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Nanostructurization in X-Ray Amorphous Organic Substances of Geological Origin

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Abstract—The nanosized structures of natural X-ray amorphous organic substances were examined with the use of atomic-force microscopy. The supramolecular structure types and particle sizes of natural solid bitumens from asphaltites to high anthraxolites were determined. It was shown that the supramolecular structure is suitable as a diagnostic structural criterion for grouping and subgrouping natural solid bitumens. Specific features of the nanostructure of Baltic amber were determined.

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Originated as early as the beginning of the XX century [1], organic mineralogy still ranks among the less thoroughly developed domains of mineralogy because of a complex heterogeneous composition and (typical) ultradispersity of natural organic compounds [2, 3]. Nevertheless, natural organic compounds, above all X-ray amorphous ones, belong to the most interesting subjects of mineralogical research owing to the diversity of nanometer-sized structural elements they comprise [2–5], which are termed supramolecular structures.

Here, we report the results of a study of the supramolecular structures in natural solid bitumens and fossil resins, which have the widest occurrence in lithosphere and the largest practical significance among X-ray amorphous organic mineral substances.

Natural Solid Bitumens

Meant by natural solid bitumens are hydrocarbon-based compounds (from high-molecular-weight hydrocarbons and complex mixtures thereof to high-carbon varieties) that have solid consistence and are the result of various geological processes. Essential implications of the molecular heterogeneity in bitumens include indistinct boiling, melting, and solidification points; variable density; broadly fluctuating solubility; and dispersed structure due to the presence of different kinds of segments: crystallites, pores, and colloid particles [3]. Researchers remain at odds over a uniform approach to systematization of natural bitumens, which is due mainly to the fact that, under geological conditions, bitumens resulted from processes of different nature may belong to the same taxon [6–10]. In this connection, the greatest popularity among foreign researchers is enjoyed by the approach based on Van Krevelen diagram [11], which is a plot of the atomic ratio of hydrogen to carbon on the ordinate vs. atomic ratio of oxygen to carbon on the abscissa. This diagram demonstrates the principle evolutionary paths followed by for organic matter nature: coalification (plant debris–coal) and bituminization (oil–bitumens).

As to approaches to systematization of bitumens, proposed by scientists in Russia and in the former USSR, nearly all of them are based on V.A. Uspenskii's concept [12, 13] which implies separation of bitumens into three groups depending on which of the transformation type, thermal-metamorphic, phase-migrational, or hypergenic, they underwent. These types underlie the modern classification of solid bitumens [6, 10] which distinguishes among three genetic sequences of which two sequences result from transformation of petroleum (carbonization and oxidation sequence) and one, from transformation of gas condensates. The carbonization sequence includes oils, malts, asphalts, asphaltites, kerites (subdivided into low and high, depending on the degree of alteration), and anthraxolites (low, medium, and high). During transformation, the high-molecular-weight part of petro-

