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On the Origin of Natural Bitumen at Yasnoye-8 (Sakhalin Island)

In this study, we analyze samples of a black substance that was used for restoring a Tym-type vessel at Yasnoye-8, Central Sakhalin. On the basis of similar finds from the Japanese archipelago, this was initially assumed to be natural bitumen. However, scientific methods have not previously been used to test this assumption. In addition to identifying natural bitumen, we sought to identify its source. The studies were carried out independently at two laboratories, using geochemical and petrographic methods, so the results may be considered reliable. For the first time in Russia, the method of pyrolysis gas chromatography-mass spectrometry was used, along with elemental and petrographic analysis, to identify hydrocarbon from an archaeological site. The results confirm the use of natural bitumen during the Early Iron Age. This can be procured in sufficient amounts on Sakhalin Island. Identification of specific sources is complicated by the virtually complete lack of geological data (bitumen is not mined for industrial purposes). Available materials suggest that the bitumen found at Yasnoye-8 originates from the northern Sakhalin petroleum zone, or from adjacent areas. No relationship to bitumen deposits in northeastern Honshu was found. Nor is it likely that the sample is related to surface hydrocarbons of Hokkaido.

Keywords: *Sakhalin, natural bitumen, Early Iron Age, Tym-type ceramics, pyrolysis gas chromatography-mass spectrometry, elemental analysis, petrography.*

Introduction

Natural bitumen represents a type of fossil hydrocarbon that humans began to use along with the development of technologies, primarily for the manufacture of hunting and fishing tools. These were employed to fasten stone tools to wooden bases as early as the Paleolithic and Neolithic Ages. The adhesive and water-proof properties of natural bitumen were highly appreciated in the various areas of human activities, from waterproofing containers to building complex engineering structures. Owing to the availability of oil deposits and active tectonic processes, Sakhalin Island, along with the Japanese archipelago, is one of the peculiar places in Northern Eurasia where humans could have been using crude hydrocarbons in their subsistence activities since extreme antiquity (Deryugin, 2014).

Object of the study

Our study is concerned with natural bitumen on a fragmented vessel from the Yasnoye-8 site, located approximately 5 km northwest of its eponym, the village of Yasnoye on the upper Tym River, Central Sakhalin (Deryugin, 2007a, b, 2010, 2015). The fragmented vessel was discovered in 2006 during excavation of a single rectangular-plan ditch with rounded corners, 22 × 19 m in size and 20–50 cm deep below the ancient surface. The structure without any distinct pillar-type constructions had a hearth at its center, near the eastern wall. The intended use of this object is unclear. However, the arrangement of goods argues for the economic use of the unearthed structure. The number of lithic artifacts (heavy-duty tools, end-scrapers, arrowheads, a borer, etc.) is negligible, and no typological variability is observed among these items. A large proportion of the flakes have been found in accumulations in the production zones along the southeastern wall of the ditch. The vast majority of ceramics have been discovered along the southwestern and northeastern walls of the ditch.

The site is single-layered, and the ceramic assemblage is morphologically consistent, which has made it possible to distinguish a separate Tym type of ceramics on Sakhalin Island. On the basis of 11 radiocarbon dates, the date of the ancient structure was determined to be within the 7th to 4th centuries BC (Deryugin, 2007b, 2015).

Test samples were taken from the vessel found as crushed vessel No. 9 in compact accumulations No. 29 and 32. The first accumulation was in pit No. 5, the second approximately 2 m from it, in a corner of the ditch. Among the 22 fragmented vessels that it was possible to reconstruct, either fully or partially, only one vessel showed traces of a restoration in ancient times that used coils of natural bitumen (Fig. 1). This is an unornamented flat-bottomed neckless vessel of open type, with a straight rim, which is not delimited from the body. The outer edge of the mouth is slightly folded outward, owing to thickening of the upper coil. There is a flange along the bottom edge. The vessel's height is 30.8 cm; its diameter is 30.5 cm at the upper edge of the rim, and 12.2 cm at the bottom. The vessel was manufactured using the coil-ring technique, and the coils were fastened together butt-to-butt. The paste contains a considerable proportion of temper in the form of rather well-graded fine sand. The vessel was exposed to bonfire baking at a rather low temperature.

