Chapter 17

Radiocarbon dating of remnants of woolly rhinoceroses and mammoth from Starunia, fore-Carpathian region, Ukraine

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Abstract

The radiocarbon method has been applied several times over the past three decades to determine the age of famous mammoth and woolly rhinoceroses remnants excavated in the Starunia area, at the beginning of the 20th century. Altogether, seven laboratories from five countries representing three different measurement techniques took part in those trials, these repeated efforts remained largely unsuccessful. The radiocarbon ages obtained to date for five different specimens of mammoth and woolly rhinoceroses range from ca. 14 to 47 kyr BP. This range is characteristic for the whole set of dated samples as well as for the same sample dated with different techniques. As a result, no conclusion can be drawn so far from radiocarbon dates with respect to mutual chronology of the excavated specimens. The peculiar nature of the dated samples (bones and soft tissue soaked with oil and brine) is the most probable reason for serious difficulties encountered in the process of obtaining reliable radiocarbon ages. Complete removal of ^{14}C-free hydrocarbons from the dated samples turned out to be very difficult. Also, long-term *in situ* interaction between liquid hydrocarbons and organic material leading to significant aging effect in terms of radiocarbon ages cannot be ruled out at this stage. Comparison of radiocarbon dates obtained recently in Kraków and Poznań suggests two probable ranges for the true age of the Starunia specimens: the range around 42 kyr BP suggested mainly by the AMS dates, and around 26 kyr BP. Both ranges appear equally probable. Comprehensive, systematic studies of suitable cleaning procedures for the Starunia specimens would be needed to resolve the ambiguity of currently available ages.

Keywords: radiocarbon dating, AMS dating, contamination, woolly rhinoceros, mammoth, Starunia, Ukraine.

1. Introduction

Palaeontological finds in the Starunia area where earth wax (ozokerite) had been exploited between 1868 and 1960 (Bojko, Sozański, 2004; Alexandrowicz, 2005, this volume; Koltun *et al.*, 2005, this volume) become famous world-wide at the beginning of 20th century. Carcasses or their fragments of large Pleistocene mammals excavated there were preserved in exceptionally good state (Stach, 1930). In two campaigns in 1907 and 1929, remnants of one woolly mammoth (*Mammuthus primigenius*) and four woolly rhinoceroses (*Coelodonta antiquitatis*) were found, among which one rhinoceros was in a completely-preserved state (Alexandrowicz, 2005, this volume; Kubiak, Drygant, 2005, this volume). The exceptionally low degree of degradation of organic tissues resulted from peculiar chemical properties of the surrounding environment. Oil, ozokerite and salty water impregnated organic material (Tokarski, 1930; Kotarba, 2005, this volume), making it resistant to decomposition by weak acids present in the soil as well as bacteria and fungi.

Attempts to date the mammoth and rhinoceroses remnants using radiocarbon technique go back to the 1970s (Kubiak, 1971; Kubiak, 2003). New ^{14}C datings of this exce-

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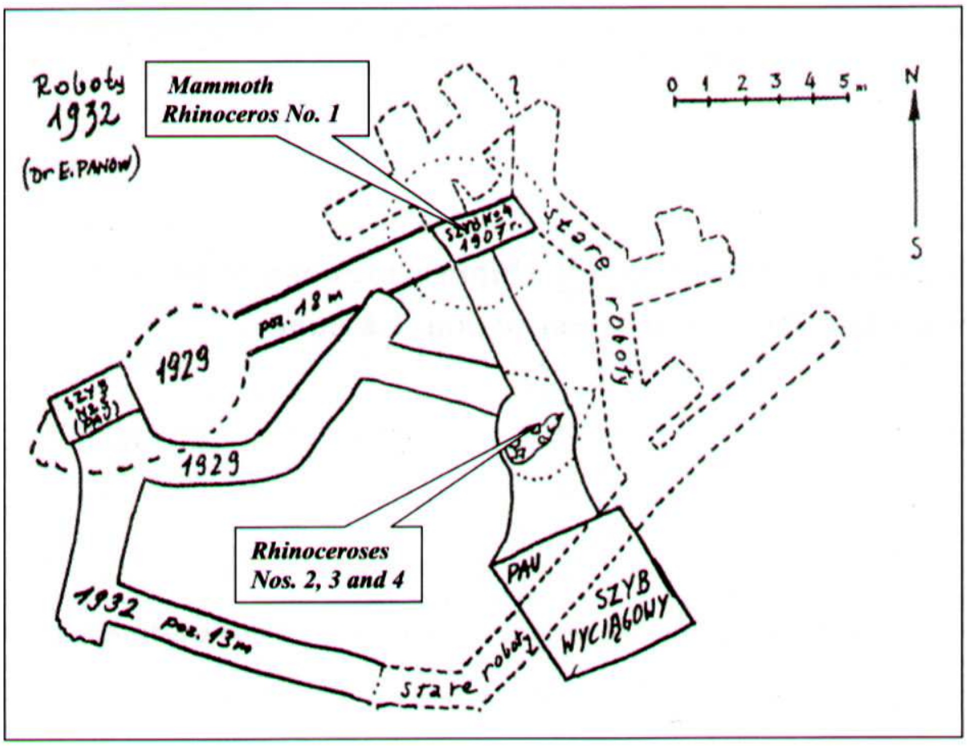

