GEOCHRONOMETRIA Vol. 21, pp 49-56, 2002 – *Journal on Methods and Applications of Absolute Chronology*

^{230}Th/U AND ^{14}C DATING OF MOLLUSC SHELLS FROM THE COASTS OF THE CASPIAN, BARENTS, WHITE AND BLACK SEAS

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Key words:
URANIUM-THORIUM DATING,
RADIOCARBON DATING,
GEOCHRONOLOGY,
TRANSGRESSION,
MOLLUSC SHELLS

Abstract: We dated Holocene and Late Pleistocene mollusc shells collected from coastal sediments of the Caspian, Barents, White and Black Seas by means of both a modified ^{230}Th/U method and the radiocarbon method. Essence of the modification is the removal of the surface (about 1/3 of the weight) of the mollusc shells by nitric acid as it may contain adsorbed detrital ^{232}Th and ^{230}Th. The ^{230}Th/U dates of the inner part of the shells do not require detrital correction with the ^{232}Th activity and well agree with the corresponding reservoir-corrected and calibrated ^{14}C ages of mollusc shells with ages between 1300 and 13,500 BP.
We tested the modified ^{230}Th/U method on thick-walled and well-preserved mollusc shells from the transgression sediments of the Barentz, White and Black Seas derived during the Mikulino Interglacial (MIS 5e) and the Early Valday Glaciation (MIS 5c). The ^{230}Th/U ages of the inner part of the shells from the Boreal (Eem) transgression sediments of the Barentz and White Seas ranged from 86 to 114 ka and those from the Karangat (Eem) transgression in the Black Sea (Maly Kut and Eltigen sections) from 95 to 115 ka. The new ^{230}Th/U dates of the shells from the section Eltigen ranged from 100 to 125 ka..

1. INTRODUCTION

^{230}Th/U dating of biogenic calcium carbonate (mollusc shells, corals etc.) depends on three basic requirements: a) uranium was incorporated into the biogenic calcium carbonate during its formation and soon after the death of the animal; b) the carbonate does not contain any noticeable amounts of ^{232}Th and detrital ^{230}Th; c) the sample behaved as closed system during aging in the sediments. That means that neither loss nor accumulation of uranium and thorium occurred.

Uranium is incorporated into corals during their formation. Migration of uranium and thorium isotopes has not been observed (Veeh, 1966; Kaufman *et al.,* 1971). However, uranium migration is recorded for fossil mollusc shells subjected to groundwater action. Kaufman *et al.* (1971) found that about 50% of ^{230}Th/U dates from 60 mollusc shells deviate from the known Pliocene or Pleistocene age. During geological time ranges (million years) mineralogical, physical and chemical processes might have accompanied by uranium migration. Obviously, comparison of the mollusc shell ages should be made within the age range of the method (300 ka).

Until now ^{230}Th/U dating has been carried out on the entire shells through radiocarbon dating of mollusc shell demonstrated that the surface part of the shells behaves as open system and often contains a secondary changed ^{14}C activity due to isotope exchange and diffusion processes (Olsson and Blake, 1961/1962; Arslanov, 1987). Similarly, the uranium isotope activity of the inner and outer parts of shells may also be modified.

We analyzed the ^{238}U, ^{234}U, ^{232}Th and ^{230}Th specific activities of the surface, the outer layer and the inner part of recent and fossil mollusc shells in order to study uranium isotope migration within the shells. For this parallel radiocarbon and uranium-thorium dating of the same samples of mollusc shell with known ages within and just above the dating range of the ^{230}Th/U method were done. As first test of the modified ^{230}Th/U dating method of mollusc shells collected from transgressive deposits of the White, Barents and Black Seas were dated and correlated with the Riss-Wrmian (Eem) transgression of the World Ocean.