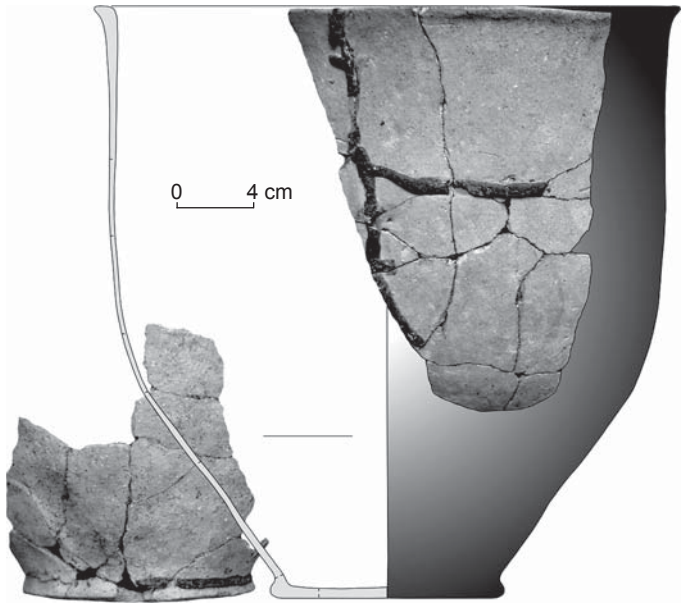

Fig. 1. The fragmented Tym-type ceramic vessel, with the remains of gluing coils of natural bitumen. Yasnoye-8.

Bands of a black substance are observed mainly on the outer side of the vessel, on the vertical crack formed as a result of the vessel's baking, and on the inner side near the mouth portion. Horizontal bands were located at the joints of clay coils, which were deformed to a near breakout condition during baking, probably because of the thinness of the vessel's walls. The majority of found coils were scaled off from the vessel's walls, and exactly these fragments were subjected to geochemical and petrological analyses.

Problem statement

In this study, we planned to address two tasks. The first was to confirm the assumption about the bitumen-component of the substance that was used for the restoration of cracked vessels in ancient times. The second, stemming from a positive result to the first, was to identify a specific source of natural bitumen from the Yasnoye-8 site. No scientific research on the ancient use of natural bitumen on Sakhalin Island has so far been conducted. More than 20 years ago, the use of coils exactly of "asphalt-bitumen paste of natural origin" for restoration of vessels in ancient times was mentioned visually (Shubina, 1992: 126). However, it has also been suggested that the black adhesive substance from Sakhalin sites had an artificial origin (Vasilevsky, Grishchenko, 2012: 37).

The second task is no less essential. While the majority of archaeological sites where natural bitumen

was found on Sakhalin Island are localized within the established oil- and gas-accumulation zone of the Northern Sakhalin oil-and-gas bearing area (Belonin, Margulis, 2006), Yasnoye-8 is situated at a considerable distance from the known deposits or manifestations of this mineral product (Fig. 2).

There are various examples of the distance of natural bitumen sources from the places of use of this raw material at various epochs in other regions. At the Middle Paleolithic site of Umm el Tlel in Syria, where stone tools were found showing traces of fastening with bitumen and dating back to ca 70 ka BP, the used fossil adhesive material originated from the source at the Djebel Bichri deposit, located 40 km from the archaeological site (Boëda et al., 2008), i.e. within one day's walk. In Azerbaijan, where various forms of natural hydrocarbons had been used since extreme antiquity, bitumens were delivered to the Menteshtepe settlement dating to ca 3500 BC from the Byandovan bitumen deposit located 460 km away (Abbasova, 2012). The origin of natural bitumen from the Tell el-Oueili site of the Ubaid period (4500–3700 BC), in Southern Mesopotamia, is related to the deposits of Northern Iraq (the area of modern Kirkuk) (Connan, 1999: 40–41), and their distance exceeded 500 km.

