

The Late Paleocene Anoxic Event in Epicontinental Seas of Peri-Tethys and Formation of the Sapropelite Unit: Sedimentology and Geochemistry

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Abstract—This work discusses the lithochemical consequences of Late Paleocene sea level fluctuations in a large water basin in the southern territory of the former Soviet Union (FSU). The sharp growth of phytoplankton bioproductivity against the background of a rapid eustatic transgression resulted in the accumulation of sediments that are highly enriched in organic matter. These sediments are characterized by increased concentrations of V, Ni, Cu, Pb, Cr, Zn, Mo, Se, Ag, Au, etc., decreased contents of CaCO_3 and Mn, and passive behavior of Ti, Zr, Nb, Sc, Hf, Y, and REE. The hydrosulfuric contamination of the basin water, which had a negative impact on the benthic fauna, governed the geochemical signature of sediments. The organic matter and carbonates in sapropelite unit were simultaneously enriched in light carbon isotope. The organic matter is of predominantly marine origin. The model proposed for the formation of the sapropelite unit is based on the interaction between the transgressing sea and coastal topography, inducing the supply of biophile elements and the bloom of phytoplankton bioproductivity in the basin.

INTRODUCTION

The Phanerozoic record of the Earth displays several relatively short periods such as Late Devonian, early Toarcian, Cenoman–Turonian, etc., when the organic-rich sediments were accumulated over very large (occasionally, global-scale) territories; the benthic and adjacent sediments strongly differed from each other in geochemical signatures; and anoxic conditions, including the hydrosulfuric contamination, were common in the water column. These anomalous conditions exerted an appreciable influence on the biota, promoting the disappearance of one group of species and the appearance of another group of species. The reasons for the origination of such geological events, the mode of their manifestation in sedimentary sections, as well as the associated changes in biota were widely discussed by geologists (Arthur *et al.*, 1990; Jenkyns, 1988; and others).

The Late Paleocene episode is among geological events of this kind. It is traced as a thin (decimeter- to meter-scale) layer of the organic-rich clayey and clayey marl rocks that are developed over a large territory of the southern Russia and adjoining regions from Crimea to Central and South Asia. Hereinafter, this layer will be labeled the sapropelite unit. The unit is not continuous; nevertheless, some of its structural features coincide in sections that are thousands of kilometers apart. Sapropel sediments were deposited in a single basin (Fig. 1); however, the basin was very large, and its various sectors were likely characterized by different

facial conditions. In an effort to elucidate the constraints of the accumulation of these sediments in different sectors of the basin and reveal the possible mechanisms of the formation of organic-rich sediments, we carried out a lithochemical study of a series of Upper Paleocene sections (Fig. 1). The results obtained are presented in this work.

Before describing the sapropelite unit features, let us briefly dwell upon the environment at the ocean and epicontinental seas that prevailed during the accumulation of the sapropelite unit sediments. In synchronous or subsynchronous Late Paleocene sediments of the ocean, the oxygen isotopic composition was strongly shifted toward the negative values in benthic and planktonic foraminifera of higher latitudes and in benthic foraminifera of other areas. Many researchers relate this phenomenon to the intense but short-period warming that was a most dramatic event in the geological history (Rea *et al.*, 1990; Kennett and Stott, 1991; and others). This event was responsible for the large-scale mortality of benthic foraminifera and extinction of up to 50% species of foraminifera. It was also accompanied by a distinct change in the global carbon cycle, which is determined from the carbon isotopic composition in carbonate shells of benthic and planktonic foraminifera (Kennett and Stott, 1991; Thomas, 1990). Thomas believes that the species composition of the oceanic benthic foraminifera in the Late Paleocene time suggests a substantial increase of the organic matter supply into sediments and possible depletion of

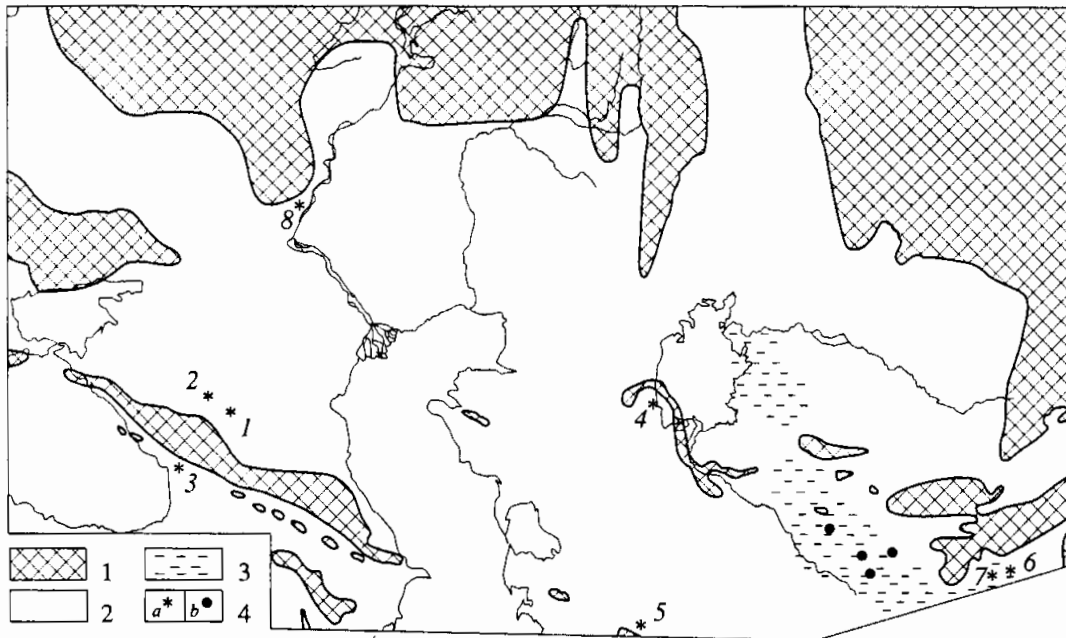


Fig. 1. Late Paleocene paleogeographic scheme (modified after *Atlas...*, 1966) and location of the sapropel unit sections studied. Sections: (1) Kheu River; (2) Baksan River; (3) Settlement of Medani; (4) Cape Aktumsuk; (5) Torangly area; (6) Kurpai area; (7) Guru Fat'ma area; (8) Lower Volga region. (1) Land; (2) sea; (3) oil shale zone; (4a) location of sections studied; (4b) position of boreholes, from which the sapropel core was collected.

oxygen in the water column or, at any rate, at the sediment–water interface (Steineck and Thomas, 1996). However, other researchers argue that the extinction of living organisms is related to environmental changes: the site of abyssal water formation shifted from the high-latitude zone to the subtropic one, resulting in the increase of water temperature, the decline of oxygen concentration, and the large-scale extinction of foraminifera (Pak and Miller, 1992; Kaiho, 1994; and others). Ostracodes also experienced a biotic crisis (Steineck and Thomas, 1996); benthic organisms disappeared not only in deep-water sectors, but also in shelf zones of oceans (Schmitz *et al.*, 1996).

In addition to temperature changes, the available data on the lithology and geochemistry of oceanic sediments made it possible to reveal the growth of bioproductivity (Kenneth and Stott, 1990, 1991) and variations of the $p\text{CO}_2$ values in the Late Paleocene ocean (Stott, 1992). This time interval was also characterized by a rather intensive volcanism (Morton and Knox, 1990).

Hence, the Late Paleocene stage was characterized by noticeable rearrangements in the biosphere, hydrosphere, and, possibly, lithosphere. At the end of Paleocene, the ocean level was about 200 m above the present-day level (Haq *et al.*, 1987); large epicontinental basins were formed owing to the occupation of a major part of land by sea; and the ocean level fluctuations were as much as 50–100 m. It should be noted that the aforesaid stratigraphic level within Paleocene sections of various continental blocks incorporates the

organic-rich units that are similar to the sapropelite unit studied. Hence, the sapropelite unit formation coincided with the timing of a series of global events and represented a regional process.

STRATIGRAPHIC POSITION AND GENERAL CHARACTERISTICS OF THE SAPROPELITE UNIT

The organic-rich unit is mentioned in several publications on the regional stratigraphy and lithology of Paleogene deposits of Central and South Asia, Caspian region, Ciscaucasus, and Transcaucasus. However, these data were not systematized, and the stratigraphic position of the dark-colored clays or marls were not always properly identified.

Our comprehensive stratigraphic studies (Muzylev *et al.*, 1989, 1994) made it possible to attribute the organic-rich interlayers to a single, narrow stratigraphic interval. The stratigraphic position of the sapropelite unit is identified with a high precision, because the boundary between the subzone *Chiasmolithus bidens* and the subzone *Campylosphaera eodela* of the zone *Discoaster multiradiatus* is drawn on the basis of nanoplankton. The stratigraphic interval of this unit corresponds with the foraminifer zone *Acarina acarinata* (layers with *Globorotalia aequa*).

The sapropelite unit area is characterized by both latitudinal and longitudinal variations of the sapropelite fabric and host rocks. The strongest differences are noted between the southern (Crimea–Caucasus–Cen-

tral and South Asia) and northern (Volga region) sections. The southern zone section consists of dominant clay-carbonate rocks without notable coarse admixture, whereas the northern type is mostly composed of sand-silt varieties. The southern Paleocene zone is divided into two subzones: the western subzone stretches from Crimea to the Aral-Kopet Dagh meridian, and the eastern subzone corresponds with the Central and South Asian territory. In the western subzone, variations of the OM content in sapropelite sections are notable, and the maximum C_{org} content does not exceed 8–10%. The eastern subzone is characterized by the accumulation of highly organic-rich sediments with a C_{org} content of up to 25% or more (e.g., the Suzak oil shales).

The **Kheu River** (Kabardin-Balkaria) section (Fig. 1, 1) is a representative example of Paleocene sapropelite sections in the Ciscaucasus (Gavrilov and Muzylev, 1991). The sapropelite unit, 0.45 m thick, is located in the upper part of about 50-m-thick, monotonous, marl clay sequence consisting of greenish gray, nonstratified layers with numerous and diverse (in shape and size) traces of bioturbation (Gavrilov and Muzylev, 1991). The sapropelite unit interval here is a transitional type formation: relatively low-carbonate ($CaCO_3 < 10\%$) clays with siliceous rock layers appear 5 m above the sapropelite interval. The dark brown sapropelite unit is clearly distinct in the host rock matrix. The unit is underlain and overlain by interlayers (8–12 cm) that are less intensively colored but still darker than host rocks. The sapropelite unit is not homogeneous: its color is deepest in the lower part; the lower part of its upper section contains a layer (10 cm) of pale-colored carbonate clays. The bedding planes of sapropelite unit contains fish scales, shark teeth, and the occasional fish skeleton. The rocks incorporate sulfide nodules and rarely, pyritized wood fragments. The upper section of the aforesaid layer (near its roof) contains worm trails in the form of lensoid patches (0.3–1 × 0.5–4 cm).

In the **Baksan River** section situated 35 km northwestward from the Kheu River counterpart, the sapropelite unit is represented by a single 25-cm-thick layer. The OM concentration is noted in the lower part (10 cm) of the layer; the upper part is darker in color, but depleted in C_{org} . The lower boundary is sharp, whereas the upper one is vague. The host rocks are composed of greenish gray silt clays with numerous traces of bioturbation. This layer is characterized by the lack of its lowermost part (corresponding to the nannoplankton subzone CP8a); i.e., the upper part of the sapropelite unit here disconformably overlies the older deposits. In the more westerly sections of the Northern Caucasus (in Stavropol, for example), the position of the sapropelite unit is highly similar: the reduced sapropelite unit disconformably overlies the silt clay bed.

In Transcaucasus, near the **settlement of Medani**, Western Georgia (Fig. 1, 3), the sapropelite-hosting

section is composed of the following beds (from the bottom to the top): alternating, decimeter-scale interlayers of compact white limestones and obscure-bedded marls (total thickness 21 m); conformably (but with a sharp contact) overlying, light gray, vague-bedded marls (6 m) with rare, more compact interlayers; relatively soft, obscure-bedded marls (3.5 m); overlying sapropelite unit (2.3 m) characterized by a distinct floor but less distinct roof and consisting of dark brown, laminated clay-carbonate rocks that are finely foliated during weathering; and a monotonous sequence of greenish gray obscure-bedded marls.

In the Eastern Ustyurt (**Cape Aktumsuk**, Fig. 1, 4), the sapropelite unit is distinctly observed along the western coastal cliffs of the Aral Sea. The unit is located within the sequence of grayish white, sometimes reddish, massive sandy limestones (Fig. 2). One can observe here at least two sapropelite sections at a distance of 1.5–2 km.

