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Mineralogy of Fossil Resins in Northern Eurasia

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Abstract—The investigation is focused on identification and origin of fossil resins from the Cretaceous, Tertiary, and Quaternary sediments of Northern Eurasia on the basis of detailed study of their physical and chemical characteristics: morphology; size; mass; density; optical, mechanical, and thermal properties; chemical composition; etc. The composition of amorphous organic minerals with polymeric structure, fossil resins included, is studied with IR spectrometry, the EPR method, derivatography at low heating rates, XRD, chemical analysis, emission spectrometry, etc. The results of investigation summarized for the Baltic–Dnieper, North Siberian, and Far East amber-bearing provinces show some similarity of fossil resins in combination with specific features inherent to each province. Resins from the Baltic–Dnieper province should be termed as amber (succinite). Their variety is the most characteristic of Northern and Eastern Europe. Amber-like fossil resins from the North Siberian and Far East provinces are irrelevant to succinite. They usually occur as brittle resins, namely, retinite and gedanite, without jewelry value. Viscous fossil resin rumänite with an expected high economic value occurs in the Far East, on the shore of Sakhalin Island.

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INTRODUCTION

The current ideas about organization of matter and poorly ordered phases, the development of the theory and analytical methods, and equipment for mineralogical investigations are expanding the sphere of mineralogical research over polymer organic minerals and other noncrystalline compounds known in the lithosphere. The main objective of such research is the revision of known mineral species, investigation of their structure and economic value, determination of role and place of these compounds in the evolution of the lithosphere, and elaboration of their structural and genetic classification.

The vast territory of Northern Eurasia (part of the continent located to the north of 40° N) is rich in fossil resin varieties, occurring in the sediments of different stratigraphic levels. The term *fossil resin* denotes secretions of terpene plants subjected to fossilization. Fossil resins are often named *amber* in spite of the fact that this term has many meanings in both the scientific and popular literature. The application of this term to any fossil resin without regard to its physical and chemical features is improper and unjustified from the scientific point of view. Therefore, the term *amber* should be applied only to a highly polymerized variety of fossil resins (succinite), occurring mainly on the southwest shore of the Baltic Sea and in the Dnieper basin. The term *amber-like resin* is reasonable to use for the fossil resins that differ from succinite in their physical and chemical characteristics (Table 1).

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Unfortunately, in spite of some progress achieved in recent years in investigation of succinite and other fossil resins, they remain poorly studied, as well as many other organic minerals. Numerous findings of resins simply remain unstudied because their scientific and applied potential is as yet unrealized. Therefore, investigations in this field are quite topical.

RESEARCH METHODS

The application of physical and physicochemical methods to analyzing the composition of amorphous organic minerals with polymer structure, including fossil resins, allowed Savkevich (1987) to recommend IR spectrometry (frequency range 2000–400 cm^{-1}), the EPR method at different temperatures (sensibility of no less than 1×10^{13} g^{-1} of unpaired electrons), derivatography at low heating rates (about 1 deg min^{-1}), XRD, chemical analysis, and determination of trace element contents in amber acid. T.N. Sokolova successfully studied plastic and thermal properties of fossil resins for their identification. Along with traditional mineralogical investigations, this method allows identification of fossil resins up to determination of a species (succinite, gedanite, etc.).

Precisely such a comprehensive approach has been used in this study for investigation of fossil resins from Northern Eurasia. In order to provide more accurate mineralogical identification of specimens, the results obtained were compared with similar data on fossil resins from the Pal'mniken deposit (Savkevich, 1970; Katinas, 1971) and Klesovo deposit (Srebrodol'sky, 1984), occurrences in the Yugorsky Peninsula (Yush-

Table 1. Physicochemical characteristics of fossil resin species, after Savkevich (1970) and Trofimov (1974)

