largely excluded in the confined conditions of interglacial peat deposits. Likewise, α-recoil only moves the uranium daughter isotopes over distances that are smaller than the common sample volume of several cm^3 (Henderson & Slowey 2000). According to the above-described scenario for the formation of interglacial fen peat deposits, the central part may be considered as a closed system with respect to uranium and thorium. However, there are several possible situations in which this may not be true. Some fen peat deposits contain thin sand layers which may be conduits for oxygenated groundwater to the middle of the deposit. In the peat adjacent to these layers, open-system conditions with respect to uranium may have been present. Occasionally samples from the central part of a deposit without visible stratigraphic peculiarities yield outlier ^{230}Th/U ages. A possible explanation is that permafrost might have expanded the frozen fen peat and on warming voids were created into which groundwater containing uranium could have penetrated before the peat was recompacted. Detailed descriptions of the sampling site may help correlate outlier ^{230}Th/U ages to stratigraphic peculiarities. There are other scenarios which may occur in permafrost regions (Schirrmeister et al. 2002). For example, superficial peat layers may become dry down to a depth of 1-2 m during the summer months, allowing oxygenated melt water to enter the deep parts of the deposit.

Many dated interglacial peat deposits in western Asia have been exposed along river banks. If the river rises above the level of the peat layers, samples collected from up to several decimetres depth may have been affected by river water. Exposed fen peat deposits well above the present river level might also have been affected by seeping rainwater. Only drill cores of sufficient length seem to guarantee suitable peat samples.

Thorium typically exists in the +4 and +5 oxidation states. The ions are readily hydrolyzed and either precipitate or are adsorbed on detrital particulates (inorganic or organic), clay minerals and iron (oxy)hydroxides. Thorium ions can be transported with humic acids (Richards & Dorale 2003). But movement of humic acids in confined peat beds can be excluded.

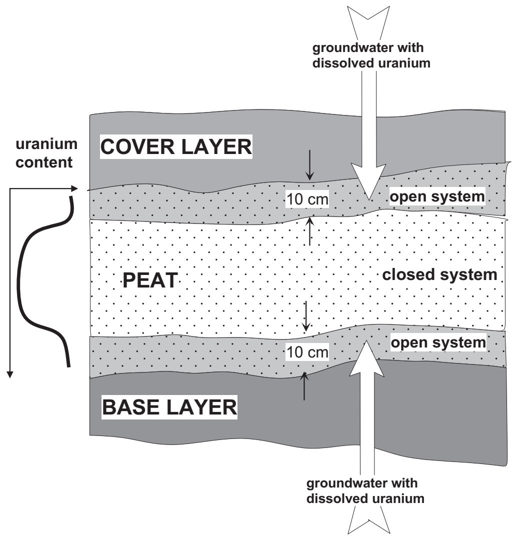

Fig. 4: Schematic of a section through a layer of interglacial fen peat: Samples suitable for ^{230}Th/U dating can only be expected in the central part of the organic deposit. The top and bottom 10 cm in most cases behaved as open systems with respect to uranium during ageing and are, therefore, unsuitable for ^{230}Th/U dating.

Abb. 4: Schematisiertes interglaziales Niedermoorprofil: Geeignete Proben für die ^{230}Th/U-Altersbestimmung können nur im zentralen Bereich des Torfes erwartet werden. Die Randbereiche von 10 cm Mächtigkeit im Hangenden und Liegenden des Torfes bilden gewöhnlich offene Systeme für Uran und erweisen sich deshalb für die ^{230}Th/U-Datierung als ungeeignet.

Detrital contamination with allochthonous ^{230}Th: Airborne dust or water-borne fine-grained material may become incorporated during the formation of fen peat. These contaminants usually contain thorium, which is often bound to detrital clay. The presence of ^{230}Th in the detrital material means that the ^{230}Th/U clock shows ^{230}Th/U ages that are too old. The allochthonous (detrital) ^{230}Th decays during ageing while the content of 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 age error caused by an initial detrital ^{230}Th content is often large and may amount to several 1000 years up to 100,000 years. Therefore, the two or more sources of ^{230}Th (one radiogenic and at least one detrital) have to be distinguished and quantified for correction of the ^{230}Th/U ages.

Limits on the ^{230}Th/U method for the dating of peat and lignite: The above-described scenario of both accumulation and binding of uranium in fen peat limits the use of the ^{230}Th/U dating method for this material. Accurate ^{230}Th/U ages of sublayers cannot be expected. During the growth of the moss the peat remains very porous and groundwater or lake water containing dissolved uranium may enter even deeper layers. Hence the ^{230}Th/U ages will always be younger than the actual ones. Moreover, as fen peat formation is restricted to shallow lakes, which exist mainly at the end of the interglacial or interstadial periods, the corresponding organic deposits often represent the end of the peat-formation period or the interglacial period rather than the beginning. Hence, suitable material of palynologically distinct sub-layers of the first part of the interglacial period can seldom be provided.

Exclusion of raised-bog peat from ^{230}Th/U dating: Raised-bog peat receives uranium mainly from particulate matter in precipitation. Therefore, the concentration is usually low and there may be different sources of thorium and uranium with different isotopic compositions. Moreover, as raised bog peat is often only

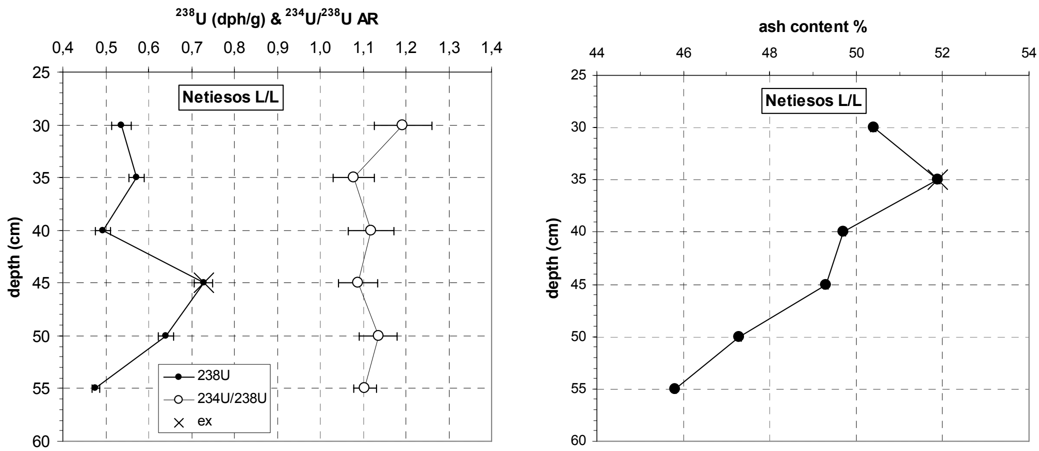

Fig. 5: Depth profiles of the specific ^{238}U activity, the ^{234}U/^{238}U AR and the ash content at the Netiesos site in Lithuania (GAIGALAS et al. 2005). Samples L-4 and L-5 (crossed dots) have a slightly elevated specific ^{238}U activity. This indicates that the premises of ^{230}Th/U dating are potentially violated.

