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The Early Cretaceous Anoxic Basin of the Russian Plate: Sedimentology and Geochemistry

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Abstract—The profile comprising a series of lower Aptian sections from Ul'yanovsk to Saratov in the Russian Plate has been studied. It is shown that the unit of organic-rich rocks is characterized by the lack of bioturbation and elevated concentration of many chemical elements. The petrography and geochemistry of organic matter (OM) indicate the prevalence of basinal OM in carbonaceous sediments, while continental OM dominates in host rocks. Sedimentological, biotic, and geochemical data testify to the deposition of organic-rich sediments under anoxic conditions. The anoxic environment in the Aptian basin of the Russian Plate correlates with the global OASE-1a anoxic event. The mechanism of Aptian carbonaceous sedimentation is discussed.

INTRODUCTION

A comprehensive lithological, geochemical, and paleoecological study is required for the reconstruction of formation conditions for organic-rich sequences that often host various mineral deposits. Sediments deposited at the stages transitional from normally aerated basins to anoxic ones attract the most interest. Such transitions are generally accompanied by the following processes: (1) abrupt variations of chemical element contents in sediments; (2) appreciable changes in geochemistry of buried OM; (3) intense negative and positive trends in the behavior of stable isotopes, first of all, $\delta^{13}C$ and $\delta^{18}O$; and (4) substantial variations of biota in the basin. Such variations bear not only regional but also global character and display certain rearrangements in biosphere. Problems of anoxic environments in paleobasins were discussed in (Strakhov, 1962, 1976; Kholodov and Nedumov, 1991; Kholodov, 2002; Gavrilov *et al.*, 1997; Jenkyns, 1980; Arthur *et al.*, 1988; Tyson, 1995; Brumsack, 1980; Hild and Brumsack, 1998; and others).

Lower Aptian sedimentary rocks of the Russian Plate are interesting as a regional manifestation of the so-called global oceanic anoxic event 1 (OAE-1) (Jenkyns, 1980; Arthur *et al.*, 1988). Aptian rocks are characterized by a terrigenous type of sedimentation, whereas the middle Eocene Kuma (anoxic) basin in southern Russia is mainly filled with carbonate rocks. In the Phanerozoic history of the central Russian Plate, the early Aptian basin with carbonaceous sediments was probably the single basin with a rather stable anoxic environment, and this also attracts the special interest to its formation conditions. This work is devoted to the lithological and geochemical characteristics of the lower Aptian sequence and the reconstruction of its formation environment.

The Aptian bituminous shale unit was studied along the profile that transects its present-day domain extending from Ul'yanovsk to Saratov. The complete sections were studied at scarps on the right bank of the Volga River in Ul'yanovsk, Sengilei, north of Khvalynsk near the Fedorovka and Yershovka villages, and in open pits of the brick yard at northern outskirts of Saratov (Guselka).

The chemical analyses were performed in the Laboratory of physicochemical analysis at the Geological Institute, RAS; C_{org}, CO_2, Fe, Mn, Ti, and P were determined by chemical analysis, while other elements were determined by emission spectroscopy (PGS-1 spectrometer). Results of the OM pyrolysis were obtained with a Rock-Eval II device at the Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS.

STRATIGRAPHIC POSITION OF LOWER APTIAN ORGANIC-RICH SEDIMENTS

The Aptian bituminous shale unit was known in the Russian Plate rather long ago (Arkhangel'skii, 1923; Sazonov, 1953; Sazonova, 1954, 1958, 1962; Sazonova and Sazonov, 1967; and others). It includes calcareous concretions locally merging into a common layer defined as the Aptian plate (Sazonova and Sazonov, 1967; Gerasimov *et al.*, 1962). It is traced almost continuously along the Volga River from Ul'yanovsk to Saratov and serves as a good reference horizon.

Sazonova and Sazonov (1967) published the detailed Aptian paleogeographic map showing sea boundaries and carbonaceous shale domain that extends from the Oka–Tsna Arch in north to the latitude of Saratov in south and further toward the northern Caspian Lowland.

In the 1980s and 1990s, the stratigraphy of Lower Cretaceous sedimentary rocks of the Russian Plate was studied in detail by Baraboshkin. The obtained results are reported in (Baraboshkin, 1998, 2001; Baraboshkin *et al.*, 1999). He proposed a refined paleogeographic scheme for the evolution of this province in the early Aptian (Baraboshkin, 2001). The scheme was compiled with the consideration of new information concerning the facies distribution and biostratigraphic data (Fig. 1). Boundaries of the domain of carbonaceous rocks within the marine paleobasin of the Russian Plate are in good agreement with the data reported by Sazonova and Sazonov (1967).

In most works published before the 1990s, the bituminous shale unit of the Russian Plate was traditionally referred to the *Deshayesites deshayesi* ammonite zone (Sazonova, 1958; Sazonova and Sazonov, 1967; Glazunova, 1973; *Stratigrafiya SSSR...*, 1986–1987). In recent years, the biostratigraphy of this interval has been substantially revised (Mikhailova and Baraboshkin, 2001). It is currently referred to the *Deshayesites volgensis = Deshayesites forbesi* ammonite zone (Casey, 1961). This provides a closer correlation with an episode of the global OAE-1 event known as OASE-1a subevent (*Deshayesites forbesi/deshayesi*), which was marked by the deposition of C_{org}-rich sediments in epicontinental marine basins of Germany (Kemper and Zimmerle, 1978; Mutterlose and Böckel, 1998), Italy, France, and Pacific Ocean (Arthur *et al.*, 1988).

The biostratigraphic position of the shale unit traced from Ul'yanovsk to Saratov varies to some extent within the same ammonite zone (Fig. 2). Variations in the structure, thickness, and certain lithogeochemical parameters are also recorded. Thus, the lower boundary of the Aptian bituminous shale unit turns out to be slightly diachronous.

The calcareous nannoplankton was also studied in the sections near Ul'yanovsk and Sengilei. In both localities, it was found only in sediments of the bituminous unit and completely lacking in host rocks. In the first section, the bituminous unit base contains a rather diverse assemblage including *Rhagodiscus angustus* and *Eprolithus floralis*, which serve as markers of the *Rhagodiscus angustus* Zone base (Thierstein, 1976; Roth, 1978), and *Braarudosphaera hockwoldensis*. At the same time, *E. floralis* appears somewhat higher than *R. angustus* in many sections of the world (Erba, 1994; Cobianchi *et al.*, 1997; Bischoff and Mutterlose, 1998; and others), suggesting that the sediments containing this assemblage in the studied area are related to the upper *Rhagodiscus angustus* Zone.