Species	Chemical composition, wt %				Color	Microhardness, kgf/mm^2	Brittleness number, g	Melting temperature, °C	Amber acid content, wt %	Traditional localities of findings
	C	H	O	S						
Gedanite	80.59	10.63	8.62	0.16	Yellow, brown	23.5–25.4	20–50	210–260	<1	Baltic region
Delatinite	80.98	10.46	7.61	0.95	Red, brown	27.7–31.3	200–250	340–380	1–3	Carpathian region
Copalite	85.45	11.46	2.55	0.54	Yellow, honey	19.0–26.5	30–40	160–240	–	England
Retinite	81.30	11.08	7.11	0.51	Yellow, brown	19.7–26.0	20–50	130–180	–	Siberia
Rumänite	81.64	9.65	7.56	1.15	Red, brown	29.6–34.1	200–250	350–390	1–5	Romania
Succinite	78.75	10.25	10.75	0.25	Yellow, honey	24.5–30.9	200–250	320–370	3–8	Baltic region

kin, 1973) and Khatanga Basin (Sokolova, 1987), and resin findings in the Far East (Trofimov, 1974).

RESULTS OF INVESTIGATION

Morphology, size, and mass. The overwhelming majority of fossil resin grains from Belarus, Siberia, and the Far East are fragments of larger lumps. Some grains are characterized by a high degree of roundness and coated with a thin oxidation crust that hampers their genetic interpretation. By analogy with samples from the Baltic region and Ukraine, the preserved large lumps may be subdivided into overtrunk and intratrunk varieties. Primary drops found in Belarus, Siberia, and the Far East are rather deformed. Stalactites are small and have a fresh fracture. Sinter plates are thin; the surface of the grains bears numerous tracks of transportation in the form of furrows and hollows. The amber samples from Belarus, Siberia, and the Far East, on the one hand, and the Baltic region and Ukraine, on the other, differ in visually discernible degree of deformation. Casts of bark, wood fibers, and leaves are absent in samples from Belarus, thus indicating their significant transfer from the places of their primary formation. This is also confirmed by the size of samples from Belarus, Siberia, and the Far East. The size and mass of the grains are variable, but the percentage of large fragments of fossil resins from the Baltic region and Ukraine is usually much higher.

Optical properties. Fossil resins from the Baltic region vary in color from pale yellow, virtually colorless, to red-brown. Resins from Ukraine are commonly yellow-brown and brownish red like the samples from the Klesovo deposit and elsewhere, where fossil resins contain up to 0.1% Fe. Palette of Belarussian resins includes almost all mentioned hues except bluish, greenish (Baltic region), and cherry red (Ukraine). The samples from Siberia and the Far East are usually yellow and yellow-brown. The transparence of the fossil resin samples varies from crystal clear to opaque in all occurrences, depending on the number, size, and distribution of air bubbles, mechanical impurities, and degree of weathering.

The fossil resins from Baltic region, Belarus, Ukraine, Siberia, and the Far East do not differ in texture. The results of electron microscopy investigation of fine textural features are given below.

Transparent varieties of fossil resins (Fig. 1) are characterized by a small amount of fine hollows 0.00005–0.0025 mm in size and are devoid of any inclusions. The hollows are spherical in shape and distinctly delineated; rare fractures do not prevent free passage of light.

Translucent grains have a more complex internal structure (Fig. 2). Small hollows (0.001–0.01 mm) con-

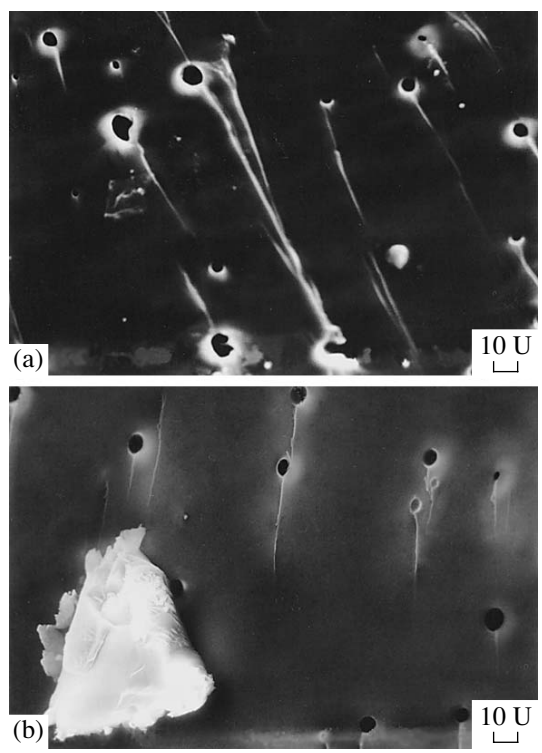

Fig. 1. SEM photomicrographs of transparent fossil resins from (a) Baltic–Dnieper and (b) North Siberian provinces. Magn. 600.

