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^{230}Th-EXCESS AND ^{14}C DATING OF PELAGIC SEDIMENTS FROM THE HYDROTHERMAL ZONE OF THE NORTH ATLANTIC

V.YU. KUZNETSOV[1], K.A. ARSLANOV[1], V.V. SHILOV[2], G.A. CHERKASHEV[2] and S.B. CHERNOV[1]

[1]*Geographical Research Institute, St. Petersburg State University, Sredny Prospect 41, 199 004 Saint-Petersburg, Russia*
[2]*Institute for Geology and Mineral Resources of the Ocean, Angliysky Prospect 1, 190 121 Saint-Petersburg, Russia*

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Abstract: **A comprehensive geochronological study of a pelagic sediment core altered by hydrothermal processes from the Mid Atlantic Ridge (14.5°N) was carried out using both the $^{230}Th_{excess}$ and the radiocarbon methods. Complementary foraminiferal tests and oxygen-isotope determinations were done. The main task was to check whether $^{230}Th_{excess}$ dating of such diagenetically changed sediments yields reliable absolute ages. For this purpose the vertical distribution of the ^{238}U, ^{234}U, ^{232}Th and ^{230}Th activities along the core was measured. The results proved that it was not disturbed during the aging of the sediment. The long-term hydrothermal influence had been constant during at least the last 300 ka and did not change the natural $^{230}Th_{excess}$ distribution along the core. Hence, $^{230}Th_{excess}$ dating yields reliable ages and allows to calculate sedimentation rate. Between the uppermost and lowermost sublayers of the core we obtained 1.35±0.15 cm/ka which agrees with 1.47±0.03 cm/ka derived from conventional ^{14}C ages. These numerical dates, the results of the foraminiferal tests and the δ^{18}O values place the studied sediments to the marine isotope stage 5 (MIS 5). These dates are well correlated with the corresponding sedimentary records from pelagic sediments of the North Atlantic Ocean.**

1. INTRODUCTION

There is a growing interest to study different types of pelagic sediments mixed with low and high temperature hydrothermal components. High temperature hydrothermal fluids are discharged into the bottom ocean water (Lisitsyn *et al.*, 1990). Part of these hydrothermal matter is deposited near the vents forming massive sulfides and metalliferous sediments. These sediments are scattered around large distances. Pelagic sediments are penetrated by hydrothermal solutions in active hydrothermal zones and chemical elements are deposited.

Many comprehensive chemical, mineralogical, geological, geophysical, biogeochemical and geochronological studies have been carried out on hydrothermal sediments. However, there are only few data on sedimentation rates and absolute ages. In most cases the uranium-disequilibrium method was applied.

As there are usually no data on the biostratigraphy of hydrothermal deposits numerical dating is essential to classify such deposits. We undertook a comprehensive biostratigraphic, isotopic and geochronological study of a sediment core from the active hydrothermal zone of the Mid-Atlantic Ridge (MAR). We investigated: 1) the vertical distribution of the uranium and thorium isotopes (^{238}U, ^{234}U, ^{232}Th and ^{230}Th), 2) checked the possibility to apply the $^{230}Th_{excess}$ dating method to oceanic hydrothermal deposits, and 3) compared the results of our geochronological, biostratigraphic and stable isotope study with those of the North Atlantic Ocean.

2. LOCATION AND MATERIALS

The core KP-145 was taken on RV "Professor Logachev" in 3105 m water depth at 14°45'44" N and 44°58'74" W in the Mid-Atlantic Ridge area in 1994. This site is located about 300 m north of the hydrothermal field "Logachev" which was discovered in 1993 (Krasnov *et al.*, 1995). The hydrothermal field is situated at the eastern slope of the rift valley about 35 miles far from the fracture zone at 15°20'N (**Fig. 1** and **2**). Two layers are distinguished in the core:

Layer 1 (0-18 cm): It consists of 90-95% grey-beige biogenic calcium carbonate (coccolites and foraminifera) with spotted ore-bearing silt. There are singular micro-inclusions of black color (Fe-Mn oxides) and fragments of ultrabasic rocks. The spherical silt spots are beige-colored, sometimes non-transparent and formed by bioturbation. The upper sublayer (0-1 cm) is saturated with seawater.