2. METHODS

Three of the authors (Kh.A.Arslanov, N.I.Tertychny and N.V.Lokshin) collected recent mollusc shells from many large rivers (Volga, Kama, Belaya, Zapadnaya Dvina, Berezina and Dnieper) and from the coasts of the Azov, White, Baltic and Caspian Seas in 1969 and 1970. These authors together with many geologists and geographers selected fossil mollusc shells from reference sections during 1969-1982. A.E.Dodonov submitted shells from the reference profile Eltigen taken in 1998. Most of the geochronological results were earlier published in Russian Journals (Arslanov *et al.* 1977, 1978, 1981 and 1983).

The protocol of the radiochemical procedure to isolate uranium and thorium from mollusc shells was published by Arslanov *et al.* (1976 and 1981). The following steps were done:

1. Separation of the surface, the outer layer and inner part of the mollusc shells by nitric acid after cleaning, washing and drying (at 105 °C).
2. Admixture of known quantities of ^{234}Th and ^{232}U spikes and $Fe(NO_3)_3$ (10 mg Fe) to the three sample fractions in solution and co-precipitation of uranium and thorium isotopes on $Fe(OH)_3$ by passing carbon-free ammonia through hot solution until pH=7-8 is attained.
3. Dissolution of the washed $Fe(OH)_3$ residue in 4.5n HCl and passing of obtained solution a column filled with Teflon powder impregnated with di-2-ethylhexyl phosphoric acid in diethyl ether.
4. Successive extraction of uranium and thorium from the column with 15 ml of concentrated HCl and with 20 ml of 0.5n oxalic acid solution, respectively.
5. Electrochemical deposition of uranium and thorium on platinum disks from ethyl alcohol solution.

Recently, the stages 3-4 was altered (Kuznetsov *et al.*, 2000):

1. Dissolution of $Fe(OH)_3$ with co-precipitated of uranium and thorium in 7n HNO_3 solution.
2. Passing of solution through the column filled with anion-exchange resin AV-17.
3. Successive extraction of thorium and uranium by 6n HCl and 0.2n HNO_3, respectively.
4. Electrochemical deposition of uranium and thorium on platinum disks from ethyl alcohol solution.

The α-activity of ^{234}U, ^{238}U, ^{232}U, ^{230}Th and ^{232}Th deposited on platinum disks was measured with a silicon detector of an area of 5 cm^2 and the pulse analyzer AI-128 and AI-1024. Chemical yields of uranium were calculated from the activities of the ^{232}U and ^{234}Th spikes. The counting efficiency for uranium and thorium isotopes was checked with a transuranium (^{239}Pu and ^{241}Am) standard of known activity. Radiocarbon dating of mollusc shells was done with benzene liquid scintillation counting (Arslanov *et al.*, 1993).

3. RESULTS

In order to study uranium transfer from groundwater into recent mollusc shells, we determined the uranium activity of 30 alive mollusc shells (*Anadonta*) from several rivers of the European part of Russia and Belarus (Volga, Kama, Oka, Belaya, Berezina, Zapadnaya Dvina and Dnieper) and marine shells from the coasts of the Azov, Black, Caspian and Baltic Seas. The uranium concentration of the river shells determined by luminescent technique ranged between 1.0-5.9·10^{-3} ppm and its distribution through the shells was uniform (Arslanov *et al.*, 1975).

The uranium concentration of marine mollusc shells ranged from 2.5·10^{-3} to 0.65 ppm (**Table 1**).

Sea molluscs *Mytilus edule* contained 3.3·10^{-3} - 8.3·10^{-3} ppm uranium (Arslanov *et al.*, 1975). Both the *Mytilus* mollusc species and the fluvial *Anadonta* shells contained high concentration of organic matter. The uranium concentration in the isolated organic matter of *Mytilus edule* shell amounted to 0.5·10^{-3} ppm while the maximum value