Fig. 1. Sketch-map of the mine workings at the Starunia site. Original drawing by E. Panow (after Alexandrowicz, 2004), with indicated places of extinct mammals findings

ptional material were undertaken in 2005, in the framework of an interdisciplinary project aimed at comprehensive characterization of the Starunia site and the surrounding region by providing new geophysical, geochemical and hydrological data related to surface appearances of oil, gas and salty water. These fluids were crucial to preservation of excavated fragments of Pleistocene mammals on this site.

The Starunia site is located in the region where brines have been exploited since the 14th century and oil was produced for local purposes. Ozokerite deposits discovered in the 19th century became the dominant raw material exploited on an industrial scale in this region (Alexandrowicz, 2004).

In shaft No. IV of the ozokerite mine in Starunia, at a depth of 12.5 m, fragments of a mammoth (*Mammuthus primigenius*) were found in 1907 (Fig. 1). Subsequent works in shaft No. IV (later re-named "Mammoth Shaft") led to the discovery of parts of the "first" woolly rhinoceros (*Coelodonta antiquitatis*), consisting of large fragments of skeleton and soft tissue. They were discovered at a depth of 17.6 m, i.e. ca. 5 m below the position of the mammoth remnants. Eventually, both findings were transported to the Dzieduszycki's Museum (today Natural History Museum) in Lviv where relevant preparatory and conservation treatment was undertaken (Alexandowicz, 2004).

In 1928, the Polish Academy of Arts and Sciences obtained funds for interdisciplinary investigations of the Starunia. A new shaft was constructed under supervision of Dr. E. Panow. About 15 m from the old shaft No. IV, a new one was dug to a depth of ca. 18 m and a gallery joining both shafts was cut (Fig. 1). In October, 1929, in another gallery, at the depth ca 12.5 m, an almost complete body of the "second" woolly rhinoceros in upside down position (lying on its back) was found (Stach, 1930). The rhinoceros was discovered at a distance of 3.3 m from the "Mammoth Shaft" (Fig. 1). In December of 1929, the rhinoceros was transported to the Museum of Physiography of the Polish Academy of Arts and Sciences in Kraków. Detailed description of this finding and associated research works were given by Nowak and Panow (1930), Tokarski (1930), Szafer (1930) and Stach (1930).

The later works revealed remnants of next, "third" rhinoceros specimen consisting only of bones, however in a good state of preservation. These were placed ca. 1.5 m above the former, "second" rhinoceros, very close to it in a horizontal direction. After a careful examination of the skeleton, some bones were found belonging to a younger specimen that was described as "fourth" woolly rhinoceros (Kubiak *in*: Alexandrowicz, 2002, Kubiak, 2003).

Pleistocene mammals excavated in Starunia are actually stored in museums of two towns: Lviv and Kraków (cf. Table 1). However, detailed studies on rhinoceroses from Starunia were continued (Kubiak, Dziurdzik, 1973; Bigaj *et al.*,1976; Kubiak, 1994).