At Aktumsuk-1, the sapropelite unit is represented by a thin (20–25 cm) interlayer. The erosion surface is traced 1 m below this unit. The overlying 16-m-thick limestones include several levels of brecciation and erosion surfaces. The Aktumsuk-2 section is characterized by a thicker sapropelite unit (up to 1.2 m) with a more sophisticated structure: a light-colored interlayer in the middle zone separates it into two parts. In this respect, the Aktumsuk-2 section is similar to the Kheu River counterpart in the Ciscaucasus. It should be noted that the lower part of the Aktumsuk-2 sapropelite unit is characterized by a low-angle cross-bedding. It is difficult to determine whether its pinchout along the strike is related to facial changes or syndepositional erosion of sapropelite rocks. The specific features of the sapropelite unit here are likely induced by the accumulation of sediments in the proximal zone of an uplift under a relatively active hydrodynamic regime.

In the **Torangly**, Kizil Cheshme, Sumbar, and other sections of the Western Kopet Dagh region (Fig. 1, 5) and Lesser Balkhan, Turkmenistan, the upper Paleocene sapropelite unit is represented by the so-called "first fish layer" within the Danatin Formation composed of dark brown foliated clays. The lower and upper boundaries of the layer, about 1.5 m in thickness, are sharp.

Southeast of the Aral Sea in the Central and South Asian region, the sapropelite unit is highly enriched in OM, and rocks of this unit can be considered oil shales. The oil shale zone encompasses a large area of the Turan Plate and its framework, i.e., the Southern Kyzyl Kum region, the Bukhara-Karshin region, and the Tajikistan-Afghanistan Depression (Fig. 1). It should be mentioned that the sapropelite unit in shallow-water deposits is facially replaced by the phosphorite-bearing rocks. In general, the phosphorite zone occupies a greater age interval than oil shales; however, the sapropelite unit is associated with a quite definite



Fig. 2. Photograph of the sapropelite unit section, Cape Aktumsuk, western coast of the Aral Sea (courtesy of E.A. Shcherbinina).

gravel-pebble layer identified as the "fourth phosphorite layer" (Rasulov *et al.*, 1990).

In the Tajik Depression (**Guru Fat'ma and Kurpai sections**, Fig. 1, 6, 7), the sapropelite unit, which is registered as a layer (about 1 m) of black-colored laminated rocks with appreciable silt admixture within the light gray marls (Givar layers), is characterized by a distinct bottom and obscure top. The Kurpai sapropelite unit has a three-member structure, and its middle inter-layer is OM-depleted. In the Guru Fat'ma section, an erosion surface is registered below the sapropelite unit. In the relatively shallow-water zones of the Tajik Depression, the sapropelite unit is underlain by coarser, locally gritstone-type rocks. In the Fergana Depression characterized by shallow-water sedimentation, oil shales are represented by the so-called "fish layers" (≈ 10 m) composed of gray, low-carbonate clays with fish detritus in rare, yellowish brown, laminated inter-layers.

In the northern zone of the Upper Paleocene deposits, the sapropelite unit of southern Russia is represented by the lower part of the Lower Kamysheh sub-formation (lower Volga region, Fig. 1, 8). The 5–7-m-thick sandy and clayey siltstones are composed of decimeter-scale interlayer alternations with variable contents of OM represented mostly by plant detritus. The disconformably underlying Lower Saratov bed is also composed of sand-clay rocks.

Based on the foregoing, we can conclude that the sapropelite unit is elsewhere distinguished by a darker color and often by typical foliation of rocks after weathering. Its lower boundary is always sharp, whereas the upper one, while also distinct, is more gradual. Several sections are characterized by the pres-

ence of an erosion surface at some depth below the unit, while some sections reveal a transgressive unconformable contact of the unit with the underlying layer. Toward the coastal-facies zone, the sapropelite unit is OM-depleted; locally, it is replaced by layers with abundant fish detritus; and, occasionally, it is replaced by or spatially associated with phosphorite-bearing rocks.

LITHOLOGY AND GEOCHEMISTRY OF THE SAPROPELITE UNIT

The objective of our research was to estimate the impact of geological events that triggered the drastic growth of bioproductivity and accumulation of organic-rich sediments in the basin on the geochemical signature of rocks. The research was based on the study of a wide range of elements and *sensu stricto* the geochemistry of OM, including the carbon isotopic composition, in particular. The sapropelite unit sections in various sectors of the Late Paleocene basin were examined for the content and distribution of the following components: C_{org} , $CaCO_3$, S, P, Fe, and Ti (chemical methods), as well as V, Cr, Ni, Co, Pb, Cu, Ga, Ge, Mo, Ag, Zn, and Sn (quantitative spectral analysis). Additionally, two representative sections in the western and eastern sectors of the basin (Kheu River section in the Northern Caucasus and Guru Fat'ma section in the Tajik Depression) were examined for the following elements: Nb, Zr, Rb, Sr, and Ba (X-ray fluorescence analysis), as well as Sc, Se, Br, Sb, Cs, Hf, Au, Th, Y, La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu (neutron activation analysis). The results obtained are given in Table 1 and Fig. 3.

Table 1. Contents of chemical elements in the sapropelite unit and host rocks

| Ciscaucasus, Kheu River | | | | | | | | | | | | | | | | | | | | | |
|-------------------------|------------------|-------------------|------|-------|------|-------|-------|------|-----|------|-------|-----|----|----|-----|------|------|------|------|-------|----|
| Sam- ple no. | C _{org} | CaCO ₃ | Fe | Mn | Ti | P | S | Cr | Ni | V | Cu | Co | Pb | Ga | Ge | Mo | Zn | Sn | Ag | As | |
| 9 | <0.1 | 13.6 | 3.36 | 0.26 | 0.44 | 0.05 | 0.78 | 122 | 97 | 140 | 68 | 33 | 26 | 19 | 2.0 | 2.0 | 60 | 1.8 | 0.08 | 8 | |
| 10 | 0.51 | 1.6 | 4.19 | 0.02 | 0.47 | 0.07 | 0.26 | 150 | 423 | 205 | 120 | 104 | 33 | 32 | 2.4 | 5.4 | 280 | 2.7 | 0.09 | n. a. | |
| 11a | 7.90 | 0.1 | 5.95 | 0.16 | 0.41 | 0.31 | 2.73 | 740 | 338 | 1100 | 172 | 53 | 69 | 21 | 3.5 | 23.1 | 175 | 2.7 | 6.5 | 32 | |
| 11b | 6.30 | 12.9 | 5.82 | 0.14 | 0.33 | 0.26 | 3.99 | 235 | 310 | 1650 | 106 | 45 | 26 | 16 | 5.3 | 63.5 | 250 | 2.7 | 2.70 | 110 | |
| 11c | 1.01 | 25.8 | 3.63 | 0.07 | 0.36 | 0.11 | 0.73 | 167 | 260 | 247 | 103 | 25 | 36 | 22 | 2.0 | 6.6 | 280 | 2.7 | 0.35 | 6 | |
| 11d | 6.00 | 1.1 | 4.74 | 0.007 | 0.38 | 0.24 | 0.82 | 1200 | 395 | 338 | 118 | 46 | 48 | 21 | 2.8 | 5.2 | 360 | 2.0 | 7.00 | 6 | |
| 12 | 0.22 | 26.1 | 3.46 | 0.12 | 0.35 | 0.1 | 0.47 | 145 | 518 | 225 | 77 | 38 | 25 | 20 | 2.2 | 4.9 | 245 | 3.0 | 0.54 | 20 | |
| 14 | 0.14 | 17.8 | 4.58 | 0.26 | 0.41 | 0.066 | 0.23 | 115 | 150 | 147 | 40 | 21 | 26 | 19 | 2.7 | 1.6 | 80 | 2.1 | 0.14 | 6 | |
| Kheu River (contd.) | | | | | | | | | | | | | | | | | | | | | |
| Sam- ple no. | Nb | Zr | Rb | Sr | Ba | Sc | Se | Br | Cs | Hf | Au | Th | La | Ce | Nd | Sm | Eu | Tb | Yb | Lu | Y |
| 9 | 3.2 | 160 | 90 | 920 | 6300 | 18 | 2.3 | 1.6 | 5.2 | 4.1 | 0.004 | 10 | 43 | 93 | 42 | 7.3 | 1.6 | 1.3 | 3.0 | 0.40 | 61 |
| 10 | 8.6 | 120 | 100 | 290 | 440 | 23 | 9.8 | 5.8 | 9.3 | 3.4 | 0.012 | 9.6 | 27 | 48 | 21 | 3.9 | 0.81 | 0.59 | 1.8 | 0.26 | 19 |
| 11a | 6.2 | 110 | 110 | 780 | 6300 | 18 | 280 | 27 | 7.8 | 2.7 | 0.024 | 7.3 | 63 | 93 | 50 | 12 | 2.4 | 1.6 | 4.8 | 0.65 | 54 |
| 11b | 6.5 | 94 | 76 | 810 | 1600 | 14 | 190 | 17 | 5.8 | 2.2 | 0.021 | 6.2 | 59 | 83 | 51 | 13 | 2.1 | 1.5 | 4.3 | 0.72 | 52 |
| 11c | 6.6 | 100 | 95 | 840 | 4200 | 18 | 26 | 10 | 10 | 3.1 | 0.016 | 8.1 | 34 | 51 | 29 | 5.9 | 1.2 | 0.86 | 2.5 | 0.36 | 24 |
| 11d | 6.8 | 120 | 105 | 740 | 6500 | 18 | 140 | 35 | 8.8 | 3.2 | 0.025 | 8.6 | 35 | 57 | 30 | 5.6 | 1.2 | 0.87 | 2.6 | 0.36 | 37 |
| 12 | 8.7 | 90 | 88 | 720 | 8900 | 15 | 13 | 2.8 | 7.7 | 2.7 | 0.016 | 7.6 | 31 | 53 | 28 | 5.4 | 1.2 | 0.89 | 2.2 | 0.35 | 18 |
| 14 | 7.2 | 100 | 120 | 780 | 2100 | 18 | 2 | 1.9 | 9.1 | 3.0 | 0.007 | 8.0 | 35 | 64 | 29 | 5.6 | 1.2 | 0.87 | 2.4 | 0.34 | 18 |
| Baksan River | | | | | | | | | | | | | | | | | | | | | |
| Sam- ple no. | C _{org} | CaCO ₃ | Fe | Mn | Ti | P | S | Cr | Ni | V | Cu | Co | Pb | Ga | Ge | Mo | Zn | Sn | Ag | As | |
| 50 | 0.33 | 36.43 | 2.98 | 0.13 | 0.32 | 0.02 | n. a. | 115 | 80 | 120 | 45 | 23 | 16 | 15 | 1.5 | 1.0 | 80 | 4.5 | 0.12 | n. a. | |
| 51 | <0.1 | 17.37 | 3.48 | 0.11 | 0.32 | 0.04 | n. a. | 120 | 115 | 115 | 25 | 27 | 11 | 13 | 1.5 | 1.0 | 60 | 4.5 | 0.12 | n. a. | |
| 52 | 0.17 | 17.82 | 3.37 | 0.08 | 0.35 | 0.04 | n. a. | 190 | 165 | 170 | 300 | 55 | 31 | 20 | 1.8 | 1.0 | 260 | 5.4 | 0.18 | n. a. | |
| 53 | 0.1 | 8.97 | 2.65 | 0.06 | 0.45 | 0.08 | n. a. | 95 | 165 | 135 | 43 | 100 | 18 | 10 | 1.4 | 0.5 | 120 | 2.6 | 0.30 | n. a. | |
| 54a | 1.07 | 9.87 | 2.63 | 0.05 | 0.44 | 0.29 | n. a. | 385 | 220 | 305 | 110 | 100 | 37 | 18 | 3.2 | 1.4 | 260 | 5.9 | 2.25 | n. a. | |
| 54b | 0.3 | 19.64 | 3.24 | 0.11 | 0.44 | 0.07 | n. a. | 125 | 140 | 145 | 24 | 32 | 14 | 10 | 1.4 | 0.5 | 130 | 3.4 | 0.20 | n. a. | |
| 54c | 0.12 | 22.53 | 2.59 | 0.12 | 0.43 | 0.07 | n. a. | 70 | 100 | 95 | 15 | 20 | 8 | 6 | 1.4 | 0.5 | 175 | 2.4 | 0.25 | n. a. | |
| 55 | <0.1 | 10.90 | 4.23 | 0.05 | 0.49 | 0.04 | n. a. | 130 | 58 | 210 | 27 | 10 | 13 | 13 | 2.2 | 0.5 | 70 | 3.5 | 0.30 | n. a. | |
| 56 | <0.1 | 3.52 | 4.37 | 0.03 | 0.38 | 0.04 | n. a. | 250 | 110 | 270 | 60 | 23 | 28 | 22 | 1.0 | 1.0 | 90 | 6.0 | 0.16 | n. a. | |

Table 1. (Contd.)

