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# RECONSTRUCTION OF PAST CLIMATE BASING ON THE ISOTOPIC COMPOSITION OF CARBON FROM FOSSIL REMAINS

**ABSTRACT.** The areas of Northern Eurasia and the Far North regions with a sharply continental climate are of particular interest to paleoclimatologists. The nature of these areas preserves many features of the Late Glacial period. However, the reliability of the classical paleoclimatic methods in these areas is low. It is known that climate may affect the  $\delta^{13}$ C value of plants, causing isotopic variations of up to 3‰. The authors propose to use the carbon isotope compositions of bone carbonate of herbivorous animals as a paleoclimatic indicator for the Polar Regions.

To test the potential of the proposed paleoclimatic indicator, the authors studied the carbon isotopic composition of carbonate of bone (reliably dated by the radiocarbon method) of Late Pleistocene mammals (mammoth mostly) from the area of the Lena River delta – the New Siberian Islands – Oyagossky Yar (the total of 43 samples). These data suggest that the Late Pleistocene climate in North Yakutia was not stable. Instability was expressed in the sharp, short-term (500-2000 years), occasional episodes of relatively warm climate that may be ranked as interstadials based on their intensity.

**KEY WORDS:** stable carbon isotopes, paleontological relics, reconstruction of palaeoclimate, mammoths

## INTRODUCTION

Paleogeographic reconstruction, especially with the relevant data on the evolution of the Pleistocene and Holocene climate, provide the basis for modeling of climate change and its prediction. Unfortunately, our understanding of the paleogeography of the continental regions of Northern Eurasia and the Far North is still largely fragmentary and contradictory. In most cases, methods of reconstruction of climatic conditions include spore-pollen analysis of different modifications [see, for example, Vasilchuk, 2007; Klimanov and Andreev, 1991], such isotopic methods as the oxygen-isotope analysis of polygonal-wedge and structureforming ice [Vasilchuk, 1992; Konyakhin, 1987; Nikolayev, Mikhalev, 1995], analysis of phosphate mammoth bone [Nikolaev et al, 2002], etc. Some of these methods provide low reliability for these regions; some require the introduction of "subjective" corrections; some are expressed in terms of isotopic composition, the amounts of positive temperature growing season, etc.;

some are obtained based on materials that can be dated with difficulty; etc. All this together shows the relevance of the development and implementation of new both quantitative and qualitative methods of reconstruction of the paleoclimate of the Polar Regions.

In 1947, G. Urey [Urey, 1947] suggested that the concentration of the heavy isotope of carbon in organic matter can reconstruct paleotemperatures.

Empirically derived relation between the carbon isotope composition of cellulose and latitude, temperature, and relative humidity show convincingly that its long-period variations carry paleoclimatic information [Alexander et al 1991]. It was shown [Ahmetkereev and Dergachev, 1980] that the average carbon isotopic composition of plant biomass (peat) reflects the climatic conditions of plant growth: comparison of the values of the isotopic composition of carbon of dated samples of peat with the curve for the average

July temperature allowed establishing their temperature dependence. The reason for the close correlation of these values, apparently, is the fact that in the case of peat land plants (the basis of peat), we can ignore the many factors (light, water stress, density of vegetation, etc.) that have a substantial influence on the carbon isotopic composition of plants.

Bone carbonate  $\delta^{13}$ C values reflect carbon isotope composition of the whole diet of herbivorous animal. Enrichment from 12 to 14 ‰ between carbonate and diet has been estimated for large mammals [Bocherens et al., 1994; Krueger, Sullivan, 1984; Lee-thorp et al., 1989].

Thus, we can assume that the "carbon isotope label" reflects the climatic conditions of the plants growing at high latitudes.

#### MATERIALS AND METHODS

The isotopic composition of carbon of bone hydroxyapatite carbonate (hereafter,



**Fig. 1. Locations of the studied paleontological samples:** 1 – New Siberian Islands; 2 – the Lena River delta; 3 – Cape Svyatoy Nos – OyagosskyYar

carbonate) of 36 <sup>14</sup>C dated (data obtained were not calibrated) mammoth remains (*Mammuthus primigenius*) from Northern Yakutia (Fig. 1) was studied. Also for comparison, several samples of horses (*Equus caballus*) and bison (*Bison priscus*) were analyzed.