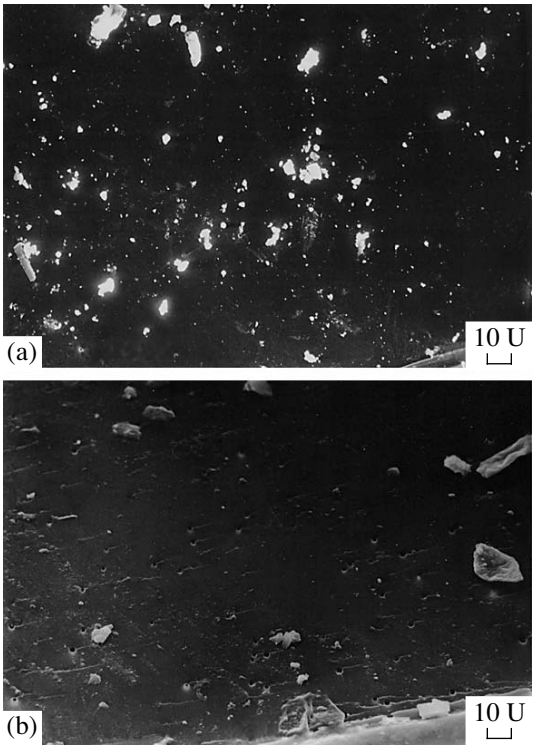

Fig. 2. SEM photomicrographs of translucent fossil resins from (a) Baltic–Dnieper and (b) North Siberian provinces. Magn. 600.

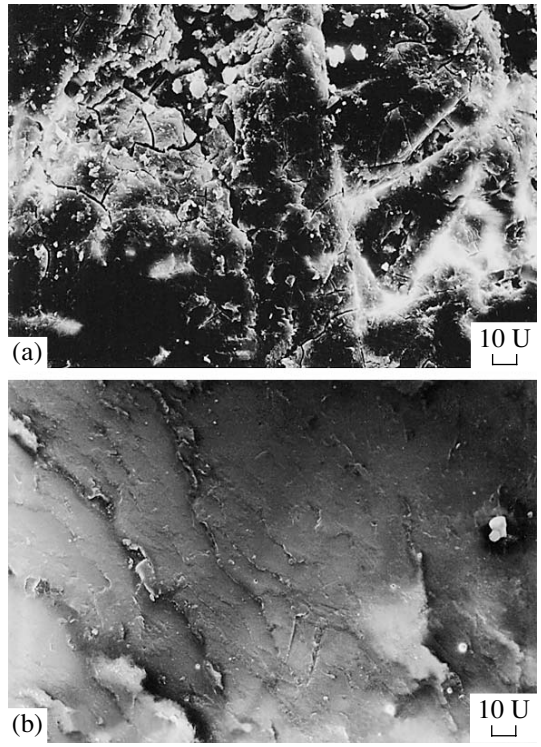

Fig. 3. SEM microphotographs of opaque fossil resins from (a) Baltic–Dnieper and (b) North Siberian provinces. Magn. 600.

centrate as irregular clusters or linear veinlets. The shape of the hollows is close to ellipsoidal; their outer boundaries are diffuse. The samples occasionally contain flakelike inclusions of unknown nature. These flakes and small fractures hinder free passage of light through samples.

Opaque samples are characterized by the most complex internal structure (Fig. 3). The hollows are large (0.0025–0.05 mm), numerous, and group into clusters and veinlets; hollow boundaries are diffuse. The samples contain flakelike inclusions of unknown nature and numerous internal fractures. The combinations of these elements are so complex and diverse that it is almost impossible to distinguish any special features.

The photoluminescence of fossil resins from the Baltic region and Ukraine are characterized by a wider emission band in the range 390–610 nm than the samples from Belarus, Siberia, and the Far East, which are distinguished by a narrow band in the range 435–560 nm.