2. Radiocarbon datings of mammoth and rhinoceros remnants

The first attempts to determine the age of the remnants of mammoth and wooly rhinoceroses excavated in the Starunia site using the radiocarbon technique were undertaken in the early 1970s. Soft tissue (skin) belonging to the "second" rhinoceros was dated to ca. 23 kyr BP and 36.2 kyr BP by two different laboratories (SI, Hv — cf. Tables 1 and 2). In subsequent years, samples of mammoth as well as the "first" and "third" rhinoceroses (both soft tissues and bones) were dated by two other laboratories which were using two different conventional techniques: gas proportional counting (GC) and benzene synthesis followed by liquid scintillation counting (LSC). New AMS radiocarbon dating technique was employed in 2002. Samples of all four rhinoceros specimens were dated by the Oxford Radiocarbon Accelerator Unit. The attempt failed except for the "first" rhinoceros for which the age of 42.1 kyr BP (BP: before present) was obtained. In the framework of the present study, a renewed attempt was made to date all available material using both conventional (radiometric) and the AMS techniques.

Table 1 summarizes the currently available information about each specimen which was subjected to radiocarbon dating. This table also contains names of radiocarbon laboratories which were engaged in ^{14}C analyses. As can be seen from Table 1, seven laboratories participating in these trials were using three different measurement techniques. Two laboratories (Radiocarbon Laboratory, Silesian University of Technology, Poland (Pazdur *et al.*, 2003), and Nieddersächsiches Landesamt für Bodenforschung, Germany), used gas proportional counters (GC), applying as a filling gas CO_2 and C_2H_2, respectively. Benzene synthesis followed by liquid scintillation spectrometry (LSC) was used by three laboratories: Smithsonian Institution, Radiation Biology Laboratory, ^{14}C Laboratory, Maryland, USA; Kraków Radiocarbon Laboratory, AGH-University of Science and Technology, Poland (Florkowski *et al.*, 1975; preparatory procedure of bones after Longin, 1971 and Arslanov, Svezhentsev, 1993) and Geological Institute of the Russian Academy of Science, Russia (Sulerzhitsky, 1997). The accelerator mass spectrometry technique (AMS) was applied by two laboratories: Poznań Radiocarbon Laboratory, Foundation of the Adam Mickiewicz University, Poland (Goslar *et al.*, 2004; preparatory procedure of bones after Longin, 1971, Piotrowska, Goslar, 2002, and Lanting *et al.*, 2001) and Oxford Radiocarbon Accelerator Unit, Research Laboratory for Archaeology and History of Art., England (Ramsey *et al.*, 2004).

Table 2 summarizes all radiocarbon dates available to date for mammoth and rhinoceroses remnants from the Starunia excavation site. For remnants of *Mammuthus primigenius* three different radiocarbon dates were obtained by three laboratories: 22.6 kyr BP, 35.1 kyr BP and 45 kyr BP. The first two were obtained for soft tissue whereas the last one is related to bone (collagen fraction).

The "first" woolly rhinoceros was dated by two laboratories which reported ages of 14.17 kyr BP and 42.15 kyr