Western Georgia, settlement of Medani

| Sample no. | C _{org} | CaCO ₃ | Fe | Mn | Ti | P | S | Cr | Ni | V | Cu | Co | Pb | Ga | Ge | Mo | Zn | Sn | Ag | As |
|------------|------------------|-------------------|------|------|------|-------|-------|-----|-----|------|----|----|----|----|-----|------|-------|-----|------|-------|
| 1 | <0.1 | 66.06 | 1.79 | 0.13 | 0.29 | 0.028 | n. a. | 51 | 43 | 25 | 31 | 14 | 6 | 4 | 1.0 | 1.0 | 30 | 1.2 | 0.03 | n. a. |
| 3 | <0.1 | 61.86 | 2.29 | 0.09 | 0.31 | 0.044 | n. a. | 62 | 63 | 45 | 24 | 30 | 8 | 5 | 1.0 | 1.5 | 30 | 1.2 | 0.03 | n. a. |
| 4 | <0.1 | 43.36 | 3.13 | 0.06 | 0.40 | 0.049 | n. a. | 65 | 150 | 50 | 35 | 58 | 11 | 6 | 1.0 | 3.5 | 60 | 1.2 | 0.03 | n. a. |
| 5 | 0.48 | 20.43 | 3.90 | 0.04 | 0.46 | 0.036 | n. a. | 70 | 105 | 85 | 55 | 32 | 13 | 13 | 1.2 | 1.0 | 135 | 1.3 | 0.06 | n. a. |
| 6 | 0.5 | 11.24 | 4.19 | 0.04 | 0.41 | 0.031 | n. a. | 85 | 115 | 90 | 55 | 30 | 9 | 8 | 1.2 | 1.7 | 125 | 1.6 | 0.11 | n. a. |
| 8 | 1.92 | 49.03 | 2.78 | 0.04 | 0.32 | 0.15 | n. a. | 270 | 90 | 1200 | 37 | 14 | 7 | 5 | 1.0 | 11.5 | 105 | 1.3 | 0.95 | n. a. |
| 10 | 2.65 | 40.07 | 3.89 | 0.04 | 0.32 | 0.19 | n. a. | 250 | 80 | 130 | 43 | 10 | 6 | 6 | 1.0 | 6.1 | 65 | 1.3 | 0.75 | n. a. |
| 11 | 3.30 | 32.01 | 3.35 | 0.03 | 0.36 | 0.14 | n. a. | 340 | 180 | 185 | 65 | 13 | 8 | 10 | 1.4 | 5.2 | 130 | 1.5 | 2.30 | n. a. |
| 12 | 3.30 | 37.46 | 2.79 | 0.03 | 0.33 | 0.14 | n. a. | 410 | 130 | 180 | 85 | 12 | 9 | 11 | 1.5 | 3.5 | 165 | 1.8 | 2.0 | n. a. |
| 13 | 0.82 | 53.35 | 2.79 | 0.04 | 0.29 | 0.081 | n. a. | 80 | 105 | 55 | 25 | 14 | 7 | 4 | 1.0 | 3.5 | 50 | 1.2 | 0.12 | n. a. |
| 15 | 0.29 | 65.94 | 2.34 | 0.04 | 0.23 | 0.050 | n. a. | 80 | 30 | 32 | 20 | 5 | 5 | 3 | 1.0 | 3.0 | 30 | 1.0 | 0.18 | n. a. |
| 16 | 1.20 | 69.80 | 2.23 | 0.04 | 0.28 | 0.053 | n. a. | 95 | 80 | 70 | 30 | 14 | 6 | 5 | 1.0 | 2.6 | 40 | 1.3 | 0.17 | n. a. |
| 17 | 0.23 | 56.98 | 2.89 | 0.06 | 0.31 | 0.058 | n. a. | 105 | 65 | 80 | 30 | 16 | 8 | 6 | 1.0 | 1.7 | 30 | 1.3 | 0.10 | n. a. |
| 18 | <0.1 | 67.53 | 1.67 | 0.07 | 0.27 | 0.026 | n. a. | 45 | 28 | 35 | 19 | 7 | 5 | 3 | 1.0 | 1.0 | 30 | 1.0 | 0.03 | n. a. |
| 19 | <0.1 | 71.73 | 1.78 | 0.09 | 0.27 | 0.027 | n. a. | 50 | 40 | 30 | 20 | 16 | 5 | 3 | 1.0 | 1.0 | 10-15 | 1.0 | 0.05 | n. a. |
| 20 | <0.1 | 69.80 | 1.56 | 0.09 | 0.27 | 0.036 | n. a. | 35 | 23 | 20 | 16 | 4 | 5 | 3 | 1.0 | 1.0 | 10-15 | 1.0 | 0.03 | n. a. |

Western Aral region, Cape Aktumusk-1

| | | | | | | | | | | | | | | | | | | | | |
|----|------|-------|------|------|------|------|------|-----|-----|-----|-----|-----|----|---|-----|-----|----|-----|------|----|
| 54 | <0.1 | 87.17 | 0.71 | 1.41 | 0.17 | 0.19 | 0.20 | 16 | 54 | 38 | 12 | 23 | 5 | 5 | 1.0 | 2.4 | 15 | 1.1 | 0.10 | 7 |
| 56 | 3.80 | 59.02 | 5.30 | <0.1 | 0.80 | 0.54 | 1.05 | 415 | 680 | 710 | 130 | 155 | 13 | 4 | 1.0 | 6.3 | 20 | 1.0 | 4.30 | 35 |
| 57 | 2.41 | 57.09 | 1.74 | 0.36 | 0.21 | 0.63 | 0.68 | 555 | 560 | 450 | 165 | 130 | 14 | 5 | 1.0 | 3.7 | 85 | 1.0 | 1.70 | 8 |
| 58 | 0.62 | 76.05 | 1.87 | 0.88 | 0.18 | 0.29 | 0.65 | 252 | 280 | 400 | 130 | 165 | 25 | 5 | 1.0 | 3.9 | 65 | 1.0 | 0.60 | 22 |
| 59 | <0.1 | 85.13 | 0.99 | 1.08 | 0.18 | 0.32 | 0.40 | 57 | 36 | 65 | 16 | 18 | 5 | 5 | 1.0 | 1.7 | 20 | 1.0 | 0.09 | 1 |
| 60 | <0.1 | 92.62 | 0.69 | 0.61 | 0.16 | 0.06 | 1.85 | 12 | 11 | 20 | 12 | 5 | 6 | 5 | 1.0 | 1.5 | 12 | 1.0 | 0.07 | 1 |

Table 1. (Contd.)

| Cape Aktumusk-2 | | | | | | | | | | | | | | | | | | | | |
|-------------------------------------|------------------|-------------------|-------|-------|-------|-------|-------|-----|-----|------|-----|----|-----|----|-----|------|------|------|------|-------|
| Sample no. | C _{org} | CaCO ₃ | Fe | Mn | Ti | P | S | Cr | Ni | V | Cu | Co | Pb | Ga | Ge | Mo | Zn | Sn | Ag | As |
| 100 | <0.1 | 77.18 | 1.04 | 0.07 | 0.15 | 0.10 | 0.62 | 520 | 20 | 45 | 10 | 6 | 5 | 3 | 1.0 | 2.0 | 40 | 1.0 | 0.23 | 17 |
| 101 | 0.95 | 56.07 | 1.36 | 0.05 | 0.17 | 0.47 | 1.72 | 400 | 105 | 1500 | 65 | 11 | 12 | 3 | 1.0 | 22.0 | 40 | 1.0 | 0.95 | 34 |
| 103 | 6.50 | 57.54 | 1.36 | 0.05 | 0.20 | 0.61 | 1.00 | 280 | 115 | 615 | 115 | 10 | 11 | 3 | 1.0 | 15.2 | 40 | 1.0 | 0.65 | 17 |
| 104 | 0.54 | 89.67 | 1.23 | 0.06 | 0.21 | 0.66 | 1.05 | 45 | 95 | 385 | 80 | 9 | 9 | 3 | 1.0 | 12.5 | 40 | 1.5 | 0.60 | 16 |
| 106 | 3.40 | 71.51 | 1.15 | 0.07 | 0.15 | 0.23 | 1.25 | 15 | 75 | 315 | 30 | 9 | 5 | 3 | 1.0 | 8.8 | 40 | 1.0 | 0.65 | 17 |
| 107 | <0.1 | 85.13 | 0.50 | 0.11 | 0.13 | 0.27 | 0.52 | 100 | 25 | 35 | 25 | 6 | 10 | 3 | 1.0 | 2.2 | 40 | 1.0 | 0.33 | 14 |
| 108 | <0.1 | 90.91 | 1.09 | 0.18 | 0.09 | 0.07 | 0.72 | 175 | 55 | 15 | 15 | 17 | 5 | 3 | 1.0 | 2.5 | 40 | 1.0 | 0.14 | 12 |
| Western Kopet Dagh, Torangly area | | | | | | | | | | | | | | | | | | | | |
| 3 | <0.1 | 17.03 | 4.11 | 0.12 | 0.40 | 0.01 | 0.10 | 110 | 60 | 135 | 65 | 13 | 19 | 16 | 1.0 | 1.1 | 100 | 2.5 | 0.10 | n. a. |
| 6 | <0.1 | 22.70 | 3.31 | 0.18 | 0.37 | 0.02 | 0.10 | 112 | 65 | 135 | 35 | 10 | 18 | 17 | 2.0 | 0.8 | 115 | 3.5 | 0.16 | n. a. |
| 8 | <0.1 | 19.86 | 2.43 | 0.12 | 0.39 | 0.01 | 0.10 | 132 | 75 | 140 | 35 | 8 | 15 | 20 | 2.3 | 0.8 | 130 | 4.0 | 0.28 | n. a. |
| 9 | <0.1 | 8.85 | 5.09 | 0.10 | 0.38 | 0.02 | 0.94 | 112 | 90 | 160 | 60 | 23 | 18 | 20 | 2.3 | 32.0 | 215 | 4.5 | 0.24 | n. a. |
| 10 | 1.81 | 5.68 | 3.29 | 0.08 | 0.45 | 0.11 | 0.27 | 275 | 160 | 3200 | 110 | 10 | 130 | 25 | 3.0 | 360 | 850 | 5.0 | 2.40 | n. a. |
| 11 | 1.02 | 1.70 | 3.90 | 0.08 | 0.36 | 0.08 | 3.65 | 325 | 90 | 515 | 35 | 17 | 40 | 21 | 3.0 | 24.5 | 280 | 5.5 | 2.10 | n. a. |
| 13 | 1.42 | 9.65 | 4.98 | 0.14 | 0.37 | 0.12 | 0.10 | 560 | 90 | 2300 | 75 | 15 | 65 | 27 | 2.3 | 25.0 | 1100 | 6.0 | 4.50 | n. a. |
| 14 | 0.75 | <0.4 | 4.70 | 0.10 | 0.41 | 0.06 | 0.10 | 165 | 75 | 375 | 40 | 13 | 43 | 34 | 3.0 | 4.5 | 330 | 5.0 | 0.85 | n. a. |
| 15 | 0.32 | 8.74 | 3.73 | 0.12 | 0.40 | 0.05 | 0.10 | 192 | 75 | 200 | 35 | 20 | 30 | 29 | 2.0 | 0.8 | 250 | 5.0 | 0.45 | n. a. |
| 22 | <0.1 | 11.92 | 3.19 | 0.11 | 0.41 | 0.04 | 0.10 | 120 | 55 | 155 | 35 | 10 | 16 | 21 | 2.3 | 1.4 | 130 | 3.5 | 0.28 | n. a. |
| Amu Darya region (Suzak) oil shales | | | | | | | | | | | | | | | | | | | | |
| 29/77 | 14.40 | 21.68 | 2.59 | 0.04 | 0.22 | 0.38 | 4.73 | 335 | 350 | 3700 | 115 | 30 | 13 | 7 | 4.5 | 700 | 105 | 9.0 | 1.0 | n. a. |
| 33/71 | 3.50 | 50.85 | n. a. | n. a. | n. a. | n. a. | n. a. | 550 | 110 | 1420 | 95 | 15 | 19 | 8 | 1.0 | 30 | 135 | 4.0 | 3.8 | n. a. |
| 71/73 | 18.00 | 14.07 | 3.91 | 0.04 | 0.21 | 0.21 | 4.97 | 215 | 430 | 3400 | 140 | 30 | 18 | 7 | 7.0 | 1760 | 200 | 14.0 | 1.0 | n. a. |
| 72/74 | 9.70 | 85.58 | n. a. | n. a. | n. a. | n. a. | n. a. | 165 | 140 | 2200 | 80 | 25 | 10 | 4 | 1.0 | 175 | 65 | 2.5 | 0.9 | n. a. |
| 80/71 | 13.90 | 51.87 | 4.27 | 0.04 | 0.18 | 0.39 | 5.72 | 230 | 390 | 3500 | 105 | 27 | 14 | 5 | 4.8 | 650 | 40 | 8.0 | 1.2 | n. a. |
| 82/72 | 9.10 | 41.31 | 2.65 | 0.04 | 0.17 | 1.28 | 3.90 | 160 | 180 | 3000 | 110 | 20 | 13 | 4 | 3.5 | 300 | 40 | 4.0 | 1.1 | n. a. |
| 96/76 | 15.20 | 30.42 | 2.38 | 0.04 | 0.15 | 0.35 | 4.56 | 215 | 185 | 3500 | 130 | 23 | 14 | 6 | 2.3 | 280 | 80 | 4.5 | 1.0 | n. a. |
| Urt-1 | 22.50 | 10.78 | 2.85 | 0.04 | 0.19 | 0.67 | 6.04 | 280 | 490 | 5400 | 180 | 27 | 14 | 6 | 6.5 | 1260 | 145 | 13.0 | 1.4 | n. a. |
| Urt-2 | 20.20 | 17.48 | 2.47 | 0.03 | 0.18 | 0.75 | 5.04 | 300 | 340 | 5800 | 110 | 27 | 12 | 6 | 3.5 | 810 | 145 | 8.0 | 1.3 | n. a. |