Table 1. *Uranium concentration in recent marine mollusc shells.*

Seashore	Mollusc species	Uranium concentration [ppm]		
		Surface	Outer layer	Inner part
Sea of Azov	*Mytilus edule*, alive	5.8· 10^{-3}	8.0· 10^{-3}	8.3· 10^{-3}
Caspian Sea	*Cardium edule*	0.65	0.59	0.2
White Sea	*Mytilus edule*, alive	4.5· 10^{-3}	-	1.7· 10^{-3}
Baltic Sea, near Klaipeda	*Chione gallina*, alive	5.0· 10^{-2}	-	-
	Chione gallina	4.7· 10^{-2}	3.0· 10^{-2}	2.1· 10^{-2}
	Cardium edule	8.4· 10^{-2}	-	-
	Anadonta	3.9· 10^{-3}	3.9· 10^{-3}	3.3· 10^{-3}
	Dreiscenia	0.16	7.5· 10^{-2}	4.5· 10^{-2}
	Dreiscenia, alive	2.0· 10^{-2}	1.8· 10^{-2}	1.2· 10^{-2}
Black Sea, Taman peninsula	*Mytulus edule*, alive	2.5· 10^{-3}	2.8· 10^{-3}	3.8· 10^{-3}
	Donox trinc, alive	0.13	0.09	0.09
	Cardium edule, alive	0.17	0.10	0.075
	Clamus glabara	2· 10^{-2}	2· 10^{-2}	2.2· 10^{-2}
	Chione gallina, alive	4.5· 10^{-2}	1.75· 10^{-2}	1.75· 10^{-2}
	Chione gallina	2.3	2.3	1.8
	Cardium elule	-	0.60	0.42
	Ostrea edulis	2.2· 10^{-2}	2.0· 10^{-2}	2.0· 10^{-2}
	Gastropod, alive	1.1· 10^{-2}	0.8· 10^{-2}	0.9· 10^{-2}

of 0.65 ppm was found in *Cardium edule* mollusc shells from the Caspian Sea. Recent shells from the Baltic and Black Seas had about 10^{-2} ppm. In general, the shells of alive molluscs contain less uranium (**Table 1**) than dead and fossil shells in river and marine young banks (**Table 2**). In recent shells with lower organic matter (*Dreissenia, Donox, Cardium edule and Chiohe gallina*), highest uranium concentration is found in the surface layer. Gener-

Table 2. *Uranium concentration and* ^{230}*Th/U ages of fossil mollusc shells (A – outer layer, B – inner part).*

Mollusc species and locality	**Lab. No**	**Age** [BP]	**Uranium** [ppm]
Cardium edule, Mamedkala Settlement, Dagestan Republic	190A 190B	2050±90 -	0.85±0.04 0.65±0.02
Same as above	LU-191A LU-191B	1570±100 1640±100	1.50±0.05 1.35±0.05
Cardium edule, Shirvan area, Azerbaijan	LU-422A LU-422B	- 3400±90	2.00±0.03 -
Undetermined species, Dzhorat settl., Apsheron peninsula, Azerbaijan	LU-421A LU-421B	- 5540±110	2.40±0.03 -
Didacna sp., Duvannye settlement Azerbaijan	LU-192A LU-192B	13,140±150 13,200±250	3.90±0.02 4.10±0.05
Didacna sp., Amia Cape, Azerbaijan	LU-193A LU-193B	- 12,480±150	1.20±0.06 1.00±0.05
Didacna sp., Shirvan area, Azerbaijan	LU-423B	12,330±140	4.5±0.02
Didacna sp., near Maloye Turaly Lake, Dagestan Republic	LU-424A LU-424B	13,110±490 12,720±400	3.60±0.18 3.80±0.19
Didacna sp. Near Manas River mouth, Dagestan Republic	LU-426A LU-426B	12,700±450 12,500±300	6.00±0.30 5.40±0.27
Didacna sp. Shamkhal-Termen Settl., Dagestan Republic	LU-432B	76,000±4000	7.30±0.30
Same as above	LU-400B	81,000±2000	2.50±0.40
Didacna sp. Shirvan, Azerbaijain	LU-430A LU-430B	109,000±5000 114,000±4000	5.50±0.20 5.70±0.20
Didacna sp, right bank of Achisu River, Dagestan Republic	LU-401B	≥300,000	2.5±0.04
Didacna sp, Apsheron peninsula, Azerbaijan	LU-434A LU-434B	≥300,000 ≥300,000	2.9±0.14 3.20±0.16
Didacna, Aljatskaya Hill, Khanaly-Kyshlak settl., Azerbaijan	LU-431A LU-431B	≥255,000 ≥300,000	15.60±0.75 14.80±0.74
Chione gallina, near Tuapse City *Dreissenia polymorpha*, Pitsunda Cape, Abkhazia	LU-308B LU-413B	≤2000 47,000±1700	0.40±0.02 1.00±0.02
Paphia senescens, Eltigen section, eastern coast of Kerch Strait	LU-402A LU-402B	96,000±2500 88,000±3000	1.20±0.06 0.95±0.03
Cardium edule, Malye Kut Section, Taman peninsula	LU-403A LU-403B	96,000±2500 85,000±3000	2.60±0.10 1.37±0.01
Chione gallina, Adler settl., near Sochi City	LU-404A LU-404B	76,000±3000 73,000±3000	1.7±0.08 2.20±0.11
Chione gallina, Tuzla Cape, Taman peninsula	LU-410A LU-410B	70,000±2500 65,000±3000	4.60±0.18 4.30±0.15
Chione gallina, Ashe River mouth, Krasnodar krai	LU-409A LU-409B	133,000±5000 139,000±12000	1.61±0.08 1.31±0.06
Cardium edule, west Manych River terrace	LU-450A LU-450B	- 33,320±520	2.12±0.06 1.81±0.06
Cardium edule, Split Chyshka, Taman Peninsula	LU-449B	40,700±1200	-
Chione gallina and *Cardium edule*, same as above	LU-448A LU-448B	- 41,250±1340	6.61±0.19 1.00±0.02
Paphia senescens, Golubaya Dacha Settl., Krasnodar Krai	LU-406A LU-406B	124,000±3500 -	1.00±0.02 1.07±0.03