Table 1

Material available for radiocarbon dating from the Starunia excavation area

Description of the object	Place of storage	Type of dated material	Dating laboratory	Laboratory code	Remarks
Mammuthus primigenius (woolly mammoth)	Museum of Natural Sciences, Lviv, Ukraine	soft tissue	Radiocarbon Laboratory, Silesian University of Technology, Poland	Gd	parts of skeleton, skin, muscle, shaft No. IV, depth: 12.5 m, found: autumn 1907
		soft tissue	Geological Institute, Russian Academy of Sciences, Russia	GIN	
		bone, part of vertebra	Poznań Radiocarbon Laboratory, Foundation of the Adam Mickiewicz University, Poland	Poz	
Coelodonta antiquitatis ("first" woolly rhinoceros)	Museum of Natural Sciences, Lviv, Ukraine	soft tissue	Radiocarbon Laboratory, Silesian University of Technology, Poland	Gd	anterior part of body, shaft No. 4, depth: 17.5 m, found: November, 1907
		soft tissue	Oxford Radiocarbon Accelerator Unit, Research Laboratory for Archaeology and History of Art., England	OxA	
Coelodonta antiquitatis ("second" woolly rhinoceros)	Polish Academy of Sciences, Kraków, Poland	soft tissue	Smithsonian Institution, Radiation Biology Laboratory, C^{14}Laboratory, Maryland, USA	SI	complete specimen, underground gallery, depth: 12.5 m, found: October 23, 1929
		soft tissue	^{14}C- und ^{3}H-Laboratorium, Nieddersächsiches Landesamt für Bodenforschung, Hannover, Germany	Hv	
		soft tissue	Poznań Radiocarbon Laboratory, Foundation of the Adam Mickiewicz University, Poland	Poz	
		soft tissue	Kraków Radiocarbon Laboratory, AGH-University of Science and Technology, Poland	KR	
Coelodonta antiquitatis "third" woolly rhinoceros)	Polish Academy of Sciences, Kraków, Poland	bone, part of a rip	Poznań Radiocarbon Laboratory, Foundation of the Adam Mickiewicz University, Poland	Poz	bones, major part of skeleton underground gallery, depth: 11.0m, found: 1929, after October 23.
			Krakow Radiocarbon Laboratory, AGH-University of Science and Technology, Poland	KR	
Coelodonta antiquitatis ("fourth" woolly rhinoceros)	Polish Academy of Sciences, Kraków, Poland	bone, part of a shoulder--blade	Poznań Radiocarbon Laboratory, Foundation of the Adam Mickiewicz University, Poland	Poz	bones, small fragments underground gallery, depth: 11.0 m, found: 1929, after October 23.

Table 2

Radiocarbon ages of remnants of a mammoth and woolly rhinoceroses, excavated in the Starunia area

Dated specimen	Type of tissue dated	Code of the laboratory /year of dating/	Dating method	Laboratory sample code	Radiocarbon age (yr BP)
Mammuthus primigenius (woolly mammoth)	soft tissue	Gd/2001	GC	Gd-17077	22,610 + 3,400 −2,380
	soft tissue	GIN/1997	LSC (?)	GIN-6633	35,100 ±1,000
	bone, part of vertebra	Poz/2005	AMS	Poz-11347	45,000 ±2,000
Coelodonta antiquitatis ("first" woolly rhinoceros)	bone, part of skull	Gd/2001	GC	Gd-16065	14,140 ±480
		Gd/2001		Gd-17061	14,200 ±490 weighted mean: 14,170 ±340
	soft tissue	OxA /2002	AMS	OxA-11413[1)]	42,150 ±750
Coelodonta antiquitatis ("second" woolly rhinoceros)	soft tissue	SI/1971	LSC (?)	SI-642	23,000 ±(ns)
	soft tissue (skin)	Hv/1974	GC	Hv-5989	36,250 ±815[2)]
	collagen?				23,255 ± (ns)
	soft tissue	Poz/2005	AMS	Poz-11348	47,000 ±3,000
	soft tissue	KR/2005	LSC	KR-200	26,750 ±450
Coelodonta antiquitatis ("third" woolly rhinoceros)	bone (collagen)	Gd/2001	GC	Gd-15241	18,440 ±310
	part of a rip (collagen)	Poz/2005	AMS	Poz-11349	41,600 ±1,400
	(carbonate fraction)			Poz-11441	26,590 ±190
	part of a rip (collagen)	KR/2005	LSC	KR-201	39,700 ±2,500
Coelodonta antiquitatis ("fourth" woolly rhinoceros)	part of a shoulder-blade (collagen)	Poz/2005	AMS	Poz-11350	40,300 ±1,200

GC: gas counters; LSC: liquid scintillation counters; AMS: accelerator mass spectrometry;
ns: not specified; [1)] — dating of rhinoceroses "second", "third" and "fourth" (three samples) failed;
[2)] — dated soft tissue not treated chemically.

BP. Four laboratories dated remnants of the "second" woolly rhinoceros and from five dates obtained, three are in the range: 23.0–26.75 kyr BP. The remaining two reveal older ages: 36.2 kyr BP and 47 kyr BP. In all cases except one, the dated sample was soft tissue. According to the comment made by laboratory manager on the data reporting sheet, the age of 23.2 kyr BP which was obtained for collagen fraction could be too young as a result of contamination by ethyl alcohol during sample preparation procedure. However, the lack of appropriate documentation does not allow to state beyond any doubt that collagen extracted from bone sample was indeed dated in this case. The AMS date (47 kyr BP) turned out to be the oldest one for this specimen.

