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Perspectives of application of the 230Th/U method of geochronometry for determining the age of Quarternary fossil fauna of the Arctic region

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Abstract. Perspectives of the 230Th/U method for dating the fossil bones of mammoths, widespread in sediments of the Arctic region, are considered. Determination of uranium and thorium contents in well-preserved mammoth bone samples with known radiocarbon age was carried out and the prerequisites for the 230Th/U method were tested. It was revealed that the external and middle layers of bones can be geochemical barriers that make it difficult for dissolved uranium to enter the internal layers during post-sedimentation time. Thus, the internal layers can be attributed to conditionally closed radiometric systems. In some cases, 230Th/U age of these layers is similar to radiocarbon data. 230Th/U age in the range of 100 thousand years was obtained for the sample with the direct radiocarbon age. The results suggest that using the 230Th/U method for determining the age of mammoth bones is possible under certain conditions.

1. Introduction

One of the actual question related to the study of the Quaternary period is the history of the settlement of the Pleistocene mammals. The determination and change of habitats of extinct animals makes it possible to significantly expand the understanding of the climate and paleobiogeographic environments in the Pleistocene. Bone residues are preserved in permafrost sediments especially well, which fully applies to the Arctic region.

Reconstruction of mammals, including large extinct species (mammoth, woolly rhino and others), is mainly carried out within the limits of the 14C method and is associated with time interval the last 40-50 thousand years (Markova et al., 2010, 2015). The widespread use of the 14C method for dating bone residues of the mammoth fauna has allowed for the past 20-30 years to obtain outstanding scientific results. On the basis of the large collections of dated bones, fluctuations of habitats and the time of local extinctions of certain species of animals were established. Morphological, paleogenetic, isotope and other analytical studies were carried out (Vartanyan et al., 1995, 2008; Sher et al., 2005; Lister, Stuart, 2008; Palkopoulou et al., 2015).

However, the chronology of the earlier stages of the settlement of mammals that are outside the limits of the action of the 14C method has been studied much worse. The stratigraphic method does not provide the necessary accuracy in determining the age of the enclosing sediments and, accordingly, fossil bones. Bone residues are easily re-deposited, sampling directly from the incisions does not guarantee the synchronicity of the sample and the layer in which it was found. In addition, most bones are found under sea, river or lake cliffs without reference to a specific horizon; the age of individual bones from one location may differ by tens of thousands of years. Finally, despite the active development of various methods of geochronometry in recent decades, still quantitative dating of fossil bones, especially outside of the capabilities of the 14C method, is under development.

2. Materials and methods

In this paper, we turned to the 230Th/U method with a dating limit of up to 350 thousand years, which is considered promising for determining the age of bone residues. According to the literature, the main difficulties in obtaining reliable quantitative estimates of 230Th/U age of fossil bone are associated with the feasibility of the assumptions of this method, which are formulated as follows: 1) at the time of its formation, natural material includes only uranium, from which, over time, as a result of radioactive decay, the daughter isotope 230Th accumulates; 2) the dated material at post-sedimentation time is a closed radiometric system for uranium and thorium isotopes. It was previously found that at the time of its formation, bone material contains small amounts of uranium, whereas fossil bones contain more than 10-100 times more (Szabo, 1980; Schwarcz, 1982). Thus, the question of the processes and time intervals of absorption of uranium and thorium in the burial of bones has appeared. Some authors proposed the "early uptake model". It was assumed that the adsorption of uranium by bone remains occurs only in the first few thousand years after their burial by infiltration of groundwater enriched in uranium (Rae, Ivanovich, 1986; Grun et al., 2010). After this period, the bone material behaves as a closed radiometric system in relation to uranium isotopes and the thorium radiogenic isotope - 230Th. Later, other approaches were proposed: «massive recent uptake» (Pike et al., 2002); «linear uptake model»; «diffusion-adsorption model»; «diffusion-adsorption-decay model» (Bischoff et al. 1995; Pike et al., 2005; Sambridge et al. 2012). The latter of the above models of the distribution of uranium and thorium are analytically laborious and difficult to calculate, and also significantly depend on many environment factors (paleo-hydrological setting, the degree of preservation of bone material, etc.). In this case, the results obtained are very conditional. In this aspect, simple models associated with direct dating (or simple correction of analytical data) of individual layers or fractions are probably more suitable for understanding the real situation. The aim of our work was to try to assess the perspectives of the application of the 230Th/U method for dating the fossil bones of mammoths, widespread in sediments of the Arctic region. Samples of well-preserved (dense) mammoth bones with known radiocarbon age, provided by S. Vartanyan (Northeast Interdisciplinary Research Institute, Far East Branch, Russian Academy of Sciences, Magadan) and Baranskaya A.V. (Lomonosov Moscow State University), were used as experimental material. To solve the problem, it was planned to perform the following analytical work. It was necessary to develop a simple method for the radiometric determination of uranium and thorium isotopes in bone material. It was necessary to study the distribution of uranium and thorium isotopes between the mineral and organic components of bone residues, as well as the layer-by- layer distribution of uranium and thorium isotopes from the edge to the center along the perpendicular sections of the bone samples.

