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^{230}Th/U Dating of Frozen Peat, Bol'shoy Lyakhovsky Island (Northern Siberia)

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The chronology of Quaternary paleoenvironment and climate in northeastern Siberia is poorly understood due to a lack of reliable numerical age determinations. The best climatic archives are ice-rich permafrost sequences, which are widely distributed in northeastern Siberia. For this study, ^{230}Th/U-ages were determined by thermal ionization mass spectrometry (TIMS) from frozen peat in a permafrost deposit at the southern cliff of the Bol'shoy Lyakhovsky Island (New Siberian Archipelago), west of the Zimov'e River. These yielded a Pre-Eemian "isochron"-corrected ^{230}Th/U-age of 200,900 ± 3400 yr. This result is reliable because permafrost deposits behave as closed systems with respect to uranium and thorium. Our findings suggest that ^{230}Th/U dating of frozen peat in permafrost deposits is a useful tool for the reconstruction of the Middle Quaternary environment of northern Siberia and of the whole Arctic.

Key Words: **Siberia; permafrost; geochronology; Uranium-series disequilibrium dating; uranium; thorium; peat; Middle Pleistocene.**

INTRODUCTION

Continuous permafrost preserves freshly deposited organic material from plants or animals. Hence, the permafrost deposits of Siberia are unique archives for Quaternary environmental conditions. They are particularly valuable because there are no other archives, such as glacier ice, tree rings, or laminated lacustrine deposits, in this part of the Arctic. Numerical age determination of permanently frozen, organic-rich material is essential to providing the basis for further environmental reconstruction in Siberia.

In 1999, a group of German and Russian scientists worked on the southernmost islands of the New Siberian Archipelago (Fig. 1) within the framework of the Russian–German research cooperative "System Laptev 2000." They studied permafrost deposits exposed on the south coast of the Bol'shoy Lyakhovsky Island (Schirrmeister and Kunitsky, 2000). The effort to date these deposits using the ^{230}Th/U approach is reported in this article.

Today tundra landscapes with large ice-wedge polygon nets are characterized by intensive peat growth. Conditions suitable for peat formation existed repeatedly during the Quaternary period. "Postsedimentary" exchange processes affecting the peat are assumed to be minimized by the freezing of the peat after its formation and subsequent preservation in permafrost deposits. The ^{230}Th/U dating method is applicable to organic sediments which adsorbed uranium dissolved in groundwater during their formation and then acted as a chemically closed systems for uranium and thorium over time (e.g., Titayeva, 1966; Vogel and Kronfeld, 1980; Geyh *et al*., 1997; Geyh, 2001). Therefore, permanently frozen peat deposits with ages of up to ~500,000 yr are promising archives for age determinations using the ^{230}Th/U method.

THE STUDY AREA

Quaternary deposits on the south coast of Bol'shoy Lyakhovsky Island were first described by Romanovsky (1958) as a sequence of Early to Late Quaternary floodplain deposits in different terrace levels with thermokarst lakes and fluvial sediment. The sea cliff near the mouth of the small river Zimov'e, which was studied in 1999, consists of different units of permafrost deposits (Figs. 2, 3). A basal layer of debris of about 5 m thickness with stones in silty matrix and peat inclusions is exposed on the cliff above a paleo-weathering crust near the shoreline. The sediment is ice-rich (ice content 60–150% of the dry weight) and dissected by ice wedges up to 3 m wide, which continue below sea level. This layer contains a lens of peat, which is 30 m long and approximately 1 m thick. The ice content of the peat is up to 400% of the dry weight. The overlying layer (up to +15 m above sea level [asl]) consists of 5 to 10 m of probably eolian loesslike silty sand with basal ice cement and a small amount of organic matter and ice (<40% of the dry weight). Only small ice wedges (0.2 m width) occur in this layer. In addition there are lacustrine deposits with ice wedge casts on