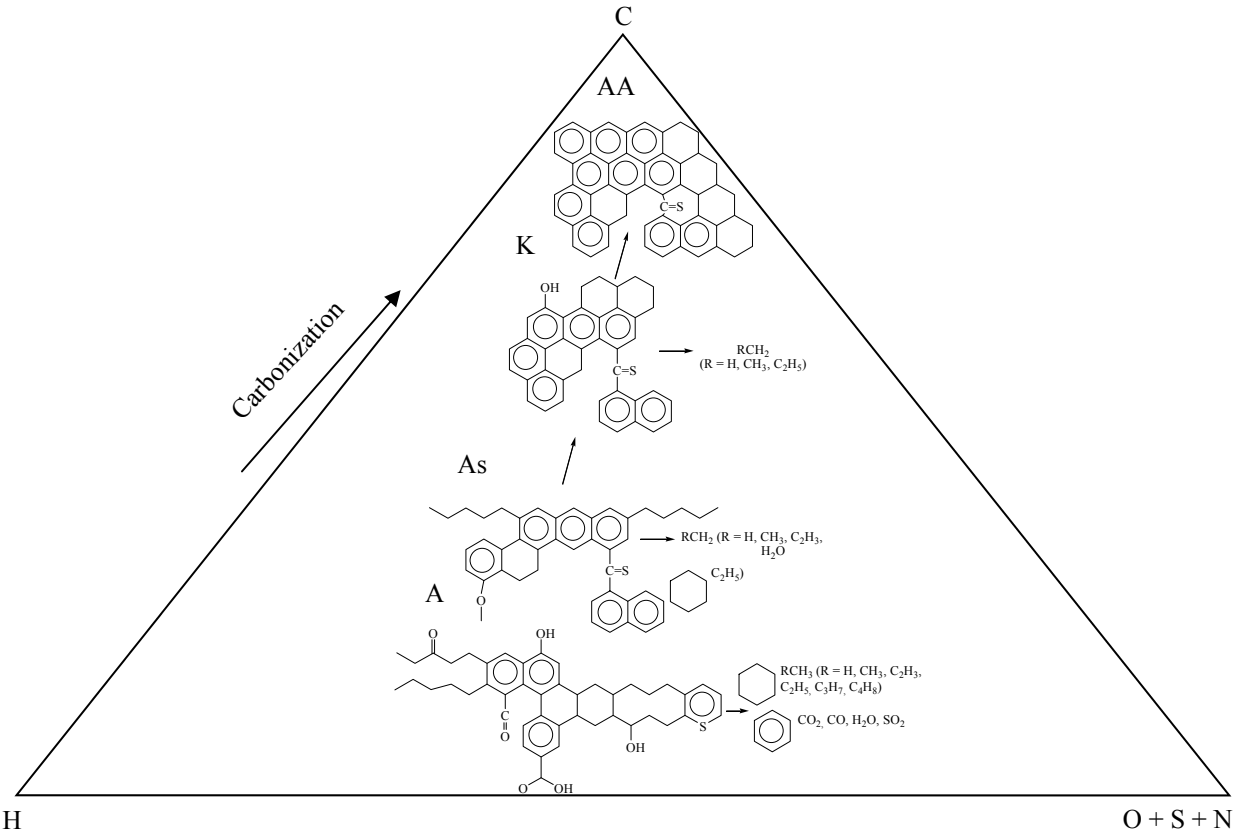


Fig. 1. Scheme of the structural transformations of solid bitumens at the molecular level in the carbonization sequence: (A) Asphalts, (As) asphaltites, (K) kerites, and (AA) anthraxolites.

leum undergoes degradation, loses hetero elements, and the carbon backbone undergoes progressive carbonization, which leads to the general carbonization till formation of virtually monocarbon substances, high anthraxolites (Table 1). The free carbon tends to form a graphite-like phase, with the interlayer spacing (d_{002}) decreased from 0.370 nm in kerites to 0.335 nm in anthraxolites.

The major criteria underlying classification of bitumens at the present time are summarized in the table. Finer differentiation of classes into subclasses is based on the use of IR spectroscopic data, X-ray diffraction patterns, etc. [2, 5, 14].

Figure 1 demonstrates the molecular transformation mechanisms [5]. The principal role in transformation of a hydrocarbon substance in the carbonization sequence belongs to thermal exposure to diversified geological factors: volcanic activity, hydrothermal processes [2, 10, 13].