Three laboratories dated bones of the "third" and "fourth" woolly rhinoceroses that were deposited in one place. The ages obtained for collagen fraction range between 18.4 kyr BP and 41.6 kyr BP. The AMS laboratory dated two fractions of the same sample: organic (collagen) and inorganic (carbonate). The carbonate fraction gave the age of 26.5 kys BP while collagen fraction turned out to be much older (41.6 kyr BP).

3. Discussion

The whole set of ^{14}C results obtained to date is very confusing. The ranges of results obtained for a single specimen are extremely wide, and there is no doubt that most of the dates given in Table 2 are wrong. Appearance of not adequate ^{14}C dates is a common problem in ^{14}C dating (as recently assessed by Buck *et al.*, 2003). On average, it concerns ca. 10% of dated samples and is caused by non-representativeness of samples for the dated event, and to a lesser extent, by gross errors made during sample preparation. If groups of related dates are available, wrong results appear as outliers, and they can be easily detected and rejected. However, in the set of samples from Starunia, no order of such a type can be found.

At the first glance one can note that ^{14}C results obtained at the AMS laboratories are older than those from the GC or LSC labs. This regularity is broken only in the case of the "third" rhinoceros, where one AMS date agrees well with the date obtained by LSC lab, while the second one (for the carbonate fraction) is distinctly younger. One can also note that the AMS dates of different specimens roughly agree with one another (except one date obtained on the carbonate fraction), while the dates obtained by conventional laboratories (GC and LSC) have a much greater scatter.

The radiocarbon dating method is based on determination of ^{14}C concentration or specific activity of carbon in the investigated material with the highest possible precision. Decades of experience of ^{14}C laboratories all over the world show with no doubt that application of different techniques of ^{14}C measurement does not cause systematic differences of ^{14}C results. Thus, the basic problem lies outside the measurement technique of ^{14}C, i.e. in selecting adequate carbon-bearing compound(s) which are to be dated and to separate them from the "raw" sample. During the first decades of application of ^{14}C dating, bones remained one of the most problematic materials, since most of the organic fraction of fossil bones buried in sediments appear susceptible to exchange of carbon with the ambient matter. It is now widely accepted that such exchange does not affect collagen, and this is the collagen fraction, which is nowadays commonly used for ^{14}C dating of bones in most laboratories. However, collagen undergoes degradation and its content in bone is decreasing with time until it entirely disappears. On the other hand, procedures for collagen extraction (Longin, 1971; Piotrowska, Goslar, 2002) are not ideal, and if collagen content in the sample is very low, concentration of other compounds (amino acids, etc.) in the extract may become significant and the resulting ^{14}C age of this fraction may be seriously biased. Anyway, the collagen content in the analysed samples was quite high. Photo 1 shows the bone fragment and the extracted collagen (ca. 5% of the total mass of the sample) for "third" rhinoceros, dated by the Kraków Radiocarbon Laboratory.

The material available from the Starunia excavation site constitutes an example of exceptional difficulties one can face at the stage of sample preparation for ^{14}C activity measurement. The mammoth and rhinoceroses remnants were buried for thousands of years in a peculiar environment where oil and earth wax were present. In addition, concentrated brines commonly occurring in the area could have penetrated into the dated material. Photo 2 shows soft tissue of the "second" rhinoceros, rep-

Photo 1. The rip fragment of the "third" woolly rhinoceros with well pronounced spongy structure of inner part. Extracted collagen in dry form is shown on the right side. Photo by T. Kuc

Photo 2. The soft tissue (skin and muscles) of the "second" woolly rhinoceros before preparation. Tissue looses its dark-brown colour after washing in organic solvents. Photo by T. Kuc

resented by skin and underlying muscles. It is dark-brown in colour and the presence of hydrocarbons could be confirmed even by their specific smell. Washing in organic solvents caused a change of colour to light brown and made the structure of tissue much more brittle. Oil and bitumens extracted from vertebra of the rhinoceros found in 1929 together with oil from surface seepage in the vicinity of Starunia were matter of detailed study (Kotarba, 2002) which confirmed impregnation of the carcasses by hydrocarbons from local sources.