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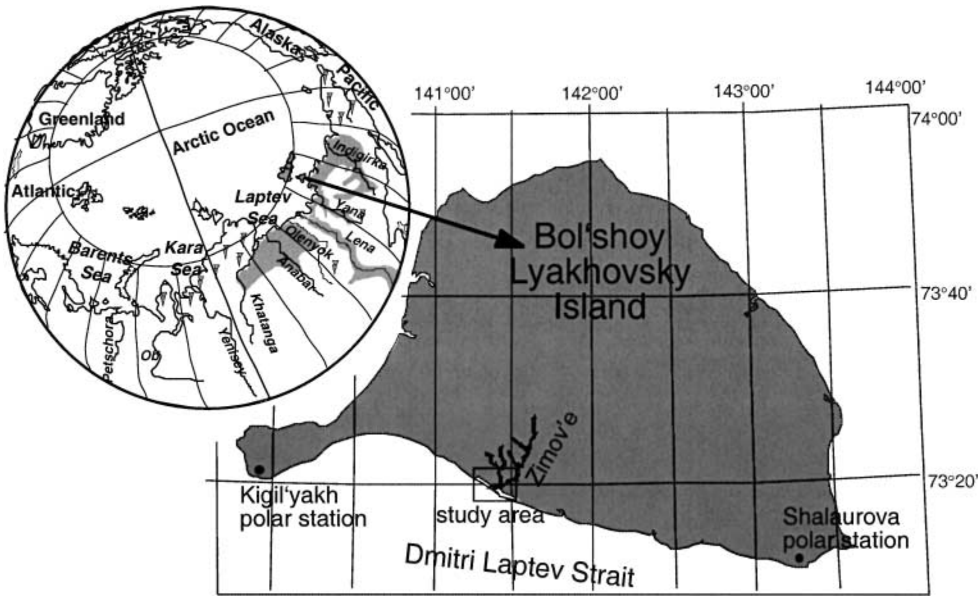


FIG. 1. Position of the study area at the south coast of Bol'shoy Lyakhovsky Island, Russia.

their bottoms at about the same elevation (0 to 10 m asl). Such lacustrine and thermokarst deposits are only located 1.5 km to the east and the west of the sampled site but not directly above it. The second layer is overlain by the 20-m-thick sequence of the Late Pleistocene Ice Complex (P. Grootes, unpublished radiocarbon dates; Nagaoka *et al*., 1995). The Ice Complex consists of ice-rich silty fine-grained sand with peat inclusions, small ice bands (2–5 cm), and a lenslike reticulated cryostructure. Large ice wedges (3–5 m wide) dissect the entire cliff, which has an elevation of about 40 m asl (Fig. 3).

MATERIAL AND METHODS

The large frozen peat lens at about 1 m above the beach level was selected for ^{230}Th/U dating. A cube with a side length of about 30 cm was cut from the central part of this peat lens (Fig. 4) using a chain saw, leaving rim layers of 15 cm above and 35 cm below the sample. This frozen peat monolith was stored in waterproof plastic wrap and shipped to Germany. There was no loss of material, but defrosting of the peat resulted in water distribution within the monolith. Three samples of less than 1 cm^3 each were chosen from the center of the monolith for ^{230}Th/U analyses, all corresponding to an original height of 0.85 m. Arctic peat accumulation is commonly low (about 0.1 mm/yr) such that the sampled peat cube may cover a time span of about 3000 yr, and each of the three samples less than

FIG. 2. The coastal outcrop at the south coast of Bol'shoy Lyakhovsky Island; the wall of the Late Pleistocene Ice Complex (background) and the Middle and Late Pleistocene permafrost deposits near sea level.

