

# The Carbon Isotope Composition of Organic Matter and the Age of Paleosols from Wurm Glaciations Interstadials to Holocene (Bryansk region, Russia)

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**Abstract.** Paleosols of Trubchevsk district of the Bryansk region (Russia) lie in landscape with its own characteristic micro-relief, called Trubchevsk Opolye. The radiocarbon data have been obtained for two interstadial soils:  $16500 \pm 230$  Ki-17 414,  $12930 \pm 170$  Ki-17 413 years ago. The ratio  $\delta^{13}\text{C}_{\text{org}}$  for underlying sandy pedosediments varies in range  $-26.5$ - $-27.2$  ‰ characterizes relatively humid climate. The most lightweight carbon isotope composition ( $\delta^{13}\text{C} = -28.4$ - $-29.5$  ‰) measured for the Holocene second humus horizon, discovered in micro-depressions of Trubchevsk opolye and dating (in its upper part)  $2180 \pm 60$  Ki-17 415 BP,  $1650 \pm 60$  Ki-18775. It is characterized by a high content of phosphorus, including its strong accumulation of organic compounds ( $635.8$  mg/kg  $\text{P}_2\text{O}_5$ ).

## 1. Introduction

The more studied and widespread Late Pleistocene soil in the East European Plain refers to the climate warming 32-24 kyr BP called Bryansk interval (Paudorf, Shtillfrid "B", etc.). Often this soil is covered by loess and modern (Holocene) soils and has well-defined horizons. However, recent research [1, 6, 11] has discovered that these Late Valdai (Wurm) loess are heterogeneous and are separated by humic or gley horizons (undeveloped soils) in many stratigraphic sections. These horizons determine regional characteristics of climatic fluctuations between 17-10.2 kyr BP. The existence of paleosols levels with different characteristics is evidence of periods with relatively mild climatic conditions or interstadials of the final stage of the Late Valdai glaciation. Another interesting feature of these deposits is the presence of thick sandy loess strata, which recorded the cryogenic deformations. The genesis of these sequences can be attributed to the water-glacial streams activities on right bank of the river Desna.

Thus, the aim of this study is to clarify the regional climate conditions on Late Glacial-Holocene boundary for the Trubchevsk district (Bryansk region), based on the studying of buried soil properties in the loess-sandy-soil series. We have previously shown [5, 6, 7, 8] that the most informative features for paleoecological recovery of the environment are such biomarkers as carbon isotope composition of humus, different characteristics of the organic matter, organic and inorganic phosphorus content and also the magnetic susceptibility.

## 2. Materials and methods

The studied sites are located in the Bryansk region on the territory of Trubchevskoe Opolye, where the agrogrey soils (WRB: Albic Luvisols / Grey Luvic Phaeozems) are formed on the Late Wurm loess. Trubchevskoe Opolye is situated on the high right bank of the middle course of the river Desna (on the watershed of the rivers Desna and Sudost) in the middle latitudes of the Russian plain ( $52^{\circ}34'80''$  N,  $33^{\circ}38'52''$  E). The average annual temperature in the study area is  $+5.4^{\circ}\text{C}$ . Amount of the precipitation



ranges from 550 to 590 mm [11]. Different types of agrogrey soil are formed of different elements of the landscape: their varieties with the second humus horizon are formed in saucer shaped micro-depressions, gleyic variants formed in the middle parts of slopes and gley ones at footslopes, deeper depressions; there are also agrogrey soils without second humus horizon on the micro-elevations. The Late Pleistocene and Holocene loess-paleosol series are presented in the sediments of quarries in villages Krasnoe (52°33'70"N, 33°42'62"E) and Telec (52°34'51"N, 33°44'71"E). These quarries expose the thickness of sand and loess deposits.

All samples taken from soil pits were air dried and sieved (<1 mm). Total C and N, as well as organic C ( $C_{org}$ ) were analyzed by dry combustion with an elemental analyzer Thermo Flash1112. The content of humic and fulvic acids in organic matter was analyzed by the Tyurin method [9]. The group phosphorus analysis allows us to divide organic and inorganic compounds of phosphorus [5]. The inorganic phosphorus content is determined by photometry after 1n  $H_2SO_4$  treatment. Total phosphorus is determined by photometry after the calcination at 500°C (for conversion of phosphorus-organic compounds to soluble forms) and 1n  $H_2SO_4$  acid treatment.