Layer 2 (19-115 cm): It mainly consists of calcium carbonate (coccolites and foraminifera) which concentration gradually decreases downward from 78 to 72%. The sublayer up to 60 cm contains hydrothermal material. There is some beige-colored silt with singular black colored (Fe-Mn oxides) micro-inclusions. The upper part of the layer (19-25 cm) is affected by bioturbation with numerous gray-beige dots and bands without sharp contours.

Our sediment core KP-145 from the active hydrothermal MAR area contains complex genetic features which could only be deciphered by a careful, comprehensive geochronological and multidisciplinary study. The common pelagic sediment is depositionarily superimposed by the penetration of hydrothermal fluids and associated and geochemical processes. Parts of the sediments were mixed by tectonics and bioturbation.

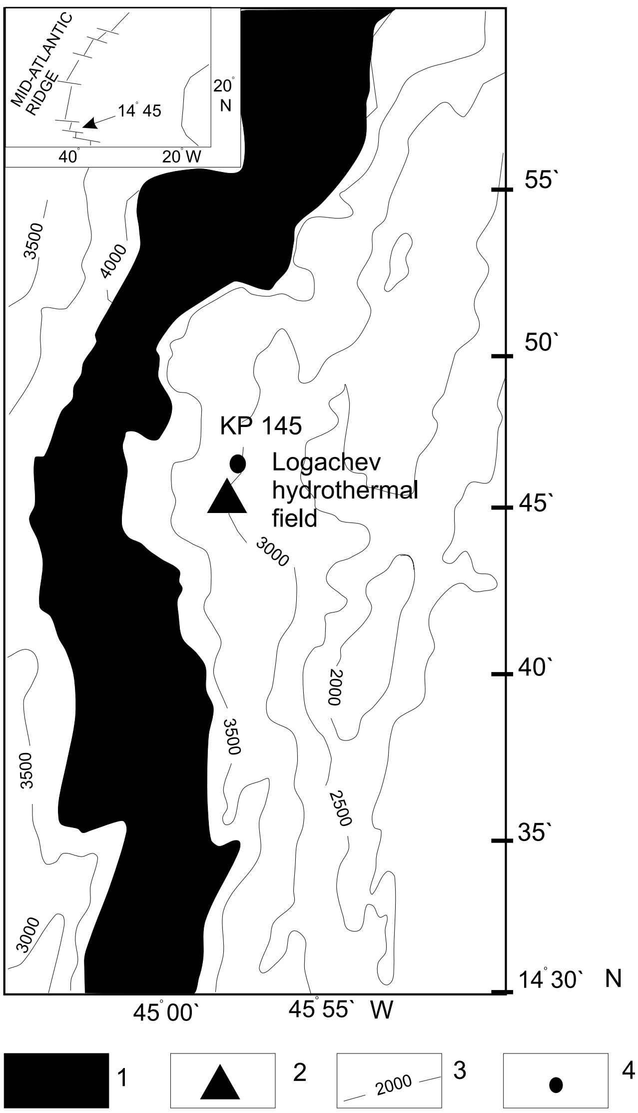

Fig. 1. Location of "Logachev" hydrothermal field and station KP 145. 1 – rift valley; 2 – "Logachev" hydrothermal field; 3 – isolines of floor relief; 4 – location of station KP 145.