The absence of nannoplankton in the middle part of the bituminous unit (at the Aptian plate level) is apparently caused by the calcium carbonate dissolution and redistribution. Dissolution was probably the main process that was responsible for the formation of monotype nannoplankton assemblage. In sediments surrounding the Aptian plate (sample U-8, Ul'yanovsk section; sample S-30, Sengilei section), the nannoplankton assemblage is dominated, for example, by the least soluble forms of *Watznaueria* spp. (*W. barnesae, W. britannica, W. ovata*) (>90%). Clear indications of dissolution and the predominance of *Watznaueria* spp. (>50%) were also noticed in nannoplankton assemblages at higher levels. All species of *Watznaueria* genus are oligotrophic forms, and their ubiqutuous prevalence over the eutrophic group (*Zeugrhabdothus* spp., *Biscutum* spp.) likely indicates a deficiency in nutrients for nannoplankton in the basin (Roth and Krumbach, 1986; Bischoff and Mutterlose, 1998; Fisher and Hay, 1999). The relative abundance of *Rhagodiscus* spp. (*R. angustus, R. splendens, R. asper*) is an indicator of a rather warm surface water (Erba *et al.*, 1992; Bischoff and Mutterlose, 1998). At the same time, the absence of nannoconids, which are commonly interpreted as warm-water oligotrophic species (Bischoff and Mutterlose, 1998), is characteristic of the studied assemblages.

LITHOLOGICAL AND PALEONTOLOGICAL CHARACTERISTICS OF SECTIONS

The most complete section of the bituminous shale unit crops out north of Ul'yanovsk near the new bridge across the Volga River (Fig. 3).

The base of exposed Aptian section is composed of the banded member (apparent thickness 1.5 m) with a frequent intercalation of wavy lenticular bands (0.5–1.5 cm) consisting of greenish gray clay and friable light gray siltstone. In some intervals, the sediments are affected by bioturbation. The roof of the banded member is deeply penetrated by large wormtrails filled with dark green friable fine-grained micaceous sand locally cemented by siderite.

The overlying unit (about 9.5 m) consists of dark gray clay with an admixture of silty material along with rare and small lenticular carbonate concretions at the base. The clay is generally massive and significantly affected by bioturbation (Fig. 4a). The siltstone interlayers within the clay are up to 10–15 cm thick and locally cemented by massive pyrite. At the roof, the clay is substantially enriched in a coarse silty material and shell fragments. This clay unit underlies the bituminous shale and belongs to the upper *Deshayesites tenuicoststus* Zone with a predominance of the mainly boreal ammonite assemblage.

The overlying unit (3.8 m) consists of dark brown thin-laminated rocks that are megascopically fairly uniform from the base to roof. These rocks are separated from the clay unit by a sharp, severely limonitized uneven boundary with indications of erosion. At the fresh fracture, the rock reveals a olive color and distinct thin horizontal bedding with laminae 1–5 mm thick. The perfectly preserved bedding with almost complete

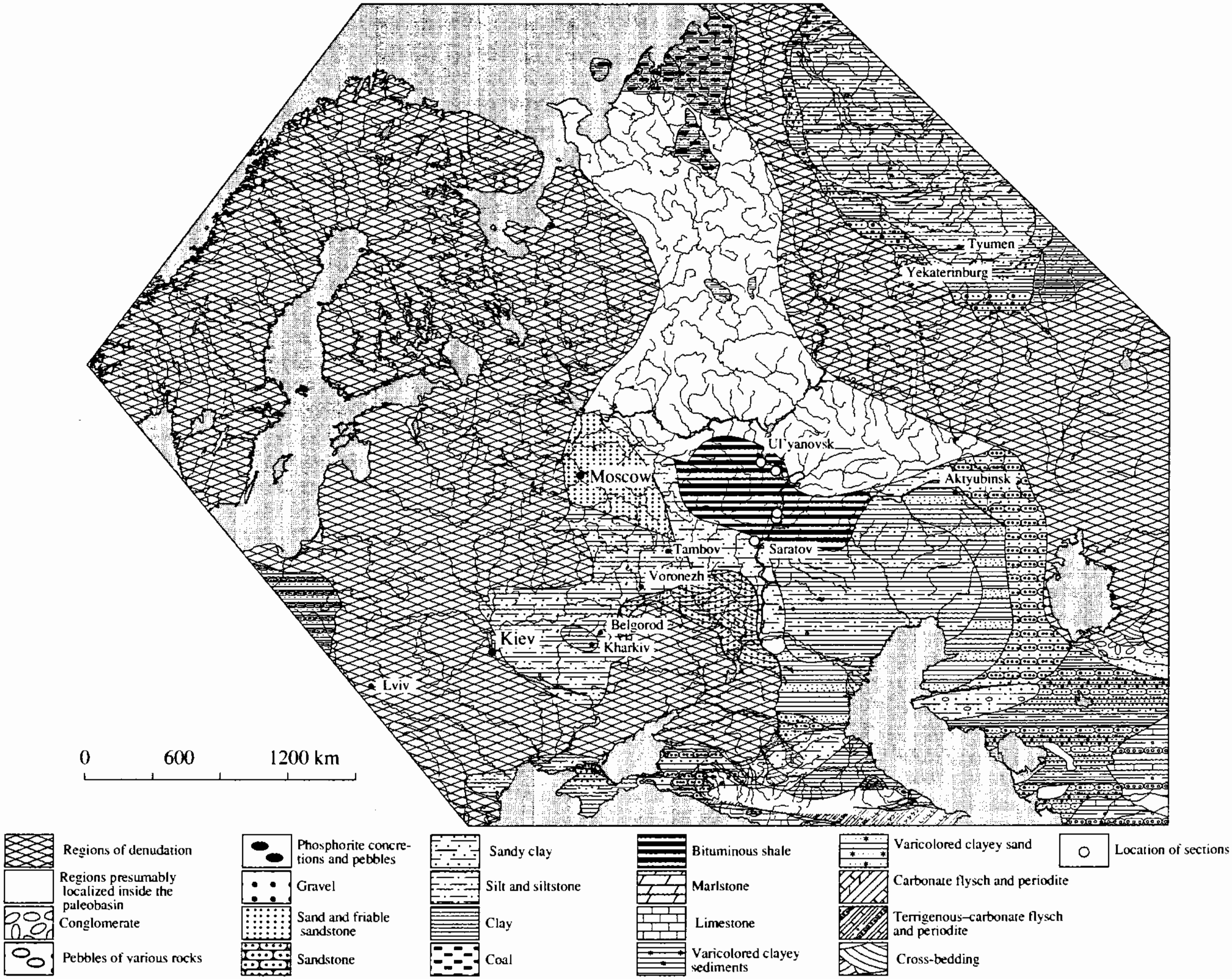

Fig. 1. Paleogeographic scheme of the Russian Plate in the early Aptian.