Radiocarbon analyses of extractable humic acids were carried out at the Kyiv Radiocarbon laboratory (Institute of Environmental Geochemistry, Ukraine). The magnetic susceptibility of soils was measured by kappameter KT-5 [3]. The  $^{13}C/^{12}C$  ( $\delta^{13}C$ ) ratio was measured on a mass spectrometer Thermo-Finnigan Delta V Plus IRMS and elemental analyzer Thermo Flash1112. Removal of carbonates from the soil was made by the method of soil fumigation [2]: by decomposing the carbonate under the concentrated hydrochloric acid. Sample of calcareous soil pulverized into powder (30 mg) was placed in open glass bottles and moistened with 50 ml of distilled water. Then weighing bottles with the sample were placed into a closed desiccator with the glass of concentrated HCl (100ml). After fumigation (24 h) the samples were dried for 4 hours at 60°C or under a hood. For the measuring of the isotopic composition of soil carbonates sample was calcined at 500°C to remove the organic substance.

### 3. Results and discussion

Last glaciation deposits on the terraces of the Desna river (middle reaches), opened in quarries near villages Krasnoe (first terrace above the floodplain) and Telec (second terrace above the floodplain), are a part of a hollow formed by melted glacial waters flowing into the river. Therefore, these sediments are presented by sandy-loam, sand deposits and loess with sand inclusions [5, 6, 7]. According to Velichko [11], second and first terraces of the river Desna were formed respectively in the first and second half of the Valdai period. Investigated deposits were formed during the Late Valdai 24-10.2 kyr BP (~Wurm IV) and correspond to isotope stage MIS 2 (25-10 kyr BP, by Svendsen et al. [10]). This phase began after Bryansk (Paudorf, Shtilfrid B) Interstadial - 32-24 kyr BP characterized by well-studied and well-expressed soils in many loess strata of the East European Plain [11].

In the studied sediments, we did not find well-expressed Bryansk soil (it is present only in the outcrops at a higher elevation on the bluff right bank of the Desna River). Investigated Last Glacial soils and pedolithosediments have traces of active freezing processes and thawing of deposits. At the same time there was an accumulation of thick sandy deposits on the study territory, which have a layered texture, solifluction traces (soil deformation processes), ferruginized horizons.

Studied sandy-loess sediments contain two sinlithogenic soils. The radiocarbon dates for these soils are  $16500 \pm 230$  BP (Ki-17414) and  $12930 \pm 170$  BP (Ki-17413), which correspond to the last stage of Valdai glaciation and reflect two interstadials corresponding to Lascaux and Belling interstadials (Wurm IV) and MIS2. Both soils have a number of common traits: gleying profile, iron accumulation, the presence of iron-manganese concretions, lower values of the magnetic susceptibility and increase in humus, organic phosphorus and calcium carbonate content (table 1).

Among the interstadial soils after Bryansk interval (younger than 24 kyr BP) there is well known Trubchevsk humus horizon (gleying level) highlighted by Velichko [11] near our research area (village Golubcha, Bryansk region, depth of the layer 3.8-4.0 m) and dated 16.5-15 kyr BP (Lascaux

interstadial, Wurm IV). The horizon is described by the authors as a weak brown level with silty loam composition, carbonates and organic stains along the pores, inclusions of sandy material. There are also signs of waterlogging: ferrugination spots and grayish tint in this horizon.

Thus, the study horizon with data 16500 BP from quarry by Telec village is close to the Trubchevsk horizon and Lascaux interstadial. It lies at the depth of 2.5-2.8 m and is represented by light loam with thin layers of sand, carbonates through the pores and Fe-Mn-concretions. Below it the clayey carbonate BCb horizon lies (2.8-3.0 m) which is underlain by ferruginate and carbonate sandy horizon (3.5-4.2 m) - BCfe,b. Perhaps the study horizon crowned permafrost level with processes of carbonates and iron pulling. Dated horizon was covered with noncarbonate loess (C1 1.0-2.5m) with humus streaks and Fe-Mn-concretions. Also the paleosol with profile Bb-BCb-BCfe,b-Gb has good spatial expression. The upper horizon Bb has slightly alkaline pH, depleted humus content (0.5%), contains 6.0% CaCO<sub>3</sub> and does not contain P<sub>2</sub>O<sub>5org</sub> (table 1). Humic acids prevail in the humus composition. Horizon BCb has relatively high content of humus (0.7%), organic phosphorus (68.0 mg/kg P<sub>2</sub>O<sub>5 org</sub>), carbonates (5.6% CaCO<sub>3</sub>) and higher values of the magnetic susceptibility. Underlying sandy horizon BCfe,b enriched with calcium carbonate (10.6%), has low humus content and 44.5 mg/kg of organic phosphorus (P<sub>2</sub>O<sub>5org</sub>).

The results of carbon isotopic composition (figure 1) of organic matter indicate a moderately humid conditions of paleosol and underlying sediments formation ( $\delta^{13}\text{C} = -25.6\text{-}26.7\text{‰}$ ). It also points to the arid climate ( $\delta^{13}\text{C} = -23.1\text{-}24.5\text{‰}$ ) during the subsequent accumulation of loess loam horizon C1 overlying the paleosol. This loess layer was probably formed during the Yaroslavl cryogenic stage of the Valdai glaciation (altynovsky loess by Velichko et. al, [11]) 13-14 kyr BP.