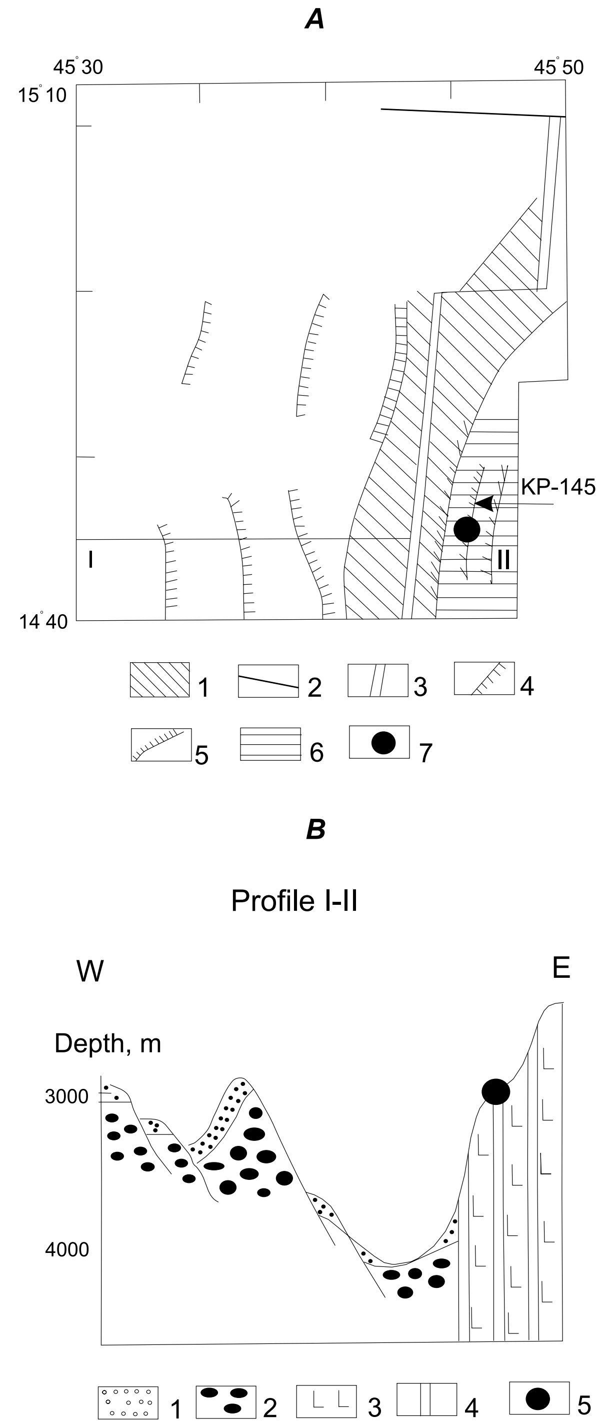

Fig. 2. Geological structure of axis region of Mid-Atlantic Ridge in the zone of hydrothermal field 14° 45 N (after Bogdanov et al., 1995).
A: 1 – rift valley; 2 – transform fault 15° 20 N; 3 – spreading axis; 4 – normal fault scarps; 5 – vertical deep-seated fault; 6 – massif of serpentinous ultrabasites and gabbroides; 7 - active hydrothermal field.
B: Profile I-II: 1 – unconsolidated sediments; 2 – extrusive basalts; 3 – serpentinous ultrabasites and gabbroides; 4 – vertical deep-seated fauls; 5 – active hydrothermal field.

3. ANALYTICAL METHODS

Uranium and thorium were radiochemically extracted (Kuznetsov, 1993; Kuznetsov *et al.*, 2000). The main steps were:

- digestion and dissolution of 5-10 g of sediment by concentrated HNO_3, HF and HCl; removal of F^- by concentrated $HClO_4$; addition of the double spike of ^{232}U and ^{234}Th;
- adsorption of uranium and thorium isotopes on iron hydrooxide in a carbonate-free ammonia solution at pH 7 to 8;
- purification of the solution from all admixtures of interfering alpha emitters; separation of the uranium and thorium by anion exchange. Anionite AV-17 was used to elute the Th fraction from the 7n HNO_3 solution and uranium from the 6n HCl/0.2n HNO_3 solution;
- electrodeposition of uranium and thorium on platinum discs from the ethyl alcohol solution (adding the 0.2 n HNO_3 solution) during 1.5 hours under current density of 60 ma/cm^2 (Kim *et al.,* 1966);
- alpha-spectrometric determination of the ^{238}U, ^{234}U, ^{232}Th and ^{230}Th activity using a semi-conductor surface-barrier silicon detector (resolution: 30 KeV/channel) and the pulse analyzer AI-1024.

The chemical yield of uranium and thorium isotopes were calculated from the activities of the ^{232}U and ^{234}Th spikes. The results of a radiochemical analysis of the sediment core KP-145 are compiled in **Table 1**.

The organogenic fraction of the pelagic sediment was transformed into benzene and ^{14}C dated by liquid scintillation counting (Arslanov, 1987). The ^{14}C dates of the various sublayers of the core are compiled in **Table 2**.