Mechanical properties. Fossil resins from all regions are characterized by similar microhardness (Table 2). According to plasticity (brittleness), fossil resins from Belarus are classified as viscous and correspond to the samples from the Baltic region and Ukraine in brittleness number (200 g or more). The oxidized, more brittle fossil resins have a brittleness number of about 150 g, while the archeological samples, up to 120 g.

The brittleness number of fossil resin samples from Siberia varies from 50–80 g for unaltered transparent and translucent varieties to 80–100 g for opaque specimens, whereas this parameter ranges from 50 to 100 g in the unoxidized samples from the Far East and decreases down to 20–70 g in oxidized varieties. Thus, the studied fossil resins from Siberia and the Far East pertain to the group of brittle resins, while fossil resins found on the southeast shore of Sakhalin have brittleness number of more than 200 g and correspond in this parameter to the viscous fossil resins from the Baltic region, Belarus, and Ukraine.

Density. Unaltered varieties from different regions are similar in density (0.98–1.13 g/cm^3). In all provinces, the density of highly oxidized grains increases owing to pore healing.

X-ray diffraction. Comparison of samples from the Baltic region, Belarus, Ukraine, Siberia, and the Far East by parameters of radial distribution of atomic density (correlation functions) attests to the amorphous state of fossil resins. In the X-ray patterns of Belarussian fossil resins, halos are within a range of $2\theta = 11°$–$20°$ with a maximum at 15°–16°. In the X-ray patterns of Siberian fossil resins, two distinct halos ($2\theta = 8°$–$9°$ and 22°–24°) are observed. The first, more distinct, halo is typical of the majority of fossil resins. No inclusions of crystalline phases have been detected in fossil resins.

Table 2. Characteristic microhardness of fossil resins, kgs/mm^2

Occurrence	Variety	Loading, g		
		5	50	100
Baltic Region	Bright yellow, transparent	25.40	32.05	30.90
″	Dark yellow, smoky	24.56	29.17	28.11
″	Yellow-brown, bastard	22.38	27.23	26.91
″	Dark yellow, smoky	23.64	30.74	27.48
″	Yellow-brown, ivory	20.45	25.85	24.45
Belarus	Yellow-brown, bastard	22.20	30.40	28.20
″	Light yellow, transparent	23.10	29.90	27.90
″	Dark yellow, opaque	22.10	28.90	28.70
″	Dark yellow, transparent	23.20	29.14	27.14
″	Light yellow, transparent	23.50	29.33	27.19
Ukraine	Light yellow, transparent	23.45	29.95	26.15
″	Red-yellow, smoky	23.46	27.49	24.87
″	Yellow-brown, bastard	24.15	28.80	26.70
″	Dark yellow, bastard	22.65	29.58	25.10
″	Light red, bastard	24.11	29.42	27.65
Siberia	Lemon yellow, smoky	20.80	26.20	23.50
″	Honey yellow, bastard	21.70	27.40	24.55
″	Honey yellow, transparent	22.15	28.47	24.13
″	Red-brown, bastard	23.78	29.03	26.49
″	Yellow-brown, opaque	22.57	28.54	25.23
Far East	White-yellow, opaque	22.23	26.76	24.68
″	Brown-yellow, bastard	22.50	26.07	24.14
″	Dark red, transparent	24.19	28.38	26.84
″	Yellow-brown, smoky	23.32	27.93	25.01
″	Light red, opaque	20.97	24.09	22.18

Electron paramagnetic resonance. Free radicals in an amount of 10^{14}–10^{16} g^{-1} at a signal width of 10–15 ergs have been detected in amber from the Pal'mniken deposit. In the samples from the Klesovo deposit, the concentration of paramagnetic centers is within the same range. EPR spectra of the samples from Belarus, Siberia, and the Far East are characterized by appearance of intense signal as a singlet line [g = 2.0036(±5), ΔH = 33 ergs] after irradiation. The concentration of spins in all samples attains 3.3–3.7(±1.1) × 10^{19} sp/g. X-ray radiation leads to breaking of bonds in molecules of amber acid and formation of free radicals.