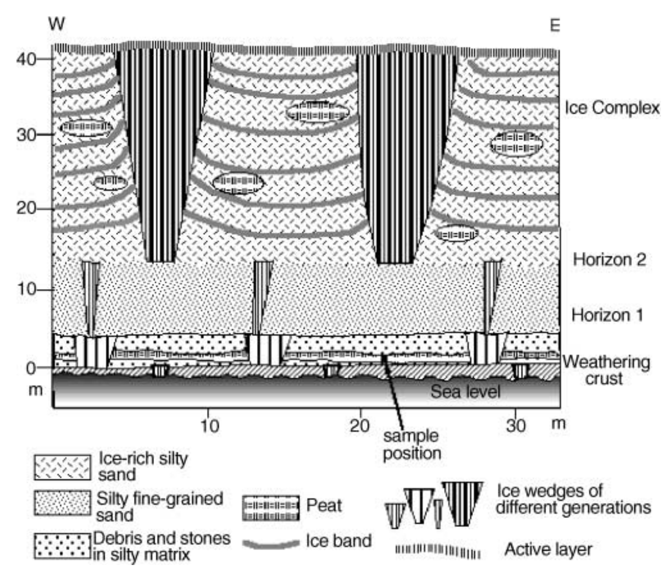
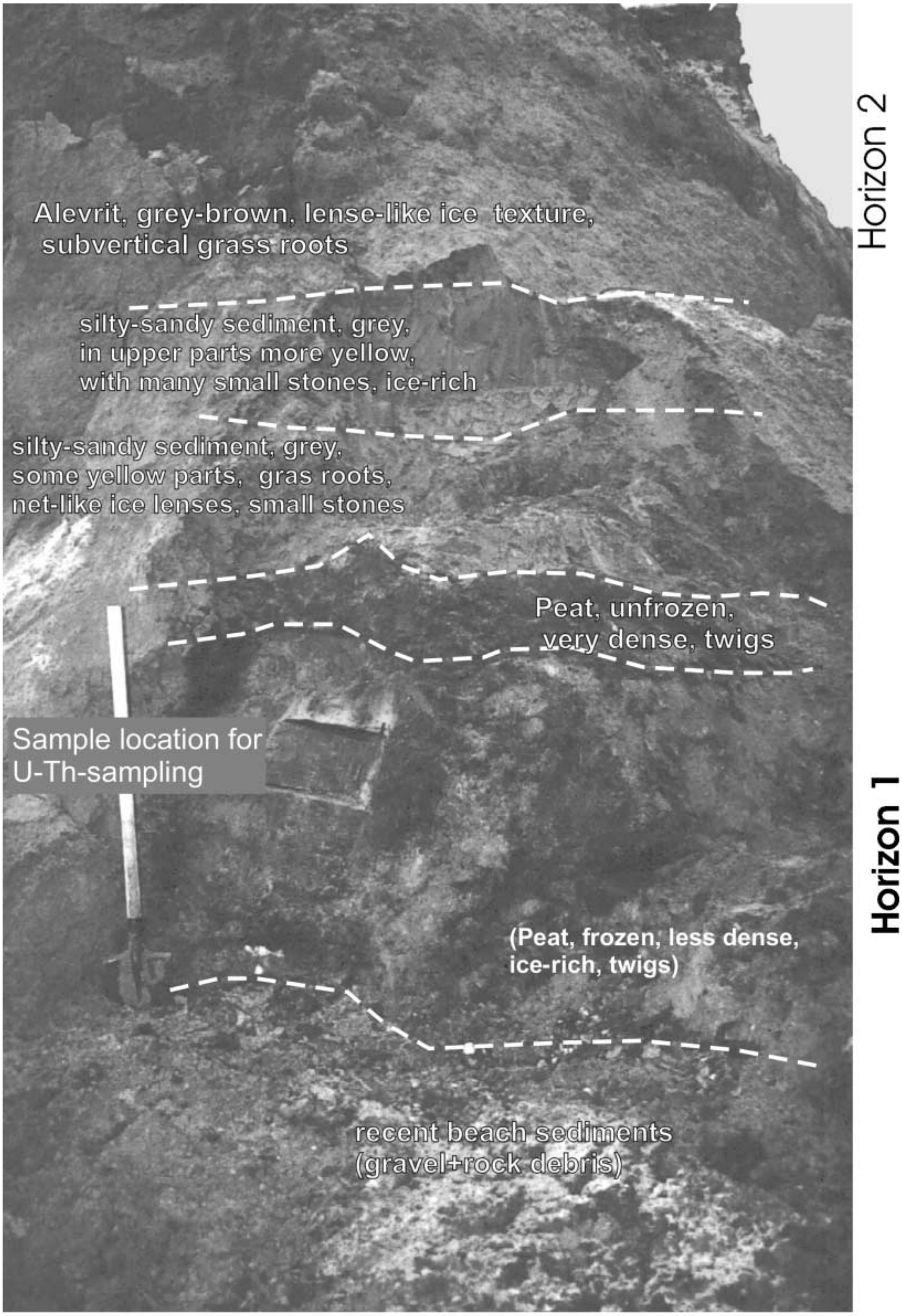


FIG. 3. Schematic profile of the studied outcrop and the position of the studied peat lens at about +0.85 m above the beach level.



Location: R8+50 (east side from the melt water creek)

FIG. 4. The sample location of the frozen peat, 0.85 m above the beach level, south coast of Bol'shoy Lyakhovsky Island (Photograph by Guido Grosse). Location: east side of the melt water creek indicated in Figure 1. Shovel for scale.