4. RESULTS

Radiometric measurements

The manifold methods of uranium-series disequilibrium dating are based on the offset of radioactive equilibrium in oceanic sediments. One of these methods is the $^{230}Th_{excess}$ method which uses the radioactive decay of the excess activity of ^{230}Th over that of the parent uranium. There are two prerequisites for the application of this method: 1) ^{230}Th may not migrate in the sedimentary strata which has never been observed (Kuznetsov, 1976; Kuznetsov and Andreev, 1995; Huh and Ku, 1984; Lalou *et al.*, 1988); 2) ^{230}Th is deposited with a constant deposition rate. This prerequisite has to be checked for each section with different genesis.

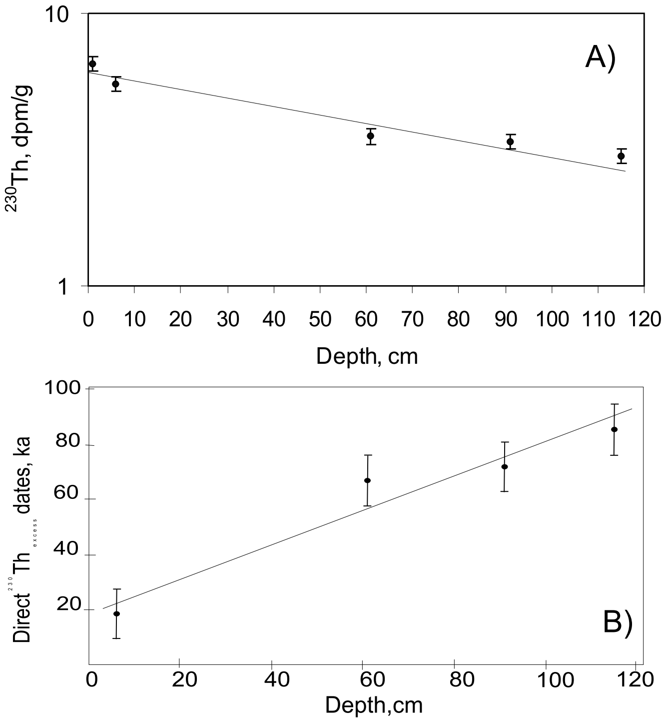

Fig. 3. *Vertical distribution of $^{230}Th_{excess}$ (A) and direct $^{230}Th_{excess}$ dates (B) along the core KP-145*

Table 2. *Absolute ages of sublayers of core KP-145.*

No.	Sublayer [cm]	Conventional ^{14}C Age [BP]	$^{230}Th/U$ age [years]*
1	0 - 1		
2	5 - 6	4100 ± 400*	
3	13 - 15	10,800 ± 200 (11,170 BC-10,485 BC)	10,400 ±1100*
4	30 - 31	20,800 ± 500	22,600 ± 2400*
5	40 - 41	27,600 ± 600	30,000 ± 3200*
6	60 - 61		44,800 ± 4800*
7	90 - 91		67,000 ± 7400*
8	114 - 115		84,800 ± 9200

Comments:
The average sedimentation rate calculated by ^{230}Th was 1.35±0.15 cm/ka; the standard deviation of the average sedimentation rate was calculated from that of the date of 84,800±9200 yr.
The average sedimentation rate calculated by ^{14}C data was 1.47±0.03 cm/ka; the standard deviation of the average sedimentation rate was calculated from that of the date of 27,600±600 yr.
*)=the age was calculated from the average sedimentation rate of 1.35±0.15 cm/ka.