Thermal properties. DTA curves of the samples from the Baltic region and Ukraine (Fig. 4) are characterized by a wide and relatively weak endoeffect with a maximum within the range 98–130°C (160–185°C for Belarussian specimens). With increasing temperature, this effect gives way to a relatively strong exothermic rise, which is followed by a sharp endothermic doublet within the temperature range 311–330°C (320–340°C for Belarussian samples). Two wide exothermic effects within the ranges 350–365 and 478–508°C (355–370 and 490–520°C for Belarussian samples) are separated by flat endoeffect with a maximum at 400–425°C (395–420°C for Belarussian samples). Further heating results in melting of the polymer as recorded in the thermogram by the endothermic effect at 540–565°C (575–605°C for Belarussian samples).

The DTA curves of Siberian fossil resins are similar to the general configuration and position of the main thermal effects. Some discrepancies arise as a wide, low-temperature exoeffect probably related to the partial molecular reorganization at a maximum temperature of about 150°C for transparent varieties of Siberian fossil resins and 190°C for translucent resins. The maximum of the second exoeffect at ~290°C that indicates oxidation of resins occupies the same position in both thermograms, but is much wider for opaque varieties, where oxidation usually starts at 265°C in comparison to 285°C for transparent resins. The melting of both transparent and opaque fossil resins begins at 330–340°C and is recorded in sharp endoeffects. The melt-