The procedures used to prepare the bone samples for mass spectrometric analysis are presented below.

Visible contamination of bone samples were removed by a drill and (or) by ultrasound. To measure the isotopic composition of carbon of bone carbonate, about 100 mg of sample were ground to a powder and treated with a solution of 2% NaOCI for one day. The sample was then repeatedly washed in distilled water and leached with 1M acetate buffer solution for 20 hr to remove diagenetic calcium carbonate [Bocherens et al., 1994; Lee-Thorpet al., 1989]. After washing and drying, the sample was dissolved overnight in vacuum at 50°C in 100% orthophosphoric acid to release CO<sub>2</sub>. After gas purification, the isotopic composition of carbon was studied by mass spectrometry.

The isotopic composition of carbon was measured concurrently with the percentage of carbon and nitrogen (as well as the atomic ratio C/N) in the samples at the elemental (CHN) analyser Carlo Erba EA 1110 in line with the mass spectrometer ThermoFinnigan delta plus XR. The samples (0,15-0,2 mg) in a foil capsule were placed in the processing system, vacuumized, and then dropped into the reactor, heated to a temperature of 1025°C. The injection of oxygen into the reactor increased the temperature to 1800°C and the sample was incinerated. After purification in the cryogenic trap, the test gas  $(CO_2)$  came through the capillary into the analyzer and then to the mass spectrometer; the flow of helium served as a carrier.

In this paper, all the isotopic data are expressed as the relative deviation ( $\delta$ ) of the content of the heavy isotope in a sample from its content in the international standards

(in ‰). The obtained isotopic results are expressed relative to the standard V-PDB (the marine carbonate of biogenic origin). The standard deviation was  $\pm 0,1\%$  (1 $\sigma$ ) for <sup>13</sup>C measurements.

To check the preservation of the oxygen isotope signal, measurements of oxygen isotope composition of bone carbonate ( $\delta^{18}O_{carb}$  and  $\delta^{18}O_{phos}$ ) were carried out on the studied samples. Plotting the oxygen values on a  $\delta^{18}O_{phos} - \delta^{18}O_{carb}$  diagram the points lie near the line of well-preserved isotope values. When carbonate oxygen retains its original isotope composition it is supposed that also carbonate carbon are not altered principally when water is not involved in diagenetic processes [see Wang and Cerling, 1994].

# CARBON ISOTOPES IN BIOLOGICAL OBJECTS

It is known that some plants absorb carbon through photosynthesis by epyCalvin cycle  $(C_3 \text{ plants})$ , and the other – through the Hatch-Slack cycle  $(C_4 \text{ plants})^1$ . In the area of our study (northern Yakutia), <sup>1</sup>C<sub>4</sub> plants are virtually absent in the present [Pyankov and Mokronosov, 1993], and judging from the values of  $\delta^{13}C$  of organic matter of buried soils, they were also absent in the Late Pleistocene [Nikolaev et al., 2000]. The  $\delta^{13}$ C values in collagen of animals whose diet contains 100% of C<sub>3</sub> plants is close to -21,5 ‰ [Van der Merwe, 1992], which corresponds to our previous results. Thus, the authors [Nikolaev et al., 2004] studied the isotopic composition of carbon in the bone collagen of 111 fossils of mammoths (Mammuthus primigenius) from Northern Yakutia (the sector between 100°E and 170°E). The average  $\delta^{13}$ C value obtained comprised  $-21,7 \pm 0,95$  %.

<sup>&</sup>lt;sup>1</sup> The difference between  $C_3$  and  $C_4$  plants is that the  $C_3$ -plants form three-carbon products of photosynthesis at the first stage (phosphoglyceric acid and phosphoglyceric aldehyde), while  $C_4$ -plants formfour-carbon compounds (oxalicacetate, malic, and aspartic acid).  $C_3$  and  $C_4$  plants differ greatly in the isotopic composition of carbon biomass (see, for example, [O'Leary, 1988]).

Current views on the fractionation of carbon isotopes by C<sub>3</sub> photosynthesis plants, suggest that most of the observed variations of  $\delta^{13}$ C of cellulose was due to changes in the geometry of cellulose stomata of the leaves with variations in light, relative humidity, and temperature [Farquhar et al., 1982; Francey and Farquhar, 1982].