Table 1. *Results of a radiochemical analysis of the sediment core KP-145.*

No.	Layer [cm]	^{238}U [dpm/g]	^{234}U [dpm/g]	$^{234}U/^{238}U$	^{232}Th [dpm/g]	^{230}Th* [dpm/g]
1	0 - 1	0.48 ± 0.02	0.51 ± 0.02	1.07 ± 0.06	0.90 ± 0.06	6.53 ± 0.37
2	5 - 6	0.51 ± 0.02	0.54 ± 0.02	1.06 ± 0.06	0.62 ± 0.04	5.51 ± 0.33
6	60 - 61	0.44 ± 0.02	0.48 ± 0.02	1.08 ± 0.06	0.55 ± 0.03	3.54 ± 0.22
7	90 - 91	0.14 ± 0.01	0.16 ± 0.01	1.11 ± 0.06	0.42 ± 0.03	3.38 ± 0.20
8	114 - 115	0.25 ± 0.01	0.25 ± 0.01	0.99 ± 0.06	0.55 ± 0.03	2.99 ± 0.19

*)=activity of ^{230}Th, excessive over the equilibrium with parent ^{234}U.

The $^{234}U/^{238}U$ AR insignificantly vary within the core. The ^{238}U concentration ranges from 0.2 - 0.7 µg/g corresponding to a specific activity of 0.14-0.51 dpm/g (**Table 1**). The ^{232}Th activity varies by a factor of two along the core.

Foraminiferal tests, oxygen-isotope composition and palaeotemperature

The composition of the well preserved and abundant planktic foraminifera, the $\delta^{18}O$ values and the ratio of biogenic and terrigenous components in the sand sediment fraction were determined on 14 sublayers. The average annual paleotemperature was reconstructed from the ratio of planktic foraminifera species *Globigerina Pachyderma* (**Fig. 4**). The determination of the oxygen-isotope analyses were done on the $CaCO_3$ of all species planktic foraminifera shells rather than an individual species as relative large quantities of samples were required for the mass-spectrometric measurement. Some of the planktic foraminifera contained Fe-Mn oxides.

5. DISCUSSION

Radiometric measurements

The $^{234}U/^{238}U$ AR and ^{238}U activities are in the range of uranium in common pelagic and metal-bearing sediments (Kuznetsov, 1976; Lalou *et al.*, 1988; Arslanov *et al.*, 1988). Hydrothermal fluid discharged from the ocean floor is usually not enriched in uranium compared to seawater (Lisitsyn *et al.*, 1990; Lisitsyn, 1970 and 1993; Arslanov *et al.*, 1988). Hence, the concentration and distribution of uranium in the pelagic sediment may be primarily determined by its terrigenous and hydrogenous origin and by the supply of endogenous ore substance. This supply decreases to some extent the uranium concentration in the sediment. This concept is in agreement with the found $^{234}U/^{238}U$ activity ratio which ranges from 1.0 (terrigenous detritus) to 1.14 (near that of seawater; see **Table 1**). The $^{230}Th_{excess}$ activity in the core decreases gradually from the surface downward as expected from radioactive decay (**Fig. 3**). The direct absolute $^{230}Th_{excess}$ dates calculated on the basis of the $^{230}Th_{excess}$ activity in the sublayers 1 and 2, 1 and 6, 1 and 7, 1 and 8 tend to increase along the core (**Fig. 3**). These findings testify that any influx of endogenous ore matter and from the hydrothermal plume was constant and did not disturb the natural distribution (**Table 1**).

The maximum thorium concentration in sublayer 1 may reflect an insignificant supply of ^{232}Th and ^{230}Th during the last several thousands of years.

Under the found conditions the $^{230}Th_{excess}$ method was used to determine the average sedimentation rate of the core. On the basis of the $^{230}Th_{excess}$ activity in the sublayers 1 and 8 we calculated the age of 84,800±9200 yr between the sublayers 0-1 cm and 114-115 cm. The data allow to calculate the average sedimentation rate of 1.35±0.15 cm/ka from which absolute ages were estimated for each sublayer (**Table 2**). The latter and the corresponding ^{14}C dates agree well with each other. On the basis of the ^{14}C date of 27,600±600 (sublayer 40-41 cm) we calculated the average sedimentation rate of 1.47±0.03 cm/ka.

Foraminiferal tests, oxygen-isotope compositions and palaeotemperature

The elaborated reliable chronology of core KP-145 explains why these sediments were chosen for the comprehensive study including foraminiferal tests and complementary isotope-oxygen analysis. The results allowed a stratigraphic and geochronological classification of the core and its correlation with MIS (Shackleton and Opdyke 1973; Barash *et al.*, 1983 and 1984; Barash, 1988; see **Fig. 4**).