The main problem arising in the quantitative determination of uranium and thorium isotopes in bone material is associated with a high phosphate content. The ion exchange resin used in the analysis loses the ability to absorb thorium isotopes after high concentrations of phosphate ions in the prepared solution (Choukri, 1994). Only when reaching sufficiently low concentrations of phosphate ions (~0.08 mol/l) does the resin begin to absorb thorium ions. On the basis of this, as well as the well-known radiochemical techniques, we proposed a method for the determination of uranium and thorium isotopes in bone material.

3. Results and discussion

It was shown for one sample that more than 95% of uranium and thorium are concentrated in the mineral skeleton, whereas the organic component of mammoth bones - collagen contains no more than 2% of their total content in bone samples (table 1). Therefore, the variant where it was proposed to use collagen as a fraction suitable for dating 230Th/U (Hercman, 2014) seems to be unproductive. The study of the layer-by-layer distribution of uranium and thorium isotopes was carried out in fractions selected along the perpendicular section of the mammoth's tusk, as well as the mammoth femur. The obtained results (table 2) indicate a low concentration of uranium and thorium isotopes in the samples provided, this applies especially to mammoth tusks. This factor explains the rather substantial errors of the specific activities of isotopes and their relations.

Table 1. The results of radiochemical analysis of U and Th isotopes in mineral and organic fractions of mammoth bone residues and their 230Th/U age.

Fraction	% by weight	^{238}U	^{234}U	^{230}Th	^{232}Th	$\frac{^{230}Th}{^{232}Th}$	$\frac{^{230}Th}{^{234}U}$	$\frac{^{234}U}{^{238}U}$	Age, ka
		dpm/g							
Mammoth lower jawbone, Chukotka, 14C-age 28680 ± 140 BP (32780± 280 calBP)									
mineral matrix	91,65	0,258± ±0,013	0,348± ±0,016	0,055± ±0,004	0,020± ±0,003	2,734± ±0,418	0,157± ±0,014	1,351± ±0,082	18,4±1,7
collagen	7,27	0,004± ±0,001	0,007± ±0,002	-	-	-	-	1,660± ±0,517	-
insoluble residue	1,08	0,011± ±0,002	0,012± ±0,002	0,010± ±0,002	0,010± ±0,001	1,037± ±0,214	0,889± ±0,198	1,119± ±0,238	-

Table 2. The results of radiochemical analysis of U and Th isotopes in different fractions of mammoth bone residues and their 230Th/U age.