Abb. 5: Die Tiefenprofile der spezifischen ^{238}U-Aktivität, des ^{234}U/^{238}U-Aktivitätsverhältnisses und des Aschegehalts vom Profil Netiesos in Litauen (GAIGALAS et al. 2005). Die Proben L-4 und L-5 (angekreuzte Punkte) haben eine leicht erhöhte ^{238}U-Konzentration und damit ein geringes Potential, für die ^{230}Th/U-Datierung geeignet zu sein.

weakly decomposed and the content of humic acids is low the ability to absorb actinides is limited. As a consequence, all attempts to date raised-bog peat using the ^{230}Th/U dating method have failed.

4 Determination of the reliability of data sets for the ^{230}Th/U dating of fen peat and lignite

Based on the above-described scenario for fen peat formation and the numerous factors that interfere with ^{230}Th/U dating of fen peat, it is necessary to identify and to discard data sets from samples that are not suitable for ^{230}Th/U dating. Such sample material does not fulfil the two basic premises of this dating method: (1) It has behaved as an open system with respect to uranium (and thorium) and/or (2) it contained more than one detrital contaminant.

Three simple tests are used for the initial reliability determination: depth profiles of (i) uranium concentration or specific ^{238}U activity, (ii) ^{234}U/^{238}U AR, and (iii) ash content.

Uranium-depth profiles may show up samples which behaved as an open system with respect to uranium on the basis of elevated uranium concentration relative to the base level in the central part of the peat profile. The ^{234}U/^{238}U AR in the top and bottom rim layers can be expected to differ from the central part if ^{234}U was preferentially leached or accumulated. The third test is determination of the ash content of the sample: an elevated ash content may indicate the presence of sand layers.

Figure 5 shows the results of the three tests for the Netiesos site (Gaigalas et al. 2005). The ^{238}U activity of samples L-4 and L-5 (45 and 50 cm) are 30-40 % above the other samples and therefore these samples potentially violate the two basic premises for ^{230}Th/U dating. The authors do not describe any disturbance of the stratigraphy, and therefore other information is necessary to determine which samples need to be excluded from the age determination. For example, the decrease in ash content with depth points to the possibility of open-system conditions in the upper part of the peat.

Examination of 222 data sets obtained from 33 fen peat sections in Eurasia (e.g. Arslanov 2005) has yielded evidence that ^{230}Th/U ages can be satisfactorily correlated with the SPECMAC chronology even from samples with considerably elevated or depleted uranium concentrations, or from samples with anomalous ^{234}U/^{238}U ARs or that contain a high ash content. Hence, the three tests do not reliably identify samples that do not fulfil the basic premises for ^{230}Th/U dating.

More sophisticated tests are required. The theoretical background was developed in the 1960s.

Kaufman & Broecker (1965) introduced the concept of a binary mixture of radiogenic ^{230}Th and allochthonous 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 (τ = 14.01×10^{9} a), it behaves similar to a stable isotope. Hence, its activity has not changed during the aging of the sample and hence is a measure of the initial detrital ^{230}Th content in the sample. One of the main tasks of ^{230}Th/U dating of fen peat and lignite is to determine the initial ^{230}Th/^{232}Th AR (thorium index) in order to correct the corresponding ages for the detrital contamination (Chapter 5).

The principal feature of binary mixing is that any two properties of the two components show a linear correlation. Hence, the plot of any two isotope ratios of uranium and/or thorium in peat samples – according to the Kaufman & Broecker concept – must also yield a straight line. If this requirement is not fulfilled, the basic premises for ^{230}Th/U dating are not fulfilled: The material did not behave as a closed system with respect to uranium and thorium and/or there were more than two sources of detrital ^{230}Th.

In 1970, Osmond et al. (1970) developed two mixing 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) (Figs. 6 and 7 bottom). Rosholt (1976) introduced two additional plots, the Rosholt-I (^{230}Th/^{232}Th AR versus ^{238}Th/^{232}Th AR) and Rosholt-II plots