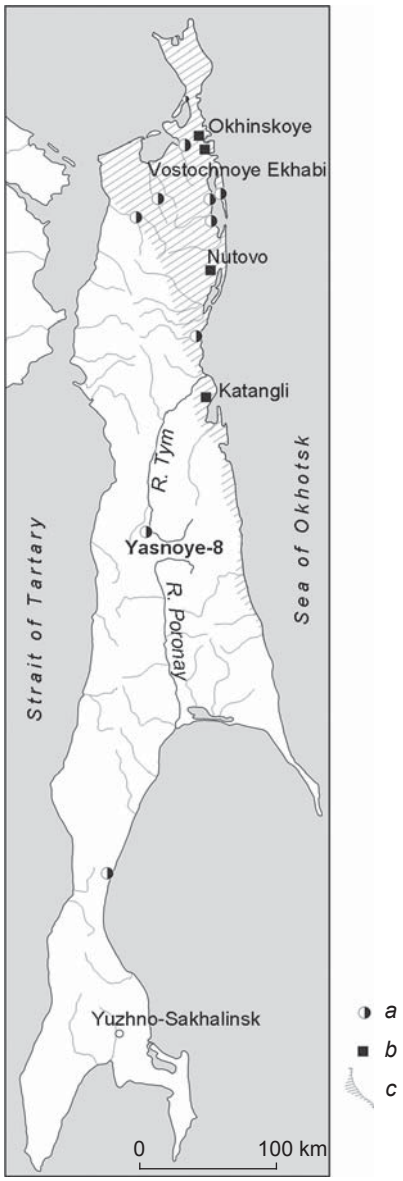

Fig. 2. Distribution of archaeological sites where natural bitumens were found (*a*) and the main manifestations of the latter (*b*) in the established oil and gas accumulation zone of the Northern Sakhalin oil-and-gas bearing area (*c*) (the data were derived from the following papers: (Belonin, Margulis, 2006; Vasilevsky, Grishchenko, 2012)).

On the neighboring Japanese archipelago, where the use of bitumens has been observed since the second half of the Initial Jōmon, while its peak is dated to the late and final periods of this epoch, three groups are distinguished according to the remoteness of the sources of raw materials from the places of consumption (Fukui Jun'ichi, 2010: 487). In the first group, the sources of fossil adhesive material were located no more than 50 km from the consumer settlement. In this case, the share of arrowheads with traces of fastening with bitumen could have reached more than 50 % of all those found at the site, such as, for example, in the territory of the Niigata Prefecture, where abundant bitumen manifestations are recorded. The sources of the second group were located at a distance of 50–100 km from the settlements; in the third group, at a distance of 100–150 km. The consumption of this material is inversely related to its remoteness.

The nearest known surface occurrences of natural bitumens south of the Yasnoye-8 site are in northern Hokkaido, in the areas adjacent to the Soya Strait. These are recorded on oil deposits of Wakkanai, Menashi, and Kita Toyotomi (Ibid.: 490). Unfortunately, we are not familiar with their identifying characteristics, owing to insufficient knowledge of both Hokkaido and Sakhalin bitumens. However, the assumption is noteworthy on the basis of the chromatography-mass spectrometry results (Kato et al., 2008: 1027), according to which, natural bitumens at a number of Hokkaido sites originate from the Nutovo deposit in the north of Sakhalin.

Study method

The nature of the organic compounds in a sample of substance from Yasnoye-8 was identified using the pyrolysis gas chromatography-mass spectrometry

method (standard conditions) (F-Search…, 2010; Sukhoverkhov et al., 2014). A Shimadzu GCMS QP-2010 gas chromatograph-mass spectrometer was employed, along with a Double-Shot PY-2020iD pyrolyzer. The temperature of the pyrolyzer furnace was 600 °C, that of the PY/GC interface was 320 °C. Separation of pyrolysis products was performed using the Ultra ALLOY-5 column with helium as carrier gas. The column's temperature was programmed from 40 to 320 °C, with a rate of 20 °C /min. The comparison of pyrograms was carried out using F-Search "All-In-One" software, Ver. 3.10.