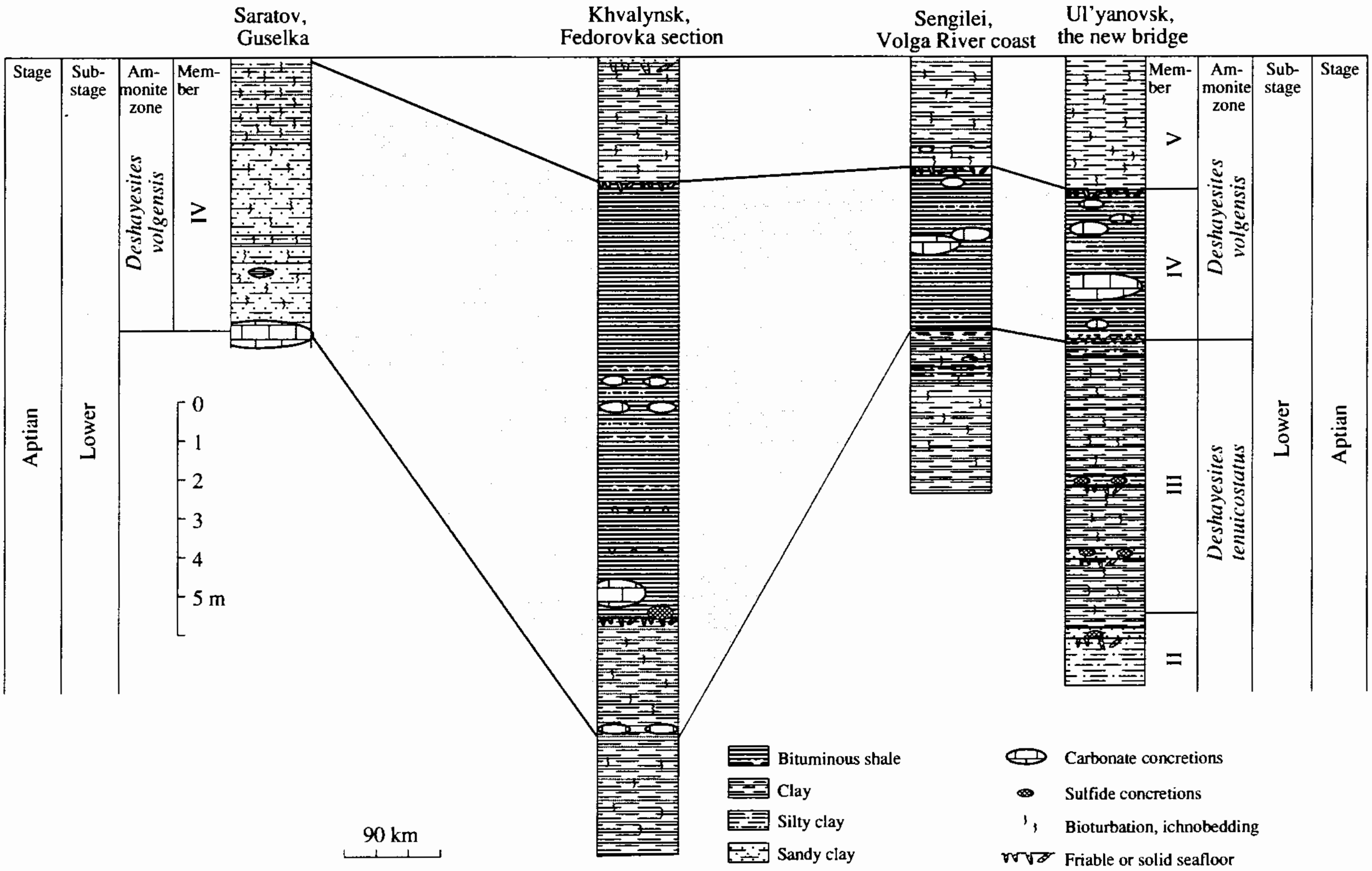

Fig. 2. Correlation of lower Aptian sections in the Ul'yanovsk–Saratov Trough, the Russian Plate.

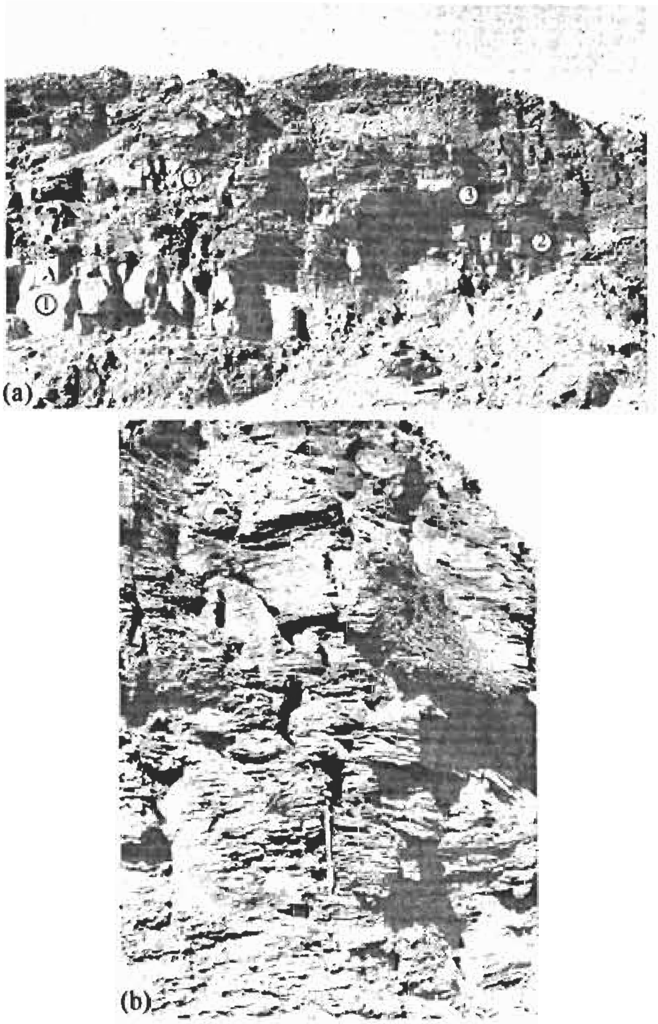

Fig. 3. Bituminous shale unit in the Ul'yanovsk section. (a) (1) Calcite lenses of the Aptian plate; (2, 3) large concretions localized above the Aptian plate; the hammer (indicated by arrow) is 0.5 m long. (b) Foliation of bituminous shale along thin horizontal bedding.

lack of bioturbation (Figs. 4b, 4c) indicates that the fossorial bottom organisms were not active during the deposition of these sediments. The thin bedding is caused by a nonuniform distribution of organic, calcareous, and terrigenous materials. The background bedding is stressed by frequent but nonuniformly distributed light interlayers, a few millimeters thick, clearly seen with the naked eye. The bedding planes of fresh interlayer surfaces exhibit clusters of flattened and heteromorphic ammonite conchs and phosphate remains of fish detritus. Some surfaces are almost completely covered by numerous embrional ammonite conchs.