Supramolecular structuring in natural solid bitumens was detected with the use of optical and

Natural bitumen classification according to V.A. Uspenskii [12, 13]

Natural bitumen class	Oils, %	Resins, %	Asphaltenes, %	Solubility in chloroform, %
Malts	45–65	30–40	5–15	100
Asphalts	25–45	30–50	15–60	100
Asphaltites	5–25	5–40	30–90	90–100
Kerites	0–1	0–5	1–50	10–20
Anthraxolites	0	0	0	insoluble

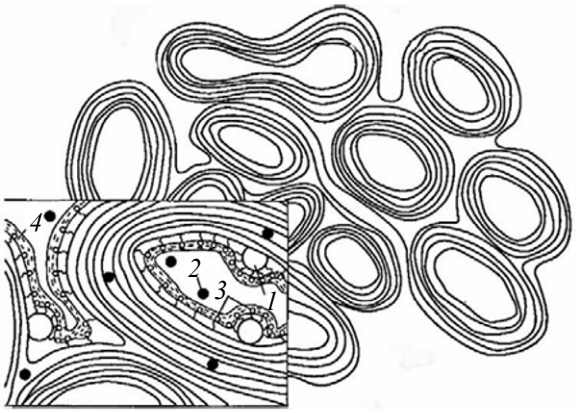


Fig. 2. Physicochemical model of the structure of high anthraxolites from Karelian shungite rocks [23]: (*1*) fullerenes, (*2*) organometal compounds, (*3*) surfactants, and (*4*) water.

electron microscopic techniques [2, 14–17]. The morphology of the heaviest bitumen components (asphaltenes) was examined for samples deposited onto substrates from solvents [18]. Those studies revealed the occurrence of diversified, mostly fibrous and globular, microstructures in bitumens. The currently prevailing view is that the structure type in each specific case depends on the balance of the intra- and intermolecular interactions and the interaction of the macromolecules with their environment [2, 15]: With the intramolecular forces outweighing the strength of interaction with the environment, the molecules are folded into globules; otherwise the macromolecules tend to unfold into fibers. The process may go further (which is a frequent event), and the subsequent aggregation of the primary particles will lead to multilevel structures, e.g., spherulites, dendrites, larger globules.

Certain distinctions were revealed among the supramolecular structures of different classes of natural bitumens; at the micrometer level such distinctions were observed even for samples from the same subclass [2, 14–18]. For example, Melkov and Sergeeva [14] believe that asphalts and asphaltites are characterized by predominantly "spheroidal aggregations of their supramolecular particles (globules)," while Pen'kov [17] reported on their having a predominantly fibrous structure.

In kerites there exist globular, fibrous, banded, dendritic, and ribbon-like supramolecular structures; their aggregation type broadly varies from subparallel to felt-like. Globules, in turn, form various aggregates, in particular, spheroidal and bunchy segregations. In anthraxolites, along with globular structures, there exist micrometer-sized (most likely, secondary) banded, fibrous, dendritic, and other structures. Presumably, these different patterns should be interpreted in the context of the supramolecular structure type as being dependent on the initial substance and geological formation conditions. Often, heterogeneities that are seen in images and interpreted as supramolecular structures correspond more closely to shear-type textures which are independent of the type and size of supramolecular particles. Comparison of relevant data reported by different researchers is complicated by the fact that they do not always clearly identify the particle size and aggregation level. For example, Pen'kov's opinion [2] that the largest size is achieved by supramolecular structures in the least (ozokerites, wurtzilites) and most highly (high kerites and the majority of anthraxolites) carbonized bitumens seems disputable from advanced viewpoint [4, 5, 19].

Among solid bitumens, the most comprehensive research effort was received by high anthraxolites of Karelian shungite rocks (often termed shungites) [20]. Their structure is described as consisting of packages of planar or twisted graphene grids with the interlayer spacing (0.34–0.36 nm) exceeding that in graphite. According to the X-ray diffraction data, these packages consist of 5–6 layers [21], and according to transmission electron microscopy data, of 5–14 layers. The layers are typically closed on themselves; they cover pores [22, 23] and form globules (Fig. 2).