Since oil is obviously free of radiocarbon, the specific problem of vital importance for Starunia samples is to complete removal of contamination by dead carbon of allochtonous origin. Incomplete removal of ^{14}C-free hydrocarbons from the dated material would then results in too high ages. Due to this fact, the procedure of removal of hydrocarbons is critical for reliable dating of the Starunia samples.

Unlike extraction of collagen, removal of hydrocarbons is not a standard procedure of sample pre-treatment for ^{14}C dating. Unfortunately, the reports of previous dating attempts of the Starunia specimens do not contain information on methods applied to remove hydrocarbons from the dated samples. Therefore, in further discussion we focus mainly on dates obtained recently in Kraków and Poznań, where procedures for hydrocarbon removal were strictly controlled.

In both laboratories removal of hydrocarbons was accomplished by washing the samples in benzene. Several (4–5) steps of washing were applied. After each step, the solution was removed and a new portion of solvent was used. In Poznań, each step took ca. 20 hours (full time of treatment ca. 5 days). In Kraków, each step took 15–20 minutes only, so the full procedure lasted approximately 2 hours. The effect of solvent was evident (especially in the first step), as it was gradually turned to yellow and light brown. In subsequent steps, coloration of the solvent was weaker and weaker. At the end, the remains of benzene were washed out with acetone (several times), and the acetone was thoroughly washed out with water.

In light of the procedures described above, the results obtained in Kraków and Poznań are rather puzzling. One date from Kraków, of the bone of "third" rhinoceros (39,700 ±2,500 BP), agrees well with the result obtained in Poznań (41,600 ±1,400 BP). Both dates were obtained on the collagen fraction. However, the dates obtained by both laboratories on skin and soft tissue of the "second" rhinoceros differ significantly (26,750 ±450 BP and 47,000 ±3,000 BP for Kraków and Poznań, respectively). At first glance, the difference between these two dates could be associated with different durations of hydrocarbon removal procedures. Indeed, the coloration of benzene during treatment of soft tissue of the "second" rhinoceros was very strong; in Poznań it became invisible only in the 4th step, and in Kraków in the 3th step. Thus it is possible that hydrocarbons were removed to a lesser degree in the Kraków laboratory than in Poznań. On the other hand, benzene coloration with bones of the "third" rhinoceros was very weak, suggesting no distinct differences in degree of hydrocarbon removal which seems to explain good agreement of both ^{14}C dates in that case.

However, the hypothesis that the Poznań sample of the "second" rhinoceros was cleaned more effectively than in Kraków does not hold with the assumption that hydrocarbon contamination was free of ^{14}C. In fact, the dates from Poznań, where the procedure of hydrocarbon removal was especially rigid and long-lasting, are in general older (not younger) than the results obtained in other laboratories. This means that either the hydrocarbons washed-out in Poznań were young (in terms of ^{14}C age), or the 5-days-long washing introduced contamination with ^{14}C-free benzene. Both possibilities are difficult to accept. Though no direct ^{14}C measurements were made on oil and earth wax present in the Starunia site, it seems very unlikely that its carbon contains any traces of ^{14}C. "Young" hydrocarbons (i.e., containing significant amounts of ^{14}C) could be easily introduced after excavation, during conservation treatment. However, ^{14}C dated fragments of skin and soft tissue of the "second" rhinoceros had never been conserved with carbon-bearing reagents (H. Kubiak, private information). The second possibility, that the samples were contaminated by benzene, is also very unlikely. Indeed, to alter ^{14}C age from ca. 26 kyr (as dated in Kraków) to more than 41 kyr (as measured in Poznań), ^{14}C-free (benzene) contamination should contribute 85% of the total mass of carbon. In fact, the reverse effect (alteration of ^{14}C age from 41–26 kyr) is much easier to imagine, as it requires only 3% contamination with modern carbon.