ally, the initial organo-mineral complex of shells contains only very little uranium.

Fossil mollusc shells have as high as two orders of magnitude higher uranium concentration (**Table 2**) than recent shells (**Table 1**). In most cases the uranium concentration was slightly lower in the inner part than in the outer layer (Arslanov *et al.*, 1975).

The $^{234}U/^{238}U$ activity ratio was higher than the average value of seawater of 1.14±0.014 (Arslanov *et al.*, 1976). It is known that groundwater often has a higher $^{234}U/^{238}U$ ratio (Cherdyntsev, 1969).

^{232}Th and ^{230}Th activities were determined from the surface of nine fossil mollusc shells (**Table 3**). All samples contained adsorbed detrital thorium. Only two out of 33 mollusc shells contained ^{232}Th in the outer layer. ^{232}Th was absent in the inner layer of all analyzed samples.

The reliability of the modified ^{230}Th/U method was checked by complementary radiocarbon dating of eight stratigraphically well-dated Holocene and Late Glacial mollusc shells (**Table 4**). In addition, fossil Pleistocene mollusc shells from Lower Khazarian deposits of the Caspian Sea with age ≥300 ka were dated. The ^{14}C dates were reservoir-corrected by subtracting of 384±59 years for Caspian shells and calibrated using the Groningen Radiocarbon Calibration Program Cal-25.

The modified ^{230}Th/U dating method was applied to transgressive sediments in the White, Barents and Black Seas. The large Karangat transgression of the Black Sea and the Boreal (Eemian) transgression and study of the White and Barents Seas are correlated with Mikulino Interglacial (MIS 5e) based on the results of microfaunal, diatom, pollen and lithostratigraphic investigations of thermophile species of shells (Arslanov *et al.*, 1981 and 1983). According to the chronology of MIS (oxygen-isotope record from deep-sea cores; Martinson *et al.*, 1987), MIS 5e (Eemian, Sangamon – 125 to 115 ka) corresponds to the Mikulino Interglacial. Hence, the mollusc shells from the geochronostratigraphic reference sections for the Karangat and Boreal transgressions are considered as stratigraphically well-dated.