Table 1. (Contd.)

| Tajik Depression, Kurpai area | | | | | | | | | | | | | | | | | | | | | |
|-------------------------------|------------------|-------------------|------|------|------|------|-------|-----|-----|------|-------|-------|----|----|-----|------|------|------|------|-------|----|
| Sample no. | C _{org} | CaCO ₃ | Fe | Mn | Ti | P | S | Cr | Ni | V | Cu | Co | Pb | Ga | Ge | Mo | Zn | Sn | Ag | As | |
| 13 | <0.1 | 5.22 | 2.85 | 0.05 | 0.41 | 0.01 | n. a. | 205 | 62 | 302 | 26 | 18 | 30 | 18 | 1.7 | 5.0 | 97 | 4.3 | 0.07 | n. a. | |
| 14 | <0.1 | 2.27 | 1.52 | 0.05 | 0.35 | 0.01 | n. a. | 139 | 58 | 242 | 36 | 13 | 47 | 13 | 1.7 | 27.0 | 900 | 2.8 | 0.10 | n. a. | |
| 15 | 7.45 | 10.22 | 2.22 | 0.07 | 0.21 | 0.30 | n. a. | 114 | 168 | 431 | 98 | 26 | 48 | 9 | 1.3 | 110 | 55 | 4.6 | 0.21 | n. a. | |
| 17 | 1.16 | 7.26 | 4.93 | 0.12 | 0.45 | 0.14 | n. a. | 122 | 100 | 298 | 54 | 18 | 44 | 23 | 1.7 | 15.9 | 165 | 5.4 | 0.10 | n. a. | |
| 18 | 13.30 | 3.86 | 4.63 | 0.15 | 0.16 | 0.49 | n. a. | 87 | 350 | 900 | 93 | n. a. | 78 | 5 | 2.7 | 157 | 64 | 4.3 | 0.30 | n. a. | |
| 19 | 17.00 | <0.4 | 6.65 | 0.14 | 0.11 | 1.01 | n. a. | 68 | 385 | 1050 | 120 | n. a. | 82 | 5 | 2.2 | 220 | 190 | 5.6 | 0.49 | n. a. | |
| 20 | 0.10 | 31.78 | 2.71 | 0.13 | 0.37 | 0.07 | n. a. | 96 | 59 | 185 | 29 | n. a. | 23 | 12 | 2.0 | 6.7 | 40 | 2.4 | 0.05 | n. a. | |
| Guru Fat'ma area | | | | | | | | | | | | | | | | | | | | | |
| 5 | 0.11 | 10.44 | 3.06 | 0.12 | 0.38 | 0.04 | 0.97 | 115 | 52 | 228 | 26 | 12 | 14 | 17 | 1.2 | 11.6 | 72 | 4.6 | 0.03 | n. a. | |
| 6 | 0.16 | 11.69 | 3.90 | 0.08 | 0.38 | 0.09 | 1.81 | 248 | 69 | 492 | 30 | 16 | 16 | 17 | 1.5 | 29.0 | 66 | 4.8 | 0.05 | n. a. | |
| 7 | 15.50 | 15.10 | 3.87 | 0.00 | 0.20 | 0.32 | 3.80 | 140 | 220 | 1550 | 110 | 29 | 9 | 6 | 1.5 | 188 | 40 | 4.8 | 0.57 | n. a. | |
| 7a | 6.40 | <0.4 | 3.90 | 0.08 | 0.41 | 0.15 | 1.67 | 125 | 102 | 345 | 80 | 14 | 20 | 19 | 1.5 | 62.5 | 45 | 4.6 | 0.35 | n. a. | |
| 7b | 2.04 | <0.4 | 3.82 | 0.02 | 0.48 | 0.10 | 1.02 | 132 | 89 | 232 | 60 | 16 | 16 | 25 | 2.2 | 15.4 | 70 | 2.6 | 0.12 | n. a. | |
| 8 | 2.12 | 3.75 | 3.69 | 0.02 | 0.45 | 0.13 | 0.93 | 60 | 38 | 100 | 26 | 8 | 6 | 10 | 1.2 | 5.2 | 45 | 2.0 | 0.30 | n. a. | |
| Sample no. | Nb | Zr | Rb | Sr | Ba | Sc | Se | Br | Cs | Hf | Au | Th | La | Ce | Nd | Sm | Eu | Tb | Yb | Lu | Y |
| 5 | 11 | 150 | 120 | 150 | 720 | 16 | 3.5 | 0.3 | 11 | 4.1 | 0.001 | 10 | 23 | 45 | 19 | 3.4 | 0.68 | 0.61 | 1.8 | 0.28 | 22 |
| 6 | 13 | 150 | 130 | 160 | 510 | 15 | 13 | 0.8 | 11 | 4.3 | 0.011 | 9.9 | 28 | 57 | 29 | 4.1 | 1.0 | 0.86 | 2.3 | 0.37 | 28 |
| 7 | 9.7 | 94 | 71 | 360 | 6100 | 8.8 | 81 | 4.1 | 6.4 | 2.5 | 0.025 | 6.3 | 34 | 56 | 25 | 5.4 | 1.1 | 0.87 | 2.7 | 0.42 | 39 |
| 7a | 12 | 120 | 150 | 150 | 970 | 18 | 13 | 0.8 | 11 | 3.2 | 0.004 | 9.2 | 30 | 55 | 30 | 6.7 | 1.3 | 1.1 | 3.0 | 0.43 | 28 |
| 7b | 16 | 150 | 160 | 130 | 750 | 20 | 6.0 | 1.2 | 14 | 3.3 | 0.029 | 12 | 33 | 62 | 28 | 6.1 | 1.2 | 1.0 | 3.0 | 0.48 | 31 |
| 8 | 14 | 140 | 150 | 190 | 730 | 19 | 6.3 | 0.7 | 12 | 3.9 | 0.011 | 11 | 32 | 64 | 30 | 6.4 | 1.2 | 1.0 | 2.6 | 0.38 | 33 |

Note: C_{org}, CaCO₃, Fe, Mn, Ti, P, and S are given in %; other elements, in ppm; n. a.—not analyzed.

Organic matter. As is evident from Table 1 and Fig. 3, the OM content in the sapropelite unit is highly variable at different sites. In the Caucasus, the highest C_{org} concentrations (up to 10%) are registered in the Kheu River section. The C_{org} content is up to 1.1% in the Baksan River section characterized by the presence of only the upper part of the sapropelite unit; as much as 3.3% in the Medani section, Transcaucasus; and up to 3.8% at Cape Aktumsuk, Aral Sea region. The C_{org} content in the Tajik Depression is up to 15–17% (Kurpai and Guru Fat'ma sections) and more than 20% in the Suzak oil shale zone, Amu Darya region. Hence, the OM content in sapropelite rocks of the Central and South Asian region is significantly higher than in its western counterparts. For example, the C_{org} content in the Volga region section does not exceed 1%.

It is worthy of mention that, irrespective of the facial position, sapropelite rocks in almost all sections are characterized by fine bedding owing to the presence of millimeter-scale OM-rich laminae that may be continuous or discontinuous. In the latter case, one can observe a series of brown (with various shades) small lenses. Generally, the organic matter is represented by an amorphous mass (colloalginite). Locally, we can also observe foraminifer shells, which are concentrated as separate bands that are not connected with the organic-rich laminae. The development of lamination owing to the stratal distribution of OM was likely induced by the seasonal phytoplankton bloom. At the same time, locally, in the Kheu River section, for example, sapropelite rocks contain small fragments of wood.

Calcium carbonate is among the major rock-forming components in Paleogene deposits, therefore, its distribution in the sapropelite unit and host rocks is of specific interest. The $CaCO_3$ distribution is variable in different sectors of the basin. In the Caucasus and Aral Sea region sections (Kheu River, settlement of Medani, and Cape Aktumsuk), where the sapropelite unit is organic-rich, the C_{org} content is negatively correlated with $CaCO_3$ (Fig. 3). In the shallow-water and subcoastal facies zones (Kuban and Malyi Zelenchuk rivers), the sapropelite unit rocks are C_{org} -depleted (0.5–0.7%); nevertheless, they contain 4–8% more carbonates than the host rocks. The sapropelite unit rocks of Central and South Asia, strongly differ in carbonate content. As is evident from Fig. 3, the C_{org} concentration in the rocks may be locally accompanied by the relative minor growth of $CaCO_3$ in sapropelites; however, the comparison of contents of carbonate and C_{org} in sapropelites demonstrates a similar inverse correlation between them. The microscopic study did not reveal any evidence of intense solution of carbonate shells of organisms (foraminifers and coccoliths); hence, the $CaCO_3$ variation observed in Paleogene rocks likely indicate the changes in bioproductivity of the Ca-generating and rock-forming species of plankton and benthos.

Phosphorus content is steadily high in all the sapropelite units studied (Table 1, Fig. 3). It is partly

concentrated in numerous organic remains (fish scale and small bone detritus) and partly scattered in rocks. Sapropelites (oil shales) of the Central and South Asian sections occasionally contain small (up to 1 cm), light gray to cream-colored, oval nodules and lenses of phosphate. The P_2O_5 content in rocks is as much as 2–3% (Oleinik, 1969).

The understanding of processes leading to formation of the sapropelite unit requires the examination of the mode of phosphate distribution in host sequences. Paleogene deposits of the Central and South Asian region contain abundant phosphorites at various stratigraphic levels, such as Middle Eocene, Lower Eocene, and Upper Paleocene (Rasulov *et al.*, 1990), but we are interested, above all, in Upper Paleocene Suzak rocks that host the sapropelite unit. In Tajikistan, only the lower part of the Suzak unit (10–40 m) contains phosphorite. Phosphorite concretions (1–5 cm, occasionally 10 cm in length), which are more or less uniformly scattered in clays, are locally concentrated in interlayers and lenses that are strongly variable in thickness along the strike. One can distinguish one to six units, 10–30 cm in thickness. The chemical composition of phosphorite concretions is rather monotonous (P_2O_5 22–27%). The phosphorite-bearing rocks contain relatively high C_{org} (up to 0.1–1%) and iron sulfides (Oleinik, 1969). In the central Kyzyl Kum region, the sapropelite unit is underlain by a gravel-pebble phosphorite layer (Rasulov *et al.*, 1990).

Paleocene phosphorites are known in the lower reaches of the Don River (Veshen deposit) of the Russian Plate. Host deposits here, however, cannot be reliably correlated with the stratigraphically similar sapropelite unit because of the lack of proper faunistic study.

Iron is among the elements that are unevenly concentrated in the sapropelite unit rocks, except for the Guru Fat'ma section where it is uniformly distributed. The thin sections studied reveal rather numerous pyritic segregations that are occasionally encountered as large nodules in the layer's lower part (Gavrilov and Muzylev, 1991).

In sapropelite rocks of the majority of sections (e.g., Kheu, Medani, Aktumsuk, and Guru Fat'ma) studied, **manganese** is relatively slightly depleted. The simultaneous decrease of $CaCO_3$ could suggest that the aforesaid depletion is induced by the isomorphic introduction of Mn into the calcite structure. However, the lack of positive correlation between Mn and $CaCO_3$ within the sapropelite unit probably testifies to their autonomous nature. This inference is also corroborated by the following observation: in sections with overall high content of carbonates in rocks (e.g., the Aktumsuk section), the $CaCO_3$ content is only slightly reduced (about 20%), but Mn is practically absent; this situation could have hardly been possible if carbonates were the main concentrator of Mn. The specific distribution mode of Mn in the Kurpai section is likely related to the diage-



Fig. 3. Distribution of chemical elements in the sapropelite unit sections. C_{org}, CaCO₃, P, Ti, Fe, Mn, and S are given in %; other elements, in ppm. (1) Shales; (2) silt clays; (3) siltstones; (4) marl clays; (5) marls; (6) limestones.