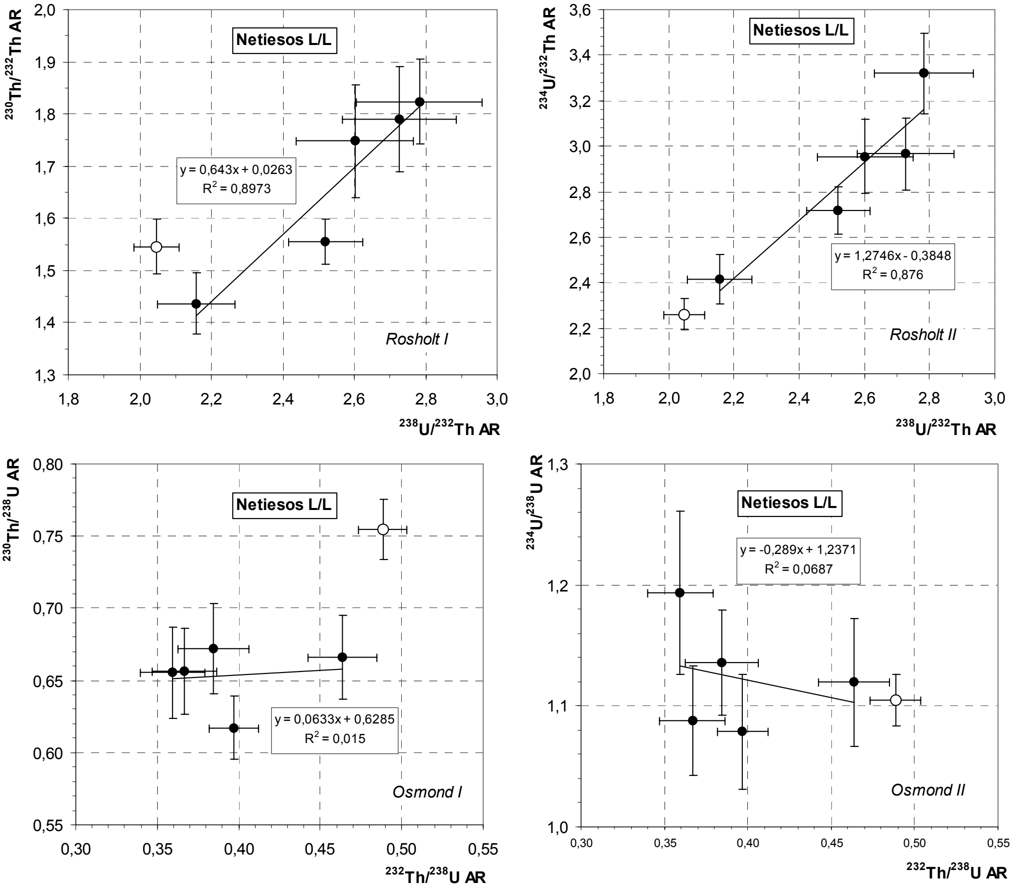

Fig. 6: Top: Rosholt I and Rosholt II plots (Rosholt 1976) of the L/L data from the Netiesos site in Lithuania (Gaigalas et al. 2005): The slopes of the mixing lines equal the $^{230}Th/^{234}U$ AR and the $^{234}U/^{238}U$ AR, respectively, and the y-intercepts give the $^{230}Th/^{232}Th$ AR and $^{234}U/^{232}Th$ ARs. The data for sample L-6 (open circle) does not fit the "isochron" and was not used for the $^{230}Th/U$ age calculation.

Bottom: Osmond I und Osmond II plots (Osmond et al. 1970) of the L/L data from the Netiesos site in Lithuania (Gaigalas et al. 2005): The slopes of the mixing lines give the $^{230}Th/^{232}Th$ AR and the $^{234}U/^{232}Th$ AR, respectively, and the y-intercepts provide the $^{230}Th/^{238}U$ AR and $^{234}U/^{238}U$ AR. The data for sample L-6 (open circle) does not fit the mixing lines and was not used for the $^{230}Th/U$ age calculation.

Abb. 6: Oben: Rosholt-I und Rosholt-II-Diagramme (Rosholt 1976) der L/L-Daten vom Netiesos-Profil in Litauen (Gaigalas et al. 2005): Die Steigungen der beiden Mischgeraden liefern die Aktivitätsverhältnisse $^{230}Th/^{234}U$ und $^{234}U/^{238}U$ sowie die Y-Achsenabschnitte die $^{230}Th/^{232}Th$- und $^{234}U/^{232}Th$-Aktivitätsverhältnisse. Der Datensatz der Probe L-6 (weißer Kreis) liegt jenseits der „Isochrone" und wurde bei der Berechnung des $^{230}Th/U$-Alters nicht berücksichtigt.

Unten: Osmond-I und Osmond-II-Diagramme (Osmond et al. 1970) der L/L-Daten vom Netiesos-Profil in Litauen (Gaigalas et al. 2005): Die Steigungen der beiden Mischgeraden liefern die Aktivitätsverhältnisse $^{230}Th/^{232}Th$ und $^{234}U/^{232}Th$ sowie die Y-Achsenabschnitte die $^{230}Th/^{238}U$- und $^{234}U/^{238}U$-Aktivitätsverhältnisse. Der Datensatz der Probe L-6 (weißer Kreis) liegt jenseits der Mischgerade und wurde nicht bei der Berechnung des $^{230}Th/U$-Alters berücksichtigt.

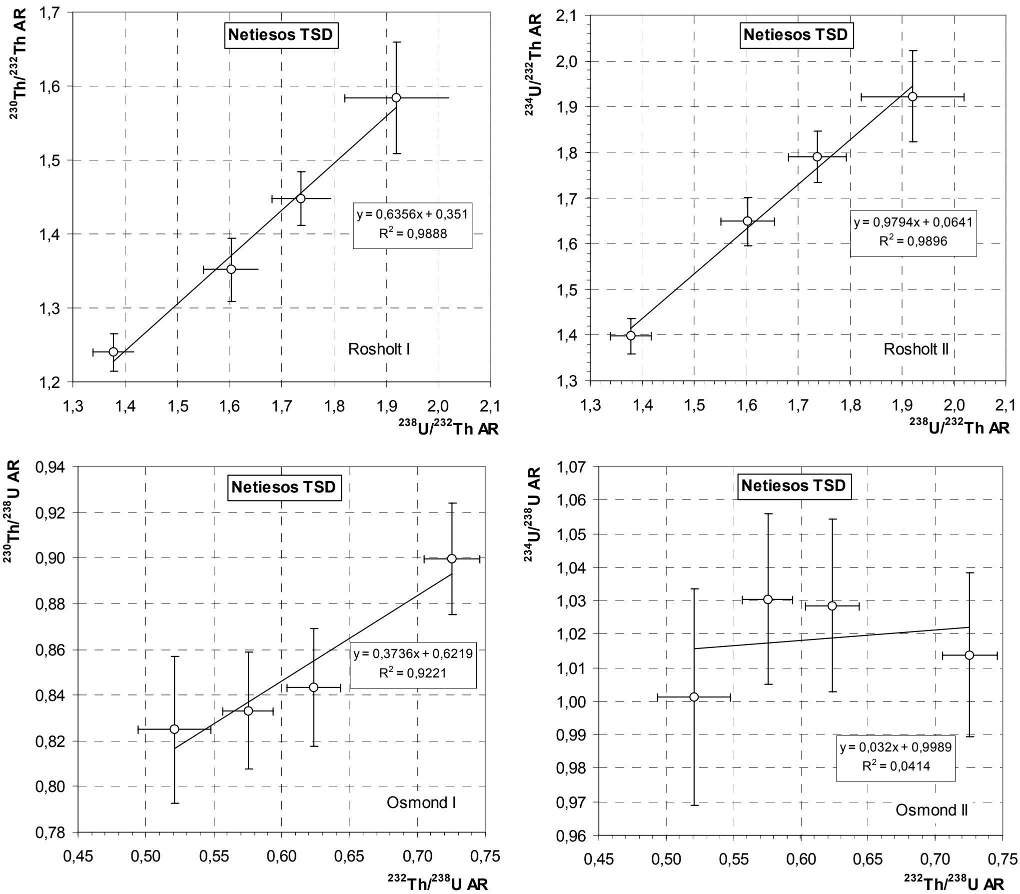

Fig. 7: Top: Rosholt I and Rosholt II plots (Rosholt 1976) of the TSD data from the Netiesos site in Lithuania (Gaigalas et al. 2005): The slopes of the mixing lines equal the ^{230}Th/^{234}U AR and the ^{234}U/^{238}U AR, respectively, and the y-intercepts give the ^{230}Th/^{232}Th AR and ^{234}U/^{232}Th AR. All data points are on the mixing lines within their uncertainty intervals and are used to calculate ^{230}Th/U ages.