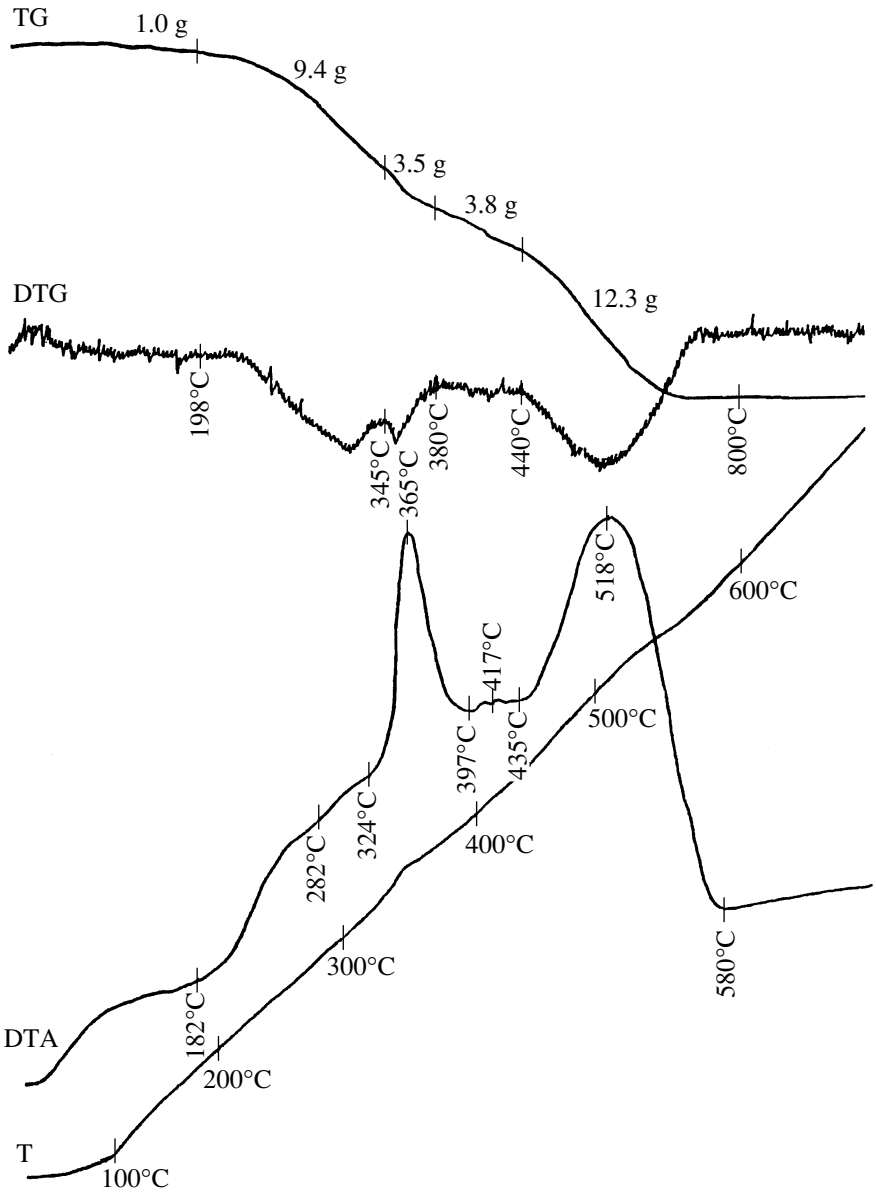

Fig. 4. Thermograms of fossil resins from the Baltic–Dnieper province (Gatcha–Osovo, Belarus).

ing is accompanied by oxidation of melting products, as is confirmed by the spectrum of effects in the interval 330–385°C, which is especially complex in the case of transparent varieties. Thermograms of Siberian fossil resins are similar to thermograms of those from the Far East; in particular, both demonstrate a complex set of effects in the range 300–400°C.

Temperatures of softening (T_s) and flow (T_f) are more informative for identification of fossil resins than the melting temperature. T_s of Belarussian resins is 120–180°C and T_s of Baltic amber is 130–170°C, while T_f of Belarussian and Baltic resins are 370–420°C and 370–410°C, respectively. According to these distinguishing features, all samples are similar and belong to the group of thermally stable and viscous resins. On the contrary, T_s of Siberian and Far East resins fall within the intervals 110–140 and 120–180°C and T_f are 150–190 and 160–250°C. Thus, these samples are thermally unstable and belong to the group of brittle resins. The data obtained for Sakhalin resins are markedly different: T_s is 180–230°C and T_f is 380–400°C, so that these samples belong to the group of viscous resins.

IR spectrometry. The IR spectra of amber samples from Belarus, the Baltic region, and Ukraine are similar in the frequency range 2000–400 cm^{-1}. They consist of the same absorption bands and differ only in intensity (Fig. 5). Interpretation of IR spectra indicates the presence of carboxyl, peroxide, hydroxyl, and complex ester functional groups (Bogdasarov, 2005) as well as single and double bonds in the structure of the studied