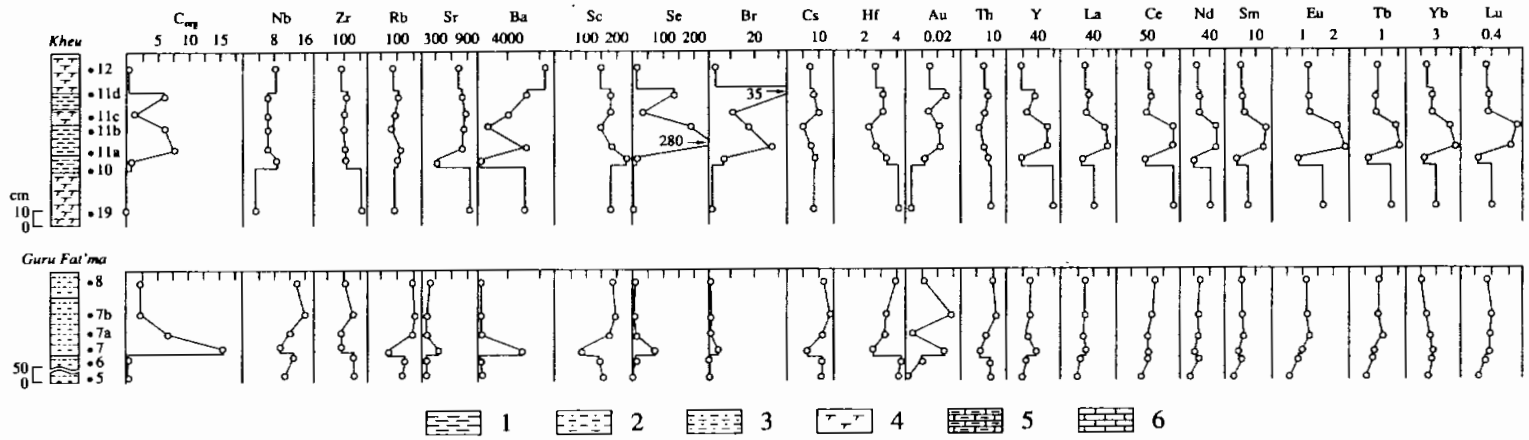


Fig. 3. (Contd.)

netic redistribution of this element in the three-member clayey siltstone unit.

The common negative correlation between Mn and C_{org} evidently indicates that Mn was diagenetically removed from sediments with the highest concentrations of OM.

Sulfur is markedly increased in all the sapropelite unit sections studied, relative to the host rocks. The sulfur content is as much as several percent. This phenomenon is quite natural, inasmuch as the sulfate-reducing and sulfide-forming processes were intense in the sapropelite unit muds. At the same time, it is highly probable that a part of S occurs in the nonsulfide form, as suggested by the infrequent lack of correlation between S and Fe. The highest concentrations of S (4–6%) are observed in the Suzak oil shales characterized by relatively low Fe content, indicating the presence of sulfur-organic compounds in the sapropelite unit rocks.

Minor elements registered in the sapropelite unit rocks can be divided into two groups. The first group includes elements, which are generally concentrated to a variable extent in the sapropelite unit, are represented by V, Cu, Mo, Ni, Ag, Au, Se, Co, Zn, Cr, Sn, Ga, Ge, Br, and possibly Ba. The second group incorporates the following elements that are characterized by very low fluctuations and even minor depletion at the transition from the host rocks to the sapropelite unit: Ti, Zr, Nb, Rb, Sr, Sc, Cs, Hf, and probably REE. The first group, which is of prime interest for estimating the formation conditions of the sapropelite unit, can be further subdivided into two subgroups: the first subgroup elements are characterized by the ubiquitous growth of content, while the second subgroup elements are only increased in particular regions.

The **vanadium** content is steadily high in the sapropelite unit, occasionally exceeding the content in clays by more than one order of magnitude; e.g., the maximum content of V in the sections studied is as follows (in ppm): Kheu 1650, Guru Fat'ma 1550, and Torangly 3200. Some Suzak oil shale samples contain more than 5000 ppm V (Table 1). At the same time, the vanadium distribution within the sapropelite unit does not always correlate with the C_{org} content (Fig. 3, Kheu section).

Another constant minor element in the sapropelite unit is **molybdenum**. The content of Mo is as much as 60 ppm in the Ciscaucasus sapropelite unit, whereas its maximum concentration in the Central and South Asian counterparts is markedly higher (in ppm): Torangly 360, Guru Fat'ma 188, Kurpai 220, and Suzak oil shales 1760 (Table 1). The **selenium** concentration is also conspicuous (more than one order of magnitude higher than in host rocks), particularly in the Kheu River section, where the selenium content rises from 2.9 ppm in the underlying rocks to 2800 ppm at the base of the sapropelite unit (Table 1). In the Suzak oil shales of other regions, the coefficient of selenium concentration ranges between 68 and 110, while the selenium

content varies from 17 to 80 ppm (Poplavko *et al.*, 1978). Based on the available published data, the average concentration of Se is 4.1 ppm in host rocks and 60 ppm in oil shales (Vorob'ev, 1969). In some samples from the middle part of the Suzak shale layer, the selenium content is as much as 200–400 ppm; a part of the element is present as native Se, but the overwhelming part is included in ferrosilite, sulfide nodules, and various OM fractions (Ivanov and Yushko-Zakharova, 1982).

Elements such as Cr, Ag, Au, etc., are regularly concentrated in the sapropelite unit. However, the regional distribution factor is more essential for these elements in the study area. The behavior of **chromium** testifies to this inference. In the Kheu River section, the chromium content is high (740 and 1200 ppm) and is correlated with C_{org} . In the Baksan River section, a minor growth of C_{org} (1.07%) is accompanied by the increase of Cr up to 385 ppm. Meanwhile, in the organic-rich (C_{org} up to 17%) sapropelite rocks of the Kurpai section, Tajik Depression, the chromium content is low, relative to the host rocks. In the sapropelite rocks of the basin's remaining territory, the chromium content is increased but still lower than the Kheu River parameters.

In the Suzak oil shales analyzed (Table 1), the chromium concentration in samples with very high C_{org} content (more than 20%) does not exceed 300 ppm, whereas it is as much as 550 ppm in sample 33/71 with only 3.5% C_{org} ; i.e., in contrast to the Ciscaucasus pattern, chromium here is not distinctly correlated with C_{org} . Hence, the behavior of Cr during the accumulation of sapropels differed in various parts of the basin. Probable reasons for the Cr-enrichment of these sediments have been discussed in our earlier work (Gavrilov and Muzylev, 1991).

An analogous pattern is typical for **silver**. Its concentration is 1–2 orders of magnitude higher in the sapropelite unit than in the host rocks, whereas the concentration growth is insignificant for both Tajik sections. The behavior of **zinc** is also similar. It is constantly present in the sapropelite unit, but the maximum concentration is observed in the Torangly section (850 and 1100 ppm). As is seen from Table 1, the host rocks are also characterized by rather high background values of Zn. Therefore, we can presume that the anomalous high concentrations of Zn in the Torangly sapropelite rocks have an inherited nature and above else are typical for this region. It is also pertinent to note that, usually, **cobalt** is only slightly concentrated in the sapropelite unit; an exception is provided by the Cape Aktumsuk section sapropelites, in which the cobalt content is appreciably greater (Table 1, Fig. 3). Moreover, it is worth noting that the cobalt content in another section located at a distance of 2 km is as usual, i.e., very low. Such drastic changes in the cobalt behavior are likely induced by the local facial features of sedimentation.

Bromium is quite distinct from the above-described elements in geochemical properties. In both sections

studied, the concentration of this element in the sapropelite unit is one order of magnitude higher than the background value in the host rocks; e.g., the respective values of Br are equal to 27–35 and 1.6–1.9 ppm for the Kheu River section and 4.1 and 0.3–0.7 ppm for the Guru Fat'ma section. Hence, the bromium content markedly differs in various parts of the region. Numerous data are available, suggesting the lifelong concentration of this element in organisms, such as phytoplankton, in particular (Selivanov, 1946; Saenko, 1992; and others). Saenko reported that the increased concentration of Br in the environment is an essential factor for the assimilation of this element by plants; moreover, plants of one species but from different sites may strongly differ in bromium content. According to Barashkov (1972), the bromium content in marine algae ranges between 0.01 and 3.0%; particularly rich in Br are red and brown algae. Presumably, these circumstances were responsible for the contrast distribution of this element in different sections of the sapropelite unit.

As for some elements that were not determined by us but were reported by other researchers, the following observations should be pointed out. The **rhennium** content is generally high in sapropelites. Numerous data are available, suggesting the presence of Re in the Suzak oil shales of Central and South Asia (Basitova *et al.*, 1972 and others). For instance, according to (Poplavko *et al.*, 1977, 1978), the coefficient of rhennium concentration in shales ranges between 881 and 4471, while its content varies from 0.24 to 3.2 ppm. Nishankhodzhaev *et al.* (1974) reported that the mean rhennium content in 39 samples is equal to 1.5 ppm, but some samples contain as much as 18 ppm, which is one order of magnitude higher than the mean value for Re in shales and four orders of magnitude higher than the clark value. According to other researchers, the rhennium content in the Suzak shales vary from 0.2 to 21 ppm, while the content in separate deposits range between 6 and 10 ppm (*Metallogeniya...*, 1987). Based on the study of rhennium behavior in the Suzak shale area (Ivanov and Poplavko, 1982), the basin's central sector is more enriched in Re than the marginal ones; within the specified shale deposits, the rhennium content is rather stable but depends on the OM concentration. High concentrations of Re are also observed in shales of Kazakhstan (Kalinin *et al.*, 1985). In the Suzak oil shales of Central and South Asia, the coefficients of concentration of other elements relative to host rocks are as follows (in ppm): **Te** from several hundreds up to 3000, **Tl** 7.4–35, **Bi** 20–300, **Sb** 4.6–5.7, and **Cd** 187–680 (Poplavko *et al.*, 1978).

The **barium** behavior is variable in two sections studied. In the Tajik section, the barium content in host rocks is low, and it is clearly correlated with C_{org} in the organic-rich interlayer. In the Kheu River section, the barium content is higher in host rocks than in the sapropelite unit. This phenomenon is likely related to the diagenetic redistribution of Ba, as evidenced by the

Table 2. The isotopic composition of organic and carbonate carbon in Paleogene rocks from the Kheu River

| Age of sediments | Sample no. | C_{org} , % | $\delta^{13}C_{org}$, ‰ | $\delta^{13}C_{carb}$, ‰ |
|------------------|------------|---------------|--------------------------|---------------------------|
| Lower Eocene | 64a | <0.1 | -27.9 | 0.4 |
| | 64c | 3.3 | -27.8 | 0.2 |
| | 64e | 0.1 | -27.8 | 0.8 |
| | 59a | <0.1 | -27.5 | 0.3 |
| | 59b | 3.7 | -27.5 | 0.1 |
| | 59e | 0.2 | -28.2 | 0.0 |
| | 55a | <0.1 | -27.2 | 0.3 |
| | 55b | 2.0 | -27.5 | 0.5 |
| | 55c | 0.3 | -27.7 | 0.1 |
| | 55e | <0.1 | -28.8 | 0.3 |
| Upper Paleocene | 14 | 0.2 | -27.4 | 0.5 |
| | 12 | 0.3 | -27.9 | -0.2 |
| | 11e | 9.2 | -30.8 | -1.7 |
| | 11c | 1.6 | -27.3 | -0.6 |
| | 11b | 10.6 | -30.3 | -1.8 |
| | 11a | 8.5 | -30.5 | -1.8 |
| | 9 | 0.1 | -27.2 | 0.3 |

presence of pyrite and barite nodules. Hence, this element can be included into the group of elements that are concentrated in the sapropelite unit.

Elements such as Ti, Zr, Nb, Sc, Cs, Rb, Hf, Th, Sr, and B are passive in relation to the sapropelite unit. The majority of these elements belong to the typical lithophile elements, whose distribution is governed by aluminosilicate components of the sediment. The REE group elements are rather close to the above-mentioned elements in the distribution mode. In the two sections studied, REE and Y were rather passive in relation to the organic-rich sediments (Fig. 3, Table 1). In the Kheu River section, the lower part of the sapropelite unit is characterized by a slight increase of REE and Y, whereas the upper part contains clark-level concentrations of these elements. In the Guru Fat'ma section, REE and Y are at normal level in the sapropelite unit but relatively increased in the underlying layer. Special attention must be given to the lack of correlation with P. The REE distribution in Paleocene deposits, in general, is similar to that in sapropels and host rocks of the Black Sea (Fomina and Volkov, 1970).