Bottom: Osmond I und Osmond II plots (Osmond et al. 1970) of the TSD data from the Netiesos data in Lithuania (Gaigalas et al. 2005): The slopes of the mixing lines give the ^{230}Th/^{232}UTh AR and the ^{234}U/^{232}Th AR, respectively, and the y-intercepts provide the ^{230}Th/^{238}U AR and ^{234}U/^{238}U AR. All data points are on the mixing lines within their uncertainty intervals and are used to calculate ^{230}Th/U ages.

Abb. 7: Oben: Rosholt-I und Rosholt-II-Diagramme (Rosholt 1976) der TSD-Daten vom Netiesos-Profil in Litauen (Gaigalas et al. 2005): Die Steigungen der beiden Mischgeraden liefern die Aktivitätsverhältnisse von ^{230}Th/^{234}U und ^{234}U/^{238}U sowie die Y-Achsenabschnitte die ^{230}Th/^{232}Th- und ^{234}U/^{232}Th-Aktivitätsverhältnisse. Alle Datensätze genügen den Mischgeraden und den Kriterien der ^{230}Th/U-Methode.

Unten: Osmond-I und Osmond-II-Diagramme (Osmond et al. 1970) der TSD-Daten vom Netiesos-Profil in Litauen (Gaigalas et al. 2005): Die Steigungen der beiden Mischgeraden liefern die Aktivitätsverhältnisse ^{230}Th/^{232}Th und ^{234}U/^{232}Th sowie die Y-Achsenabschnitte die ^{230}Th/^{238}U- und ^{234}U/^{238}U-Aktivitätsverhältnisse.

($^{234}U/^{232}Th$ AR versus $^{238}U/^{232}Th$ AR; Figs. 6 and 7 top). The Rosholt-I plot is often incorrectly referred to as an "isochron" plot. The slope of the least-squares fitted straight line in a plot of the $^{230}Th/^{232}Th$ versus $^{238}U/^{232}Th$ activity ratios of coeval samples equals the $^{230}Th^{*}/^{234}U$ AR of the radiogenic $^{230}Th^{*}$ and its intercept on the y-axis equals the decay-corrected initial $^{230}Th/^{232}Th$ AR (detrital correction factor = f). The Rosholt-II plot yields the present $^{234}U/^{238}U$ AR. Both ARs are required to calculate the $^{230}Th/U$ ages (Eq. 1). An "isochron" slope of 0 corresponds to a $^{230}Th/U$ age of zero; an "infinite" age has a slope of 1 (radioactive equilibrium).

Figures 6 and 7 show two sets of the four Rosholt-Osmond plots of the ARs obtained from the uranium and thorium analyses of the fen peat at the Netiesos site using the L/L and TSD methods. The displacement of any pair of AR values from any of the four mixing lines indicates that the corresponding sample may not fulfill the basic premises for $^{230}Th/U$ dating. Especially, the Rosholt I and II plots give "a misleading impression of an well-defined isochron for data of little statistical power" (LUDWIG 2003). LUDWIG mentions three factors as the reason. (1) The $^{238}U/^{232}Th$ and $^{234}U/^{232}Th$ ARs tend to reflect the U/Th element ratio. The abundances of both ^{234}U and ^{230}Th of non-zero-age materials are generally highly correlated with the concentration of uranium. Therefore, the scatter of the $^{238}U/^{232}Th$ AR greatly amplifies even a dubious isochron trend. As a result the correlation coefficient of the Rosholt isochrons are usually higher than 0.90 and also considerably greater than those of the Osmond plots. (2) The ARs, especially if measured radiometrically, are highly correlated if the denominator isotope ^{232}Th activity is low. Due to the large analytical error the data scatter along lines subparallel to most isochrons and paradoxically strengthen the visual impression of an isochron. 3) The data points of radiometrically measured ARs plotted with error ranges appear to fall more precisely on the regression line than the error ranges imply, even if there is much more scatter than the errors would otherwise indicate ("zero"-correlation problem; CHAYES 1949, 1971).

To obtain a well defined mixing line, (LUDWIG & TITTERINGTON 1994), data sets from at least two coeval samples with widely differing detrital ^{230}Th content must be available. In the case of fen peat, a much larger number of samples should be analysed.

Coeval samples with similar detrital contamination yield a data cluster, which excludes the possibility of a mixing line. Moreover, the y-axis intercept of the mixing line must be positive, as a decay-corrected negative initial $^{230}Th/^{232}Th$ AR is theoretically excluded. The mean of negative decay-corrected AR values can be accepted only if its confidence interval includes zero.

The four mixing plot tests – especially those by Osmond – are a sensitive check for identifying unsuitable data sets. However, it is recommended to include the three simple tests described above in a rigorous examination of the reliability of U/Th age data. Moreover, supplementary tests should be found which also allow an objective and reproducible identification of suitable and unsuitable data sets.

5 Detrital contamination and the correction factors

According to the KAUFMAN & BROECKER (1965) concept, the radiogenic ^{230}Th activity ($[^{230}Th]^*$) can be calculated from the measured activity $[^{230}Th]$ as follows:

$$(2) \qquad [^{230}Th]^{*} = [^{230}Th] - [^{232}Th] \cdot f_o \cdot e^{-\lambda_{230} \cdot t}$$

$$= [^{230}Th] - f \times [^{232}Th],$$

where f_o is the initial $^{230}Th/^{232}Th$ AR and f is the decay-corrected f_o.

Any correction of radiometrically determined $^{230}Th/U$ ages for detrital ^{230}Th is negligible if the measured $^{230}Th/^{232}Th$ AR of any sample is smaller than 20 because in this case the detrital ^{230}Th activity is very low.

The detritus-corrected ^{234}U activity ($[^{234}U]^*$) can be calculated from the Rosholt II plot using an analogous equation:

(3) $$[^{234}U]^* = [^{234}U] - [^{232}Th] \cdot g_o \cdot e^{-\lambda_{234} \cdot t}$$
$$= [^{234}U] - g \cdot [^{232}Th],$$

where g_o is initial $^{234}U/^{232}Th$ AR and g is the decay-corrected g_o.

