Unique Quaternary environment for discoveries of woolly rhinoceroses in Starunia, fore-Carpathian region, Ukraine: Geochemical and geoelectric studies

Maciej J. Kotarba*
Marek Dzieniewicz
Włodzimierz J. Mościcki
Henryk Sechman

AGH-University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Mickiewicza Av. 30, 30-059 Kraków, Poland

ABSTRACT

In 1907, remnants of a mammoth and a woolly rhinoceros were discovered in the Pleistocene clays of an earth-wax mine in Starunia village. Then, in 1929, a nearly fully preserved woolly rhinoceros was found in the same mine. The unique combination of clays, oil, and brine into which the animals had sunk is responsible for their almost perfect preservation. During the late Pleistocene winters, when the ice and snow cover was present in the tundra "paleoswamp," areas of inflow of brines, oils, and hydrocarbon gases had a higher temperature, which resulted in melting and cracking of the cover, and large mammals could be trapped. Geoelectric measurements, as well as molecular and stable isotope analyses of gases in the near-surface zone within the "paleoswamp" performed in 2004–2005, reveal a few places favorable to the burial and preservation of Pleistocene vertebrates.

Keywords: woolly rhinoceros, ozokerite, Pleistocene, surface geochemical survey, DC resistivity, stable carbon isotopes, Ukraine.

INTRODUCTION

The discoveries of large Pleistocene mammals at the Starunia ozokerite (earth-wax) mine, situated in the fore-Carpathian region in Ukraine (Fig. 1), were spectacular scientific events on a worldwide scale (e.g., Alexandrowicz, 2005). In 1907, a partially preserved mammoth was found at a depth of 12.5 m, and a woolly rhinoceros at a depth of 17.6 m. In 1929, Polish scientists discovered a unique, nearly complete woolly rhinoceros carcass at a depth of 12.5 m. Radiocarbon dating determined two probable ranges for the age of the remnants of these mammals: one around 42 ka, and another around 26 ka (Kuc et al., 2005). The woolly rhinoceros excavated in 1929 is displayed at the Natural History Museum in Kraków (Fig. 1). The fossil flora and fauna excavated in Starunia in 1907 and 1929 were subjected to various scientific investigations for identification, determination of ecology, age, and other purposes (Alexandrowicz, 2005, and references therein). In 2004, Polish and Ukrainian scientists restarted studies in the Starunia area.

Quaternary deposits of the Velyky Lukavets River valley in Starunia are developed as clays containing plant remains and large Pleistocene mammals, as well as gravels, sands, and peats. The top of the Lower Miocene Vorotyshcha Salt-bearing Formation of the Boryslav–Pokuttya Unit, which underlies the Quaternary deposits, occurs at depths from 8 to 20 m. The ozokerite deposit occurs in a Miocene molasse sequence.

Pleistocene clays were saturated with brines that migrated from the underlying Lower Miocene Vorotyshcha beds rich in halite and sylvite, and oil from Oligocene and Eocene strata of the Boryslav-Pokuttya Unit (Koltun et al., 2005; Kotarba et al., 2005a). Small oil seeps and ponds, mud volcanoes, and saltwater springs are present in Starunia and nearby. The almost perfect preservation of skin and some soft tissues (e.g., tongue, trachea, palate; Kubiak, 1969) as well as collagen in bones (Kuc et al., 2005) of the woolly rhinoceros discovered in 1929 was a result of natural processes, owing to the brine- and oil saturation of the "spongy" microporous body structures. Unfortunately, the DNA of the rhinoceros has not been investigated yet. The purpose of our geochemical and geoelectric studies was to investigate the geologic setting and environment of the Pleistocene sediments, as well as to assess the possibility of new discoveries of large, extinct mammals.

FIELD AND ANALYTICAL PROCEDURES

For a near-surface geochemical survey, the patented sampling procedure of Sechman and Dzieniewicz (2007) was used. The sampling depth was ~1.2 m. Natural gas samples from wells and surface seeps were placed into 500 mL glass vessels filled with saturated NaCl solution. The molecular composition of gases was analyzed in a set of columns on gas chromatographs equipped with flame ionization (FID) and thermal conductivity (TCD) detectors. Stable carbon isotope analyses were performed using a mass spectrometer, and results are presented in the δ notation relative to the Peedee belemnite (PDB) standard. The geoelectric method applied was DC resistivity sounding. A four-electrode Schlumberger array with the largest spacing, AB/2 = 100 m, was used (Mościcki, 2005).