In order to correlate the Yasnoye-8 sample with some specific surface manifestation of natural bitumens, additional studies were conducted for identification of the elemental composition of bitumens and the composition and properties (reflective power) of macerals. A Yanagimoto MT-5 gas chromatograph was used for the CHNO analysis. The method was implemented under the standard conditions: helium as carrier gas, and a flow rate of 180 ml/min. During determination of the carbon, hydrogen, and nitrogen contents, the temperature in the combustion chamber was 950 °C, that in the oxidation chamber was 850 °C, in the reduction chamber 550 °C; for the oxygen, 1050, 1000, and 300 °C, respectively. Immediately before the analysis, the sample was dried in a vacuum desiccator for more than 24 hours.

The percentage material composition of macerals (organic microcomponents) of bitumen and the reflectivity coefficient of one of these were used as a supplemental marker for comparison with materials from the Japanese archipelago (Stach et al., 1982; Xiao Xianming et al., 1998). The material's composition was studied using an Axio Imager A2m microscope made by Carl Zeiss MicroImaging, at 500x magnification in reflected light. The quantitative relationship between macerals was determined on the basis of 400 reference points per 100 μm, using IBM SPSS Statistics software, Ver. 21.0. Determination of macerals based on the reflection coefficient and morphological characteristics was performed using the International Classification (The New Vitrinite Classification…, 1998; The New Inertinite Classification…, 2001).

Results

It has been established that the substance used at Yasnoye-8 pertains to natural bitumens that are well represented in northeastern Sakhalin as surface manifestations in the form of asphalt lakes and deposits of bituminous sand (Yaroshevich, Kravchenko, 1984). Analysis of the sample by the pyrolysis gas chromatography-mass spectrometry method showed no more than 30 per cent of coincidences with the majority of known natural and synthetic polymers in the standard library of the F-Search "All-In-One" software, Ver. 3.10. The search for matches in the library of oils and waxes from the Western Siberian and Sakhalin deposits* has established that the substance under study contains oil hydrocarbons, and is most similar to waxes (coincidence 71 %) and oil (coincidence 53 %) from the Sakhalin deposits (Fig. 3). The coincidence of 30 % to 45 % with oil and wax samples from other areas also unambiguously points to the petroleum nature of this substance.

The CHNO-analysis has demonstrated the following elemental composition of bitumen sample from Yasnoye-8 site:

H	6.02
C	66.39
N	1.14
O	19.78
Ashes	2.97
H/C	1.09
O/C	0.22

Most conspicuous is a low carbon-content. Judging by the relationship between the main elements, some similarity of this sample to Nutovo bitumen manifestations can be observed (Osnovniye puti…, 1961: 152–153). However, there is no overall database on small bitumen-manifestations and deposits of bituminous sand, which does not allow an exact determination of the source of bitumen used at Yasnoye-8.

In terms of the composition of macerals, the studied sample differs from natural bitumens found on some sites in northeastern Honshu (see *Table*). Though amorfinit predominates in all cases, its content is considerably higher in the bitumens originating from the deposits on Honshu Island. As for macerals of the vitrinite and inertinite groups, their amount is greater in the studied sample.

The reflection coefficient of amorfinit contained in bitumen from Yasnoye-8 is 5.68 %. This suggests a higher reflective power as compared to samples from the earlier studied deposits and archaeological sites in northeastern Honshu (Ujiie Yoshihiro, 2013). The data on reflective power of amorfinit of natural bitumens from Sakhalin and Hokkaido deposits are currently absent or understudied.

*The library was created by the authors on the basis of all available samples, and does not cover all deposits.