Both of these equations to correct for detrital thorium and detrital uranium assume there was only source of contamination.

No detrital correction is needed if most of the samples contain little or no detrital contamination and inferring effects can be excluded, like in the case for speleothems and or corals. In such cases the slope of the mixing lines of the Rosholt-I and Rosholt-II plots equal the $^{230}Th/^{238}U$ AR and $^{234}U/^{238}U$ AR, respectively, which are required to calculate the ^{230}Th/U age (Equation 1). The computer program ISOPLOT (Ludwig 2003) can be used to calculate the corrected ^{230}Th/U age and its standard deviation. The theoretical background for calculating the "error-correlated" standard deviation is given by Ludwig & Titterington (1994) and Ludwig (2001; 2003).

In the case of fen-peat dating a statistical check of the individual ^{230}Th/U ages is recommended in order to identify outliers. This cannot be done with the ISOPLOT program. Therefore, Equations 2 and 3 should be applied to each data set of peat and lignite samples (Geyh 1994; 2001). The required *f* and *g* values and their standard deviations are obtained from the intercept of the mixing lines with the y-axis of the Rosholt-I and Rosholt-II plots or the iterative approximation of the decay-corrected initial $^{230}Th/^{232}Th$ AR described below. The standard deviation of the detritus-corrected ^{230}Th activity is calculated using the usual error propagation equations. In most cases the correction for detrital uranium is not necessary because the $^{234}U/^{238}U$ AR and $^{232}Th/^{238}U$ AR do not correlate for most peat samples. This is also the case for the Netiesos site (Figs. 6 and 7 bottom).

An independent approach to the determination of the detrital correction factor *f* is to approximate the decay-corrected initial $^{230}Th/^{232}Th$ AR iteratively. The $^{230}Th/^{232}Th$ AR and $^{234}U/^{232}Th$ AR

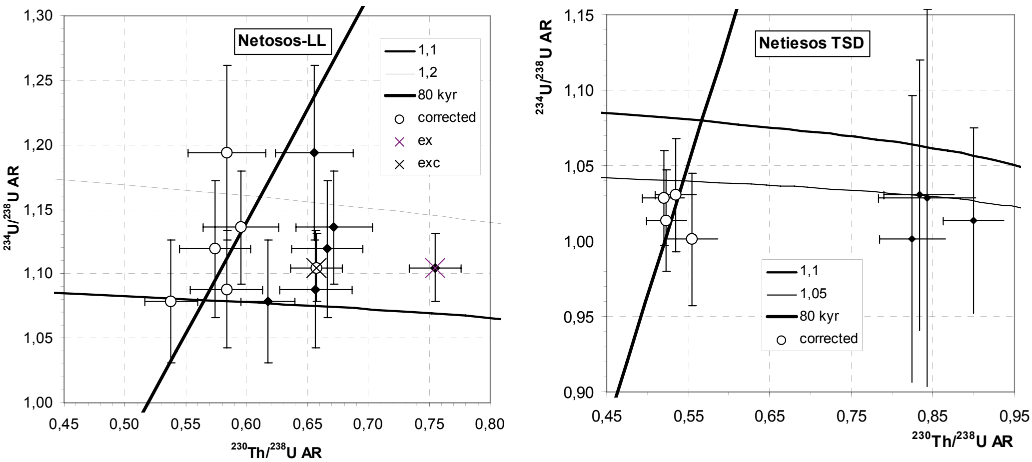

Fig. 8: Isotope-ratio evolution plot: Scatter of the L/L (left) and TSD ARs and their standard deviations in the $^{230}Th/^{232}Th$- $^{234}U/^{232}Th$ diagram for the Netiesos site in Lithuania (Gaigalas et al. 2005). This scatter decreases with increasing detrital correction factor. The L/L data of sample L-6 (crossed symbols) remains far from the cluster.

Abb. 8: Isotopen-Evolutionsdiagramm: Die Streuweite der L/L- und TSD-Aktivitätsverhältnisse des Netiesos-Profils in Litauen (Gaigalas et al. 2005) nimmt im $^{230}Th/^{232}Th$- $^{234}U/^{232}Th$-Diagramm mit steigendem detritischen Korrekturfaktor ab. Die L/L-Daten der Probe L-6 (gekreuzter Punkt) bleibt der Punkthäufung fern.

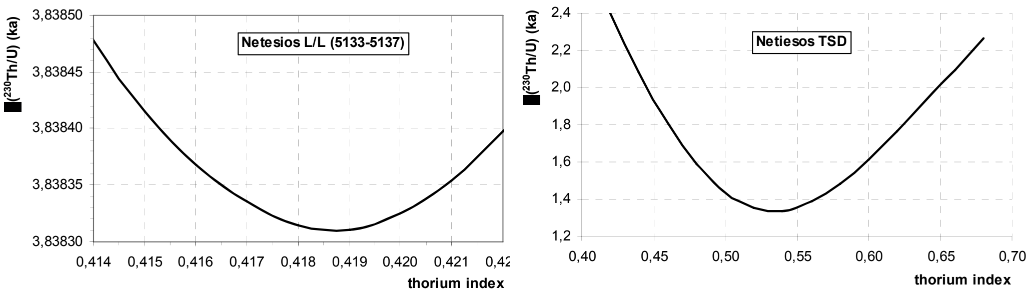

Fig. 9: The scatter represented by the standard deviations of the iteratively corrected L/L and TSD ^{230}Th/U ages of the Netiesos site in Lithuania (GAIGALAS et al. 2005) approaches a minimum at f(L/L) = 0.412 ± 0.080 and f(TSD) = 0.534 ± 0.011. The values for sample L-6 were discarded.

Abb. 9: Streuweite der iterativ-korrigierten ^{230}Th/U-Alter vom Netiesos-Profil in Litauen (GAIGALAS et al. 2005) erreicht Minima bei f(L/L) = 0.412 ± 0.080 bzw. f(TDS) = 0.534 ± 0.011. Der Datensatz der Probe L-6 wurde ausgeschlossen.

of coeval samples containing contamination from different sources scatter widely. Iteratively increasing the detrital correction factor *f* causes the points to move to the left in the isotope-ratio evolution plot of KAUFMAN & BROECKER (1965). The higher the detrital contamination the faster the points move to the left. The optimum detrital correction factor *f* is obtained when the points of the cluster are the closest together. The points in the cluster move further apart when the *f* value is increased beyond the value for the minimum width of the cluster. An elliptical shape of the cluster is caused by differences in the initial ^{234}U/^{238}U AR (Fig. 8). An effect resulting from α-recoil as observed in carbonates (HENDERSON & SLOWEY 2000) cannot be completely excluded for fen peat.