Remains of benthic fauna are extremely rare and represented by small shells of ecologically tolerant bivalves *Nuculana*, *Cymbula*, and *Neocomiceramus*. The light concretion massive limestone (so-called Aptian plate), which lies 1.2 m above the shale unit base, makes up a chain of closely spaced and tens of

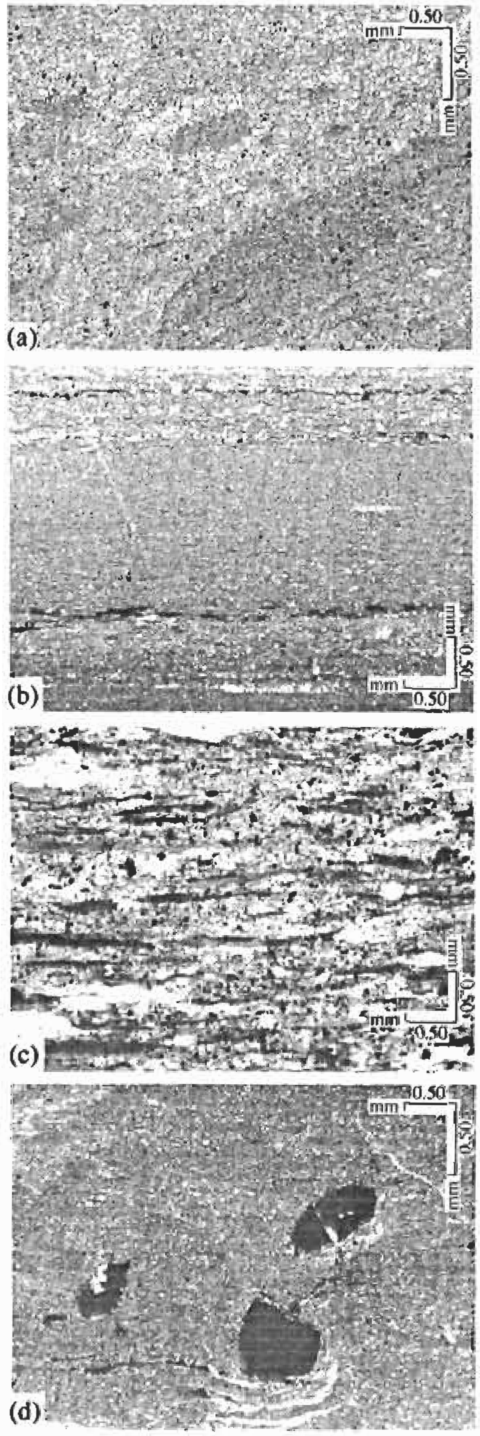

Fig. 4. Microstructures of the lower Aptian bituminous shale and host rocks. (a) Clay underlying the bituminous shale unit (primary sediment structure is strongly disturbed by bioturbation); (b) bituminous shale (thin horizontal bedding without signs of bioturbation); (c) distribution of organic matter (colloalginite) in bituminous shale; (d) bioturbated clay overlying the bituminous shale unit (black spots are cross sections of pyritized tubular wormtrails).

meters long lenses. In the Ul'yanovsk section, the concretions attain 0.7–0.8 m in thickness. Upward the section, three other levels of smaller carbonate concretions, 0.15–0.20 m thick and 0.3–0.8 m in diameter, are traced at a distance of a few meters from each other.

Below and slightly above the Aptian plate, the bituminous shale includes thin (few centimeters) siltstone interlayers completely cemented by microgranular pyrite. These interlayers are rather systematically spaced with an interval of 0.3 m.

The bituminous shale is overlain by dark gray massive monotonous and strongly bioturbated clay with an apparent thickness of 3.5 m (Fig. 4d).

The shale unit and the overlying clay member are referred to the *Deshayesites volgensis–Volgoceratoides schilkovkensis* Zone. They contain the assemblage of mainly boreal ammonites including heteromorphic species. The Tethyan ammonite species, which are close to those reported by Bogdanova (1991, 1999) from Aptian sediments of Turkmenistan, first appear at this level. It should be mentioned that the overlying clays of the *Deshayesites deshayesi–Ancyloceras matheronianum* ammonite zone clearly correlate with the synonymous zone in Turkmenistan, northern Caucasus, England, Germany, and France. The clays contain similar ammonite assemblages, indicating the existence of a broad marine communication between basins of the Russian Plate and Tethys.

A similar (in structure and thickness) section of carbonaceous shales was studied at scarps along the Volga River down- and upstream the Sengilei area (thickness 4.5 m; C_{org} 3.2–7.8%). The visual appearance of carbonaceous shales is the same as in Ul'yanovsk.

A somewhat different structure of this interval was observed in the southern Ul'yanovsk–Saratov Trough, particularly, in the Fedorovka section. Aptian sedimentary rocks crop out here at the scarps along the Volga River, 20 km upstream the Khvalynsk area (south of the Fedorovka Village).

The underlying unit is composed of dark gray silty clay (apparent thickness ~10 m) with interlayers of gray friable siltstone up to 0.1 m thick. Signs of erosion are noticed at the roof. The unit includes several levels of small lenticular carbonate concretions. The first *Deshayesites volgensis* ammonites were found in carbonate concretions 4 m below the base of the shale unit.

A sharp boundary separates these rocks from the overlying thick-platy, in places coarse-laminated, brownish gray clayey rocks attaining 10.5 m in thickness. Although these rocks look lighter-colored in comparison with varieties observed near Ul'yanovsk and Sengilei, the C_{org} content remains approximately at the same level. The primary bedding is locally disturbed by bioturbation. The bioturbated shales occur as thin interlayers at the unit base and roof. The rocks are rather uniformly enriched in a fine silty material, which also makes up thin laminae (< 1 mm) as particular elements of the thin bedding. Therefore, the weathered Fedorovka shale has a more massive appearance than the rocks occurring at the same level in Ul'yanovsk and Sengilei (i.e., fine foliation is atypical for the Fedorovka shale).

Large carbonate concretions (Aptian plate) are absent in the Fedorovka section. However, a horizon of much smaller concretions (up to 0.3 m in diameter), which most likely corresponds to the Aptian plate, is locally traced in the lower part of the shale unit.

Two more horizons of small lenticular carbonate concretions closely spaced in vertical direction occur within the platy clay with *Deshayesites volgensis*. Heteromorphic ammonites were not found here. Mikhailova and Baraboshkin (2001) suggested that this section was located closer to the paleobasin shore. Thin interlayers (up to 0.1 m) of light fine-grained sandstone sporadically occur in the bituminous shale above the concretions.