GEOCHEMICAL STUDY

In the Starunia area (Fig. 1), gas samples were collected from five wells in Oligocene and Eocene reservoirs and from two oil seeps. The molecular composition, gas indices, and stable isotope ratios vary within the following ranges (Kotarba et al., 2005a): CH_4 85.6%–95.9%, C_2H_6 1.76%–4.78%, C_3H_8 0.41%–2.20%, N_2 0.92%–2.40%, CO_2 0.01%–3.49%, hydrocarbon C_{HC} index [$C_{HC} = CH_4/(C_2H_6 + C_3H_8)$] from 12 to 44, carbon dioxide–methane (CDMI) index [$CDMI = CO_2/(CO_2 + CH_4)100(\%)$] from 0.09% to 3.92%, $\delta^{13}C(CH_4)$ from –46.6‰ to –27.1‰, $\delta D(CH_4)$ from –187‰ to –150‰, $\delta^{13}C(C_2H_6)$ from –33.1‰ to –26.5‰, and $\delta^{13}C(CO_2)$ from –15.6‰ to +20.0‰. Moreover, slight concentrations of helium, up to 0.011% (N-1 well, Fig. 1) as well as hydrogen (0.25%) in the "upper oil eye" are present.

Subsurface hydrocarbon gases accumulated in Oligocene and Eocene reservoirs as well as gases connected with two oil seeps in the Starunia area were generated from type II kerogen during low-temperature thermogenic processes (Figs. 2A and 2C). The thermogenic hydrocarbons migrated together with helium (Fig. 3A) to the surface along the "Rinne" fault zone directly from deep accumulations (Kotarba et al., 2005a). Carbon dioxide is also of thermogenic origin, with the exception of gas from the "upper oil eye," which was generated during microbial processes (Fig. 2B).

The near-surface geochemical studies were run along three measurement lines (Fig. 1, lines P-0, P-2, and P-3). The analyzed gases are more variable in their molecular and isotopic compositions than gases from deep accumulations and seeps (Kotarba et al., 2005a, 2005b). Concentrations of components of near-surface gases for 111 samples are presented in Table 1. Gas indices and stable carbon isotope ratios for 24 selected samples vary within the following ranges: hydrocarbon (C_{HC}) index 12–4543, carbon dioxide methane (CDMI) index from 2.3%–100%, $\delta^{13}C(CH_4)$ from –70.9‰ to –32.4‰, $\delta^{13}C(C_2H_6)$ from –29.9‰ to –25.4‰, and $\delta^{13}C(CO_2)$ from –26.3‰ to +1.9‰. These ranges indicate that genetic history and gas migration to the near-surface zone were complicated. The highest concentrations of analyzed gases occur in the central and southeastern parts of the study area, whereas in the northwestern and western parts,

*E-mail: kotarba@agh.edu.pl.