Hence, in addition to C_{org} , a large group of elements are concentrated in the sapropelite unit. However, we do not observe any distinct correlation between C_{org} and the majority of the minor elements within the layer or over the area. Some of these elements are characterized by conspicuous variations over the sapropelite area irrespective of the OM content. The regional-scale, possibly inherited-type increase of concentrations of these elements in the sapropelite unit may be induced

by specific features of the geological setting of particular regions. It may be governed, in particular, by the type of weathering in the coastal denudation zones and the specific conditions of sedimentation.

Evidently, the concentration of various elements in the sapropelite unit was a complex process affected by different factors, such as the accumulation of certain elements in tissues of living organisms during metabolism, the sorption of elements by remnants of atrophied organisms and hydroxides of Fe and Mn during sedimentation, the diagenetic processes of the accumulation or removal of elements, the direct precipitation of sulfides of certain metals from suspension in the H₂S-contaminated basin waters, etc. Obviously, the passive attitude of a group of elements (Ti, Hf, Sc, Nb, Zr, and others) in relation to sapropel sediments was mainly dictated by the terrigenous sedimentary material, and the role of the above-mentioned factors was insignificant.

The comparative analysis of the ranges of elements that are intensely or weakly concentrated in the Thanetian sapropelite unit and sapropels of the Black Sea (Volkov, 1973 and others) and Mediterranean Sea (Calvert, 1983, 1990; Pryusers *et al.*, 1991; and others) indicates that these ranges are generally similar, although one can observe certain differences in the behavior of separate elements and the degree of their concentration.

GEOCHEMISTRY OF ORGANIC MATTER IN THE SAPROPELITE UNIT SECTIONS

The isotope analysis of carbon and characteristic molecular structure of organic matter may be crucial for respective paleoreconstructions. With this objective in mind, we studied two sections in the following two sectors of the Late Paleocene basin: the Kheu River section in the Ciscaucasus and the Kurpai section in Tajikistan.

In the Kheu River section, we studied the isotopic composition of organic and carbonate carbon in the Upper Paleocene–Lower Eocene deposits, as well as the pyrolytic characteristics of OM. The bitumoid extracted from rocks with the application of a benzene–methanol mixture (9 : 1 v/v) was used to analyze the distribution of *n*-alkanes and porphyrine pigments by chromatography and optical spectroscopy, respectively. We also obtained the IR spectra and distribution of carbon isotopes in different-polarity bitumoid fractions.

The Isotopic Composition of Carbon

Based on data on the Upper Paleocene–Lower Eocene section including the sapropelite unit and the less organic-rich sapropel interlayers of Lower Eocene (Table 2), we can deduce the following regularities in the distribution of carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$ values). First, the isotopic composition of organic carbon is homogeneous along the entire time interval studied: the $\delta^{13}\text{C}_{\text{org}}$ values for all samples except those of the Pale-

ocene sapropelite unit fall within the -27 to -28‰ range, which characterizes Cretaceous marine sediments (Dean *et al.*, 1986; Kodina, 1987). The higher content of light carbon isotope in Cretaceous and older marine sediments, relative to Late Cenozoic and present-day sediments of seas and oceans, is attributed to the influence of climatic variations in the Earth's history on the global carbon cycle (Galimov, 1995). The isotopic composition of organic carbon suggests that the sedimentation here in Paleocene and at least Early Eocene occurred under an environment of warm climate that is typical of the first half of the Tertiary period.

Second, the sapropelite unit is enriched in light carbon isotope, relative to the host rocks. For instance, the carbon isotopic composition of the sapropelite unit with a C_{org} content equal to 8–10% ranges from -30.3 to -30.8‰ .

Third, the sapropelite unit with the lightest carbon isotope contains carbonates that are also enriched in this isotope ($\delta^{13}\text{C}$ up to -1.8‰). Consequently, the section is characterized by the presence of a parallel trend of isotope values of both organic and carbonate carbons (Fig. 4). More often, one can observe the following situation in nature: during the intensified bioproductivity and accumulation of organic-rich sediments, the carbon pool is depleted in light isotope owing to the isotopic fractionation at the stage of bioassimilation and preferential involvement of ^{12}C isotope in organic matter. Consequently, the carbonate carbon is enriched in heavy isotope. This phenomenon has been reported in several publications.

Hence, the above-described regularity, which was revealed by us, likely represents an exception from the general trend, and the reasons should be searched for in specific features of the sedimentational environment in the basin studied. An analogous isotope anomaly has been reported in Carboniferous black shales of Kansas and Oklahoma (Wenger and Baker, 1986) and Lower Toarcian (Posidonian) shales of southern Germany (Kuspert, 1982; Moldovan *et al.*, 1985). In the latter case, the concentration of organic carbon in bituminous shales and the parallelism of isotopic compositions of the organic and carbonate carbons were attributed to the participation of organogenic carbon dioxide in the assimilation cycle under the conditions of highly productive stagnated basin and anaerobic diagenesis.

The adequate appraisal of the geochemical environment in the intracontinental, relatively shallow-water basin studied requires the elucidation of the nature of organic matter in sapropel interlayers with the application of autonomous research methods. Based on modern concepts about the invariability of the carbon isotopic composition in terrestrial plants over the geological history and the isotope value for these plants at the level of -26‰ (Galimov, 1995; Pope *et al.*, 1989), we should acknowledge that even if the contribution of terrestrial biomass was conspicuous, it could not have served as

Table 3. Pyrolytic parameters of organic matter in the Ciscaucasus and Tajikistan sections

| Sample no. | S ₂ | S ₃ | TOC | HI | OI | Sampling site |
|------------|----------------|----------------|-------|-----|-----|--------------------|
| 64c | 5.46 | 1.40 | 3.28 | 166 | 42 | Kheu River section |
| 59c | 6.36 | 1.48 | 3.51 | 181 | 42 | " |
| 55b | 2.68 | 1.02 | 1.96 | 136 | 52 | " |
| 12 | 0.46 | 0.42 | 0.51 | 90 | 82 | " |
| 11e | 25.23 | 3.31 | 9.17 | 275 | 36 | " |
| 11c | 2.04 | 0.72 | 1.62 | 125 | 44 | " |
| 11b | 24.62 | 2.48 | 8.49 | 289 | 29 | " |
| 11a | 29.86 | 3.02 | 10.65 | 280 | 28 | " |
| 20 | 113.37 | 5.57 | 21.52 | 526 | 25 | Kurpai section |
| 19 | 91.54 | 5.14 | 17.62 | 519 | 28 | " |
| 17 | 2.88 | 1.12 | 1.33 | 216 | 82 | " |
| 15 | 51.95 | 3.08 | 9.37 | 545 | 32 | " |
| 13 | 0.43 | 0.72 | 0.28 | 153 | 257 | " |

Note: S₂ is given in mg OM/g rock; S₃, mg CO₂/g rock; (HI) hydrogen index; (OI) oxygen index; (TOC) total organic carbon, %.

the sole factor for depletion of the isotope value of organic carbon in sapropels up to -30‰.

The express pyrolytic analysis of rocks with the use of Rock-Eval II device coupled with the isotope analysis of carbon, the chromatography, and the molecular mass-spectrometry provided additional information about the nature of organic matter, its geochemical maturity, and sedimentational environment. Table 3 presents summarized results of the pyrolytic investigation of samples with C_{org} > 0.2% (indications of the detector below this value are nonlinear).

Based on the hydrogen index (HI), i.e., the function of the H/C ratio in kerogen, which is an essential parameter of pyrolysis, the organic matter is divided into three facial and genetic types (Table 3). In the Kheu River section, the maximum values of HI (275–

289 mg) are noted in the Upper Paleocene interlayer with the highest content of OM. However, it is worthy of noting that the absolute value of HI here is below the limit (HI = 300) set for organic matter of the genetic type II (Tisso and Welte, 1978) associated with the phytoplankton biomass. Therefore, the Kheu River variety should be classified as a mixed II–III-type organic matter with appreciable terrigenous admixture. According to the interpretation of facial affinity of shales in (Demaison and Moore, 1980), rocks with the aforesaid HI value are identified as bituminous shales that are accumulated in anoxic near-bottom waters and regulated by the contribution of plankton biomass.

The HI versus TOC plot demonstrates a correlation at the 1–8% interval (Fig. 5). Above the 8% concentration level, the HI value remains constant. The aforesaid

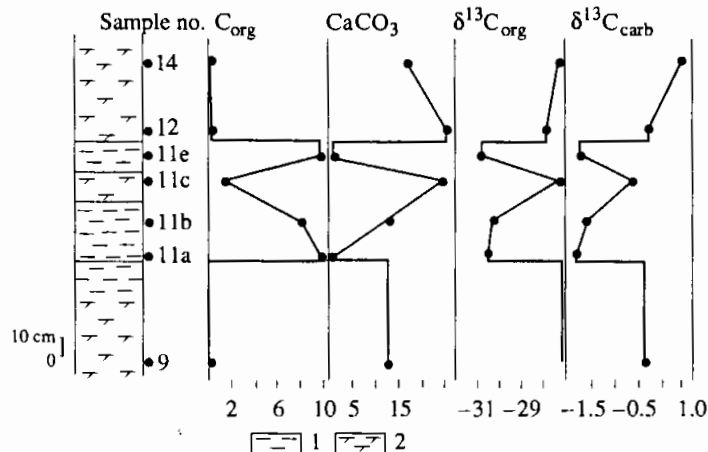


Fig. 4. Distribution of C_{org} and CaCO₃ (%) and δ¹³C (‰) in organic matter and carbonates from the Kheu River sapropelite unit section. (1) Clays; (2) marl clays.

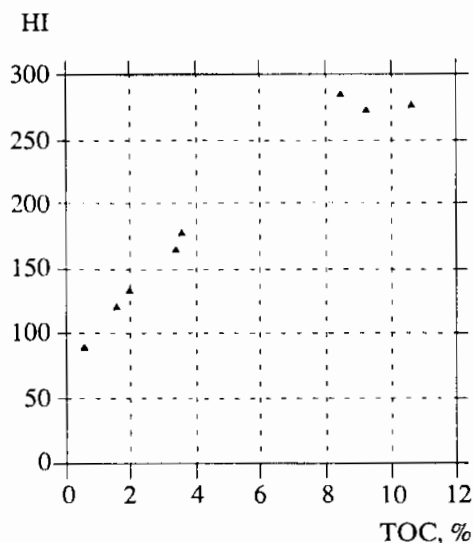


Fig. 5. The hydrogen index (HI, mg CM/g C_{org}) vs. C_{org} (TOC, %) correlation in the Kheu River rocks.

correlation testifies to the mixed composition of organic matter. Above the 1% TOC level related to the terrigenous admixture with HI < 100, the TOC value increases on account of the supply of H-rich, planktonogenic organic matter. The lesser the organic matter in rock, the higher the oxygen index (OI) and, consequently, the higher the proportion of terrigenous or recycled material.

The study of IR spectra of bitumoids and their separate fractions in slides with the aid of Specord-75 IR-spectrometer revealed that the sapropelite OM (samples 11a, 11d, 64c) is generally aliphatic, as indicated by intense absorption bands of long aliphatic chains and esters in all the low-polar fractions. The characteristic bands of aromatic structures are weakly developed.

The chromatograms of hydrocarbon fraction contain *n*-alkanes from C₁₅ to C₃₄; it is likely that the low-molecular *n*-alkanes C₁₅–C₁₉, which are observed as minor spikes on an appreciable peak, were partially lost owing to biodegradation. The alkane spectrum is characterized by equal numbers of even and odd homologues, the maximum concentration being for *n*-C₂₅.

The porphyrine metal complexes were detected in bitumoids of all the sapropelite unit samples studied on the basis of the characteristic optical absorption spectra. The presence of porphyrine pigments in the sapropelite OM is an indicator of reductive diagenesis of the planktonogenic OM. The positions of maximum absorption (396, 516, 552, and 585 nm) make it possible to suppose the presence of two types of nickel complexes: the low-polar DPEP- and etio-type and the more polar rhodo-type. The lack of vanadyl-porphyrines in bitumoid, despite the high concentration of V in sapropelites, is natural for the geochemically immature rocks. As is well known (Baker and Louda, 1986), vanadyl-porphyrines are incorporated into the kerogen

matrix and are only released during its thermic destruction.

The Kurpai Section, Tajikistan

Organic matter of the Kurpai sapropelite unit retains certain features of the Caucasian sapropelites but displays a contrast planktonogenic pattern.

Organic matter was more intensely accumulated in this basin. Based on the pyrolysis data (Table 3), as well as chromatographic and mass-spectrometric investigations of biomarkers, the plankton biomass served as the source of OM. The terrigenous contribution was minimum; the amorphous OM contains microscopic inclusions of spores, pollen, and vitrinite (Kodina *et al.*, 1995). In contrast to the Caucasian counterpart, the HI value here, however, is as much as 545; the OI value is low (25–32); and the share of the pyrolyzed carbon is two times more than in the Kheu River section. The Kurpai variety definitely belongs to the genetic type II. Samples 319 and 315 are characterized by the prevalence of the typical (for the planktonogenic OM) low-molecular *n*-alkanes with maximums in the C₁₇–C₁₉ zone and Ni-porphyrines. The sapropelite OM is enriched in biomarkers, such as triterpanes and, especially, steranes. Steranes are typical of eucaryote biomass, whereas C₂₇-homologue (cholestene) is a geochemical marker of algal biomass. Based on the mass-spectrometry (Kodina *et al.*, 1995), the Kurpai sapropelites are dominated by cholestene with the bioconfiguration $\alpha\alpha\alpha$ -20R.