Thick-walled and well-preserved mollusc shells from transgressive sediments of the Barents, White and Black Seas were selected for dating. Most of the results are

Table 3. *Specific activity of thorium isotopes of fossil mollusc shells (in dpm/g).*

Sample No	Surface		Outer layer		Inner part	
	^{232}Th	^{230}Th	^{232}Th	^{230}Th	^{232}Th	^{230}Th
LU-424	0.036	0.283	≤ 0.005	0.181	≤ 0.005	0.200
LU-421	0.015	0.076	≤ 0.005	0.060	≤ 0.005	0.066
LU-420	0.012	0.031	≤ 0.005	0.012	≤ 0.005	0.016
LU-413	0.029	0.219	≤ 0.005	0.150	≤ 0.005	0.150
LU-430	0.140	1.712	≤ 0.005	1.669	≤ 0.005	1.662
LU-436	0.086	0.952	≤ 0.005	0.752	≤ 0.005	-
LU-414	0.079	0.136	≤ 0.005	0.043	≤ 0.005	0.043
LU-432	0.040	1.940	≤ 0.005	1.916	≤ 0.005	1.916
LU-428	0.050	1.079	≤ 0.005	0.993	≤ 0.005	0.993
LU-192	-	-	≤ 0.005	0.428	≤ 0.005	0.400
LU-424	-	-	≤ 0.005	0.181	≤ 0.005	0.200
LU-190	-	-	≤ 0.005	0.010	≤ 0.005	0.012
LU-191	-	-	≤ 0.005	0.050	≤ 0.005	0.040
LU-422	-	-	≤ 0.005	-	≤ 0.005	0.040
LU-193	-	-	≤ 0.005	0.143	≤ 0.005	0.179
LU-423	-	-	≤ 0.005	-	≤ 0.005	0.234
LU-400	-	-	≤ 0.005	-	≤ 0.005	1.310
LU-429	-	-	≤ 0.005	1.134	≤ 0.005	-
LU-435	-	-	≤ 0.005	-	≤ 0.005	2.266
LU-401	-	-	≤ 0.005	-	≤ 0.005	1.735
LU-434	-	-	≤ 0.005	1.362	≤ 0.005	1.307
LU-431	-	-	≤ 0.005	8.619	≤ 0.005	8.595
LU-308	-	-	≤ 0.005	-	≤ 0.005	0.007
LU-413	-	-	≤ 0.005	-	≤ 0.005	0.150
LU-402	-	-	≤ 0.005	0.229	≤ 0.005	0.193
LU-403	-	-	≤ 0.005	0.738	≤ 0.005	0.679
LU-404	-	-	≤ 0.005	0.400	≤ 0.005	0.522
LU-410	-	-	≤ 0.005	1.059	≤ 0.005	0.926
LU-406	-	-	≤ 0.005	0.415	≤ 0.005	0.362
LU-450	-	-	≤ 0.224	0.245	≤ 0.005	0.243
LU-448	-	-	≤ 0.166	1.053	≤ 0.005	0.759
LU-449	-	-	≤ 0.005	-	≤ 0.005	0.522

Table 4. *^{230}Th/U and ^{14}C ages of mollusc shells from the Caspian Sea. A=outer layer and B=inner part.*

Mollusc species and location	Lab. No	^{14}C Age [BP]	Age [Cal BP]	^{230}Th / U Age [BP]
Cardium edule, Zorat Settl., Azerbaijan	LU-476B	1510±70	1511 – 1313	1330±300
Cardium edule, Mamedkala Settl., Dagestan Republic	LU-190B	2050±90	2145 – 1897	≤ 2450
Cardium edule, Shirvan area, Azerbaijan	LU-422B	3400±90	3821 – 3481	4100±300
Dzhorat settl., Apsheron peningula, Azerbaijan	LU-421B	5540±110	6445 – 6200	6400±300
Didacna paralella, near Manas River mouth,	LU-426A	11,600±400	14,000 – 13,100	12,700±450
Dagestan Republic	LU-426B	-	-	12,700±450
At 48-th km from Baku, between railway stations	LU-479B	11,550±90	13,795 – 13,425	11,800±350
Nasosnaya and Jashma, Azerbaijan	LU-479A	11,680±160	13,820 – 13,485	12,900±350
Didacna sp. Shirvan, Azerbaijan	LU-423B	12,330±140	15,055 – 14,125	14,400±400
Didacna sp., near Maloye Turaly Lake, Dagestan Republic	LU-424B	12,720±400	15,600 – 14,425	13,800±440

already published in Russian (Arslanov *et al.*, 1981 and 1983). Only the samples LU-4202-4215 submitted by A. Dodonov in 1998 were recently analyzed **Table 5**.