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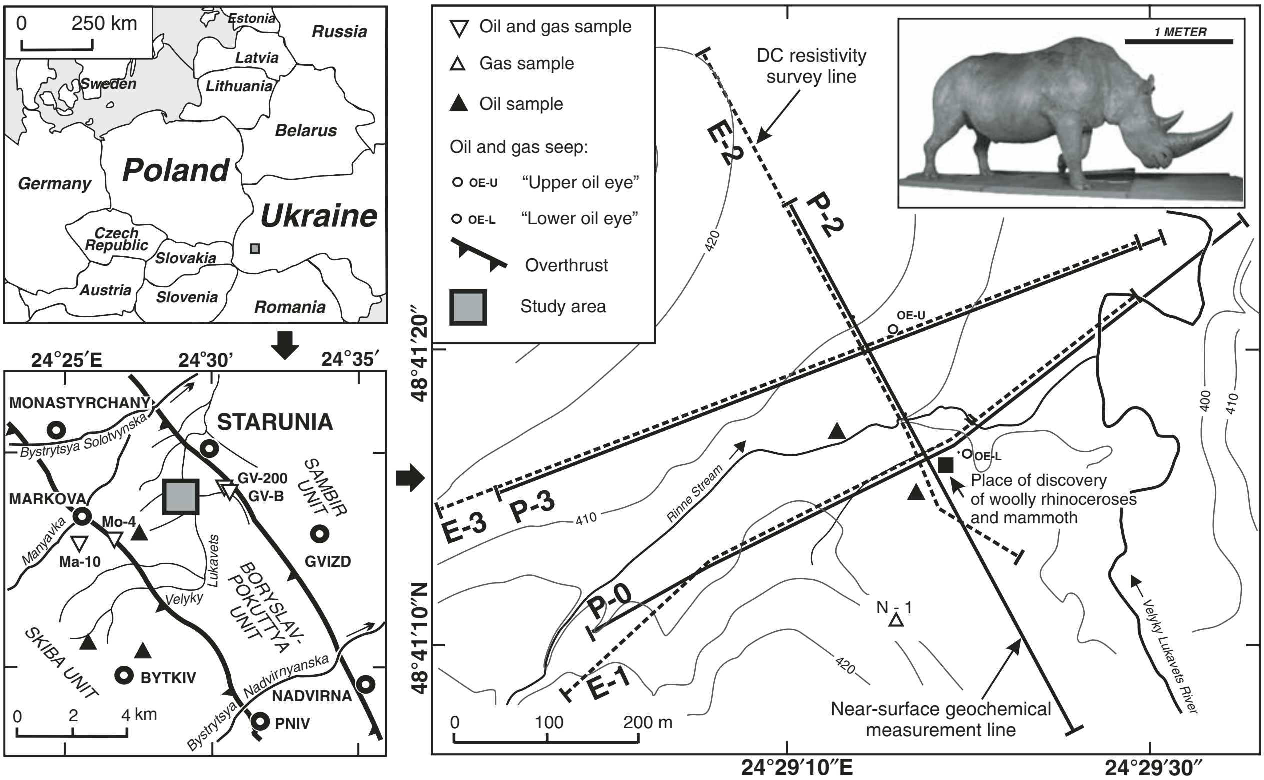

Figure 1. Location map of study area. Photo of unique woolly rhinoceros in Natural History Museum in Kraków by W.J. Mościcki.

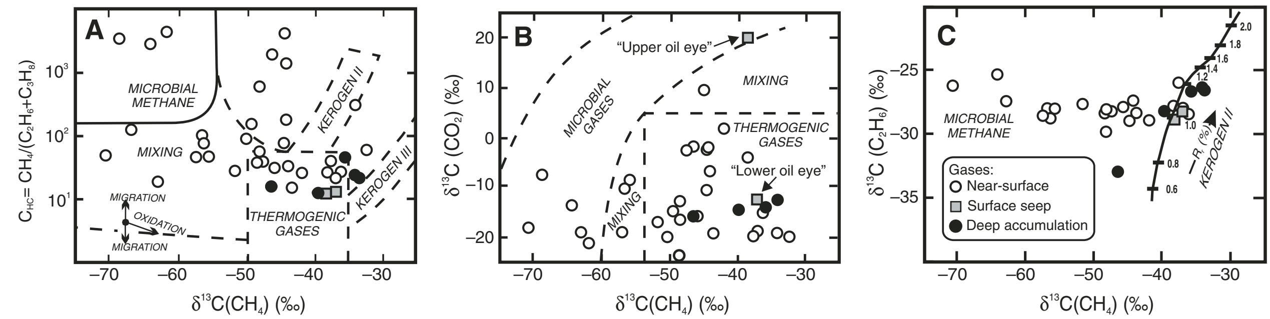

Figure 2. Genetic characterization of natural subsurface and near-surface gases using (A) hydrocarbon index (C_{HC}), (B) $\delta^{13}C(CO_2)$, and (C) $\delta^{13}C(C_2H_6)$ versus $\delta^{13}C(CH_4)$. Compositional fields in A are after Whiticar (1994), and compositional fields in B are after Kotarba and Rice (2001) modified by Kotarba. Positions of vitrinite reflectance curves for type II kerogen in C are after Berner and Faber (1996) and have been shifted based on average of $\delta^{13}C$ values of Oligocene Menilite Formation type II kerogen (25.2‰) after Kotarba et al. (2005a).