Shungites are geological materials in which fullerenes were first detected [24]. More recently, fullerenes were found in genetically different organic substances, e.g., in lightning-induced products (fulgurites) in Florida (US) [25] and in carbonaceous substances of suwites of Sudbury astroblem in Onaping Formation (Canada) [26]. Today, the occurrence of fullerenes in Karelian shungites is a disputable issue [27], but researchers tend to accept the opinion that the supramolecular structure in shungites is of the fullerene type, which suggests that simplest fullerenes constitute only a small part of the carbon cluster family [22]. Diagnostics of simplest fullerenes in shungites may be a problem because the physicochemical bonds they form within the structure of shungite carbon prevent the use of conventional procedures for their extraction and analysis [20].

The boundary criterion for differentiation between the molecular and supramolecular levels is based on

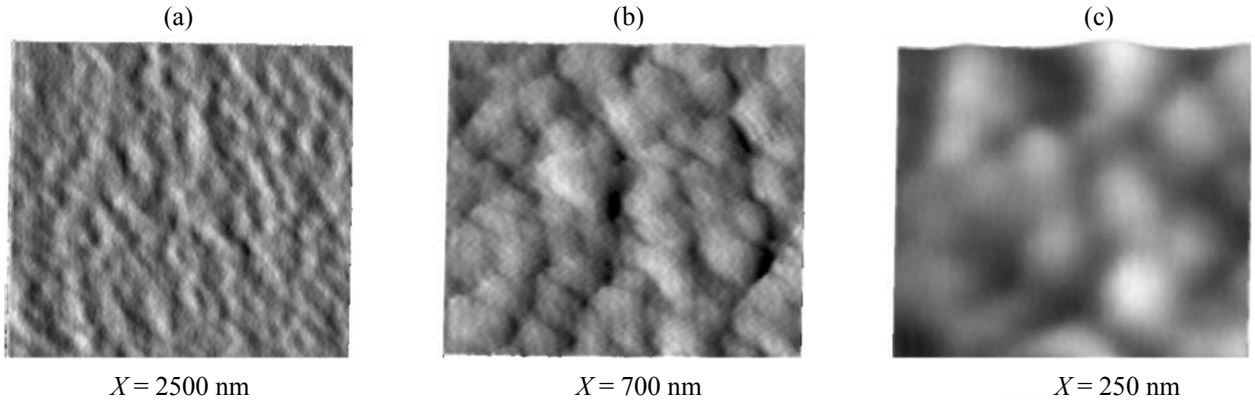


Fig. 3. Typical supramolecular structures for (a) low kerite, (b) high kerite, and (c) high anthraxolite.

the principal physical difference between molecules and supramolecules, which consists in that the latter have a surface. Overall, optical and electron microscopic examinations of the supramolecular structures of organic substances are complicated in view of the specific features of application of these techniques on the nanosize scale [28]. Recent introduction into the mineralogical practice of more advanced scanning probe microscopic techniques suitable for observation of nanosized particles has brought the understanding of supramolecular structuring in natural solid bitumens to a new level.

Scanning tunneling (STM) and atomic-force (AFM) microscopic examinations of solid bitumens have been carried out since the middle of 1990s and allowed visualization of asphaltene components isolated with the use of solvents from natural (corresponding to asphaltites in Uspenskii's classification) and artificial bitumens and deposited onto various substrates [30–35] However, this multistep procedure of isolation of supramolecular particles from a bitumen substance poses significant limitation on the amount and nature of the information derived thereby. For example, the mutual arrangement of supramolecular particles and their contacts in the substance cannot be examined. It is not improbable that the size and morphology of the particles are modified by the extraction and "purification" procedures. Therefore, in the current stage the greatest interest is focused on direct observation of the structure, without chemical treatment of the samples. Examples of such observation can be found in STM visualization of the globular structure of a high anthraxolite from Karelian shungite rocks by N.P. Yushkin [36] for Shun'ga deposit samples, as well as in the AFM examination by Loeber et al. [37, 38] who revealed spherical particles with the diameter of 100–200 nm, that constitute artificial asphalt and asphaltite and are integrated into grid structures. It should be mentioned, however, that in the last-named studies the samples were prepared by deposition of hot asphalt and asphaltite onto a substrate, so that the original supramolecular structure might be perturbed.