The inner part of the mollusc shells from Boreal transgression deposits of the White and Barents Seas yielded ^{230}Th/U ages of 86-114 ka, whereas that of shells from the Karangat transgression of the Black Sea (Maly Kut, Eltigen sequences) ranged between 102 and 130 ka. Mollusc shells found with paired valves under living conditions from the estuary clay section of Cape Krotkov were dated to 98-100 ka (**Table 5**). This clay sequence contained 93 – 98% pollen of wood species (pine pollen: 55-65%; spruce pollen: 27-35%; birch pollen: 12%; Arslanov *et al.*, 1983). Single pollen of beech, elm and oak represent broad-leaved species. This pollen assemblage essentially corresponds to that of the taiga forest and, most likely, correlates with the beginning of the Valdai (Weichselian) Glaciation.

4. DISCUSSION

Shells of an age of 1.5-2.0 ka contained up to two orders of magnitude more uranium than recent shells. However, we did not found a strong correlation between the uranium concentration and the ^{230}Th/U age. Hence, the incorporation of the major portion of uranium into shells ceases after several thousands of years in agreement with the findings by Broecker (1963). The decomposition of the organic matter of the mollusc shells enables the incorporation of uranium into the porous structure. Uranium is incorporated into mollusc shells as more or less soluble salts (uranotallite, swartzite and andersonite) or as complex uranium compounds with albumen present in the conchiolin of the shells.

The ^{234}U/^{238}U activity ratio >1.15 gives evidence that the major portion of uranium in shells stems from groundwater and is postsedimentarily incorporated.

Table 5. *^{230}Th /U Ages of marine mollusc shells from transgression sediments of the Barents, White and Black Seas. A = outer layer and B = inner part.*

Lab. No	Age [BP]	Mollusc species and location
LU-455B	97,000±4000	*Cyprina islandica* from the section base, Svjatonossky gulf, Kola peninsula
LU-452A	102,000±4000	*Astarta borealis* from the Malaja Kachovka exposure, Kola peninsula
LU-452B	114,000±4000	
LU-464A	85,500±3200	*Cyprina islandica* from the exposure On Chapoma River, Kola peninsula
LU-464B	86,000±3900	
LU-808A	129,400±4900	*Cardium edule* from the marine sediments of Maly Kut section, Taman peninsula
LU-808B	115,000±3100	Same as above
LU-805A	125,000±5000	*Paphia senessens* from the middle part of the marine sediments of Eltigen section, eastem coast of Kerch strait
LU-805B	102,290±3200	*Paphia senessens* from the middle part of the marine sediments of Eltigen section, eastem coast of Kerch strait
LU-802A	90,600±3100	*Cardium tuberculatum* from the same layer
LU-802B	107,400±3800	*Cardium tuberculatum* from the same layer
LU-804-1A	88,900±2200	*Cardium edule* from the Krotkov cape section, westem part of Taman peninsula
LU-804-1B	98,000±2400	Same as above
LU-804-2A	98,900±2200	Same as above
LU-804-2B	100,500±2100	Same as above
LU-4022B	127,000±8900	Thick-wall, good preserved shells from the marine sediments of Eltigen Sections, eastern coast of Kerch strait depth 2.6 m a.s.l.
LU-4203	107,000±7700	Same as above, depth 8.0 m a.s.l.
LU-4214	127,000±7700	Same as above, depth 13.8 m a.s.l.
LU-4205	117,000±11000	Same as above, depth 14.3 m a.s.l.
LU-4215	122,000±9600	Same as above, depth 14.8 – 15,8 m a.s.l.