The shale grades into the dark gray silty clay (7.5 m) with a splintery parting and rare thin (up to 0.25 m) interlayers of friable cross-bedded fine-grained sandstone near the base. This part of sequence is related to the *Deshayesites deshayesi* ammonite zone. Heteromorphic ammonites are not found here. This structure of the Aptian bituminous shale unit is retained up to the Khvalynsk and Shirokii Buerak Village areas on the right bank of the Volga River.

Southward, this interval was studied at outskirts of Saratov in small open pits of the brick yard (Guselka section). The clay unit, 6.5 m thick, is exposed here above the massive limestone of the Aptian plate. The biostratigraphic position of the clay is determined by numerous findings of *Deshayesites volgensis* and clearly correlated with that of carbonaceous shales elsewhere. The clay is generally massive; the primary thin bedding is almost completely destroyed by bioturbation; and the relict bedding can only be observed at high magnification in thin sections.

The lower part of the unit (1.5 m) is composed of the greenish gray locally brownish sandy clay. A layer with small (a few centimeters) light spherical carbonate concretions occurs in the roof of this unit.

The rocks in the upper part of the section are darker and consist of finer-grained silty clay. The pelitic fraction content gradually increases upsection.

In all of the lower Aptian sequences of the Russian Plate, the shale unit with elevated C_{org} content is clearly recognized by a dark color and symptomatic sedimentological features. As a rule, the lower boundary of the unit is sharp and bears indications of erosion, whereas the upper boundary is gradual and distinct.

As can be seen from the data mentioned above, the thickness of the carbonaceous shale unit (up to 10.5 m) is maximal in the vicinity of Khvalynsk and gradually decreased both southward and northward. When moving to the south toward Saratov, the bituminous sediments are increasingly enriched in silty and sandy materials. They pinch out in zones of near-shore sedimentation. When moving to the north toward Ul'yanovsk and Sengilei, they become finer-grained (pelagic), and this is mirrored in the ammonite fauna. In addition, only the bituminous shale unit is related to the *Deshayesites vogensis* Zone in the north (Ul'yanovsk and Sengilei), whereas the underlying clay unit is also attributed to this zone in the south (Fedorovka and Ershovka sections). This implies that the upper part of the sequence below the shale unit could be eroded in some sections.

LITHOLOGICAL, MINERALOGICAL, AND GEOCHEMICAL FEATURES OF APTIAN SEDIMENTS

Aptian sediments of the Russian Plate are composed of the terrigenous material. As was shown above, pelitic fractions largely dominate in the lower Aptian, whereas silty and sandy fractions mainly occur as an admixture in clayey rocks. The mineral assemblage of the clayey fraction remains practically unchanged both in bituminous shales and in host sediments. It almost does not vary in vertical and lateral directions over the whole investigated area. Based on XRD data, smectite and mixed-layered (smectite–mica) minerals with 20–40% of mica layers, kaolinite, and hydromica with 5–10% of swelling layers are major constituents of the <0.001-mm fraction. Chlorite with various degrees of structural defectiveness is always present in a subordinate amount. Quartz and feldspar are noticed as admixtures.

Relationships between chlorite and kaolinite reflections (3.53 and 3.57 Å, respectively) suggest the trend of some enrichment of bituminous shale in kaolinite relative to host rocks. The amount of kaolinite and quartz markedly increases in the Guselka section (Saratov), which is situated closer to the paleobasin shore in comparison with other sections.

Fine silty fractions occur in the bituminous shale as an admixture (up to 5% in Ul'yanovsk and Sengilei, as much as 20–30% in the Fedorovka section, and 50% or more in Saratov). The coarser silty and fine sandy materials make up separate interlayers. The composition of silty and sandy fractions is similar and practically constant in both vertical and lateral directions. As a rule, quartz and various micas are predominant; feldspar is present in a lesser amount; epidote and garnet are accessory minerals. In general, the composition of admixture in clayey sediments did not substantially vary during the deposition of organic-rich sediments.

The content of *carbonate material* in Aptian clayey rocks is low. As can be seen from Table 1, the CO_2 content in rocks hosting the bituminous shale unit and in the clay of coastal zone (Guselka) is commonly not higher than 0.*n* %. Let us mention that siderite concretions are abundant beyond the bituminous unit.

The rock-forming significance of carbonate material in bituminous shales is especially appreciable in the Ul'yanovsk and Sengilei areas (Table 1). The carbonate is mainly composed of calcite, as indicated by the typical reflection (d = 3.03 Å) on X-ray patterns for samples from bituminous shales taken from Ul'yanovsk and Sengilei. In samples from host rocks and from the bituminous shale of the Fedorovka section, such reflections were not recorded. The abrupt increase both in $CaCO_3$ and C_{org} contents is noticed in transitional zones between host rocks and bituminous shales. However, calcite is distributed nonuniformly within the shale unit and mainly concentrated in intervals below the Aptian concretion plate ($CaCO_3$ up to 21–22% in Ul'yanovsk and as much as 15–17% in Sengilei). Above this level, the calcium carbonate content gradually decreases to the background values near the section roof. At the same time, the highest C_{org} contents are commonly attained in the bituminous shale above the Aptian plate. Thus, an inverse relationship between calcium carbonate and C_{org} contents is established. Near Ul'yanovsk and Sengilei, the calcium carbonate in bituminous shales is mostly related to remains of calcareous nannoplankton that enriches the Aptian sediments at this level.

It is evident that the observed distribution of dispersed carbonate material in bituminous rocks differs from the pattern in primary sediments of the Aptian paleobasin. This is evident from the presence of several levels of large carbonate concretions formed due to dissolution and redistribution of the primary biogenic carbonate material during the early diagenesis.

In thin sections of samples from the lower part of sections with the highest carbonate content (i.e., below the Aptian plate), one can observe clots of pelitomorphic calcite material in the form of strongly flattened oblong lenses grouped into discontinuous laminae.

Petrographic data indicate that the *organic matter* is ubiquitous throughout the Aptian rocks; however, its forms and content are variable. In the clay hosting the bituminous shale, the elevated C_{org} contents (up to 1–2%) are often related to the presence of kerogen as a finely dispersed carbonized plant detritus (5–20%), whose amount and size increase in samples with coarser-grained terrigenous fractions.

In passing from host rocks to the bituminous shale, the C_{org} content abruptly increases up to 4.0–9.6% (6–8% on the average). The C_{org} content in bituminous shales from different sections does not change markedly. The organic matter is largely related to the structureless OM (colloalginite, after Ginzburg, 1991) occurring as a system of thin lenses elongated parallel to the bedding (Fig. 4c). Solitary spore and pollen remains are also noticed. As can be seen under a microscope, the plant detritus is also always present in bituminous shales being oriented along the bedding. Its amount does not exceed a few percents in shales of the Ul'yanovsk and Sengilei sections and increases up to 10–20% in the Fedorovka shale.

Results of the microscopic examination are consistent with the data obtained from the pyrolytic analysis.