We applied the STM and AFM techniques in study of the evolution of the micro- and nanosized supramolecular structures in the carbonization sequence of natural solid bitumens.

The collection that we examined was basically made of samples of solid bitumens from Timan-Pechora province (Komi Republic), including asphaltites and kerites from Yarega, Voya, and Izhma deposits and occurrences, as well as a kerite sample from Yaman-Kasy deposit (South Ural) and medium anthraxolite from the lower Lena river basin. The supramolecular structure of high anthraxolites was examined for reference representative samples of Karelian shungite rocks, which were available from Zazhogino, Maksovo, Nigozero, Shun'ga, and Chebolaksha deposits and Shardon Isles occurrences [3, 19, 39].

The main types of the observed nanometer-sized elements of supramolecular structures are identical to those detected on the micrometer scale. Specifically, there are globules and fibers and, additionally, more complex forms of supramolecular elements, as well as aggregates thereof [3–5, 39]. Figure 3 shows typical images of various supramolecular structures.

Analysis of the supramolecular elements at the initial aggregation level revealed a typically fibrous structure for the asphaltites examined. The fibers have a diameter of 200 nm and a visible length of no larger

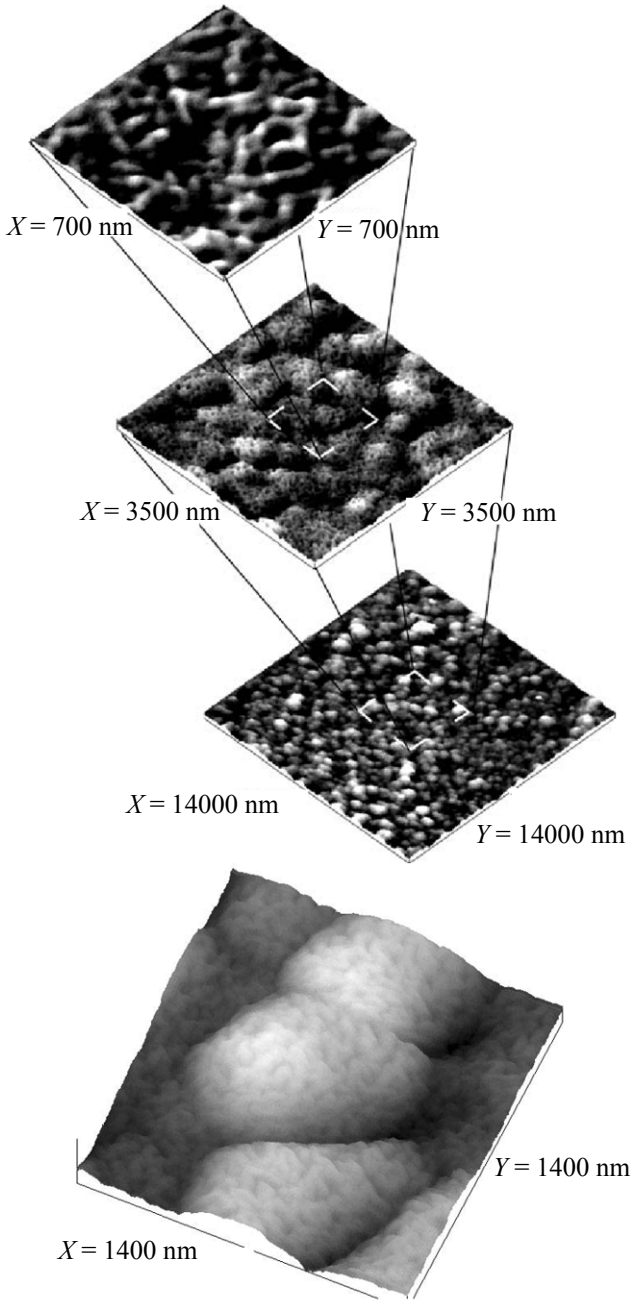


Fig. 4. Multilevel structure of anthraxolite.

than several micrometers; they are always bent and have three-dimensional interlacings and intergrowths arranged into chaotic structures. Low kerites are dominated by a fibrous supramolecular structure, with the fiber lengths and diameters analogous to those of asphaltites. However, they differ substantially from the latter in having a generally unidirectional orientation of fibers, despite of local branching, as confirmed by the Fourier spectra of the images [4].