100 yr. Therefore the whole peat lens is thought to have been formed during a period of about 10,000 yr.

The ^{230}Th/U dating method is based on the radioactive disequilibrium between ^{238}U and its radioactive daughters. The basic concept assumes that the dated material contained only uranium and negligible initial ^{230}Th at the time of its formation and remained a closed system thereafter. ^{230}Th/U-ages can then be calculated using the following equation:

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

These two assumptions are not necessarily fullfilled and must be confirmed for each dating attempt.

To meet the closed system requirement no uranium or thorium migration may have occurred after the formation of the peat. A postsedimentary mobilization of thorium can be excluded due to its geochemical properties. Uranium uptake, or more likely a loss of uranium by contact with oxygenated water (e.g., through intercalated sand layers), would change the isotopic composition and therefore the ^{230}Th/U age. The inner portion of undisturbed peat deposits might be considered closed. This assumption is checked by the plot of the ^{234}U/^{238}U activity ratios versus the ^{230}Th/^{238}U activity ratios (Ivanovitch and Harmon, 1992). Regarding the studied permafrost peat from Lyakovsky Island there are no visible indications of strong "postsedimentary" events such as thermokarst, thawing, or percolation of melt water. This can be assumed to be due to the banded, netlike ice structure, the very high ice content, as well as the undisturbed bedding of the peat and the low rate of peat decomposition. Subsequent strong influences on sediments below the permafrost table from deposits above can most likely be excluded after the completed freezing of peat. The system is therefore geologically considered a closed system.

The second assumption of absent initial ^{230}Th is usually not fullfilled for peat deposits. Thorium is adsorbed onto clay minerals, which are admixed by dust into the peat during its formation. This can be identified by small ^{230}Th/^{232}Th activity ratios. To correct for admixed detritus with a uniform ^{230}Th/^{232}Th activity ratio at the time of formation, the isochron method (e.g., Osmond *et al.*, 1970; Kaufman, 1971; Ku and Liang, 1984; Schwarcz and Latham, 1989; Luo and Ku, 1991) is applied. The method is based on the assumption of a two-component mixing of radiogenic and detrital ^{230}Th. At least two or preferably more coeval samples with different uranium and thorium concentrations, and therefore different detrital components, must be analyzed to construct isochrons. The ^{234}U/^{238}U and the ^{230}Th/^{234}U activity ratios for the age calculation after Equation 1 are obtained from the slope of the best fit line of the two activity ratio diagrams ^{234}U/^{232}Th versus ^{238}U/^{232}Th and ^{230}Th/^{232}Th versus ^{234}U/^{232}Th activity ratios.

To avoid methodically enlarged errors we used a modified procedure for the calculation of the isochron age (Geyh, 1994), which considers the normalization of ^{230}Th and ^{234}U to ^{232}Th. The plot of the ^{230}U/^{232}Th activity ratios versus the ^{234}U/^{232}Th activity ratios is used for determination of the global detrital correction factor ^{230}Th/^{232}Th and its standard deviation. This factor is then used to correct each coeval sample separately. The weighted mean of these corrected ages is the isochron-corrected ^{230}Th/U-age. A chi-square test is applied to verify whether the corrected dates belong to the same normal distribution and should not be much larger than the number of samples used to calculate the isochron.

The chemistry for the extraction of uranium and thorium from the samples was adapted from the leachate/leachate technique (Schwarcz and Latham, 1989; Kaufman, 1993). To meet the isochron requirement three separate coeval dry peat samples from the same depth of $\sim$0.4 g each were combusted in an O_2 flow at 800°C, treated with NaOH, and dissolved in a HNO_3/HCl mixture. A ^{229}Th spike and a ^{233}U-^{236}U doublespike were added to each sample before uranium and thorium were separated from the equilibrated leach solution by co-precipitation with Fe $(OH)_3$. The final separation was achieved by conventional ion-exchange chromatography. The purified uranium and thorium fractions were loaded separately without any carrier on rhenium filaments. The isotopic ratios were measured by thermal ionization mass spectrometry (TIMS; Finnigan MAT 262 RPQ) applying the double filament technique.