The assemblage of planktic foraminifera in the subsamples 0-1 cm, 5-6 cm and 10-11 cm depth contains mainly the species *Globigerinoides sacculifer* (Brady) (**Fig. 4**), *Gs. ruber d'Orbigny; Globorotalia menardii* (d'Orbigny), *Sphaeroidinella dehiscens* (Parker et Jones). It corresponds to the tropical type of thanatocenosis of the equatorial subtype. Due to the dominance of *Globorotalia menardii* (d'Orbigny) these subsamples belong to the Zone Z defined by Eriksson *et al.* (1961 and 1963) which was deposited during the last 11,000 years.

The palaeotemperature was reconstructed according to Barash *et al*. (1983 and 1988) and yielded an mean annual temperature of the surface water of +25.0 to +26.5°C (**Fig. 4**). The Holocene climatic optimum is reflected by an insignificant temperature increase and a mould of the isotope-oxygen curve at the layer between 5 and 6 cm (**Fig. 4**). The $^{230}Th_{excess}$ date of 4100±400 yr was determined for this sublayer (**Table 2**). The conventional ^{14}C and $^{230}Th_{excess}$ dates of the 13-15 cm are 10,800±200 yr BP (the calibrated ^{14}C date is 11,170 BC –10,485 BC, with 1σ confidence interval analysis) and 10,400±1100, respectively (**Table 2**). The sedimentation rate for MIS 1 adopting the age of the boundary between MIS 1 and MIS 2 of ~11 ka (Morley and Hays, 1981) is about 1.35 cm/ka (**Table 3**).

The dominant species of planktonic foraminifera of Layer 2 (18-110 cm) were *Globigerinoides ruber d'Orbigny*, *Gs. sacculifer* (Brady) (**Fig. 4**), *Globorotalia truncatulinoides* (d'Orbigny) with single individuals of *Globorotalia menardii flexuosa* (Koch). This assemblage is characteristic for Zone Y (Eriksson *et al.*, 1961 and 1963) which lasted from 75-11 ka.

The sublayers between 15-43 cm (15-16 cm, 20-21 cm, 30-31 cm and 40-41 cm) contained planktic foraminifera of the tropical type of thanatocenosis tending to the equatorial subtype (Barash, 1988). The reconstructed paleotemperature of the mean annual surface water was closely to +25.0°C (**Fig. 4**). The $\delta^{18}O$ value and the assemblage of planktic foraminifera as *Globigerinoides sacculifer* (**Fig. 4**), *Gs. ruber, Globorotalia truncatulinoides* are related to MIS 2 lasting from 27 to 11 ka. The conventional ^{14}C dates of the 30-31 cm and 40-41 cm are 20,800±500 and 27,600±600 BP, respectively (**Table 2**). The $^{230}Th_{excess}$ dates of 22,600±2400 and 30,000±3200 ka were determined for these sublayers. The sedimentation rate for MIS 2 adopting the age of the boundary between MIS 2 and 3 of ~27 ka (Morley and Hays, 1981) is about 1.75 cm/ka (**Table 3**).

The sublayers between 43-85 cm (50-51 cm, 60- 61 cm, 70-71 cm and 80-81 cm) contained planktic foraminifera of the tropical type of thanatocenosis tending to the equatorial subtype (Barash, 1988). The mean annual temperature of the surface water was estimated to +26.0 ±0.5°C (**Fig. 4**). Both the isotope-oxygen curve and that of the planktic foraminifera (**Fig. 4**) correspond to MIS 3 and the time range from 58 to 27 ka. The sample from 60-61 cm ($^{230}Th_{excess}$) yielded 44,800±4800 yr (**Table 2**). The age of ~58 ka between MIS 3 and 4 (Morley and Hays, 1981) yielded a sedimentation rate of about 1.35 cm/ka for MIS 3 (**Table 3**).

The planktic foraminifera in the section of 85-105 cm (90-91 cm and 100-101 cm) belonged to the tropical type of thanatocenosis tending to the equatorial subtype (Barash, 1988). The mean annual temperature of the surface water was close to +25.0°C (**Fig. 4**). The assemblage of planktic foraminifera and the $\delta^{18}O$ values allow a correlation with MIS 4 (72-58 ka). The $^{230}Th_{excess}$ date for the 90-91 cm sublayer is 67,000±7400 yr (**Table 2**). The age of ~72 ka between MIS 4 and 5 yielded a sedimentation rate of about 1.43 cm/ka for MIS 4 (**Table 3**).