High kerites are also characterized by a dominating fibrous structure, with the orientation ordering of fibers, characteristic for low kerites, preserved, but the fibers are much shorter than those in asphaltites and low kerites. Moreover, this bitumen subclass is characterized by a more complex supramolecular struc-ture in which, along with fibrils, there exist numerous diversely configured (dumbbell-, globule-, and drop-shaped) structural elements.

Typical for high anthraxolites in Karelian shungites is the globular supramolecular structure. Depending on the deposit, the globule size ranges from 25 to 40 nm on the average along the Zazhogino–Maksovo–Shun'ga–Nigozero–Shardon Isles series. A minimal globule size is characteristic for anthraxolites that were exposed to the highest temperatures in Maksovo–Zazhogino field [20]. As supported by the results of Fourier analysis of images, no regular arrangement of the globules was detected in anthraxolites on the whole, but certain regular features can be statistically identified in the arrangement of globules, which are associated with their grouping. Such aggregates are most often represented by chains or isolated accumulations having various shapes and sizes, and seldom, by local regular structures.

The Maksovo anthraxolite is distinguished by the largest length of the subparallel chains of the globules arranged into multiple-connected oriented and dendritic structures. As to the Shun'ga anthraxolite, it is dominated by chain-like aggregation, though on a much smaller scale compared to the Maksovo anthraxolite; some independent lumpy accumulations are also observed. Anthraxolites from Zazhogino and Nigozero deposits are composed of a uniform globular mass. The microscopic probe images of bulky globular structures [4, 36, 39] may be interpreted in terms of the above-mentioned Kovalevskii's model as well [22].

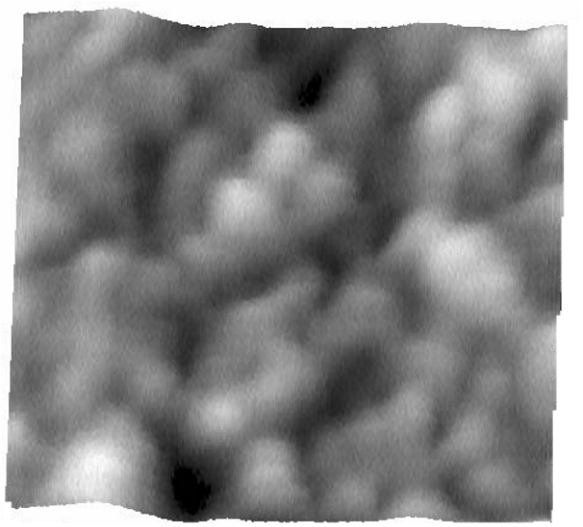
As noted above, the supramolecular structures in bitumens often exhibit hierarchic patterns, as perfectly exemplified by a medium anthraxolite sample from lower Lena river basin [4, 5, 39]. This anthraxolite sample is characterized by regular three-dimensional packing of monodispersed spherulitic grains measuring 300–500 nm in size, which makes it similar to noble opal [40]. Units having such structure fill voids between the spherulites, which measure from several tens to several hundreds of micrometers in size and are comprised by gently bent plates and spheroidolitic dendrites. For description and ontogenetic interpretation of these structures, see [40]. Using the AFM

technique we identified, along with the anthraxolite textures described in that study, peculiar supramolecular structures [4, 5], specifically, segments composed of globules measuring 1–2 μm in size (Fig. 4).