Table 1. Contents of chemical elements in lower Aptian sedimentary rocks of the Russian Plate

Ammonite zone	Member no.	Sample no.	C_{org}	CO_2	Fe	Mn	Ti	P	S	Cr	Ni	V	Cu	Co	Pb	Ga	Ge	Mo	Zn	Se	Sn	Ag	As	Hg
Ul'yanovsk section																								
	II	U-1	1.22	0.015	5.4	0.059	0.58	0.07	0.50	85	45	130	45	14	29	24	1.4	1.4	140	0.7	3.7	0.1	12	0.19
Deshayesites tenuicostatus	III	U-4	1.38	0.40	6.2	0.14	0.6	0.08	0.32	80	48	120	65	16	26	24	1.2	0.8	180	0.7	3.3	<0.10	1	0.10
		U-4B	1.24	0.30	5.1	0.19	0.56	0.08	0.24	90	55	170	38	13	28	25	1.4	0.5	185	n.d.	3.5	<0.10	34	0.07
		U-4S	1.16	0.50	4.8	0.037	0.54	0.08	0.46	125	52	195	60	23	24	26	1.6	0.8	115	0.7	4.2	<0.10	6	0.17
		U-4L	1.27	<0.30	5.3	0.042	0.3	0.08	0.57	85	55	140	65	16	28	25	1.2	2.4	140	0.7	4.0	0.11	14	0.17
		U-5B	0.99	<0.30	4.8	0.04	0.47	0.08	1.79	100	53	180	35	14	24	23	2.5	0.5	115	n.d.	4.3	0.08	10	0.06
		U-5	1.39	<0.30	5.6	0.031	0.53	0.08	2.34	120	60	200	100	18	26	30	1.4	3.8	130	2.5	4.2	<0.10	4	0.08
Deshayesites volgensis	IV	U-6	2.27	9.65	3.9	0.05	0.38	0.06	1.83	120	78	250	85	19	19	14	1.4	50	60	6.0	3.7	0.13	7	0.13
		U-6-1	4.70	9.50	4.4	0.07	0.31	0.1	2.67	115	88	290	90	35	15	11	1.4	85	60	5.8	5.0	0.11	3	0.10
		U-7B	4.20	2.75	4	0.05	0.58	0.1	2.23	140	70	440	55	14	18	17	1.4	<0.8	80	n.d.	6.0	<0.10	1	0.04
		U-8	6.40	3.55	5.8	0.056	0.36	0.09	3.94	125	93	375	100	38	19	18	1.4	100	70	7.0	5.3	0.13	17	0.12
		U-8-1	6.80	6.90	4.8	0.06	0.36	0.1	3.45	125	90	360	90	25	17	18	1.6	130	65	6.2	5.5	0.15	11	0.12
		U-12a	6.60	1.20	6.8	0.042	0.35	0.09	5.17	150	100	400	110	45	17	17	2.1	61	65	6.0	5.5	0.15	20	0.13
		U-12b	6.30	0.95	6.4	0.035	0.37	0.1	4.92	125	90	300	120	43	20	18	2.1	45	90	5.8	5.8	0.23	18	0.08
	V	U-15	3.00	0.60	5.6	0.028	0.51	0.07	2.23	130	60	175	110	14	24	23	1.6	3.8	95	1.7	4.2	<0.10	16	0.10
		U-15-1	1.28	<0.30	5.5	0.033	0.54	0.03	2.18	110	60	160	100	18	27	27	1.4	3.2	150	1.7	4.5	<0.10	2.5	0.15
		U-15-1B	1.55	<0.30	5.1	0.05	0.58	0.03	1.84	125	65	220	55	18	25	25	2	2	160	n.d.	5.0	<0.10	30	0.04
Fedorovka section																								
Deshayesites volgensis	IV	F-9/1	2.25	0.50	3.24	0.012	0.64	0.03	0.18	107	107	155	65	10	23	17	1.1	11	96	4.4	4	0.14	5.7	n.d.
		F-9/3	2.25	0.25	4.19	0.018	0.6	0.04	0.22	100	100	210	65	15	21	16	1.2	17	152	7.2	3.7	0.14	9.1	n.d.
		F-9/4	1.58	<0.25	3.54	0.014	0.59	0.03	0.49	115	115	300	75	14	23	19	1	27	125	9.0	3.6	0.17	9.5	n.d.
		F-9/6	3.35	<0.25	5.58	0.044	0.54	0.07	0.68	125	125	300	95	25	17	20	1.1	81	145	9.5	4	0.10	7.7	n.d.
		F-9/9	5.20	0.25	4.57	0.01	0.59	0.05	1.25	140	140	325	72	12	21	15	1.2	47	84	17	3.9	0.16	6.7	n.d.
		F-9/12	9.60	0.25	2.79	0.008	0.58	0.03	0.53	115	115	245	72	10	21	17	1.4	49	78	13	3.7	0.19	5.7	n.d.

Table 1. (Contd.)