The sublayers between 105-115 cm (110-111 cm and 114-115 cm) contained well-preserved planktonic foraminifera of the tropical type of thanatocenosis tending to the equatorial subtype without secondary changes (Barash, 1988). The estimated mean annual temperature of the surface water was close to +26°C (**Fig. 4**). The biostratigraphic and isotopic results allowed a connection to MIS 5 (128 to 72 ka). The absolute $^{230}Th_{excess}$ date of the sample from 115-114 cm is 84,800±9200 yr (**Table 2**).

Zone X is represented by sediments below 110 cm. It contained species of *Globorotalia menardii: Globorotalia menardii* (d'Orbigny) and *Globorotalia menardii flexuosa* (Koch) which were deposited between 128-75 ka.

The good agreement between the results of the geochronological, biostratigraphic and isotopic analyses testifies the reliability of the derived climate-geochronological course (**Fig. 4**).

Table 3. *The sedimentation rates between the boundaries of MIS in cores L-66 and KP-145.*

Marine isotope stage	**L-66** [cm/ka]	**KP-145** [cm/ka]
MIS 7	1.6	
MIS 6	0.4	
MIS 5e	1.2	
MIS 5d - 5a	1.0	
MIS 4	1.7	1.43
MIS 3	0.5	1.35
MIS 2	1.45	1.75
MIS 1	1.2	1.35

6. STRATIGRAPHICAL AND GEOCHRONOLOGICAL COMPARISON OF THE CORES KP-145 AND L-66

We compared our results from core KP-145 representing the hydrothermal activity zone with the corresponding data of the sediment core L-66 from the pelagic zone of the North Atlantic (Arslanov *et al.,* 1988). By this the geological section was correlated with the climate-stratigraphic events for the Late Pleistocene-Holocene of the Central and North Atlantic Oceans.

Core L-66 was taken on the second cruise of RV "Mikhail Lomonosov" (1958) in the European basin (49°04´ N, 20°18´ W) in a water depth of 4000 m. The core length is 298 cm. It contains alternating layers of white to light-gray silt (0-12, 134-149 and 168-255 cm). The terrigenous material of sandy silt with gravel, pebble and detritus (12-134, 149-168 and 255-298 cm) dominates over the biogenic, coccolite-foraminifera silt. In the 26-39 cm sublayer, volcanic ash is present. The terrigenous sublayers, especially the thickest sublayer at 12-134 cm,