A plot of the standard deviation of the ^{230}Th/U age versus the *f* value provides a measure of the scatter of the individual ages. For the case study from the Netiesos site , the scatter of the L/L and TSD ^{230}Th/U ages approaches a minimum at *f(L/L)* = 0.412 ± 0.080 and *f(TSD)* = 0.534 ± 0.011 (Fig. 9). The plots again show that sample L-6 does not fulfill the premises for ^{230}Th/U dating.

An iterative method developed to determine the decay-corrected initial ^{230}Th/^{232}Th AR provides an additional test for a rigorous examination of the reliability of the data sets (GEYH 2001). The iteratively detritus-corrected ^{230}Th/U ages plotted against the iteratively determined detrital correction factor yields lines with different slopes. If all samples behaved as closed systems with respect to uranium and only one detritus component was present in the samples, the lines should intersect at only one point – the actual *f* value. If one or more lines do not pass through this point the corresponding sample is identified as unsuitable.

For the case study of the Netiesos site, the bold line for sample L-6 in the L/L plot belongs to outlier data which do not fulfill the premises of the ^{230}Th/U dating method. This line does not pass through the common intersection point.

6 ^{230}Th/U age and random uncertainty

The data sets suitable for calculation of a ^{230}Th/U age and its standard deviation are selected on the basis of the rigorous examination of their reliability described above. The detrital correction is applied to each measured ^{230}Th activity (Equation 2; Chapter 5) and the ^{230}Th/U ages are calculated using Equation 1. The χ^2 test is then applied to the corrected ^{230}Th/U ages, outliers are discarded, and the mean ^{230}Th/U age is calculated. The standard deviation of the mean ^{230}Th/U age is obtained using the Gaussian method for error determination of the ^{230}Th/U ages of the samples.

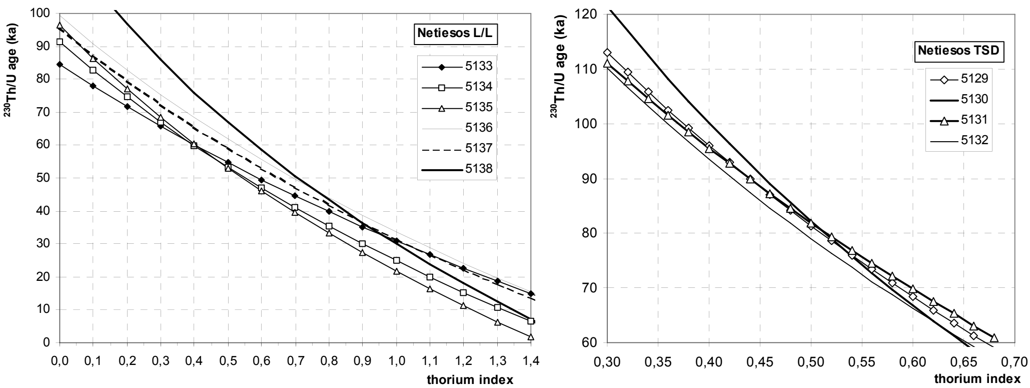

Fig. 10: Change of the detritus-corrected ^{230}Th/U ages with the iteratively increased f. Five lines of the L/L data and all lines of the TSD data have common intersection points at 61.6 ka and 76.4 ka, respectively. The bold line of the sample L-6 does not.

Abb. 10: Änderung der detritus-korrigierten ^{230}Th/U-Alter bei iterativ erhöhtem f-Wert. Fünf Linien der L/L-Daten und alle der TSD-Daten haben nahe zusammen liegende Schnittpunkte bei 61.6 ka und 76.4 ka. Die dicke Linie des L/L-Datensatzes der Probe L-6 liefert davon entfernte Schnittpunkte.

7 Minimum ^{230}Th/U age of samples

The limited precision of uranium and thorium isotope activity measurements means that there is an upper limit of the ^{230}Th/U age that can be determined. This limit is the minimum ^{230}Th/U age of a sample, corresponding to the maximum ^{230}Th/U age that can be determined with the ^{230}Th/U dating method. This minimum ^{230}Th/U age is expressed, for example, as >350 ka. Surprisingly, minimum ages are usually not estimated.

The isotope-ratio evolution plot of Kaufman & Broecker (1965) can be used to develop a method for calculating the minimum ^{230}Th/U age (Geyh & Müller 2005). X in Equation 1 is replaced by ^{230}Th/^{238}U AR and Y by the decay-corrected initial ^{234}U/^{238}U AR. Thus,

$$(4) \qquad X = \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}}(Y-1)\cdot (1-e^{-(\lambda_{230}-\lambda_{234})\cdot t}) + (1-e^{-\lambda_{230}\cdot t})$$

The decay-corrected initial ^{234}U/^{238}U (Y) is given by

$$(5) \qquad Y = (Y_o - 1)\cdot e^{-\lambda_{234}\cdot t} + 1$$

The uranium and thorium ARs of an infinitely old sample are given by a straight line in the isotope-ratio evolution plot. The equation for this isochron is derived from Equation 4 assuming an age $t = \infty$:

$$(6) \qquad X = \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}}\cdot Y - \frac{\lambda_{234}}{\lambda_{230} - \lambda_{234}} + 1$$

The ellipse defined by the X and Y random uncertainties of any data point should touch but never cut the infinite-age isochron. When the infinite-age isochron is tangent to the ellipse of the X and Y random uncertainties, the minimum ^{230}Th/U age $t_{\min}$ of the sample can be determined from the X_{min} and Y_{min} (Fig. 11). The equation of the ellipse with maximum axis lengths of $\pm 2\sigma X$ and $\pm 2\sigma Y$ around X_{min} and Y_{min} is given by

$$(7) \qquad \left(\frac{X - X_{\min}}{2\sigma X}\right)^2 + \left(\frac{Y - Y_{\min}}{2\sigma Y}\right)^2 = 1$$

Equations 4-7 are solved iteratively by decreasing or increasing the age until the error ellipse of a date touches the infinite-age isochron. A detritus-corrected ^{230}Th/U date is considered reasonable if it is smaller than the corresponding minimum ^{230}Th/U sample age t_{min} (Geyh &

MÜLLER 2005). Otherwise the result has to be expressed as the minimum ^{230}Th/U age.