A more detailed examination reveals a primary supramolecular organization of this anthraxolite sample as represented by truncated "wormlike" fibers having the diameter of 30–40 nm. These are for the most part dendritic formations arranged into a disordered felt-like structure, but single fibers are also observed. Some of the bent fibers are characterized by fairly sharp fractures, which fact may be interpreted as indirectly evidencing the occurrence of cavities, because such phenomenon is typical for any tubular body. Examination of adjacent globules shows that their constituting fibers may belong simultaneously to two globules which are "sewn together" by them. Also, there are segments in which the fibers of adjacent globules do not intersect and form a specific "brain-like" supramolecular structure (Fig. 4). Such isolated globules reach 700 nm in size.

On the whole, in the carbonization sequence of solid bitumens from Timan-Pechora province, the supramolecular structure elements tend to decrease in size in going from asphaltites to medium anthraxolites. The particle size varies within 400–500 nm (occasionally particles measure up to 200 nm) in asphaltites, 200–300 nm in low kerites, 50–100 nm in high kerites, and 30–40 nm in medium anthraxolite [5, 39]. The fibers in asphaltites are chaotically interwoven; low kerites exhibit mutually oriented elongated fibers. High kerites preserve the oriented arrangement of fibers which are, however, markedly truncated, and globular formations appear in the generally fibrous mass. Globules account for an increased proportion of the supramolecular structure of antraxolites and totally dominate in high anthraxolites [19].

Nanosized structures in asphaltites and kerites can be interpreted as supramolecules constituted by asphaltene associates. Resins and oils act as host medium with respect to supramolecules, which is distinct in the AFM images of asphaltites and low kerites. The shape of the supramolecular elements is determined by the nature of aggregation of the initial asphaltene particles in a resinous-oily medium under various physicochemical conditions, giving rise to diversified aggregates: The higher the resin (dispersion medium) content, the better the opportunities for asphaltenes to form large supramolecular particles. High kerites display a compact structure at the supramolecular level, and the diversity of the types of structural elements in them is associated with that of the molecular composition: There are asphaltene associates at a significant content of graphene structural elements. In laboratory experiments, asphaltenes are typically aggregated into spherical particles [33–35], but under geological conditions aggregation may be affected by various factors, leading to diversified shapes and sizes of supramolecules, as actually observed in natural solid bitumens.



X = 800 nm

Fig. 5. Supramolecular structure of Baltic succinite.

Fossil Resins (Ambers)

Fossil resins are essentially fossilized soft resin of pine trees that flourished mostly in Paleogene and Neogene periods [41, 42]. Regardless of the origin, composition, structure, and properties, fossil resins are sometimes collectively called amber, which term is of great current importance for everyday life and production activities. In the absence of a generally recognized classification [43], fossil resins are practically subdivided into viscous (succinites, rumenites, synetites) and fragile (often collectively called retinites), with the latter group comprising most of the remaining kinds of fossil resins.

To choose between the above-mentioned two groups in attribution of fossil resins it is sufficient to determine its fragility number, i.e., the load (in grams) which causes formation of the first visible fracture on the sample surface. In experiments in which a four-faced diamond pyramid indenter is impressed into the

samples, viscous resins typically display fragility numbers of over 200 g, and fragile resins, of no larger than 100 g. This division criterion proved to be fairly efficient, because specifically the first group includes ambers proper which serve as raw materials in jewelry, and the second group is of no commercial significance today.

Mineralogical examinations of fossil resins for diagnostic purposes widely apply differential thermal analysis (DTA), as well as IR- and NMR-spectroscopic techniques [42, 44].

The physical and chemical properties of fossil resins were described in detail in [41–43]. The available publications concerning optical- and electron-microscopic examinations of fossil resins do not contain information about the corresponding supramolecular structural elements [41–46]. These methods are still used for determining the shape, size, and distribution of micrometer-sized voids (air bubbles) and microfractures that are of decisive significance for the transparency and color, which characteristics are very important for succinite (amber) when regarded as a jewelry and decorative stone.