Relative to host rocks, sapropelites were accumulated under a reductive environment and a higher preservation of components of the alga-producer biomass. This conclusion is based on several parameters of the molecular composition of OM, e.g., the increased values of phitane/pristane, moretane/gopane, and less stable tris-norgopane (T_M)/more stable tris-norneogopane (T_S) ratios, as well as the presence of gopanes with bioconfiguration 17 β (H), 21 β (H). Besides, sapropelites are almost devoid of diasteranes that are abundant in host rocks. Diasteranes are developed during the diagenetic transformations of OM as a result of the interaction between steranes and clay minerals in an oxidative environment (Moldovan *et al.*, 1985).

The isotope anomaly in the Kurpai sedimentary section is somewhat distinct from the Kheu counterpart: it is detected at the molecular level, i.e., in the isotopic composition of individual *n*-alkanes. Alkanes are isotopically lighter in sapropelite interlayers than in host rocks. Relative to samples 313 and 317, samples 319 and 315 are characterized by a lighter carbon isotopic composition in the C₁₅–C₂₉ alkane series. The isotopic effect value ranges from +0.5 to –4.3‰ (average –1.27‰), irrespective of the number of carbon atoms in the alkane molecule; the averaged value of $\delta^{13}\text{C}$ is –30.6‰ for sapropelite alkanes and –29.3‰ for host rocks. As in the case of enrichment of the total organic carbon in

light isotope in the Kheu sapropels, the manifestation of isotopic effect here at the scale of individual *n*-alkanes is evidently related to the assimilation of isotopically light carbon dioxide. The question to be resolved concerns the nature of the source of isotopically light carbon dioxide.

Based on general notions and the concrete paleogeographic situation in the basin during sea transgression, the light carbon dioxide could have two sources: (1) the supply from coastal waterlogged soils during sea transgression and (2) the recycling of organogenic carbon dioxide during the possible development of anoxic conditions in the marine basin.

The first model can be observed in the Caucasian part of Peri-Tethys where the planktonogenic, sedimentary organic matter bears distinct signs of extensive supply of terrigenous material. Naturally, terrigenous supplies consisted not only of remains of plants or humus of waterlogged soils. A large amount of carbon dioxide dissolved in coastal waters was also introduced into the basin. Unlike the typical marine counterpart, the carbon dioxide of terrestrial ecosystems is enriched in light carbon isotope. According to Galimov (1966, 1981), the isotopic composition of pedogenic carbon dioxide is similar to that of plant biomass (-23 to -27‰); the isotopic composition of the suprasoil CO₂ is -8 to 11‰; and the isotopic composition of bicarbonate, which is dissolved in fresh waters, is up to -14‰. The supply of carbon dioxide and its additional generation due to the mineralization of the bog biomass could strongly affect the carbon isotopic signatures of both the planktonogenic organic matter, which developed under a large-scale supply of biogenic material during sea transgression, and the carbonates.

The second mechanism likely prevailed in the Central and South Asian part of the basin, as is evidenced by the detection of trimethyl benzenes in the aromatic fraction of sapropelite OM (Kodina *et al.*, 1995). Nowadays, the presence of these biomarkers is recognized as evidence of the hydrosulfuric contamination of the basin's water body up to the lower boundary of the photic layer (Summons and Powell, 1986, 1987). The bioprecursor of alkyl-trimethylbenzene homologues is represented by isorenieraten carotenoid, which is one of the components of pigment complex of the photosynthetic alga of the species *Chlorobium* (Damste *et al.*, 1993, 1995). In addition to the characteristic molecular structure, these biomarkers have a specific isotopic signature represented by the heavy isotopic composition of carbon. *Chlorobium* assimilates carbon dioxide according to the mechanism of anoxygenic photosynthesis, i.e., in the absence of oxygen and with the application of hydrogen sulfide as the reducer of CO₂. The ecological niche for these bacteria is provided by the lower boundary of the H₂S-contaminated photic layer of water column.

The finding of the specific biomarkers, isorenieraten derivatives, in the Kurpai sediments suggests that the sedimentational paleoenvironment was characterized

by a short-period stagnation of the basin, hydrosulfuric contamination of the water column, and consequent geochemical and isotopic alterations.

Obviously, the present-day analogue of such an environment is the Black Sea, where the typical biomarkers *Chlorobium* have been found in the suspended material and sediments (Damste *et al.*, 1993; Repeta and Simpson, 1991; Repeta *et al.*, 1989), and the organic matter in Holocene sediments are enriched in light carbon isotope (Kodina and Bogacheva, 1991).

Several works are devoted to the description of OM in the Suzak oil shales from other regions of Central and South Asia. Based on the analysis of the composition of *n*-alkanes and fatty acids in shales, Bondar' *et al.* (1991) concluded that the organic matter is predominantly planktonogenic, but locally (e.g., at the Dzham shale occurrence) it contains a significant amount of terrestrial higher plant. V. Oleinik and E. Oleinik (1979) reported that the organic matter in oil shales of the Hissar Range and Tajik Depression is mainly composed of the yellow amorphous substance (colloalginite); the tissue element, if it is present, accounts for not more than 10–15%; other subordinate components include spores, pollen, microscopic fragments of plant tissue, and rather abundant remains of peridiniids; remains of acritarchs are also encountered. Based on these observations and the fact that peridiniids were among the main producers of OM in the Late Paleocene basin of Central and South Asia, these researchers inferred that the origin of organic matter in oil shales is mostly sapropelic.

The recent analysis of phytoplankton from the sapropelite unit sections of Torangly and Medani (Akhmet'ev and Zaporozhets, 1996) also revealed that sapropelites are highly saturated in organic-walled phytoplankton, although usually *phytoplankton is distinctly subordinate to amorphous OM*. It is worth noting that layers underlying and overlying the sapropelite unit are depleted in phytoplankton. The thick-walled cysts, which represent specific forms or autonomous species and doubtless endemics of the Crimean-Caucasian zone and Central and South Asia, play an extraordinary role in the sapropelite complex. Beyond the sapropelite unit, the thick-walled cysts are one order of magnitude less abundant; moreover, the thickness and color of their walls are decreased. These observations suggest the following conclusions: phytoplankton and dinoflagellates, in particular, were indeed among the main producers of OM during the accumulation of sapropels; the basin waters were characterized by ecologically extreme conditions; and morphologically anomalous cysts were consequently developed with very thick shells.

Hence, the comprehensive investigation of organic matter in the sapropelite unit indicates that the organic matter was of predominantly marine origin and it acquired a mixed structure in sites with terrestrial supply of material. The chief marine source of OM was the

organic-walled phytoplankton with a perceptible content of dinoflagellates. However, the major forms were represented by green algae, cyanobacteria, and other species of microphytoplankton, whose decomposition during diagenesis produced abundant colloalginite material in sapropel sediments.

FORMATION MODEL FOR THE UPPER PALEOCENE SAPROPELITE UNIT

The paleoreconstruction of formation conditions of the sapropelite unit requires the elucidation of processes that were responsible for the intensification of bioproductivity of the organic-walled phytoplankton and the accumulation of a great amount of OM in sediments.

The upwelling is a well-known and rather scrutinized mechanism for the supply of biophile elements into the zone with a very high bioproductivity of marine organisms. It is manifested in relatively narrow oceanic shelf zones and induced by the ascent of abyssal waters from zones having markedly different pressure and temperature.

The large and relatively shallow-water Late Paleocene basin was remote and separated by a system of archipelagoes from zones where one could suppose the existence of fairly deep sectors required for the functioning of the upwelling mechanism. Therefore, we do not have strong grounds for applying the upwelling mechanism to elucidate the sapropelite unit formation. Besides, it is extremely difficult to imagine that the upwelling mechanism could function during the relatively short period of sapropel accumulation and that it did not exist before and after the accumulation episode. Difficulties emerge when we attempt to explain the sapropelite formation with the aid of other mechanisms that have been proposed by some researchers (Kidd *et al.*, 1978; Calvert, 1983; Sutherland *et al.*, 1984; and others) for the genesis of the eastern Mediterranean sapropels.

Strakhov (1971) proposed the following model for the origin of sapropel sediments in the Black Sea (Holocene Euxinian sediments): As a result of the breakthrough of the heavy, saline Mediterranean waters into the relatively brackish basin and flow along the bottom, the Euxinian waters, which were enriched in biophile elements, were forced upward. The ascent of Euxinian waters into the photic zone resulted in the activation of plankton bioproductivity and the accumulation of organic-rich sediments. After the exhaustion of the biophile element reserve, the intense phytoplankton bloom was terminated, and the OM content in sediments was reduced. However, this scheme is inapplicable for the Late Paleocene basin, because it existed in a basically different geological and paleogeographic environment.

Based on the foregoing, we believe that the model of the sapropelite unit formation should consider the following circumstances: Sapropel sediments were accumulated in a large, relatively shallow-water, epicontinental basin against the background of rapid transgression that mirrored the eustatic rise of the sealevel at the end of the Thanetian age. The transgression was preceded by a regressive episode, which is traced in some sections on the basis of respective hiatuses and erosional overlapping of older deposits by the sapropelite unit. Along the latitude, the sapropelite unit stretches for more than 2500 km with local gaps. The highest concentration of OM in the sapropelite unit is registered in Central and South Asia, where the organic matter associates with phosphorite-bearing rocks. The sapropelite unit sediments are enriched in several minor elements that are irregularly distributed over the area and are not commonly correlated with C_{org} . The OM-enrichment was basically induced by the intensification of various types of organic-walled phytoplankton; i.e., the organic matter was predominantly marine but, locally, the fraction of land-derived OM was increased. Various sectors of the basin substantially differed in facial respect; nevertheless, the transgression was accompanied elsewhere by the formation of sapropel sediments.

In our case, the model for the accumulation of organic-rich sediments, which is in best agreement with the available factual data, can be based on the mechanism of biophile element supply into the basin from coastal land during a rapid eustatic transgression (Gavrilov, 1992, 1994; Gavrilov and Kopaeovich, 1996).

The sapropelite unit formation was governed not only by the transgressive stage, during which sapropel sediments were accumulated, but also by the preceding regressive stage of the basin development, as well as the type of sediments that were mainly accumulated along the basin periphery and in interior rises during the "pre-sapropel time." As a result of the regression, large areas, which generally represent flattened (by marine erosion and sedimentation) lowlands, were developed along the periphery of a relatively shallow, epicontinental sea and around archipelagoes. It is pertinent to note that a noticeable peneplanation of the topography occurred during Late Cretaceous and Paleogene (Gerasimov and Meshcheryakov, 1964; Gorelov, 1971; Troitskii, 1974; and others); consequently, even minor fluctuations of the sea level resulted in substantial displacements of the coast line. The sector, which was released from sea, was covered by loose nonlithified sediments that recently were marine sediments, and specific coastal landscapes were developed. Nonlithified and usually reduced sediments, which contained sulfide and authigenic phosphate minerals, were subjected to subaerial weathering. The oxidation of sulfide minerals resulted in the formation of sulfuric and sulfonic acids that actively reacted with host rocks and significantly intensified the weathering. Occasionally, during the warm climate, in particular, phosphates could accumulate on carbonate rocks as a

result of the supergenic weathering. In some places of Central and South Asia, under the conditions of sea-level drop owing to erosion of the underlying bed, the gravel-pebble unit was formed.

As was noted earlier (Oleinik, 1969), the lower part of the Suzak layer, which underlies the oil shale unit, contains abundant phosphate concretions, suggesting that a high concentration of P in mud waters of sediments was accumulated before the formation of the sapropelite unit. The degree of phosphorus concentration was naturally variable in different sectors of the basin. It should be pointed out that, in specific cases, supergenic weathering leads to the formation of different-scale phosphate deposits. In Central Russia, for example, phosphate eluvium is widespread on the outcrops of Cretaceous carbonate deposits (Mikhailov, 1986).