they decrease (Figs. 3A–3D). Eight anomalous methane concentrations over 10% were found in the area. In the case of the sum of C_2-C_5 alkane concentrations, the distribution of anomalous zones with concentrations over 1% is similar. Sites of anomalous carbon dioxide concentrations over 5% are generally in the same places. These relationships are most clearly visible on measurement line P-2 (Figs. 4A–4C). High helium concentrations on the P-2 and P-3 lines were grouped near the "Rinne" fault zone (Figs. 3 and 4). Stable carbon isotope analyses of methane and ethane of near-surface gases (Fig. 2) indicate that ethane and higher gaseous hydrocarbons from all sampled sites, and methane from a majority of the sites, are thermogenic in origin and migrated to the near-surface zone from deep accumulations. However, microbial methane or mixing of microbial and thermogenic methanes also has occurred (Figs. 2 and 4), as indicated by the isotopic composition of the gases and the presence of hydrogen. The stable carbon isotope composition of carbon dioxide (Fig. 2B) also suggests a variety of origins: thermogenic (most frequent), recent microbial processes, and secondary microbial oxidation of hydrocarbons.

High variability in the concentrations of gas components and multiple origins of individual gaseous components in the near-surface zone provide insight into the lithological diversification of Quaternary sediments. These data suggest that the most favorable conditions for preservation of large Pleistocene mammals and even for people who were living at that time and hunting for them (Matskevyj, 2005) occur at locations associated with the flux of thermogenic gases to the near-surface zone from deep accumulations. These places are connected mainly with fault zones, which can also be proved by increased helium concentrations as well as oil and brine fluxes.

GEOELECTRIC STUDY

DC resistivity soundings were grouped in three measurement lines E-1, E-2, and E-3 (Fig. 1). The thickness of Quaternary deposits (natural and/or human-altered), their electrical resistivity, and hydrogeologic conditions in the area were studied. The thickness of the uppermost Quaternary deposits is ~10 m in places where no influences of human activity