The isotopic composition of carbon of plants is also sensitive to changes of in the ratio of  $C_i/C_a$  ( $C_i$  = internal leaf  $CO_2$  concentration of  $CO_2$ ;  $C_3 = air CO_2$  concentration). For example, the re-assimilation of the exhaled CO<sub>2</sub>, reduction of light under a very dense and closed forest canopy, or reduction in the content of nutrients in the soil lead to the a <sup>13</sup>C depletion in plant tissues. The opposite effect is observed with an increase in water stress (a decrease of relative humidity and (or) of annual precipitation and temperature increase) or a decrease of the partial pressure of CO<sub>2</sub>. All plants decrease their absorption of CO<sub>2</sub> at temperatures below the optimum, and this causes an increase of the  $C_i/C_a$  ratio and a reduction of the  $\delta^{13}$ C value [Tieszen, 1991]. It seems, in our study area (tundra), we can neglect the many effects caused by the local environmental conditions (e.g., density of forest, luminance, etc.).

Mammoths were herbivorous animals who consumed low-protein high fiber foods: in the snow-free period, they fed on meadow grasses, and in the snow period–woody forage. It is possible that, raking the snow with the tusks, they were able to get the fallen leaves of some shrubs and trees, as well as some grasses with green low parts of the stems and shoots [Vereshchagin and Tikhonov, 1990].

According to the results obtained by different authors, the values of carbon isotopic composition of collagen of bones and teeth of large mammals differ from the isotopic composition of consumed protein by 5 ‰ [Schoeninger, 1985; Van der Merwe, 1982]. The values of  $\delta^{13}$ C of carbonate reflect better the isotopic composition of carbon nutrition in general compared to collagen,

as collagen is primarily associated with the  $\delta^{13}$ C of proteins and their percentage composition in the overall diet [Ambrose and Norr, 1993; Tieszen and Fagre, 1993]. Experimental studies in rats with a controlled diet showed a constant difference of 9.5 ‰ between the carbon isotopic composition of bone carbonate and food intake. At the same time, the difference between the  $\delta^{13}C$ values of carbonate and collagen varies (about 5,7‰ for pure  $C_3$  or  $C_4$  diets). In the case of natural food, the increase from 7 to 10‰ between carbonate and collagen, and from 12 to 14‰ between the carbonate and the food was calculated for large mammals [Bocherens et al., 1994; Krueger and Sullivan, 1984; Lee-Thorp et al., 1989]. A big difference in the values of  $\delta^{13}$ C was detected between collagen and carbonate, and a lesserone was between the carbon isotopic composition of the protein component and of  $\delta^{13}C$  of the food in general.

In summary, we can state that different foods represent different "isotopic (climatic) tags" that, moving through food chains, vary in a predictable manner. Thus, if the average carbon isotopic composition of the food is largely determined by climatic conditions, there is a potential of using the abovementioned patterns for reconstruction of the features of past climate.

#### RESULTS

Above, it was assumed that by studying the isotopic composition of organic and of mineral carbon components of the bone (collagen and carbonate, respectively), we can register a "tag" (a climatic signal) fixed in the process of photosynthesis and passed through the food chain to our sample. To test this hypothesis, we studied the isotopic composition of carbon of bone carbonate hydroxylapatite of 36 dated remains of mammoths (Mammuthus primigenius) from the New Siberian Islands (mostly from Bolshoi Lyakhovsky Island) (20 samples), from the Lena River delta (8 samples), and from the southern coast of Dmitry Laptev Strait (Cape Svyatoy Nos – Oyagossky Yar) Table 1. Isotope composition of carbon (δ<sup>13</sup>Ccarb and δ<sup>13</sup>Ccoll, ‰) from the carbonate and collagen of bones of the Late Pleistocene mammoth complex of Northen Yakutia (dating of samples is according to [Schirrmeister et al., 2002] and other sources)