The Poznań ^{14}C date of the carbonate fraction from bone of the "third" rhinoceros (preparation of carbonate after Lanting *et al.*, 2001) constitutes an additional puzzle. This date (26,590 ±190 BP) is much younger than the dates obtained on the collagen fraction by the AMS and LSC technique, but it perfectly agrees with the Kraków date for skin and soft tissue of the "second" rhinoceros (26,750 ±450 BP). The ^{14}C date of the carbonate fraction should not be affected by hydrocarbons, although the procedure of hydrocarbons removal was applied also to this sample. Consequently, this result could be regarded as more reliable. It is thus tempting to accept ca. 26 kyr BP as the true age of the Starunia specimens. However, it is difficult to imagine that the benzene washing applied in Kraków to soft tissue of the "second" rhinoceros was successful, whereas it failed in the case of bone of the "third" rhinoceros, which contained much less hydrocarbons. It is also difficult to imagine that the "weaker" benzene washing applied in Kraków was more effective that the stronger washing applied in Poznań. Therefore, the coincidence of the above mentioned results should be regarded for the time being as accidental.

The ^{14}C dates of carbonate fraction of bones are considered reliable if no secondary carbonate was precipitated within bone structure. Therefore, carbonate fraction cannot be dated if the bones were buried in contact with groundwater rich in carbonate ions. However, it is very unlikely that such a process was taking place at the Starunia site due to a perfect isolation of the dated specimens from active groundwater circulation. However, after excavation, the bones have been stored in air for almost 100 years, in conditions of uncontrolled humidity. In such conditions, some exchange of carbon between bone carbonate and atmospheric CO_2 characterized by high ^{14}C levels cannot be excluded. This process, if occuring, would lead to younger apparent ages of carbonate fraction.

It is also not clear how collagen behaves in such a unique environment for periods of time extending to thousands of years. For instance, it is not unreasonable to imagine a possibility of interaction/exchange between liquid hydrocarbons penetrating the buried bones and collagen, eventually leading to replacement of carbon in some functional groups within the collagen structure. However, the existence of such an effect can only be proved or rejected by further detailed studies. On the other hand, relatively low ages obtained for some samples seem to preclude such a possibility.

4. Conclusions

Renewed attempts have been made over the past three decades to determine the radiocarbon age of famous mammoth and four woolly rhinoceroses remnants excavated in the Starunia area at the beginning of the 20th century. Altogether, seven laboratories from five countries took part in those trials using three different measurement techniques. In spite of a great effort, these efforts appeared to be largely unsuccessful.

The radiocarbon ages obtained to date for five different specimens described in detail in Table 1 range from ca. 14–47 kyr BP. This range is characteristic of the whole set of dated samples as well as for the same material dated by different techniques ("second" rhinoceros). It is, therefore, evident that no conclusion can be drawn so far from radiocarbon dates with respect to mutual chronology of the excavated specimens.

The peculiar nature of the dated samples (bones and soft tissue soaked with oil and brine) is the most probable reason for serious difficulties encountered in the process of obtaining reliable radiocarbon ages. Complete removal of ^{14}C-free hydrocarbons from the dated samples turned out to be very difficult and so far no procedure was applied to control the degree of this removal. Also, long-term (millennia) *in situ* interaction between liquid hydrocarbons and organic material leading to significant aging effects in terms of radiocarbon ages cannot be ruled out at this stage.

Comparison of radiocarbon dates obtained recently in Kraków and Poznań (Table 2) suggests two probable ranges for the true age of the Starunia specimens. The range around 42,000 years is suggested by the AMS dates (three dates on collagen fraction and one on soft tissue obtained in Poznań, plus one date obtained in Oxford), in agreement with the Kraków date of collagen fraction obtained for the "third" rhinoceros. On the other hand, the second date from Kraków (soft tissue of "second" rhinoceros), in close agreement with the Poznań date of the carbonate fraction (bone of "third" rhinoceros), suggest that the findings from Starunia are ca. 26,000 years old. Whichever option is true, mechanisms responsible for occurrence of contradictory dates are far from being understood. Therefore, comprehensive systematic studies of the nature of contamination occuring in the case of the Starunia specimens are needed.