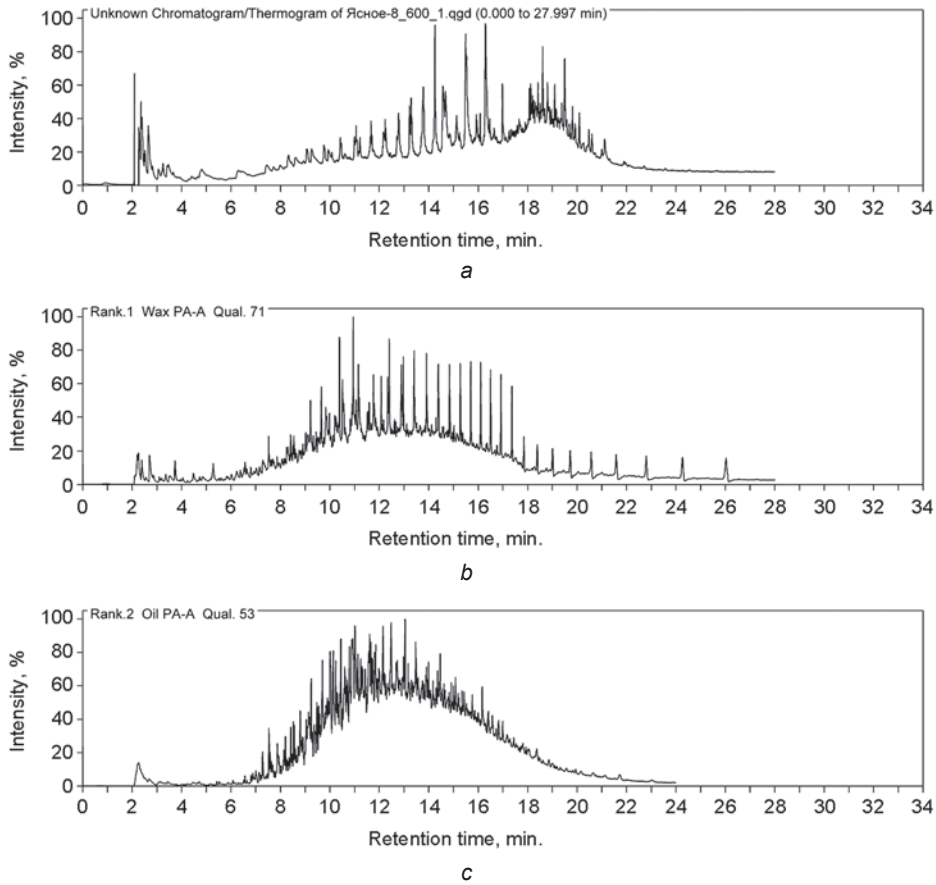

Fig. 3. Pyrograms of natural bitumen samples from Yasnoye-8 site (*a*), wax (*b*), and oil (*c*) from Sakhalin deposits.

Content of macerals in bitumen samples from the Yasnoye-8 site and a group of sites in northeastern Honshu, %

Group of macerals	Maceral	Yasnoye-8, the Yasnoye village	Shinmichi, the Kikonai village	Tangoyachi, the Hachinohe city	Tangoyachi (dump site), the Hachinohe city	Kazahari, the Hachinohe city	Matsugasaki, the Hachinohe city
Liptinites	Amorfinit	87.50	98.00	98.25	98.50	98.75	92.75
	Total	87.50	98.00	98.25	98.50	98.75	92.75
Vitrinites	Telinit	1.50	0.25	0.50	0.25	0.25	1.00
	Vitrodetrinit	4.25	0.75	0.75	0.50	0.50	1.75
	Korpokolinit	0.75	0.00	0.00	0.00	0.00	0.00
	Gelinit	2.50	0.00	0.00	0.00	0.00	0.75
	Total	9.00	1.00	1.25	0.75	0.75	3.50
Inertinites	Fyuzinit	0.25	0.25	0.00	0.00	0.25	0.25
	Semifyuzenit	0.75	0.25	0.25	0.50	0.25	0.50
	Funginit	0.00	0.50	0.00	0.00	0.00	0.75
	Inertodetrinit	2.50	0.00	0.25	0.25	0.00	2.25
	Total	3.50	1.00	0.50	0.75	0.50	3.75

Conclusions

As a result of undertaken geochemical and petrographic studies of adhesive black substance on the vessel from Yasnoye-8 site, it has been fully confirmed that this is a natural bitumen, whose surface manifestations are well represented in northeastern Sakhalin. At present, it is impossible to determine the specific source of the raw materials because of the complete absence of data on the abundant small surface manifestations of hydrocarbons, and the insufficient exploration of the large manifestations that were partly studied for industrial purposes. Judging by the presence of certain mechanical admixtures, it cannot be ruled out that natural bitumen from Yasnoye-8 originates from some unknown small manifestation of bituminous sand in the site's neighborhood. This bitumen is obviously unrelated to the deposits in northeastern Honshu. Any relation to surface manifestations of Hokkaido hydrocarbons remains to be determined; however, it is hardly likely.

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