<sup>14</sup> C dating	±σ	Laboratory number	Region	Latitude, °N	Longitude, °E	$\delta^{13}C_{carbr}\%$				
Mammuthus primigenius										
12030	60	ГИН-10713	1	73,32	141,39	-13,4				
12500	50	ГИН-10716	1	73,33	141,37	-15,85				
13100	500	ГИН-10242	2	71,79	129,40	-13,8				
17100	300	ГИН-9556	3	72,22	143,51	-13,6				
20800	100	ГИН-11084	1	73,33	141,37	-14,15				
20800	600	ГИН-10248	2	71,79	129,38	-13,6				
22100	1000	ГИН-10707	1	73,32	141,37	-12,6				
23600	500	ГИН-13229	1	74,25	140,35	-14,50				
24300	200	ГИН-10264	2	71,79	129,40	-13,2				
24600	900	ГИН-13224	1	74,25	140,35	-13,40				
24750	210	ГИН-13221	3	72,66	143,72	-14,75				
25150	360	ГИН-13228	1	75,01	147,05	-12,70				
25900	600	ГИН-10708	1	73,33	141,33	-14,8				
26100	600	ГИН-9563	3	72,22	143,51	-14,2				
27400	800	ГИН-10262	2	71,79	129,40	-14,6				
28000	180	ГИН-10706	1	73,32	141,37	-14,1				
30100	450	ГИН-13222	1	74,25	140,35	-15,45				
30200	400	ГИН-10719	2	72,90	123,35	-14,6				
31500	650	ГИН-10249	2	71,78	129,42	-14,4				
32500	500	ГИН-10659	1	73,33	141,40	-15,3				
33000	320	ГИН-11085	1	73,33	141,37	-15,40				
34000	500	ГИН-10261	2	71,79	129,40	-13,7				
>34600	-	ГИН-10246	2	71,79	129,40	-14,0				
37800	900	ГИН-10660	1	73,34	141,28	-12,7				
38700	500	ГИН-11705	1	73,33	141,37	-14,75				
39600	1000	ГИН-10714	1	73,34	141,31	-14,8				
40200	900	ГИН-10703	1	73,34	141,31	-14,1				
40900	1200	ГИН-9566	1	72,25	141,90	-14,7				
42200	600	ГИН-13218	1	75,47	136,0	-13,35				
42900	900	ГИН-9552	3	72,25	141,90	-15,2				
43100	1000	ГИН-9568	3	72,22	143,51	-14,5				
43600	1000	ГИН-10717	1	73,34	141,31	-16,4				
47400	1200	ГИН-9557	3	72,22	143,51	-13,8				
48000	2000	ГИН-10709	1	73,34	141,31	-12,7				
48800	1400	ГИН-9044	3	72,61	141,10	-13,1				
50650	1820	KIA-10681	1	73,28	141,82	-13,5				

**Continue Table** 

<sup>14</sup> C dating	±σ	Laboratory number	Region	Latitude, °N	Longitude, °E	$\delta^{13}C_{carb},$ ‰				
Equus caballus										
2310	80	ЛУ-1084	3	Chromskaya Guba	-14,4					
16380	120	ГИН-10233	2	71,79	129,38	-13,0				
26340	140	GrA-43065	3	Muksun- uokha Mount	-12,2					
29500	?	?	3	Dukarskoye Lake	-12,9					
35900	600	ГИН-10262	2	71,79	129,40	-12,8				
Bison priscus										
38200	700	ГИН-10663	1	73,34	141,31	-11,6				
41500	1100	ГИН-10686	1	73,33	141,33	-14,7				

**Regions:** 1 – New Siberian Islands (mainly the Large Lyakhovsky Island); 2 – the Lena River delta; 3 – Cape Svyatoy Nos and OyagosskyYar.

(8 samples). Also for comparison, sevaral samples of horses (*Equus caballus*) and of bison (*Bison priscus*) of these same regions were analyzed (Table 1). Strictly speaking, such combined use of different species is not quite valid because of differences in carbon isotope composition of bones due to differences in metabolism. Thus, the carbon isotopic composition of bone collagen (and, hence, of carbonate) has somewhat lower negative values for horses ( $-21,0 \pm 0,7\%$ ) compared with that of mammoths ( $-21,4 \pm 0,6\%$ ) [Bocherens, 2003].