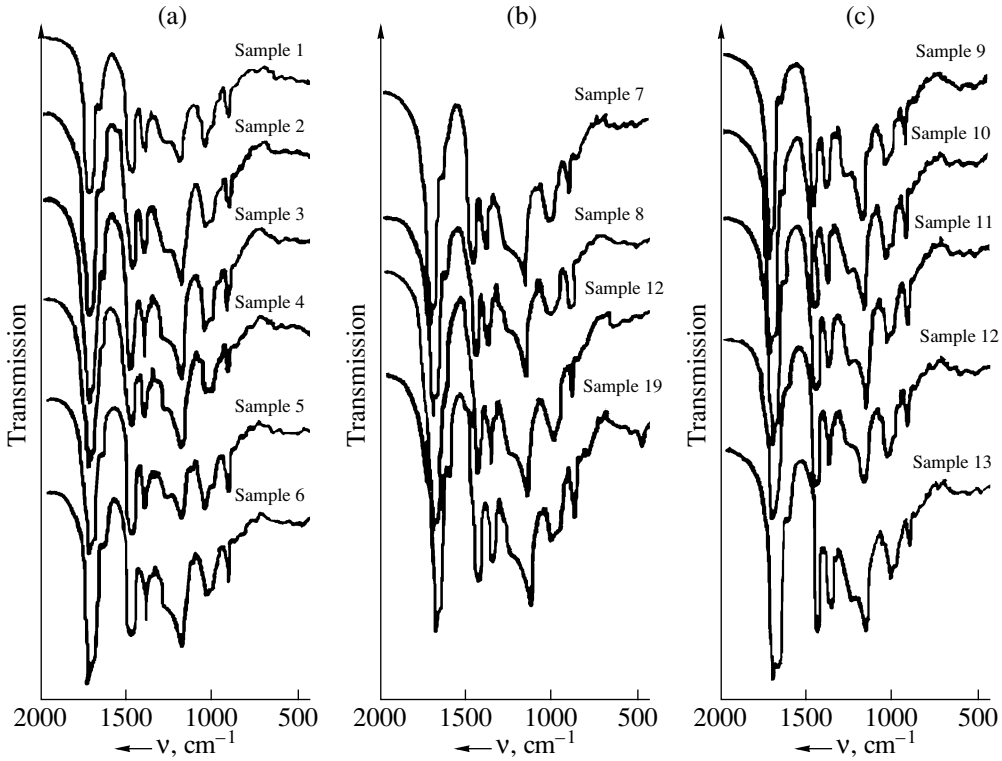

Fig. 5. IR spectra of fossil resins from the Baltic–Dnieper province, frequency range 2000–400 cm^{-1}. (a) Belarus: (1–5) Gatcha-Osovo, (6) Mikashevichi; (b) Ukraine: (7, 8, 18) Klesovo, (19) Novye Petrovtsy; (c) Baltic region (9, 10) Svetlogorsk, (11–13) Yantarny.

fossil resin varieties. Hence, these resins may be identified as succinite.

According to the IR spectra, fossil resins from Siberia fit gedanite from the Baltic region. Two retinite varieties of the so-called Yantardakh and Begichevo types are distinguished by IR spectra among the resin samples from the Khatanga Basin (Sokolova, 1987). Fossil resins from the Far East correspond to retinite, which is widespread in Primorye, and rumänite found on the southeastern shore of Sakhalin (Bogdasarov, 2005).

Chemical composition. The fossil resins from the Baltic region, Belarus, Ukraine, Siberia, and the Far East are similar in C, H, O contents and differ in S concentrations (Table 3).

Results of chemical analysis of fossil resin samples and coating reaction crust are of special interest. As a rule, the outer crust differs from the inner unaltered part of a specimen in noticeable enrichment in O and depletion in C and H (Table 4). This difference is typical of fossil resins from all provinces: oxidation results in an increase in O content and a decrease in other elements.

Fossil resins contain a rather wide range of trace elements, but their contents are somewhat lower in the Baltic region and Belarus than in Ukraine (Table 5). The Ukrainian amber contains Y, Zr, Pb, Zn, and some other elements, which are not detected in amber from the Baltic region and Belarus or are present there in lesser amounts. Ash of fossil resins from Northern Siberia and the Far East contains Ca, Mg, Si, Al, Fe, Mn, and Cu. The data obtained coincide with trace element contents in gum of contemporary conifers. The detected trace elements likely participated in physiological processes accompanying the growth and development of amber-bearing conifers.

The content of amber acid is of special importance for identification of fossil resins. Free amber acid concentrates in an amount of 3.20–7.80 wt % in Baltic amber, 3.25–7.87 wt % in fossil resins from Belarus, and 0.90–6.40 wt % in samples from Ukraine. The amount of amber acid is variable not only in fossil resins from different occurrences but also in different grains of the same occurrence and even in one sample from zones of nonuniform oxidation. The higher oxidation degree, the higher the content of amber acid. In the most oxidized grains, the content of amber acid reaches 8.11–9.44 wt %. Amber acid has not been found in the products of dry distillation of fossil resin samples from different occurrences in Siberia and the Far East.

CONCLUSIONS

The performed mineralogical study of fossil resins from Northern Eurasia allows the resins from the Baltic region, Belarus, and Ukraine to be identified as amber (succinite). Fossil resins from Siberia and the Far East usually pertain to brittle varieties: gedanite, which is