8 Precision and accuracy of ^{230}Th/U dating of fen peat

The precision and accuracy of ^{230}Th/U dating of fen peat may be illustrated by three case studies. GAIGALAS et al. (2005) published L/L and TSD ^{230}Th/U ages of 108.8 ± 8.7 ka and 80.3 ± 5.9 ka, respectively, for fen peat deposits at the Netiesos site in Lithuania. The higher value from the L/L data was obtained after rejection of the data from the uppermost (L-1: 30 cm) and lowermost (L-6: 55 cm) peat samples. A rigorous examination of the sample data sets was not carried out. The decision to reject these two values was based neither on an elevated ^{238}U activity nor on ash content (Fig. 5).

A rigorous check of the reliability of the L/L data sets identified only sample L-6 as unsuitable for ^{230}Th/U dating. The L-6 data do not fit the mixing lines of the Rosholt-I and Osmond-I plots (Fig. 6), no minimum cluster size was found when the L-6 data was included in the evolution plot (Fig. 8), and in the iterative plot the L-6 line does not pass through the common intersection point of the L-1 to L-5 lines. Sample L-2 has a slightly elevated ash content (Fig. 5) and its AR values do not fit well the mixing lines of the Rosholt-I and Osmond-I plots (Fig. 7). Other indications that L-2 is unsuitable were not found.

A rigorous check of the reliability of the TSD data sets does not identify any outliers. The ^{230}Th/U age was calculated with the Equations 1 and 2 and yielded 78.4 ± 4.3 ka and a detrital correction factor of 0.519 ± 0.161. The χ^2 test applied to the four data sets yields $\chi^2 = 0.4$. Iterative evaluation yielded an age of 76.4 ± 1.3 ka with a detrital correction factor of 0.534 ± 0.010.

A ^{230}Th/U age of 72.6 ± 10.0 ka and a detrital correction factor of 0.268 ± 0.365 and a χ^2 = 0.8 were calculated using Equations 1 and 2, discarding the data from samples L-2 and L-6. Iterative evaluation yielded a detrital correction factor f = 0.456 ± 0.060. An age of 77.0 ± 11.1 ka and a detrital correction factor f = 0.199 ± 0.381 (χ^2 = 0.4) were obtained when only the data from sample L-6 was discarded and the iterative evaluation yielded f = 0.419 ± 0.080.

Disregarding sample L-6 shifts the calculated lines in the Rosholt-I and Osmond-I of the L/L data plots to the right and downwards, respectively. This yields an acceptable ^{230}Th/U age of 77.0 ± 11.1 ka. It is in agreement with the TSD ^{230}Th/U age of 78.4 ± 4.3 ka. This age falls within the time span of MIS 5a (Brørup interstadial) between 76 and 78 ka of the SPECMAP time scale (MARTINSON et al. 1987).

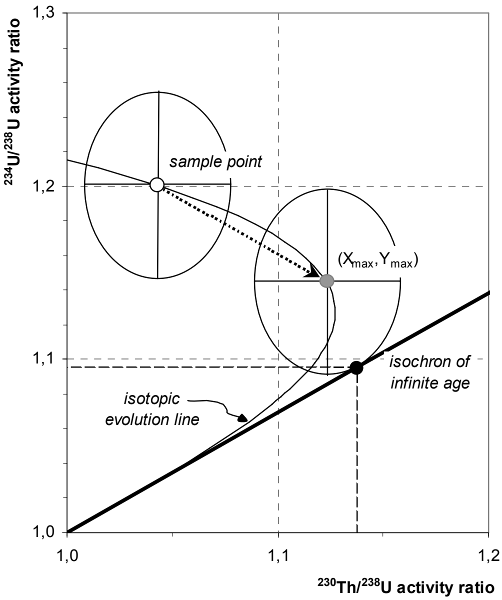

Fig. 11: Isotope-ratio evolution plot (KAUFMAN & BROECKER 1965) to determine the minimum ^{230}Th/U age t_{min} of a sample. When the data point (open circle) moves on the evolution line to the right with increasing age (grey circle) until its ellipse of 2σ X and Y uncertainties touches the infinite-age isochron (grey circle), the corresponding X_{min} = ^{230}Th/^{238}U AR and Y_{min} = ^{234}U/^{238}U AR yield the minimum age t_{min}.

Abb. 11: Isotopenentwicklungsdiagramm nach KAUFMAN & BROECKER (1965) zur Bestimmung des methodischen Minimum-^{230}Th/U-Alters einer Probe. Der weiße Punkt bewegt sich mit wachsendem Alter auf der Entwicklungslinie bis zu dem grauen Punkt, an dem die Ellipse der 2σ Y- und Y-Standardabweichungen die Isochrone für unendliche Alter trifft (schwarzer Punkt). Die entsprechenden X_{min} = ^{230}Th/^{238}U- und Y_{min} = ^{234}U/^{238}U- Aktivitätsverhältnisse liefern das Minimum-^{230}Th/U-Alter der Probe.

The second case study presented here was the first attempt to check whether it is possible to date fen peat and lignite by the ^{230}Th/U dating method (Geyh 2001). Eemian peat deposits in Europe seemed to be the most suitable for this as they contain the only Quaternary interglacial material that can be palynologically firmly identified and related to the SPECMAP timescale (Geyh 2001). Unfortunately, no cores were available and all samples were collected from exposures with the associated risk of interfering processes.

Seven sites in Germany yielded a mean ^{230}Th/U age of 111.9 ± 1.2 ka for the detritus-corrected ^{230}Th/U ages and 114.4 ± 1.9 ka using Equations 1 and 2. The agreement is good but the ages are below what is expected from SPECMAP chronology. There are several possible reasons for this. The data sets were not subjected to a rigorous reliability test. The samples might not have completely fulfilled the two basic premises for ^{230}Th/U dating due to the lack of optimum sampling conditions. In any case, the ^{230}Th/U ages and their standard deviations for these seven sites may be considered as representative of the attainable accuracy of ^{230}Th/U dating of fen peat. The precision, however, is good enough to firmly assign the dated Eemian interglacial deposits to MIS 5e but is not sufficient to assign a precise chronological age to sub-layers.