As noted above, the  $\delta^{13}$ C values of carbonate better than that of collagen reflect the carbon isotope composition of food in general. So we decided to build a cumulative (summary) curve of  $\delta^{13}$ C values of bone carbonate for the region of the Lena River Delta the New Siberian Islands – Oyagossky Yar. Earlier [Nikolaev et al., 2011], we evaluated the significance of differences of three random average (mean, standard deviation, and maximum and minimum values) for our three areas of research. The results of calculations (t-test, etc.) show that the differences between them are insignificant (at least at P > 0,06). Thus, the isotopic data from all three regions can be used together, particularly for the construction of the cumulative paleoclimatic ( $\delta^{13}C_{\text{carb}}$ ) curve (Fig. 2).

On the cumulative curve one can distinguish several phases characterized by low and high  $\delta^{13}$ C values corresponding to the warm and cold intervals: before 46,5÷48,5 (51–46,5) <sup>14</sup>C thousand years ago (cold), 4,5–38 thousand years ago (cold), 33,5–24,5 thousand years ago (warm), and 24÷26–12 thousand years ago (cold).

Let us compare the reconstructed paleoclimatic stages with the known paleogeographic data.

The first phase of high isotopic values (lower paleotemperatures) is noted in the earlier stageprior to 46,5÷48,5 <sup>14</sup>C thousand years ago. It may correspond to the Late Zyransky stage with the age of 60–50 thousand years ago. In northern Yakutia, according to biogeochemical and paleontological data, this period was characterized by dry and cold summers with a low biological productivity; the isotopic data for repeatedwedge ice showed extremely cold winter temperatures that were lower than in the last cold stage (24÷26–12 thousand ÷years ago). Sediments with high ice content





(ice complex, yedoma), covered the Arctic lowlands; in the surrounding mountains, glaciers locally developed [Mikhalev et al., 2006; Schirrmeister et al., 2002; etc.].

According to the isotope data that we received, in the range of  $46,5\div48,5$  to  $24\div26$  thousand years ago, there were predominantly relatively warm conditions with the exception of a cold episode of  $33,5\div38$  (39) thousand years ago. A warm interstadial called in Siberia the Karginsky stage (marine isotope stage MIS 3), according to various <sup>14</sup>C dating for many regions of the north-east Siberia, occurred between 50 and 25 thousand years ago [Zubakov, 1986]. This was the period with an arid continental

climate and with dry and hot summers, when within the territory of Yakutia, cryoxerophyte plants with low productivity of green mass were widely spread [Tomskaya, 2000].Two identified warm episodes of the Karginsky stage are likely to correspond to such climatic events as the European Hengelo and Denekamp [Dansgaard et al, 1993].

Our data showed that significant cooling began in the interval between  $39600 \pm 1000$  and  $38200 \pm 700$  years ago (see Fig. 2). This is confirmed by the following data. Mammoth (41750  $\pm$  1290 years ago) from the Shandrin River (a tributary of the Indigirka River) lived in a "warm time" when larch moved 200 miles north of its modern limits [Solonevich et al.,

1977]. Based on the spore-pollen data of A.I. Tomskaya [2000], the climate was similar to the present. A baby mammoth Dima (39570  $\pm$  870 years ago) of the Kirgilyah River valley lived in conditions similar to those

existing in the middle Holocene [Anderson, Lozhkin, 2001], while the horse ( $38590 \pm 1120$  years ago) from the River Selerikan (a tributary of the Indigirka River) lived in more severe conditions than at present [The



# **GRIP Dust-record**

Fig. 3. Comparison of the Late Pleistocene climatic events in Greenland (based on the study of dust particles in the ice core, see [Svensson et al., 2000]; etc.) and in North Yakutia (based on the results of the isotope analysis of bone remains of the mammoth fauna (the authors' data).
IS – (Greenland glacial) isotope stages [Johnsen et al., 1992]; B – bison, H – horse (mammoth)

Geochronology of the Quaternary Period, 1980; etc.]. We took a cold episode in the oxygen isotope curve of Summit Station in Greenland with the same age. It testified to the number of short but intense cold episodes [Dansgaard et al., 1993].

The thermal optimum of our isotope curve corresponds to  $32500 \pm 500^{14}$ C years ago (see Fig. 2). According to paleobotanical data [Anderson and Lozhkin, 2001], in this period, Beringia was covered with forests and the maximum warming took place  $35-33^{14}$ C thousand years ago [Elias, 2001].