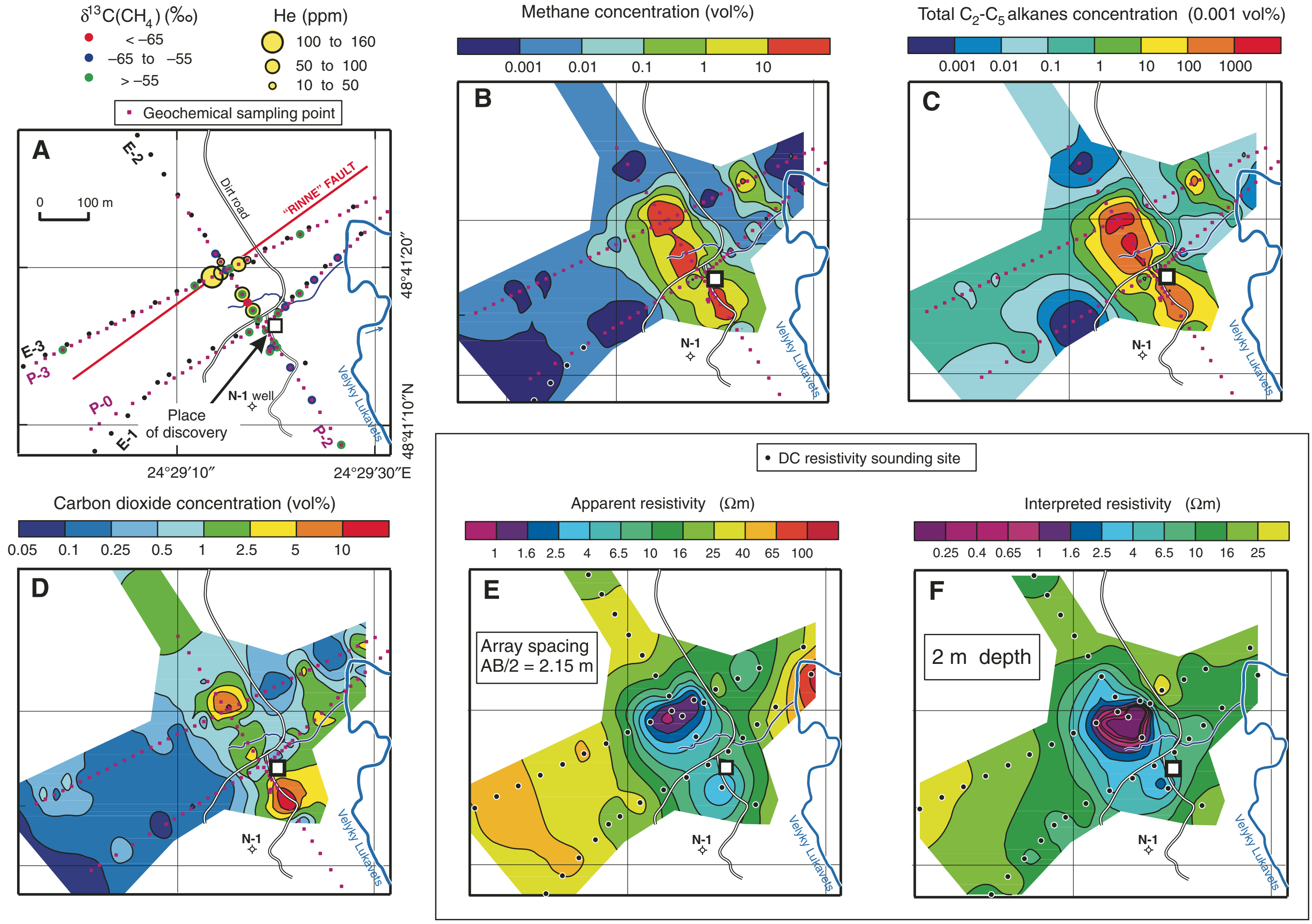

Figure 3. Maps of geochemical indices and sediment resistivity, based on DC resistivity soundings in near-surface zone of Starunia area. A: Location of geochemical profiles, stable carbon isotope composition of methane (lack of color dots in sampling point means no analyses of isotope composition were made) and helium concentration (helium concentration was measured in all sampling points. The lack of yellow circles means that helium concentration is less than 10 ppm). B: Methane concentration. C: Sum of C_2-C_5 alkanes concentration. D: Carbon dioxide concentration. E: Apparent resistivity for 2.15 m spacing. F: Interpreted resistivity at 2 m depth. E-1, E-2, and E-3 are DC resistivity survey lines, and P-0, P-2, and P-3 are near-surface geochemical measurement lines.

TABLE 1. SELECTED STATISTICAL PARAMETERS FOR ALKANE, ALKENE, CARBON DIOXIDE, HYDROGEN, AND HELIUM CONCENTRATIONS MEASURED IN NEAR-SURFACE GAS SAMPLES

Statistical parameters	Unit	Alkanes							Sum of alkanes			
		CH_4	C_2H_6	C_3H_8	iC_4H_{10}	nC_4H_{10}	iC_5H_{12}	nC_5H_{12}	C_2-C_5	CO_2	H_2	He
Minimum values	(ppm)	0.6	0	0	0	0	0	0	0	0.03*	0*	0
Maximum values	(ppm)	824000.0	32700.0	3810.0	2120.0	2850.0	2210.0	1460.0	44800.0	22.0*	0.032*	110.0
Median values	(ppm)	13.4	0.26	0.00	0.06	0	0	0	0.55	0.21*	0*	0
Mean values	(ppm)	80300.0	1530.0	149.0	108.0	50.0	72.2	14.1	1930.0	1.89*	0.002*	2.72
Number of samples		217	178	108	114	87	92	26	181	11	7	44
Percentage of samples	(%)	100.0	82.0	49.8	52.5	40.1	42.4	12.0	83.4	5.1	3.2	20.3

Note: C_2-C_5 = C_2H_6 + C_3H_8 + C_4H_{10} + C_5H_{12}.
*Values in vol%.

were noted. A very distinct low-resistivity anomaly (LRA), lower than 0.5 Ωm, was registered in the central part of the area.

Generally, the electrical resistivity of Quaternary deposits decreases with depth. The top layer has a resistivity of 30 Ωm or higher and a thickness of 1–2 m. The next layer is 4–8 m thick and has 10–25 Ωm resistivity. Deeper sediments have very low resistivity, below 5 Ωm. The aforementioned LRA is readily visible on apparent resistivity contours made for all sounding spacings used (Mościcki, 2005). An example map corresponding to penetration depths of not more than 1 m is shown in Fig. 3E. Quantitative, one-dimensional (1-D) interpretation of the DC soundings—the distribution of the interpreted resistivity at a depth of 2 m—shows a distinct LRA pattern (Fig. 3F). This pattern is probably caused by relatively salty water filling the pores of unconsolidated Quaternary sediments at shallow depth.