Certain efforts were undertaken to determine the particle size distribution for fossil resins with the use of mechanical and chemical dispersing, followed by electron-microscopic examination of the dispersion products. For Baltic succinite (Poland) the minimal size was estimated at 450 nm [45], and Chinese researchers observed ellipsoidal particles measuring 170–420 nm in size for fossil resins from Xixia province. However, it is not clear from the above-mentioned publications whether it were primary elements of the supramolecular structure or their aggregates.

The largest and most extensively studied resin-containing province is the Baltic-Dnieper province incorporating Kaliningrad oblast, Poland, Lithuania, Western Latvia, South-Western Belarus, and Right-Bank Ukraine [41, 43]. We examined fragments and transparent grains of succinites (from Kalinigrad oblast, Lithuania, and Poland) and succeeded in obtaining images of supramolecular structures from viscous fossil resins solely [47, 48]. Their elements, measuring tens and first few hundreds of nanometers in size (Fig. 5), have diversified shapes and are characterized by different degrees of isolation, ranging from clearly free-standing globules in Baltic succinites to poorly shaped particles in the succinite sample taken near Vitebsk. Examinations of fragile fossil resins (gedanites and retinites) did not reveal any reliable signs of supramolecular structuring.

The micrometer-sized AFM images [47] of the succinite surface are in a good correspondence with the electron-microscopic data. The surface has a complex microrelief with humps and hollows; some segments exhibit fluidity manifested in the directional orientation of microfractures and bubbles. The images taken at higher magnifications display a distinct supramolecular structure (Fig. 5) consisting of predominantly globular elements of diversified shape and size. These are for the most part drop-like and ellipsoidal moieties measuring from 50 to 140 nm in size and having the average longitudinal and transversal sizes of 110 and 70, respectively. Rarely occurring free-standing globules are typically organized into densely intergrown aggregates comprised of 5–10 particles.

The main aggregation types can be described as extended or twisted chains and lumpy or bunchy segregations. The morphologically isolated segregations of globule-like particles range from 300 nm to 1 μm in size. Ellipsoidal globules are integrated into aggregates, typically at the point of exit of their long axes. Also, there exist transitional forms between ellipsoidal globules and truncated fibers having the diameter of 70–80 nm and the length of up to 500 nm. Globules characterized by a chain-like aggregation motif form extended, unidirectionally oriented fluidal structures characterized by not very dense packing.

The reason for such diversity of aggregation forms and modes, characteristic for the supramolecular particles in fossil resins, may lie in the fact that, when occurring in the elastic state, they underwent contact interaction with one another during macromolecular structuring of a substance and deformation under plastic flow of resin.

Supramolecular structuring significantly affects the polymer properties, which allows the results of supramolecular structure examination to be invoked for interpreting the viscosity and fragility of fossil resins, specifically, a higher viscosity of succinites and a much higher fragility of retinites and gedanites. For example, a binding action produced by submicrometer-sized supramolecular particles may be associated with changes in the overstress conditions at the fracture edges and stress relaxation and redistribution to a larger number of microfracture formation sites, which causes the breaking stress to increase [49]. Polymers constituted by densely packed macromolecules often

are less capable of deformation, which makes them close in properties to glasses.

CONCLUSIONS

The structural features of natural solid bitumens in the carbonization sequence, from asphaltites to high anthraxolites, were examined by scanning probe microscopy, on which basis the characteristic supramolecular structure types and primary particle sizes were determined for each of the subclasses. The quailtative trends in supramolecular evolution of solid bitumens in the carbonization sequence were established.

An atomic-force microscopic examination visualized the nanosized supramolecular structure of succinites (ambers). They are formed predominantly by loose accumulations of densely aggregated globules which measure from 50 to 120 nm in size and are associated into various accumulations, rather than constitute a uniform mass. High-resolution examinations did not reveal signs of nanosized structuring in fragile fossil resins.

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