Buried soil with age  $12930 \pm 170$  BP (interstadial Belling) lies in the sediments in a quarry near the village Krasnoe. The study paleosol unlike previously described Trubchevsk soil has a deformed character and stands out in the lenses of humified loam material between ferruginate sandy layers. It has a profile Bca b-BCca,fe b-Gb. Horizon Bb contains a relatively high amount of humus (0.7%) and total phosphorus (409.7 mg / kg, P<sub>2</sub>O<sub>5</sub>), which corresponds to the humus horizon of the present agrogrey arable soil. It has relatively high values of magnetic susceptibility judging by the increase in humus content. Perhaps it was formed during periods of surface stabilization in drier than Lascaux interstadial conditions. Drier conditions are also illustrated by the results of the carbon isotopic composition of organic matter (heavier values of  $\delta^{13}\text{C} = -24.9\text{‰}$ , figure1a) and the high content of calcium carbonate (39.1% CaCO<sub>3</sub>) (table 1). The horizons lying above and below this soil are not enriched with calcium carbonate. Organic matter from buried soil is saturated with humic acids and do not contain soluble fulvic acids. High amount of organic phosphorus compounds is probably due to greater biological productivity of the landscape. Thus, the interstadial Belling is characterized by drier climate than Lascaux Interstadial (Trubchevsk Interstadial).

However, the beginning of the Holocene is featured by a catastrophic change of climate, vegetation and atmosphere chemical composition. The concentration of carbon dioxide in the atmosphere increased sharply and C-3 plants with strong root systems developed on the waterlogged soil. The low values of the isotopic ratio  $\delta^{13}\text{C}$  of organic carbon (to  $\delta^{13}\text{C} = -28.4 \text{‰}$ ), high content of humus, phosphorus in the second humus horizons (Ab, 50-85 cm) of agrogrey soils (table1) that are common for the investigated territory characterize humid and warm climatic conditions. Second humus horizons distinguished by black color, slightly acidic pH, relatively high humus content (2.6%), are more than in the modern plow horizon. Second humus horizon is characterized by high phosphorus content, including organic phosphorus accumulation (635.8 mg/kg P<sub>2</sub>O<sub>5</sub>), while the amount of organic phosphorus compounds in modern humus horizon reaches only 178.7 mg/kg of P<sub>2</sub>O<sub>5</sub>. Among the low magnetic susceptibility values, a small maximum allocated is caused by the humus accumulation.  $\delta^{13}\text{C}$  ratio have the lowest values in the profile ( $\delta^{13}\text{C} = -28.4 \text{-}29.5\text{‰}$ ). Thus, the climate was more humid and had more favorable conditions for the accumulation of organic matter than the modern one. About 2 thousand years ago ( $2180 \pm 60$  BP Ki-17415,  $1650 \pm 60$  Ki-18775) chernozem under meadow vegetation with C-3 type of photosynthesis on this area of modern gray forest soils was formed.

Accumulation of stable highly condensed molecules of organic matter in the second humus horizons of modern soils, apparently, is a relic of the chernozem soil formation stage [4, 8].

Atlantic Chernozem soil is separated from modern gray soil by the Late Holocene podzolic horizon (AE 30-50 cm) with date 2180±60 cal BP. Colder conditions are indicated by lower values of humus and organic phosphorus content as indicators of reduction in biological activity. There is increase in weight values of the isotopic ratios  $\delta^{13}\text{C}$  to -26 ‰. The lignin phenols ratio for the observed horizons also typical for small-leaved species of wood have been described in our previous studies [6, 7].

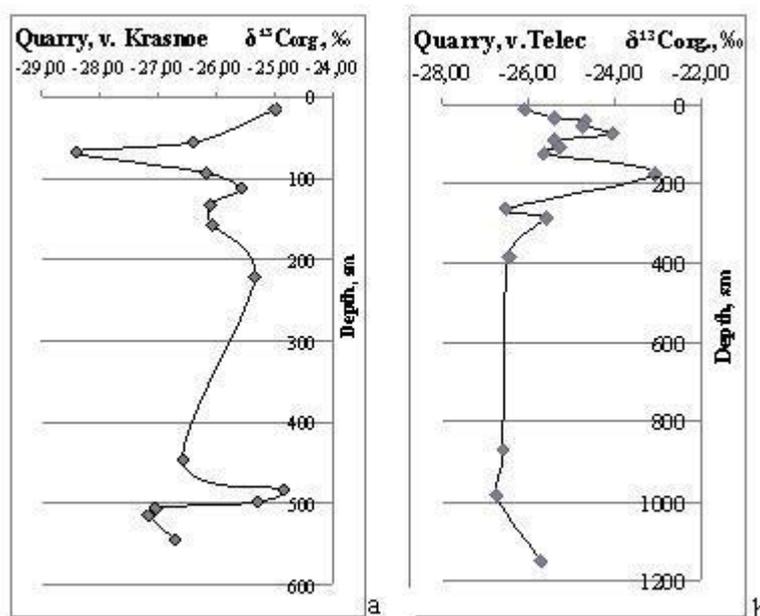
**Table 1.** Paleoecological indicators of soils.