Ammonite zone	Member no.	Sample no.	C_{org}	CO_2	Fe	Mn	Ti	P	S	Cr	Ni	V	Cu	Co	Pb	Ga	Ge	Mo	Zn	Se	Sn	Ag	As	Hg
Deshayesites volgensis	IV	F-9/16	5.30	0.25	5.2	0.02	0.54	0.07	0.97	118	118	300	65	25	20	19	1.4	81	122	12	3.7	0.13	13	n.d.
		F-9/18	4.70	<0.25	3.09	0.039	0.48	0.03	2.96	110	110	290	52	33	19	26	1.7	110	105	14	3.1	0.13	14	n.d.
		F-9/22	6.40	0.45	2.48	0.008	0.57	0.04	0.96	140	140	180	88	12	14	30	1.1	25	78	5.0	3.6	0.16	8.4	n.d.
		F-9/24	5.40	<0.25	2.52	0.013	0.54	0.04	1.03	115	115	185	84	12	18	25	1.4	25	78	4.5	4	0.17	6.2	n.d.
		F-9/26	4.80	1.05	3.34	0.018	0.5	0.05	2.32	155	155	220	62	22	17	30	1	19	76	4.5	3.3	0.13	8.1	n.d.
		F-9/29	5.00	0.65	2.34	0.012	0.54	0.04	1.23	130	130	170	88	12	19	28	1.4	24	69	5.6	3.7	0.19	13	n.d.
		F-9/35	6.50	0.70	2.81	0.023	0.5	0.06	1.69	140	140	165	62	12	18	26	1.5	20	58	4.5	3.4	0.13	12	n.d.
	V	F-9/36	7.00	1.40	3.66	0.038	0.52	0.02	1.48	125	125	160	67	27	18	25	1	1.4	140	1.5	4	<0.08	9.2	n.d.
		F-9/40	1.77	1.15	3.4	0.029	0.62	0.04	0.89	140	140	180	72	30	18	27	1.3	1.5	124	1.2	3.8	<0.08	5.2	n.d.
Sengilei section																								
Deshayesites volgensis	IV	S-1	1.38	<0.30	3.8	0.009	0.6	0.03	0.20	90	28	175	35	7	25	31	2.8	4.4	52	0.8	3.8	0.12	18	0.06
		S-2	4.2	<0.30	2.6	0.007	0.53	0.02	0.40	125	53	315	170	9	13	29	2.3	14	49	10.0	4.4	0.47	18	0.05
		S-4	3.6	<0.30	4.6	0.023	0.53	0.07	0.46	140	78	315	72	30	21	22	1.3	63	155	10.0	3.6	0.16	22	n.d.
		S-10	3.65	<0.30	4.4	0.019	0.51	0.04	0.55	140	53	265	95	17	20	23	1.3	50	132	10.0	3.4	0.17	21	n.d.
		S-13	5.7	<0.30	3.1	0.009	0.51	0.04	0.57	125	68	320	80	14	18	28	2.0	68	98	6.3	3.8	0.25	18	0.06
		S-14	4.7	<0.30	4.0	0.013	0.49	0.06	0.58	110	75	298	110	17	19	24	1.4	75	122	7.3	4	0.2	22	0.04
		S-15	5.8	<0.30	3.6	0.011	0.5	0.05	1.00	115	80	310	90	19	18	24	2.0	74	165	8.0	4	0.23	28	0.05
		S-16	4.7	<0.30	4.3	0.013	0.51	0.05	0.51	90	68	310	90	19	13	26	1.4	68	140	5.5	4	0.20	30	0.04
		S-17	4.3	<0.30	5.8	0.023	0.48	0.07	1.66	55	75	125	30	13	9	20	1.0	56	78	5.5	2.8	0.08	38	0.05
		S-18	6.2	<0.30	5.6	0.027	0.44	0.08	0.92	100	290	310	70	30	19	18	1.2	110	275	7.2	4.4	0.12	36	0.05
		S-19	6.0	<0.30	6.0	0.032	0.41	0.10	0.86	105	280	350	70	36	19	19	1.4	130	350	6.2	4.5	0.14	38	0.04
		S-21	7.0	0.55	7.4	0.140	0.43	0.10	0.61	105	115	345	80	47	19	21	1.2	112	280	5.6	4.9	0.12	28	0.04
		S-22	6.5	0.90	8.9	0.120	0.43	0.11	0.69	115	125	340	80	52	20	22	2.0	125	140	5.0	5	0.1	34	0.05
		S-23	6.3	1.00	7.4	0.039	0.43	0.10	0.65	115	100	350	70	32	20	22	1.4	110	122	7.3	4.5	0.12	30	0.05
		S-24	7.3	4.25	9.8	0.260	0.45	0.09	0.81	105	120	320	50	60	17	20	1.2	105	110	4.8	5.0	0.10	36	0.07
		S-25	7.8	1.15	8.4	0.120	0.39	0.10	2.15	110	105	345	60	42	17	18	1.4	115	82	6.7	5.0	0.12	36	0.06
		S-26	6.4	0.50	6.6	0.068	0.4	0.09	1.50	120	105	375	70	46	19	23	1.4	110	118	6.1	5.0	0.12	38	0.06

Table 1. (Contd.)

Ammonite zone	Member no.	Sample no.	C_{org}	CO_2	Fe	Mn	Ti	P	S	Cr	Ni	V	Cu	Co	Pb	Ga	Ge	Mo	Zn	Se	Sn	Ag	As	Hg
Deshayesites volgensis	IV	S-27	6.5	0.50	6.6	0.068	0.41	0.09	1.34	110	95	345	60	40	20	22	1.4	112	142	5.6	4.4	0.12	36	0.05
		S-28	5.7	6.50	7.1	0.130	0.4	0.09	3.08	95	100	305	50	44	16	17	1.2	92	85	7.2	4.5	0.1	34	0.06
		S-29	5.7	5.00	6.7	0.098	0.4	0.09	2.29	105	90	310	50	38	16	16	1.0	88	102	7.5	4.5	0.1	32	0.05
		S-30	6.8	3.70	6.9	0.063	0.42	0.11	0.95	105	100	340	70	44	18	19	1.4	105	155	7.2	4.5	0.12	26	0.06
		S-31	7.8	4.70	6.2	0.051	0.44	0.1	0.75	100	85	310	50	32	19	20	1.4	100	135	6.7	4.0	0.12	24	0.06
		S-32	5.8	7.60	6.2	0.087	0.41	0.08	2.15	85	80	235	50	30	16	15	1.4	78	92	7.1	4.0	0.12	24	0.05
		S-38	6.35	0.15	4.1	0.023	0.47	0.05	1.26	140	61	375	62	17	9	17	1.5	100	105	10	3.6	0.12	31	n.d.
		S-46	7.1	0.15	4.4	0.024	0.51	0.06	1.41	140	56	355	72	21	16	19	1.5	100	96	9.7	4.0	0.11	33	n.d.
		S-50	5.2	0.75	2.4	0.011	0.56	0.03	0.90	120	53	278	35	14	17	26	2.5	22	98	5.2	3.5	0.15	8	0.07
		S-51	5.5	1.15	2.3	0.007	0.51	0.04	0.89	135	55	330	140	15	15	30	2.7	32	100	4.2	3.8	0.3	18	0.10
		S-52	4.8	0.15	2.4	0.006	0.52	0.03	1.03	110	50	245	80	14	18	25	2.3	30	88	4.7	3.5	0.32	16	0.10
		S-53	5.2	0.70	3.7	0.006	0.53	0.02	2.00	135	48	250	140	14	16	30	2.2	19	72	5.0	4.5	0.38	14	0.10
		S-54	5.2	0.50	3.4	0.006	0.54	0.03	1.34	145	50	240	120	13	14	28	2.2	16	78	4.0	3.8	0.35	5	0.12
		S-55	5.2	0.90	3.8	0.008	0.51	0.04	1.50	115	45	198	160	13	20	26	2.3	11	88	3.4	3.5	0.28	6	0.21
	V	S-56	3.6	0.50	3.6	0.012	0.53	0.05	1.05	120	48	195	120	12	18	25	2.2	6.5	90	2.7	3.5	0.24	6	0.25
		S-57	3.2	2.00	3.4	0.012	0.55	0.05	0.75	100	48	155	100	12	22	27	2.0	2.5	80	0.05	3.4	0.14	8	0.14
Guselka section																								
Deshayesites volgensis	IV	2319/2	0.14	<0.25	3.29	0.010	0.69	0.03	0.05	95	36	140	62	10	16	27	1.2	1.1	88	0.7	3.7	<0.08	5.4	n.d.
		2319/4	0.42	<0.25	2.85	0.014	0.68	0.02	<0.05	107	39	135	34	10	15	30	1.3	1.5	83	0.5	3.7	<0.08	5.0	n.d.
		2319/5	0.60	<0.25	3.78	0.016	0.65	0.06	<0.05	109	45	140	31	13	20	25	1.1	0.8	110	0.7	4.0	<0.08	6.0	n.d.
		2319/8	0.52	<0.25	3.60	0.017	0.61	0.04	<0.05	95	40	140	39	13	20	24	1.2	<0.8	106	0.8	3.6	0.08	11.0	n.d.
		2319/12	0.47	<0.25	2.90	0.011	0.58	0.03	0.12	89	35	123	34	10	16	20	1.3	0.8	80	0.4	2.9	0.08	7.6	n.d.
		2319/13	0.68	<0.25	3.41	0.018	0.57	0.04	0.06	85	35	110	37	10	18	19	1.0	<0.8	78	0.6	3.1	<0.08	8.1	n.d.
		2319/16	0.19	<0.25	3.35	0.018	0.53	0.04	0.19	82	43	123	28	10	15	21	1.2	0.8	95	0.6	3.4	<0.08	9.3	n.d.
		2319/18	0.47	<0.25	4.08	0.027	0.52	0.07	0.16	107	52	137	28	13	21	20	1.3	0.9	96	0.9	3.4	<0.08	13.0	n.d.
		2319/20	0.65	<0.25	4.20	0.035	0.52	0.05	0.30	95	46	135	34	20	16	19	1.0	0.8	115	0.7	3.1	<0.08	12.0	n.d.
		2319/23	0.52	<0.25	3.88	0.024	0.55	0.05	0.15	100	44	123	28	17	21	19	1.0	0.8	108	1.1	3.7	<0.08	15.0	n.d.