The LRA zone is also readily visible on the profile data. The apparent resistivity pseudosection and results of 1-D quantitative interpretation are set together with geochemical data for survey line P-2 in Figure 4. The interpreted resistivity within the LRA zone falls below 0.5 Ωm. The NE boundary of the anomaly is sharper than the SW one.

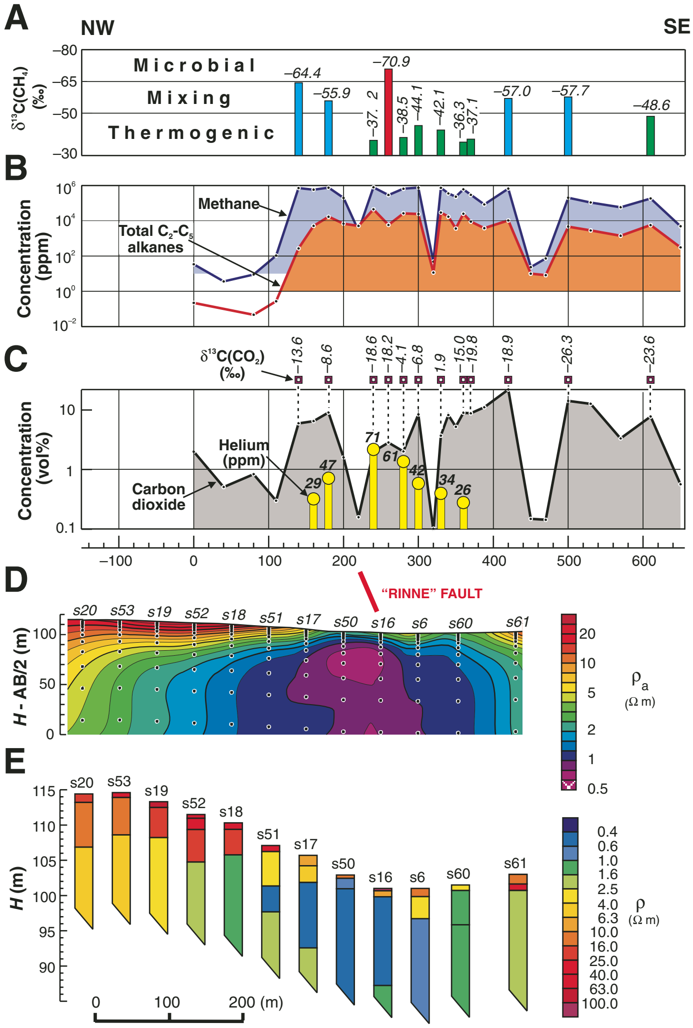

Figure 4. Results of research along P-2 measurement line. A: Stable carbon isotope composition of methane. B: Distribution of methane and sum of C_2-C_5 alkanes. C: Distribution of carbon dioxide and helium, and stable carbon isotope composition of carbon dioxide. D: Apparent resistivity pseudosection based on DC resistivity soundings. E: One-dimensional (1-D) interpretation of resistivity soundings.

A comparison of geoelectrical and geochemical maps shows a correlation between the two data sets (Fig. 3). We hypothesize that there is a geological trap here containing brines and hydrocarbons. That zone, in the area where the "paleoswamp" developed in the past, likely had a tectonic origin.

CONCLUSIONS

Geochemical and geoelectric studies indicate that large mammals sank into a Pleistocene water reservoir ("paleoswamp") that had developed in the fault zone and may have had a rectangular shape, 350 ×150 m, extending NW-SE (Fig. 3). The herbivorous mammals migrating in search of food and water could be trapped in such places and drowned in the clayey substance that was saturated with brines and oils. It seems possible that during the Pleistocene tundra winters, when a thick ice and snow cover was present in the "paleoswamp," areas of inflow of brines, oils, helium, and thermogenic hydrocarbon gases had a higher temperature, which resulted in melting and cracking of the cover. The identification of several places within the "paleoswamp" where thermogenic gases occur indicates sites favorable to burial and preservation of Pleistocene large mammals and probably also human remains. Locally, in recent swamps, large quantities of microbial methane have been generated. Unlike the places of helium and thermogenic (hydrocarbons and carbon dioxide) gas fluxes, such locations would be less likely locations for future discovery of well-preserved large vertebrates.

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