Location	Age, years BP	Horizon, depth, cm	C <sub>org.</sub> , %	P <sub>2</sub> O <sub>5</sub> org, mg/kg	$\delta^{13}\text{C}$ org, ‰	CaCO <sub>3</sub> , %	Cha/Cfa*	$\chi \times 10^{-6}$ , SGSM	P <sub>2</sub> O <sub>5</sub> inorg, mg/kg
Quarry, v. Telec with micro-elevation soil	6690±110	Ap 0-30	1.2	115.0	-26.1	0	0.69	31.5	325.7
		AE 30-35	0.4	17.8	-25.4	0	0.95	31.5	253.4
		EB 35-46	0.2	18.4	-24.7	0		21.1	205.2
		BC 46-65	0.2	10.6	-24.7	0		19.5	186.4
		C 65-85	0.2	0.0	-24.1	0		16.8	232.0
		Ab 85-99	0.4	97.2	-25.4	16.7		17.1	258.7
		C1 99-120	0.3	83.9	-25.3	46.0		13.2	261.4
		C2 120-150	0.2	38.9	-25.7	41.3		9.6	258.7
	16500 ± 230	C3 150-250	0.5	29.9	-23.1	42.0	0.14	12.0	118.03
		Bb 250-275	0.3	0.0	-26.5	6.0	4.00	2.5	24.48
		BCb 275-300	0.4	68.0	-25.6	5.6	2.00	23.6	65.08
		ORTZ1 350-420	0.3	44.5	-26.5	10.6		15.3	42.76
		G 770-970	0.1	0.0	-26.6	11.1		2.2	141.74
		C4 970-1000	0.1	0.0	-26.7	10.7		0.0	11.25
Quarry, v.Krasnoe with microdepression soil	2180±60, 1650±60	C5 1000-1300	0.2	0.0	-25.7	9.9		6.9	123.96
		Ap 0-30	1.8	178.7	-25.0	0	0.92	16.1	334.2
	12930 ± 170	AE 30-50	1.5	311.9	-26.4	0	0.82	11.3	246.8
		Ab 50-85	2.3	635.8	-28.4	0	1.08	19.4	421.6
		AEb 85-100	1.3	389.8	-26.2	0	0.54	13.2	596.4
		Eb 100-125	0.4	125.4	-25.6	0		13.9	591.1
		EBb 124-140	0.6	0.0	-26.1	0		8.7	712.0
		Bb 140-175	0.3	0.0	-26.1	0		11	383.5
		C 175-270	0.2	0.0	-25.3	0		1.1	265.4
		C3,fe,1 445-470	0.2	0.0	-26.6	0		8.6	132.26
Bb 470-495	0.4	106.3	-24.8	39.1	4.00	13.1	303.42		
BCfe,b2 495-500	0.1	0.0	-25.3	35.6		5.4	101.14		
G, 500-510	0.1	0.0	-27.0	0		3.1	129.67		
BCfe,b3 510-520	0.1	7.8	-27.2	0		5.2	62.24		
C4 520-570	0.1	2.6	-26.7	7.6		2.8	77.80		

\* - Cha - C from humic acids. Cfa - C from fulvic acids

Thus, loess-sandy-soil series are an archive of paleoecological information about the planet global climate system restructuring, which occurred on the investigated territory at the Late Glacial-Holocene boundary. This restructuring had a pulsating character, accompanied by sharp fluctuations in climate,

vegetation composition and appearance of new landscapes. There are at least two different interstadials by latest wave of the Valdai (Wurm) glaciation, corresponding to the two buried soils: dry arid episode about 12930 years BP and temperate - humid period - about 16500 years BP for the territory of the middle reaches of the river Desna. Despite rather harsh climate characteristic of this area there is a large number of Paleolithic sites (Borschevo, Khotylevo, Suponevo, Timonovka etc. [11]) which acted both in warmer (interstadials) and cooling (stadials) periods. A sharp increase in the humidity of landscapes in the first half of the Holocene and cooling - in the second half were unidirectional and global.



**Figure 1.** Carbon isotopic composition of organic matter: a - sequence of quarry v. Krasnoe, b - sequence of quarry v. Telec.

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