fraction	R1-R2[1], mm	^{238}U	^{234}U	^{230}Th	^{232}Th	$\frac{^{230}Th}{^{232}Th}$	$\frac{^{230}Th}{^{234}U}$	$\frac{^{234}U}{^{238}U}$	Age, ka
		dpm/g							
Sample № 1 – mammoth femur, Chukotka, 14C-age 46350 ± 650 BP (49720 ± 1970 calBP)									
external	-15 – -9	0,181± ±0,012	0,279± ±0,015	0,036± ±0,003	0,013± ±0,002	2,67± ±0,42	0,13± ±0,01	1,54± ±0,12	15±2
middle	-9 – -2	0,057± ±0,004	0,061± ±0,005	0,011± ±0,001	0,005± ±0,001	2,17± ±0,48	0,19± ±0,03	1,06± ±0,11	22±3
internal	-2 – 2	0,055± ±0,005	0,057± ±0,006	0,020± ±0,003	0,020± ±0,003	0,99± ±0,22	0,34± ±0,07	1,04± ±0,15	45±12
middle	4 – 10	0,018± ±0,001	0,020± ±0,002	0,007± ±0,002	0,006± ±0,001	1,16± ±0,35	0,36± ±0,09	1,16± ±0,14	48±15
external	10 – 15	0,118± ±0,008	0,162± ±0,009	0,024± ±0,002	0,023± ±0,002	1,03± ±0,12	0,15± ±0,01	1,37± ±0,12	17±2
Sample № 2 – fragment of mammoth tusk, Yamal, 14C-age 35130±790 BP (39780±840 calBP)									
external	30-38	0,030± ±0,012	0,059± ±0,014	0,025± ±0,005	0,019± ±0,005	1,31± ± 0,42	0,43± ± 0,13	1,99± ±0,93	58±25
middle	14-23	≤0,020	≤0,029	≤0,018	≤0,012		≤0,62	≤ ,45	≤98
middle	10-14	0,042± ±0,009	0,089± ±0,012	0,032± ±0,006	0,017± ±0,006	1,92± ± 0,74	0,36± ±0,08	2,10± ±0,54	46±13
internal	0-10	≤0,010	≤0,025	≤ 0,009	≤ 0,003		≤ 0,35	≤ 2,43	≤45
Sample № 3 – fragment of mammoth tusk, Chukotka, 14C-age 31470±180 BP (35350±230 calBP)									
middle	10-23	0,033± ±0,004	0,044± ±0,004	0,020± ±0,003	0,012± ±0,002	1,59± ±0,38	0,45± ±0,07	1,33± ±0,18	63±14
internal	0-10	0,049± ±0,004	0,070± ±0,005	0,038± ±0,003	0,029± ±0,003	1,29± ±0,18	0,54± ±0,06	1,43± ±0,16	80±13
Sample № 4 – fragment of mammoth tusk (end section), Chukotka, 14C-age ≥ 55700 BP									
external	30-40	0,023± ±0,003	0,035± ±0,004	0,013± ±0,003	-	-	0,36± ±0,10	1,55± ±0,25	47±16
internal	0-10	0,016± ±0,002	0,030± ±0,003	0,020± ±0,002	≤ 0,005	≥ 4,21	0,67± ±0,10	1,88± ±0,32	108±28

[1]R1-R2 is a bone layer enclosed between R1 and R2, where R1 and R2 are the distances in mm from the center ("0" mm) along the perpendicular section to the edges of the sample.

Experimental data show a relatively regular distribution of uranium in layers along the perpendicular section of the mammoth femur (sample № 1). The highest concentrations of uranium are recorded in the external layers and the lowest in the internal layers. The smallest values of the direct 230Th/U age are noted for the external layers and the largest for the internal layers. Moreover, for the external and middle layers, rejuvenation compared to the radiocarbon age is very significant, whereas for the internal layers of the direct 230Th/U age is conventionally close to the radiocarbon. These data allow us to make an assumption about the post-sedimentary uptake of dissolved uranium into the external and middle layers, probably not only during the first few thousand years after the burial of the bones, but at a much later period. At the same time, these layers act as a kind of geochemical barrier and to some extent prevent the penetration of uranium into the internal layers of bone material. Thus, the inside of the bone can more corresponding to a closed radiometric system (Maksimov et al., 2017). However, this is rather conditional, since 232Th was found in the internal layers (as in the others), indicating that the carbonate-phosphate skeleton is contaminated with thorium and uranium isotopes of the mineral detritus, which can distort the direct 230Th/U age of dated material.