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Datowania metodą ^{14}C szczątków nosorożców włochatych i mamuta ze Staruni (region podkarpacki, Ukraina)

Streszczenie

Metoda radiowęglowa była kilkakrotnie stosowana w ciągu ostatnich trzydziestu lat do określenia wieku szczątków mamuta i czterech nosorożców włochatych znalezionych na terenie Staruni. Ogółem siedem laboratoriów reprezentujących trzy różne techniki pomiarowe wzięło udział w tych badaniach. Niestety, dotychczasowe wysiłki nie zostały uwieńczone sukcesem. Wiek radiowęglowy uzyskany do chwili obecnej dla pięciu różnych osobników wykopanych na terenie Staruni mieści się w przedziale między 14 a 47 tys. lat radiowęglowych. Ten rozrzut charakteryzuje zarówno cały zbiór uzyskanych dat, jak i daty uzyskane różnymi metodami dla tego samego materiału. Stąd, jak na razie nie można wyciągnąć żadnych wniosków co do wzajemnej chronologii badanego materiału. Specyficzne warunki w jakich przebywały znalezione fragmenty oraz kompletny nosorożec włochaty (iły przesiąknięte ropą i solanką) są najbardziej prawdopodobną przyczyną trudności w uzyskaniu dat radiowęglowych wiarygodnie określających wiek. Całkowite usunięcie ropy z badanych próbek okazało się bardzo trudne. Również, długotrwałe oddziaływanie ropy na składniki organiczne (mięśnie, skóra, kolagen) *in situ*, z ewentualną wymianą grup funkcjonalnych zawierających węgiel, mogło doprowadzić do sztucznego zawyżenia wieku badanej frakcji organicznej. Porównanie datowań wykonanych ostatnio w laboratoriach radiowęglowych w Krakowie i w Poznaniu sugeruje dwa prawdopodobne przedziały wiekowe dla znalezisk staruńskich: około 42 tys. lat, wynikające głównie z datowań wykonanych techniką AMS, oraz około 26 tys. lat radiowęglowych. Oba przedziały wiekowe są jednakowo prawdopodobne. Wiarygodnego rozstrzygnięcia obecnego dylematu niejednoznaczności datowań radiowęglowych szczątków mamuta i nosorożców włochatych znalezionych na terenie Staruni mogą dostarczyć jedynie systematyczne studia natury i stopnia kontaminacji tego materiału.

Датування методом ^{14}C останків волохатих носорогів і мамонта із Старуні (передкарпатський регіон, Україна)

Резюме

Радіовуглецевий метод був застосований декілька разів протягом останніх тридцяти років для визначення віку останків мамонта і чотирьох волохатих носорогів, знайдених в районі Старуні. Загалом в цих дослідженнях взяли участь сім лабораторій, які представляли три різні методики замірів. Нажаль, всі зусилля досі не увінчалися успіхом. Визначення радіовуглецевого віку, одержані на сьогоднішній день для п'яти різних екземплярів, викопаних в районі Старуні, знаходяться в діапазоні між 14 і 47 тис. радіовуглецевих років. Цей діапазон характеризує як цілий ряд одержаних датувань, так і датування, одержані різними методами для одного і того ж матеріалу. Із цих даних поки що не можна зробити жодних висновків щодо взаємної хронології досліджуваного матеріалу. Специфічні умови, в яких перебували знайдені фрагменти і цілий волохатий носоріг (глини, просякнуті нафтою і розсолом) є найправдоподібнішою причиною труднощів в одержанні радіовуглецевих датувань, які б вірогідно показували вік. Цілком усунути нафту із досліджуваних проб виявилось дуже важко. Також довготривалий вплив нафти на органічні складники (м'язи, шкіра, колаген) *in situ*, з ймовірною зміною функціональних груп, що вміщують вуглець, міг привести до штучного завищення віку досліджуваної органічної фракції. Порівняння датувань, виконаних недавно в радіовуглецевих лабораторіях в Кракові і в Познані показує два правдоподібних значення віку для старунських знахідок: близько 42 тис. років, як показують в основному датування, виконані технікою AMS, і 26 тис. радіовуглецевих років. Обидва значення віку є однаково правдоподібними. Вірогідного вирішення існуючої дилеми неоднозначності радіовуглецевих датувань останків мамонта і волохатих носорогів, знайдених в районі Старуні, можна досягнути лише шляхом систематичного вивчення природи і ступеня контамінації цього матеріалу.