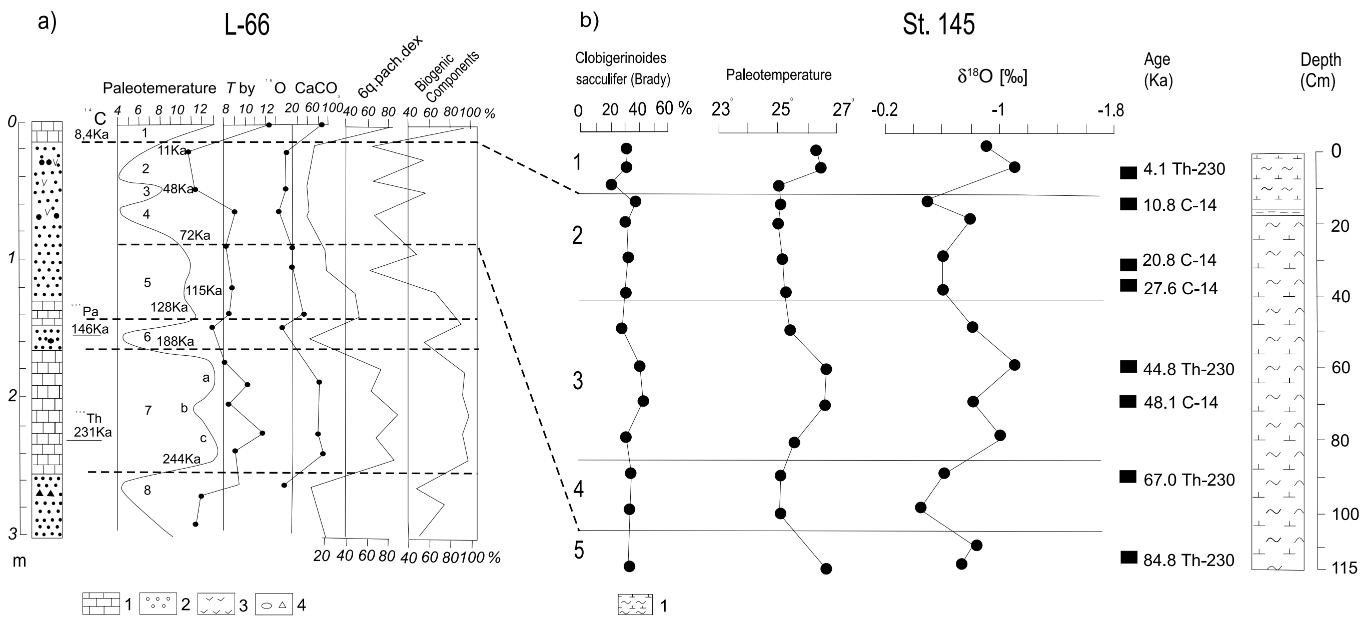

Fig. 4. *Results of geochronological study of cores KP-145 and L-66, their stratigraphical classification and correlation.*
a) 1 – coccolith-foraminiferal ooze; 2 – terrigenous mud; 3 – volcanic ash; 4 – gravel, pebble, rock debris;
b) 1 – coccolith-foraminiferal ooze.

are lithologically heterogeneous. They contain fine- to coarse-grained interlayers with micro-laminated texture. They are interpreted as reflection of significant changes of the palaeo-oceanographic sedimentation.

From this core, 18 quantitative analyses of the composition of planktic foraminifera were done, the palaeotemperature and the ratio of biogenic to terrigenous components in the sandy fraction of the sediment (>0.1 mm) were calculated. In addition, 16 isotope-oxygen analyses and 12 analyses of the carbonate concentration were performed. Uranium, thorium and protactinium measurements were carried out on eight sublayers between 0-6 cm and 229-234 cm.

The sample from 150-154 cm yielded the $^{231}Pa_{excess}$ date of 146,000±18,000 years representing the boundary of MIS 5/MIS 6. The $^{230}Th_{excess}$ date of 231,000±15,000 years for the 229-234 cm sublayer corresponds to the early climatic optimum of MIS 7 which is well correlated with the course of the $\delta^{18}O$ values (Morley and Hays, 1981; see **Fig. 4**).

The stratigraphic classification of L-66 allows an estimate of the absolute ages and the sedimentation rates between the boundaries of MIS (Morley and Hays, 1981). The sedimentation rate in core L-66 and KP-145 varied noticeably (**Table 3**).

In agreement with other findings the sedimentation rate of both cores KP-145 and L-66 is higher during the cold periods (MIS 2 and 4) than during the warm periods (MIS 1 and 3) in the Central and North Atlantic. This is explained by an increased supply of terrigenous material during the cold epochs as plant cover fixes loose sediments.

The average sedimentation rate of 1.4 ($^{230}Th_{excess}$, ^{14}C) and 1,0 ka/cm ($^{230}Th_{excess}$, $^{231}Pa_{excess}$) in the cores KP-145 and L-66 for MIS 1-4 deviate slightly from each other. This may indicate that the hydrothermal influence at the site of KP-145 was insignificant and constant along the core.

7. CONCLUSIONS

The comprehensive geochronological study of the core KP-145 proved that the $^{230}Th_{excess}$ dating method yielded reliable dates since the influx of hydrothermal matter was constant or negligible and did not influence the vertical distribution of uranium and thorium isotopes. The biostratigraphic and oxygen-isotope results allowed a stratigraphic and the $^{230}Th_{excess}$ ages for chronological classification of the sediment core from the MAR hydrothermal zone and their correlation with MIS. The palaeotemperature for the Late Pleistocene-Holocene was reconstructed for the surface water from the Central and North Atlantic.

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