Territories, which were released from sea, were characterized by the formation of lakes and waterlogged sectors (lacustrine bog landscape) on newly developed coastal plains. Judging from the present-day analogues (Timofeev and Bogolyubova, 1997 and others), peat bogs were formed very rapidly. The analysis of mineralogical and geochemical environment in present-day bog systems makes it possible to conclude that the peat-forming process promotes the geochemical activity of P, which is an essential agent of the biological cycle. In general, the bog-forming process can be considered a typical mode of phosphorus migration in the supergenic zone (Kovalev, 1985). The aggressive medium of bog systems stipulated reworking of the imported sedimentary material and alteration of the underlying sediments; several terrigenous minerals, which were relatively stable in weathering conditions, were dissolved in peat bogs; and bog waters were enriched in many microelements. In addition to the solid phase OM, the waterlogged basins contain abundant dissolved OM, which formed as a result of decomposition of the constantly regenerating reserves of OM. The accumulation and partial transfer of OM into the dissolved state were constantly proceeding during the whole life period of the aforesaid landscapes. Phyto-genic accumulations of OM in this environment were characterized by the relatively light isotopic composition of carbon, which is known to be typical of terrestrial plants.

Obviously, large territories of coastal-marine plains were occupied by soil-forming processes, and soils inherited various elements, including biophile ones, from the underlying nonlithified or weakly lithified sediments.

Hence, it is quite probable that coastal lowlands, which were formed during the sea regression, were characterized by landscapes where diverse geochemical processes were highly active owing to the eluvial, soil-forming, and bog-forming processes that were responsible for the accumulation of various, primarily

biophile elements and their conversion into the mobile reactive state.

The Late Paleocene basin was very large; therefore, the coastal terrestrial landscapes were distinguished by specific features. First, the geomorphologic factor governed the development or absence of large coastal plains. The steep seafloor slope was devoid of the wide coastal zone even at a substantial drop of the water level, whereas the low-angle seafloor, which was the most widespread situation, promoted the formation of such a zone. Second, the pattern of coastal landscapes was strongly influenced by climatic variations. As the mode of these variations is insufficiently studied, we can only assume that the basin's eastern sector had an arid-type climate. Third, coastal landscapes differed in the geochemical specialization owing to differences in the older marine sediments, which in turn were characterized by specific geochemical signatures inherited from the older rocks of the terrigenous provenance.

The regression was dynamically replaced by transgression, against the background of which the organic-rich sediments were accumulated. The sealevel rise was quite significant, i.e., not less than dozens of meters; a similar estimate is given in (Haq *et al.*, 1987). Despite the rapid transgression, the occupation of the previously abandoned territories by sea was not immediate. In the Baksan River section, Northern Caucasus, for instance, the sea covered the previously existing rise only at the end of the transgression; therefore, the eroded older surface was only overlain by the topmost part of the sapropelite unit, whereas the lower part is absent (Muzylev *et al.*, 1996).

The transgressive sea dynamically interacted with coastal-marine landscapes. Under the conditions of a flat coastal plain, even a relatively minor rise of the sealevel resulted in flooding of large territories. The organic matter, which was concentrated in peat bogs and soils, was transported into the sea. The solid phase OM was reworked and redeposited in marine muds, leading to the C_{org} -enrichment of the muds. The dissolved OM, which was abundant in peat bogs, was utilized by plankton during a new biological cycle, promoting the activation of plankton bioproductivity.

In addition to OM, several biophile elements, including, above all, P, were transported from coastal landscapes into the basin. As was mentioned above, relative to host rocks, majority of the sapropelite unit sections are enriched in P. The introduction of P into the basin stipulated a drastic intensification of bioproductivity of diverse organic-walled phytoplanktons that served as the main supplier of OM in sediments. At the same time, the productivity of the Ca-generating plankton relatively declined. The role of the additional supply of P into the Late Paleocene sea was likely crucial for the growth of phytoplankton bioproductivity. This inference is supported by the following fact: the basin's Central and South Asian sectors, where the sapropelite unit is closely associated with the phosphate-bearing

rocks and phosphorite units, are the sites, where one can encounter the maximum concentration of OM; e.g., the C_{org} content in the Suzak oil shales is as much as 20% or more (Table 1).

The model proposed by us for the sapropelite unit formation is also corroborated by the artificial reservoir-filling data that simulate the evolution of transgression at a microscale. It was reported that, during the initial reservoir-filling period, the phytoplankton bioproductivity is found to be extremely intensive owing to the high concentration of biogenic elements that were washed off from flooded soils (Petrova, 1990 and others). Actually, this phenomenon represents a model of processes during the development of the full-scale sea transgressions.

The role of bogs in the supply of biophile substances into transgressive sea and the consecutive intensification of the marine alga bioproductivity is believed to be essential for the genesis of the Pennsylvanian black shales of Kansas and Oklahoma (Wenger and Baker, 1986).

As is evident from Fig. 3 and Table 1, the sapropelite unit sections are often enriched in Fe. In this connection, it is pertinent to emphasize the following: The recent experiments in the Pacific Ocean (Martin *et al.*, 1994; Coale *et al.*, 1996; Frost, 1996) revealed that the import of Fe into the surficial layer of water column leads to the introduction of this element into the chlorophyll structure and intensifies the plankton bioproductivity. Thus, Fe can behave as a biophile element in certain circumstances. In our situation, the existence of lacustrine bog systems in Late Paleocene could serve as a powerful factor for the supergenic migration of Fe, its export into the marine basin (Strakhov, 1962 and others), and subsequent participation in the biological cycle, which would promote the phytoplankton bioproductivity.

The mechanism of the supply of biophiles into sea and intensification of phytoplankton bioproductivity was analogous in various sectors of the Late Paleocene basin that could appreciably differ in facial environment and predominant sediment type. The regional specific feature, however, strongly governed the geochemical signature of the sapropelite unit. The North Caucasian sections, for example, are characterized by a high content of Cr, while the South Turkmenian sections are distinguished by high contents of Pb, Zn, etc. The possible reasons for the Cr-enrichment of sediments have been discussed in our previous work (Gavrilov and Muzylev, 1991). Here, we shall only recall that, obviously, the geochemical signature of the sapropelite unit in different areas was significantly governed by local sources of the sedimentary material. However, this was not a simple washout-transportation-deposition scheme. Most likely, the system included optional members that were largely regulated by biogenic processes.

ANOXIC CONDITIONS IN THE WATER COLUMN

The accumulation of abundant OM in sediments triggered the generation of a large amount of H₂S that diffused into the suprabottom water and stipulated the hydrosulfuric contamination of the basin. Since the basin was relatively shallow, the contamination primarily occupied the bottom part of water column and locally the photic zone as well, as evidenced by the geochemistry of OM (Kodina *et al.*, 1995).

The development of anoxic conditions is responsible for the lack or suppressed state of benthic fauna and foraminifera, in particular (Muzylev *et al.*, 1996). As was mentioned above, sapropel sediments were OM-enriched to a variable extent in different sectors of the sea. Anoxic conditions, likely a widespread phenomenon at the Late Thanetian sea, were not, however, pervasive, and were developed as large spots (lenses) stretching over hundreds of kilometers, depending on the geomorphology of the basin floor. The degree of anoxia could strongly vary; its attenuation promoted the origination of some forms of benthic organisms that were able to withstand the unfavorable suboxic environment.

Anoxic conditions in the Late Thanetian basin rendered a negative influence not only on the benthic fauna, but on planktonic organisms as well, whose life cycle required submergence into deeper zones of the water column at certain stages of their development. This circumstance could induce the origination of anomalous thick-walled species of dinoflagellates in the sapropelite unit rocks (Akhmet'ev and Zaporozhets, 1996). At the same time, one should not exclude the alternative possibility of the origination of anomalous plankton forms owing to the development of the so-called "red tides," including toxic ones, in seas (Gavrilov and Kopaevich, 1996).

The hydrosulfuric contamination of basin waters was among the essential factors controlling the geochemical signature of sediments. Special attention must be given to the following fact: all the sapropelite unit sections, where one can suppose a rather intense development of the hydrosulfuric contamination of suprabottom waters, contain very high concentrations of Mo (maximum values, in ppm): Kheu 63, Torangly 360, Suzak oil shales 300–500, Kurpai 220, Guru Fat'ma 188, and Amu Darya region oil shales 1760. Based on the available data on some sections, the sapropelite unit rocks are one order of magnitude more enriched in Se than the host rocks. It should be noted that Mo and Se form insoluble sulfides within the H₂S-contaminated water column and are precipitated on the seafloor along with other sediments (Volkov and Sokolova, 1976 and others), promoting the rise of their concentration in rocks. This mechanism functioned in combination with other mechanisms of the concentration of minor elements in sediments. This group of minor elements also includes Re, which is anomalously high (hundreds and thousands of times higher, relative

to the content in host rocks) in the Suzak oil shales, and some other elements. At the same time, anoxic conditions were unfavorable for the precipitation of Mn; therefore, its concentration is decreased in the sapropelite unit, relative to host rocks. Hence, the hydrosulfuric contamination of seawater actively regulated the geochemical signature of the sapropelite unit sediments.

The Late Thanetian transgression was rapid but relatively short-lived. How long was the duration of the accumulation of sapropel sediments? Since the sapropelite unit is characterized by small thickness and the methods of zonal stratigraphy do not offer the required "resolution," it is rather difficult to unambiguously answer this question. The duration can be only approximately estimated by comparing it with analogous formations. According to (Vinogradov *et al.*, 1962; Degens and Ross, 1972), the similar (in thickness) sapropelite unit at the Black Sea was accumulated over a period of about 4–5 ka. The carbon isotope estimates of the duration of the Mediterranean sapropels of analogous thickness also yield values of several thousand years, and the accumulation rate of sapropels is 3–5 times greater than the rate of host sediments (Sutherland *et al.*, 1984). Obviously, the Thanetian sapropelite unit was accumulated during a similar or slightly longer period of time, however, not exceeding 10 ka.

After the culmination of transgression and the cessation of biophile element supply into the basin, the intense bloom of diverse forms of phytoplankton and the consequent concentration of OM in muds was terminated. Owing to the inherent conservative nature of the basin (as a system) and the gradual evolution of the final stage of transgression, the termination of the sapropel-accumulating process was less abrupt than its starting period. Several factors, including the relatively shallow-water basin, the lack of density stratification of waters, the cessation of generation of great amounts of H₂S in sediments, and the diffusion of H₂S into suprabottom waters, promoted a rather rapid oxidation of H₂S in the seawater and disappearance of anoxic conditions. Therein lies the essential difference between the "postsapropel" stages of evolution of the Late Paleocene basin and the Black Sea. In the latter case, thanks to the basin-type morphology and density stratification of waters, the hydrosulfuric contamination did not disappear after the cessation of sapropel accumulation, but continued to exist as a result of both the generation of H₂S in present-day sediments and the sulfate-reducing processes within the water column.

CONCLUSION

In a large territory of the epicontinental sea located in the southern part of the FSU, the Late Thanetian time was characterized by the accumulation of organic-rich sediments against the background of a rapid eustatic transgression. The abundance of organic matter in the sedimentary material balance was mainly induced by a

drastic boost of bioproductivity of the organic-walled phytoplankton, presumably including the bacterial variety, as evidenced by the geochemistry of OM and paleomicroflora data. Simultaneously with the accumulation of OM, sediments were enriched in a wide and similar range of elements over the entire basin; some of these elements are likely more concentrated in certain areas owing to specific facial features and different sedimentary provenances. The sapropelite unit is characterized by the presence of OM and carbonates with a light isotopic composition of carbon as a result of the origination of isotopically light CO₂ and its participation in the bioassimilation process. This carbon dioxide could be supplied by both terrestrial ecosystems and products of the biogeochemical decomposition of planktonic OM associated with the hydrosulfuric contamination of water column.

The concentration of OM in muds created anoxic conditions that were unfavorable for biota in the basin and responsible to a certain extent for the increase of concentrations of Mo, Se, Re, etc. and the decrease of Mn and other minor elements. Anoxic conditions were terminated after the cessation of accumulation of the sapropelite unit sediments in the basin.

The drastic enhancement of bioproductivity in the basin was induced by the supply of an optional amount of biophile elements in connection with specific features of the dynamics of its evolution. The sapropelite unit accumulation was predated by regression that exposed a large territory of the seafloor composed of "geochemically active" landscapes, such as soil cover, lacustrine bog systems, and zones of supergene weathering of phosphate-bearing sediments. At the rapid transgression stage, biophile elements derived from the aforesaid landscapes migrated into the sea and participated in the biological cycle, resulting in the activation of phytoplankton bioproductivity. The bioproductivity of the organic-walled phytoplankton abruptly decreased after the termination of transgression and removal of biophile elements from the aqueous system.

The sealevel fluctuations over the entire territory of the Late Paleocene basin created prerequisites for the accumulation of sapropel sediments in this region; however, differences in the geomorphology of the basin bed and coastal land, the geochemical features of coastal landscapes, the fabric of older sediments, the regional climatic features, etc. stipulated local deviations in sedimentation and, consequently, variations in composition and structure of the sapropelite unit in different sectors of the basin; and the sapropelite unit disappeared in certain places.

The accumulation of the sapropelite unit sediments in the Late Thanetian time was a synchronous or sub-synchronous reflection of the global, predominantly biotic and abiotic events.

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