The second thermal optimum was  $43600 \pm 1000$  years ago. Analysis of the beetles fauna from 20 sections of Western Europe has shown that, in a narrow time interval of about 43 thousand years, summer temperatures were higher than today [Coope, 1977]. Examples of warm conditions in other regions at this time are given in [Zubakov, 1986, etc.].

The last identified cold stage of 24÷26 to 12 thousand years ago, obviously coincides with the last glacial maximum (the marine isotope stage MIS 2). During this period (between 22 and 15 thousand years ago) in North Yakutia, extremely cold climatic conditions were reconstructed. There were widespread waterlogged meadows and peatlands. In wet habitats, there grew most valuable fodder plants that stored in winter much of their green mass; in addition, they had high productivity. They probably comprised an important part of the mammoth diet [Tomskaya, 2000].

Thus, it is clear that within the accuracy of radiocarbon dating, we have reconstructed evolution of the thermal regime (see Fig. 2) based on the isotopic data confirmed by independent paleogeographical data. Therefore, we can conclude that the carbon isotopic composition of bone carbonate can be used as a new (additional) paleoclimatic indicator in the high latitudesand in the areas of extreme continental climate where many of the classical methods have relatively low reliability. Mammoths, in accordance with existing ideas (Ye.N. Mashchenko, personal communication), were able to survive to the age of 60-yr. or older. Consequently, the isotopic results obtained based on the bones of mammoths represent a discrete signal – individual samples correspond to time intervals of a few tens of years (although, at times, have significant uncertainty of the geological age due to the errors in the determination of <sup>14</sup>C age). The spore-pollen, paleopedological, and several other methods have much greater inertia (response time to climate change) due to the fact that the relevant samples, because of the low rate of sedimentation and bioturbation processes in the surface layer of soil, represent a signal averaged over a few hundred or even thousands of years. These features of used methods may cause differences in the interpretation of climatic events (their duration and intensity). The proposed method of studying the isotopic composition of mammoth bones can detect very short-duration climate fluctuations and identify its instability, while other methods give, as a rule, the averaged smoothed picture.

In support of our discussion, in Fig. 3 we plotted together the data on the content of dust (Ca) in the ice core of the station GRIP (Greenland) and the results of our isotopic studies. The data for Greenland show the extreme instability of the late Pleistocene climate. Instability was expressed in the sharp, short-term (500-2000 years), occasional episodes of relatively warm climate that can be ranked in terms of intensity as interstadials. [Dansgaard et al., 1993]. For the most part of the curve 10–46 thousand years ago, these climatic variations, in general, are confirmed by the isotopic data for Yakutia (within the accuracy of dating of bones and glacial ice). Taking into account these phenomena we may propose similar instability of Late Pleistocene climate in Yakutia In the range of 47400 ± 1200-50650 ± 1820 (at the limit of the radiocarbon method), the isotope data contradict the Greenland climatostratigraphic curve (accuracy of the estimates

of ice age in this range can reach 10%, see, for example, Nikolaev, 1997). The isotopic data indicate cooling in Greenland while the curve indicates the warm conditions (see Fig. 3) at least since the turn of 51 thousand years ago. It is clear that these contradictions are due to errors in estimating the age of the events.

Analysis of the published paleoclimatic data shows that in the Karginsky time, there was instability of climate (the sharp fluctuations between the "glacial" and the interglacial conditions). Perhaps the climate of its optimum in intensity of the thermal regime was comparable to the interglacial conditions [Velichko, 2009; Dansgaard et al., 1993]. This is also confirmed by the authors' data on the carbon isotopic composition of bones of the mammoth fauna (including the Yakut horses).

## CONCLUSIONS

In summary, we should note that the carbon isotope studies of fossil remains can yield

new data on the Pleistocene fauna habitat in the high latitudes, where the results of many paleogeographic methods have limited reliability. The data based on  $\delta^{13}$ C of bone carbonate hydroxylapatite allowed reconstructing the evolution of climate (in this case in Northern Yakutia in the range 50–10 thousand years ago).

These data suggest that the Late Pleistocene climate in North Yakutia was not stable. Instability was expressed in the sharp, short-term (500–2000 years), occasional episodes of relatively warm climate that can be ranked in terms of intensity as interstadials.

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