RESULTS

Mass spectrometric ^{230}Th/U-ages, ^{234}U/^{238}U, ^{230}Th/^{234}U, and ^{230}Th/^{232}Th activity ratios, as well as uranium and thorium concentrations, are compiled in Table 1. Two sigma standard deviations are reported. We calculated the ^{230}Th/^{232}Th, ^{230}Th/^{234}U, ^{234}U/^{232}Th, ^{234}U/^{238}U, and ^{230}Th/^{238}U activity ratios of the measured atomic ratios after normalizing to ^{233}U/^{236}U. Thermal fractionation for uranium was less than 0.2% per mass unit (determined from the ^{233}U/^{236}U spike ratio). For thorium no normalization was applied due to unknown instrumental fractionation. The external reproducibility was determined by measurements of standard solution NBL (former National Brunswick Laboratories) 112A and yields a value of 0.7% (2σ). Procedural blanks were on the order of 0.03 ng U and 0.03 ng Th, respectively.

Initial ^{234}U/^{238}U activity ratios range between 1.384 and 1.415; the uranium and thorium concentrations range from 1.5 to 3.0 and from 4.7 to 5.4 ppm, respectively. The ^{230}Th/^{232}Th activity ratios are smaller than 2.1, indicating a contamination of the peat by detrital ^{230}Th. The isochron-corrected ages of the three samples were corrected with a ^{230}Th/^{232}Th ratio of 0.083 ± 1.013 (Fig. 5) and agree within the 2σ standard deviation. The isochron ^{230}Th/U-age of the studied peat, respective of the weighted mean, is $200{,}900 \pm 3400$ yr. The plot of the ^{234}U/^{238}U activity ratios versus the detritus-corrected ^{230}U/^{238}U activity ratios is used to verify closed-system conditions. The

TABLE 1
Data of the Peat Lens from the Bol'shoy Lyakhovsky Island, West of the Zimov'e River Deposits

Sample TIMS-Hv	$[^{234}U/^{238}U]_t$ $\pm 2\sigma$	$[^{234}U/^{238}U]_0$ $\pm 2\sigma$	$[^{230}Th/^{234}U]_t$ $\pm 2\sigma$	$[^{230}Th/^{232}Th]_t$ $\pm 2\sigma$	$[^{234}U/^{232}Th]_t$ $\pm 2\sigma$	U-conc. [ppm]	Th-conc. [ppm]	^{230}Th/U-age [10^3 yr] $\pm 2\sigma$	"Isochron"-corr. ^{230}Th/U-age [10^3 yr] $\pm 2\sigma$
334	1.215 ± 0.002	1.387 ± 0.002	0.953 ± 0.007	1.020 ± 0.008	1.071 ± 0.003	1.52	5.23	258.3 ± 7.1	199.4 ± 9.1
335	1.227 ± 0.006	1.409 ± 0.006	0.941 ± 0.006	1.321 ± 0.008	1.404 ± 0.006	2.03	5.37	245.0 ± 6.6	202.0 ± 7.8
336	1.215 ± 0.003	1.386 ± 0.002	0.913 ± 0.003	2.141 ± 0.008	2.346 ± 0.006	2.98	4.69	224.2 ± 2.7	200.6 ± 4.3
"Isochron" age ($\chi^2 = 4$)									200.9 ± 3.4

three analyzed peat samples (Fig. 6) form a cluster in this diagram, indicating that there was no gain or loss of uranium. This, together with the geological investigations reported above, suggests that postsedimentary mobilization processes most likely did not affect the uranium or thorium isotopic compositions in the peat after its formation and during aging.

DISCUSSION AND CONCLUSIONS

The ^{230}Th/U isochron age significantly differs from the thermoluminescence age of $980{,}000 \pm 250{,}000$ yr and magnetostratigraphic assignment to the Jamarillo event of the same horizon, both formerly published by Archangelov *et al.* (1996) and designated by these authors as Olyorian-Suite (Late Pliocene/Early Pleistocene). However, thermoluminescence ages of this age range are questionable and the chronological assignment by Archangelov *et al.* (1996) is based on only three single paleomagnetic samples instead of a continuous profile. Therefore, the magnetic excursion could be interpreted equally well as the Jamaica or Pringle Falls event (between 205,000 and 215,000 yr B.P.; Langereis *et al.*, 1997), the Biwa I event (about 180,000 yr B.P.; Kawai *et al.*, 1972), or the Biwa II event (about 200,000 yr B.P.; Machida *et al.*, 1991). New Russian paleomagnetic investigations at the same locality on Bol'shoy Lyakhovsky Island support the latter interpretation (Schirrmeister *et al.*, 2000).