Recent mollusc shells do not contain noticeable specific activities of ^{232}Th and ^{230}Th while fossil mollusc shells often do. Sometimes, the activity of ^{232}Th even exceeds that of ^{230}Th (Blanchard *et al.*, 1967).

At pH>5 soluble thorium compounds become hydrolyzed and dissolved as colloids in groundwater even if thorium is present in micro quantities (Starik, 1959). Generation of colloids $Th(OH)_5$ hydroxyd is possible due to the product of solubility PS $[Th(OH)_5] = 10^{-45}$. Colloids are easily adsorbed on the surface of shells; diffusion does not seem to play any role as reflected from comparison of the ^{232}Th and ^{230}Th activity ratio for the surface, the outer layer and the inner part of fossil mollusc shells (**Table 3**).

This finding confirms that the main prerequisites of the uranium-thorium method are fulfilled for the dating of mollusc shells: 1) thorium migration in shells is strongly limited to the surface; 2) removal of the surface and the outer layer discards all detrital thorium and allows ^{230}Th/U dating of mollusc shells without the ambiguous detrital correction with the ^{232}Th.

The common ^{230}Th/U and calibrated ^{14}C dates of most samples (LU-423, 424, 426 and 479; **Table 4**) agree within their two-sigma confidence intervals. This gave evidence that the basic assumption conditions of the ^{230}Th/U method were fulfilled: uranium became incorporated into the mollusc shells soon after their deposition into sediments. The reliability of the concordant dates of the two geochemically different elements uranium and carbon is confirmed.

The ^{230}Th/U age of ≥300 ka of the fossil mollusc shells from the Lower Khazarian also confirm the fulfillment of the principles this ^{230}Th/U dating method: any uranium and ^{230}Th migration (diffusion) at a later time would have resulted in a deviation of the ^{230}Th/^{234}U ratio from unity.

Based on our experience and described findings mollusc shells to be used for ^{230}Th/U dating should have the following properties (Arslanov *et al.*, 1976):

1) they should be at least 1 mm thick, not weathered or calcified, non-layered and mechanically stable, not ferruginous and consists of aragonite;

2) suitable mollusc species are: *Cardium edule, Chione gallina, Paphia senescens, Cyprina islandica, Astarta borealis* and Caspian *Didacna*. Shells with flaky structure such as *Mytilus edule, Clamus glabra, Ostrea edulis* were often been poorly preserved and may give ambiguous dates;

3) mollusc shells should not contain ^{232}Th in the dated fraction or anomalous concentrations of uranium.

5. CONCLUSIONS

The major part of uranium is incorporated into mollusc shells during no more than 1.5-2 ka after their deposition into sediments. The inner part of recent and fossil shells did never not contain ^{232}Th and are suitable for ^{230}Th/U dating. ^{232}Th became only adsorbed at the surface of shells.

^{230}Th/U and calibrated ^{14}C dates agree well for shells with ages up to 15 ka. Similar agreement is found with the stratigraphically dated mollusc shells of Middle Pleistocene age.

The ^{230}Th/U ages of the inner part of shells from Boreal (Eem) transgression sediments of both the Barents and White Seas ranged from 86 to 114 ka while those from the Black Sea Karangat transgression ranged from 102 to 130 ka. The lower limit of these dates may indicate a slight uranium accumulation as the Mikulino (Eem) Interglacial lasted from 116 to 128 ka (MIS 5e). In any case, the modified ^{230}Th/U method yields most reliable absolute dates in the age of 0-350 ka.

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Table 6. *Comparison of Russian terms for glacials, interglacials and marine transgressions with corresponding European terms and global term MIS.*

Russian term	European term	MIS
Late Valdai	Late Weichselian	2
Middle Valdai	Middle Weichselian	3
Early Valdai	Early Weichselian	4, 5a,b,c
Mikulino Interglacial	Eemian	5e
Boreal transgression	Eemian, Boreal	5e
Karangat transgressiion (Eltigen, Maly Kut sections)	Eemian	5e
Late Khazar transgression	Late Weichselian	2
Lower Khazar transgression	Holsteinian	9 and/or 11

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