Table 3. Chemical composition of fossil resins

No.	Location of finding	Color	Content, wt %					C/H
			C	H	S	N	O	
1	Baltic region	Yellow, transparent	80.84	10.48	0.18	0.15	8.35	7.71
2	″	Dark yellow, transparent	79.75	10.50	0.10	0.15	9.50	7.60
3	″	Light yellow, bastard	80.08	10.38	0.31	0.27	8.96	7.71
4	″	Light yellow, bastard	79.71	10.47	0.10	0.17	9.55	7.61
5	Belarus	Yellow, translucent	79.75	10.25	0.25	n.d.	9.75	7.60
6	″	Honey yellow, translucent	80.38	10.83	0.25	n.a.	8.54	7.42
7	″	Light yellow, opaque	80.85	11.37	n.d.	″	7.78	7.11
8	″	Red-orange, transparent	77.03	9.80	0.37	n.d.	12.80	7.86
9	Ukraine	Reddish, transparent	78.93	9.14	1.45	n.a.	10.48	8.64
10	″	Light yellow, opaque	80.25	10.15	1.20	″	8.40	7.90
11	″	Yellow-brown, transparent	75.39	9.43	1.24	″	13.94	7.99
12	″	Honey yellow, smoky	80.39	10.18	1.04	″	8.39	7.90
13	Siberia	Dark yellow, transparent	80.54	10.56	n.d.	″	8.90	7.62
14	″	Light yellow, transparent	79.83	11.74	0.05	1.12	7.26	6.80
15	″	Yellow-brown, opaque	79.59	11.55	0.04	1.07	7.75	6.89
16	Far East	Dark brown, opaque	78.57	10.76	0.10	n.a.	10.57	7.30
17	″	Red-brown, transparent	79.58	10.03	0.07	″	10.32	7.93
18	″	Honey yellow, smoky	78.41	10.93	0.08	″	10.58	7.17

Note: n.d. is not detected; n.a. is not analyzed.

Table 4. Chemical composition of the inner part and the outer oxidation crust of fossil resins

No.	Location of finding	Color	Content, wt %			
			C	H	S	O + N
1	Baltic region	Light yellow, translucent	78.15	10.20	0.30	11.35
		Crust	74.43	10.08	0.35	15.24
2	″	Dark yellow, opaque	78.89	10.24	0.35	10.52
		Crust	75.20	10.00	0.30	14.50
3	Belarus	Orange, translucent	79.80	10.47	0.57	9.16
		Crust	73.88	9.91	0.06	16.15
4	″	White, opaque	79.65	10.67	0.30	9.38
		Crust	75.93	10.56	0.35	13.16
5	″	Yellow-brown, opaque	77.44	10.75	0.35	11.46
		Crust	74.59	9.51	0.80	15.72
6	Ukraine	Yellow-red, translucent	77.20	10.30	0.45	12.05
		Crust	75.63	10.03	0.80	13.54
7	″	Yellow, opaque	80.15	10.05	0.50	9.30
		Crust	74.70	9.60	0.50	15.20

more abundant in Siberia than in the Baltic region, and retinite, which is not of gem value. Viscous fossil resin rumänite with a possible economic value occurs on the shore of Sakhalin Island. The eventual settling of the question about the position of these resin varieties in the mineralogical classification is a subject of future research. The solution of this problem depends on the accumulation of valid and systematized information

Table 5. Trace element contents in fossil resins, wt %

Element	Baltic Region	Belarus	Ukraine	Siberia	Far East
Al	0.0003–0.003	0.0003–0.009	0.0003–0.003	0.0003–0.004	0.0003–0.005
Ba	–	0.0001	0.0001	–	–
V	–	0.000–0.0005	0.0001–0.0005	–	–
Fe	0.01	0.005	0.003–0.1	0.005–0.01	0.005–0.01
Y	–	–	0.0005	–	–
Ca	0.1–0.3	0.01–0.05	0.05–0.5	0.01–0.5	0.05–0.5
Co	0.0003	0.0001	–	–	–
Si	0.003–0.03	0.001–0.1	0.003–0.1	0.001–0.1	0.007–0.1
Mg	0.003–0.01	0.0001	0.001–0.1	0.003–0.01	0.001–0.1
Mn	0.001	0.0002	0.003–0.005	0.001–0.005	0.003–0.005
Cu	0.0003–0.001	0.0001	0.0003–0.001	0.0003–0.001	0.0003–0.001
Mo	–	0.0001	–	–	–
Na	0.001–0.003	0.0001	–	–	–
Pb	–	–	0.001–0.005	–	–
Ti	0.001–0.01	0.005	0.001–0.002	–	–
Cr	–	0.0005	0.0007	–	–
Zn	–	–	0.001–0.003	–	–
Zr	–	–	0.003	–	–

about amber-like fossil resins over the world by analogy with the data presented in this paper.

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