There are two main conclusions associated with the isochron-corrected ^{230}Th/U-age. First, ^{230}Th/U-age determination using the isochron method is valuable for permanently frozen peat in permafrost deposits. Second, the results clearly show that the deposits exposed by up to 5 m at the southern cliff of the Bol'shoy Lyakhovsky Island, west of the Zimov'e River, are older than the Eemian and correspond to marine isotope stage 7. Therefore, if the upper ice-rich deposits of the Ice Complex are dated as Late Pleistocene (Weichselian) (Kunitsky, 1996, 1998; Nagaoka, 1994; Nagaoka *et al.*, 1995; L. Schirrmeister, unpublished data), the lower ice-rich deposits were formed during the Saalian. This means the oldest, well-preserved Ice Complex cannot be considered a stratigraphic analogy of the Olyorian Suite (Late Pliocene/Early Pleistocene), as it was by Archangelov *et al.* (1996). The horizons with ice wedge casts between these two ice complexes might have been formed during the Eemian Interglacial period.

The ice-rich permafrost deposits on the coastal lowland in northeastern Siberia and on the New Siberian Islands often

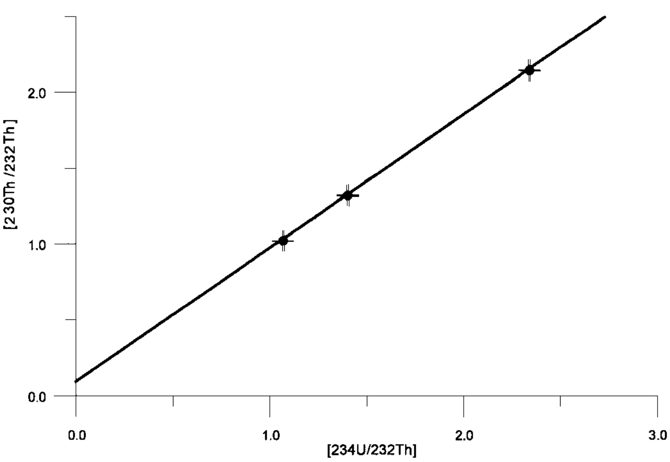


FIG. 5. ^{230}Th/^{232}Th–^{234}U/^{232}Th activity ratio isochron diagram showing the activity ratios $\pm 2\sigma$ of the three peat samples. The detrital correction factor is $[^{230}Th/^{232}Th]_t = 0.083 \pm 0.013$.

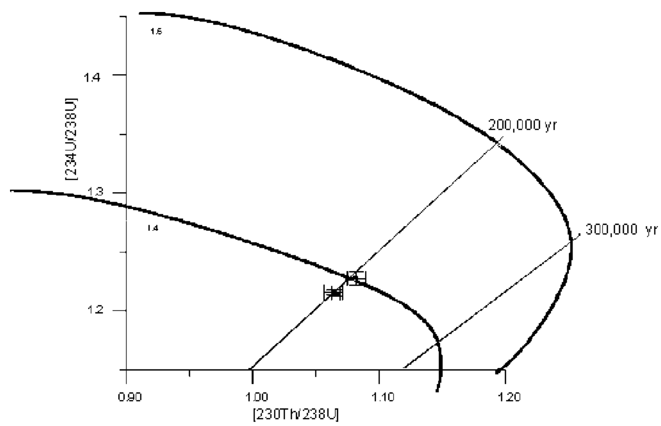


FIG. 6. ^{234}U/^{238}U–^{230}Th/^{238}U activity ratio diagram demonstrating the geochemical closed system conditions for the three "isochron"-corrected samples from the Lyakhovsky peat lens. The dotted lines are isochrons for 200,000 and 300,000 yr; the solid lines show the change in the ^{234}U/^{238}U activity ratio for initial values of 1.4 and 1.6 (after Ivanovitch and Harmon, 1992). Present ^{234}U/^{238}U and detritus corrected ^{230}Th/^{238}U activity ratios with 2σ standard deviations are shown.

contain layers, lenses, and inclusions of peat that are too old to be dated by AMS. Application of ^{230}Th/U disequilibrium dating is therefore regarded as indispensable for the reconstruction of the Quaternary Arctic environment.

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