In the third case study, the ^{230}Th/U ages for Holsteinian/Hoxnian Interglacial peat were obtained from drill cores and agree better with the SPECMAP chronology (Geyh & Müller 2005). The Hoxnian Interglacial in England has been correlated with the Holsteinian Interglacial (Turner 1970). A mean ^{230}Th/U age of 317 ± 14 ka was obtained from the fen peat at Tottenhill in the Nar Valley of NW Norfolk (Rowe et al. 1997). The ^{230}Th/U ages from the Marks Tey site in the UK, which has been palynologically classified as Holsteinian, (Rowe et al. 1999), have a very low precision and could be interpreted only by using a probabilistic approach. The authors concluded that these deposits correlate with MIS 11 or some older stage with 87 % confidence. Using Equations 4 to 7, ^{230}Th/U minimum ages of >165 to >245 ka were obtained for their data (Geyh & Müller 2005). This implies that the measured U and Th data reliably allow only the statement that the geological age of the Holsteinian samples is greater than MIS 7.

B

The Bossel site about 30 km west of Hamburg contains two organic layers: one above and one below the sediments of the Holsteinian Sea. This location became the reference site for the Holsteinian Interglacial in northern Germany as declared by the European Commission on the Stratigraphy of the Quaternary. The “isochron” plot of the AR of ten samples from both peat layers yielded a mean detritus-corrected ^{230}Th/U age of 323 ± 5 ka with individual detritus-corrected ^{230}Th/U ages between 298 and 347 ka. The lower peat layer yielded a mean detritus-corrected ^{230}Th/U age of 312 ± 3 ka with individual detritus-corrected ^{230}Th/U ages between 293 and 369 ka. The four ^{230}Th/U ages of the upper peat layer yielded a detritus-corrected mean age of 327+50/-37 ka.

These case studies provide evidence that ^{230}Th/U dating of fen peat and lignite does not yield high-precision ages. The accuracy may be around 10,000 a. But this is adequate to reliably relate any interglacial peat deposit to only one of the documented warm periods of the SPECMAP chronology (Martinson et al. 1987).

9 Sampling, analysis and isotope ratio determination

To fulfil the requirements for isochron ^{230}Th/U dating the samples must be coeval from the same interglacial or interstadial. For this it is sufficient to take samples from anywhere within the centre of the fen peat deposit. Rim layers of at least 10 cm thickness have to be excluded from the analysis. It is recommended to take the samples from a monolith or a drill core. At least four samples with a wide range of concentration of the detrital contamination, but even better more should be dated.

The sample preparation is more or less the same for both measurement methods for determining the ARs and consists of several steps. Ultrapure acids which are free of even traces of uranium and thorium have to be used. The chemical preparation should be done in a clean-air laboratory in order to lower the risk of any detrital contamination. This is especially important if small samples are treated for measurement in a TIMS (thermal-ion mass spectrometer) or MC-ICP-MS (multi-collector inductively coupled plasma mass spectrometer). In radiometric laboratories repeated and comprehensive contamination tests have to be carried out.

Preferentially, peat should be treated by "total sample dissolution" (TSD) (BISCHOFF & FITZPATRICK 1991; LUO & KU 1991). This method includes both lattice-bound and adsorbed thorium. Empirically it has been found that $^{230}Th/U$ ages obtained by the "leachate/leachate" method (SCHWARCZ & LATHAM 1989; KAUFMAN 1993) often deviate from the palynologically expected age and do not fit the SPECMAP timescale. Selective leaching of peat samples does not adequately separate the radiogenic and detrital ^{230}Th components. In addition, the radiogenic ^{230}Th may become readsorbed on detrital material during incomplete dissolution. The following steps are taken in the "total sample dissolution" method:

- The samples of 3-5 g of fresh or 0.3-0.5 g of dry peat are taken from visibly undisturbed micro ranges within monoliths or cores.
- The surface of each sample is removed. The peat is then broken into pieces, dried and ignited in a quartz tube at a maximum temperature of about 800 °C in a stream of oxygen to burn all organic material. Insoluble glass beads do not form below this temperature and, therefore, loss of uranium and thorium is avoided.
- The weighed peat ash is treated with NaOH in order to remove traces of humic acids. The residue is completely dissolved in a con. $HF/HNO_3/HCL$ mixture to completely dissolve uranium and thorium. If the L/L technique is applied, the sample is leached with a HNO_3/HCl mixture for at least 6 h. Next, 0.5 mL of a ^{229}Th spike and 0.5 mL of a $^{233}U/^{236}U$ double spike are added as a check of thermal fractionation in the ion source. The solution is heated with an infrared lamp for up to 20 h in order to ensure perfect mixing of sample and spike.
- The leachate is separated from the residue by centrifuging.
- Uranium and thorium are co-precipitated with $Fe(OH)_3$.
- The precipitate is dissolved in con. HNO_3.
- Uranium and thorium are separated from the mixture by standard ion-exchange chemistry using an actinide-specific resin (DOWEX 1×8 100-200 mesh). Thorium is eluted from the column by dilute HCl, uranium is then removed with HBr.

$^{230}Th/U$ age determinations are preferentially done now by TIMS and MC-ICP-MS. Details are given by SCHOLZ & HOFFMANN (2008). Radiometric measurements of the ARs require at least ten times more material and are less precise by one order of magnitude. The extracted uranium and thorium are electroplated on stainless steel discs. The latter are put into an alpha spectrometer and the emitted alpha particles are counted. Due to the long ^{230}Th half-life of 75,690 ka, only one out of 6×10^6 atoms of ^{230}Th decays during the common measurement time of one week. Hence, especially the counting statistics limits the precision of radiometric $^{230}Th/U$ ages.

10 Conclusions

Interglacial fen peat and lignite with ages of up to 350-500 ka can be dated with the $^{230}Th/U$ dating method. The main prerequisite is that the samples are collected from the parts of a deposit that behaved as closed system with respect to uranium during ageing and have no more than one detrital component. In the case of fen peat, the bottom and top rim layers of about 10 cm have to be discarded. Drill cores yield better samples than monoliths collected from exposed outcrops. Small samples of a few cm^3 (about 1 g of dry peat) are sufficient for TIMS and MC-ICP-MS $^{230}Th/U$ dating. Radiometric $^{230}Th/U$ dating requires at least ten times more material. The coeval samples should have a wide range in the amount of detrital contamination. A single uranium and thorium isotope analysis of peat does not yield a reliable ^{230}Th/U age. The TSD analytical method seems to be superior to the L/L method. Reliable ^{230}Th/U ages, however, always require a comprehensive and rigorous reliability check of the measured data in order to identify samples that were unsuitable for ^{230}Th/U dating. The accuracy of ^{230}Th/U ages of fen peat and lignite is around 10 ka, which is sufficient for reliable correlation with the warm periods of the global marine δ^{18}O chronology.

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