The uranium content along the end section of sample № 2 varies little, only in the internal layers it is less than in the rest. The detrital contamination in the internal layers is also the smallest (or even it may even be said not), and here the smallest direct 230Th/U age is recorded. Despite a approximate estimate of 230Th/U age, only it can correlate with a calibrated radiocarbon age.

The concentration of uranium in the internal layers is higher than in the middle fraction in sample № 3. Detrital contamination is higher also in the internal layers. At the same time, the direct 230Th/U age of both fractions clearly exceeds the calibrated radiocarbon age. Taking into account the fairly significant amount of detrital contamination, it can be assumed that mineral detritus got into the bone material at the time close to its burial. Accordingly, the aging of the direct 230Th/U age occurs. A simple detrital correction can be introduced to exclude from calculations uranium and thorium isotopes belonging to the mineral detritus (Allard et al., 2012). In this case, the corrected 230Th/U age of both fractions will be close to the calibrated radiocarbon age. This circumstance indicates that the infiltration of dissolved uranium to the mammoth tusk during the post-sedimentation time did not occur or was minimized.

Finally, let us turn to the results of the study of sample № 4, for which an nonfinite radiocarbon age was previously established. The uranium content in the internal layers is somewhat less than in the external layers. Detrital contamination is minimally in both fractions. Direct 230Th/U dates are significantly different from each other and, apparently, indicate the post-sedimentation uptake of dissolved uranium in the bone material. At the same time, the entry of uranium into the external layers rejuvenated their 230Th/U age, which is less than the radiocarbon data. Less uranium has entered the internal layers and their 230Th/U age does not contradict the radiocarbon data. Therefore, it can be assumed that the external layers act as a geochemical barrier and impede the infiltration of uranium into the internal layers of bone material. The internal layers can be considered conditionally closed radiometric system, since it is impossible to completely exclude the uptake of uranium into them in the post-sedimentation time. Accordingly, their direct 230Th/U-ages can be considered the minimum possible age estimate.

Obtained data on samples № 2 and № 3 do not deny the «early uptake model», in which uranium is absorbed only in the first few thousand years after the burial of bone material. Whereas «massive recent uptake» model is realized for samples № 1 and № 4. In this case the post-sedimentation uptake of dissolved uranium into bones occurred in a much later period after their burial. The external and middle layers of all studied samples are open radiometric systems. They are also geochemical barriers and make it difficult for uranium to uptake into the internal layers. Latter can be attributed to conditionally closed radiometric systems. Partial contamination of the carbonate-phosphate skeleton with thorium and uranium of detrital origin complicates the situation. This distorts (most likely increases) the direct 230Th/U age. Detritus enters the bone material, probably immediately after burial. Only in this case, correction of analytical data is possible, but only with the known isotopic composition of detritus.

Thus, the basic assumptions of the 230Th/U method for a number of fractions (more often external) of mammoth bones are not fulfilled, whereas for the internal layers it is possible to implement them (sometimes partial). Estimation of the direct 230Th/U age of the internal layers does not contradict the radiocarbon data.

4. Conclusions

The results obtained by us suggest that the possibility of determining the age of the mammoth bones by 230Th/U method is quite realistic under certain conditions. For dating it is better to use dense, well-preserved fragments of bones, preferably selected in permafrost. Due to the low concentrations of uranium and thorium isotopes in the bone material, large weights should be taken for analysis or mass spectrometry should be used (more preferably). It is necessary to determine the content of uranium and thorium isotopes in layers from the external layer of the bone to the internal layer. All this will allow us to test the feasibility of the prerequisites for the 230Th/U method and to obtain adequate estimates of the quantitative age of bone.

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