Note: C_{org}, CO_2, Fe, Mn, Ti, P, and S contents are given in wt %; other elements, in ppm.

Table 2. Pyrolytic and isotopic parameters of organic matter in samples from lower Aptian rocks, Ulyanovsk section

Rock, sample no.	S_1, mg HC/g of rock	S_2, mg HC/g of rock	T_{max}, °C	TOC, % of rock	HI, mg HC/g TOC	OI, mg CO/g TOC	$^{13}C_{org}$, ‰
Clay, sample U-5	0.13	1.03	403	2.41	42	52	–26
Bituminous shale, sample U-8	1.56	38.81	413	9.55	406	32	–28

The organic matter in both bituminous shales and host rocks is characterized by a low degree of thermal maturity. The temperature of maximal hydrocarbon (HC) extraction during the heating of samples in an inert atmosphere is below 430°C (Table 2). The OM generation potential is commonly determined from the $S_1 + S_2$ sum that corresponds to the total HC amount released from OM as a result of heating to 300°C (S_1) and in the range of 300–600°C (S_2). The potential of bituminous shale generation is relatively high (40.37 mg HC/g), whereas the clay yields a low value (1.16 mg HC/g). The total organic carbon (TOC) is a sum of the pyrolyzed and residual organic carbon (in % of rock). The absolute value of the hydrogen index (HI = S_2/g TOC) for kerogen from the bituminous shale is equal to 406 mg HC/g TOC and indicates its marine origin (Tissot and Welte, 1984). The biomass of marine plankton was a major source of this kerogen. On the Van Krevelen diagram in HI–OI coordinates (Tissot and Welte, 1984; Tyson, 1995), the kerogen from bituminous shales falls into the field of the mixed type II–III due to some admixture of terrestrial OM. Kerogen from the host clay is confined to the field of the terrestrial kerogen in good agreement with the petrographic data. The organic carbon in bituminous shales is enriched in light carbon isotope relative to the clay (Table 2), providing an additional evidence for different forms of the origin of kerogen in bituminous shales and host clays.

The distribution of various chemical elements was also studied in Aptian rocks of the Russian Plate (Table 1; Fig. 5). It was established that the Aptian bituminous shale is enriched in many elements in comparison with both host rocks and mean contents in clayey rocks (Turekian and Wedepohl, 1961; Wedepohl, 1991) (Fig. 6).

The chemical element distribution in Aptian rocks reveals a substantial variation in both vertical and lateral directions. The most conspicuous difference in element distribution between the bituminous unit and host rocks is displayed in the Ul'yanovsk section. As can be seen from Table 1 and Fig. 5, the C_{org} content markedly increases up to 6–8% in the bituminous unit and is only 1.0–1.5% in the host rocks. The latter value is, however, somewhat higher than the mean for clayey rocks (Turekian and Wedepohl, 1961; Wedepohl, 1991).

The host rocks are practically carbonate-free; however, bituminous shales contain the biogenic $CaCO_3$ up to 20% in some beds.

Like for C_{org}, a distinct tendency to concentrate in bituminous shales is revealed for S, P, Cr, Ni, V, Cu, Co, Mo, Se, and Ag. The highest degree of concentration is mostly typical of Mo, Se, and Ag; Fe, As, and Mg behave in the same way; however, the degree of their concentration is not high. At the same time, bituminous shales display a slight depletion in Ti, Ga, Pb, and Zn. This is likely related to the diluting effect of C_{org} and $CaCO_3$ in the case of Ti and Ga. However, the cause of such behavior of Pb and Zn remains obscure so far.

Figure 6 shows coefficients of the concentration of different elements in bituminous shales versus the host clay and the host clay versus the mean contents in clayey rocks (Turekian and Wedepohl, 1961; Wedepohl, 1991). The coefficient were calculated from chemical analyses for the sections near Ul'yanovsk and Fedorovka. The highest coefficients of concentration are typical of Mo, Se, and S.

The same patterns are observed in the Sengilei section; however, some elements behave in a somewhat different way. For example, Cu, Ag, and partly Hg contents increase at the base and roof of the bituminous unit, while the middle of the section is characterized by the lowest concentrations.

The distribution of chemical elements in the Fedorovka section, in turn, is somewhat different from the Ul'yanovsk and Sengilei sections. The relatively thick Fedorovka section is characterized by a high C_{org} content and more or less uniform distribution in rocks. However, only Ag clearly correlates with C_{org}; Mo, Se, and V are mostly concentrated in the lower part of the bituminous unit. In the upper part of the section, their contents are much lower, though they remain above the background level. Such behavior of elements-indicators of anoxia degree reflects various geochemical conditions during the deposition of carbonaceous sediments in this part of basin.

In sediments deposited close to the coast (Guselka section near Saratov), all elements are distributed more or less uniformly throughout the entire Aptian sequence. The organic-rich sediments were not deposited here, and offshore geochemical environments in deep-water regions of the basin did not affect the distribution of elements. Therefore, their contents are close to the mean values in clayey rocks (Turekian and Wedepohl, 1961; Wedepohl, 1991). The relative decrease of chemical elements in some cases is caused by a diluting effect of the sandy–silty admixture in the sediments.

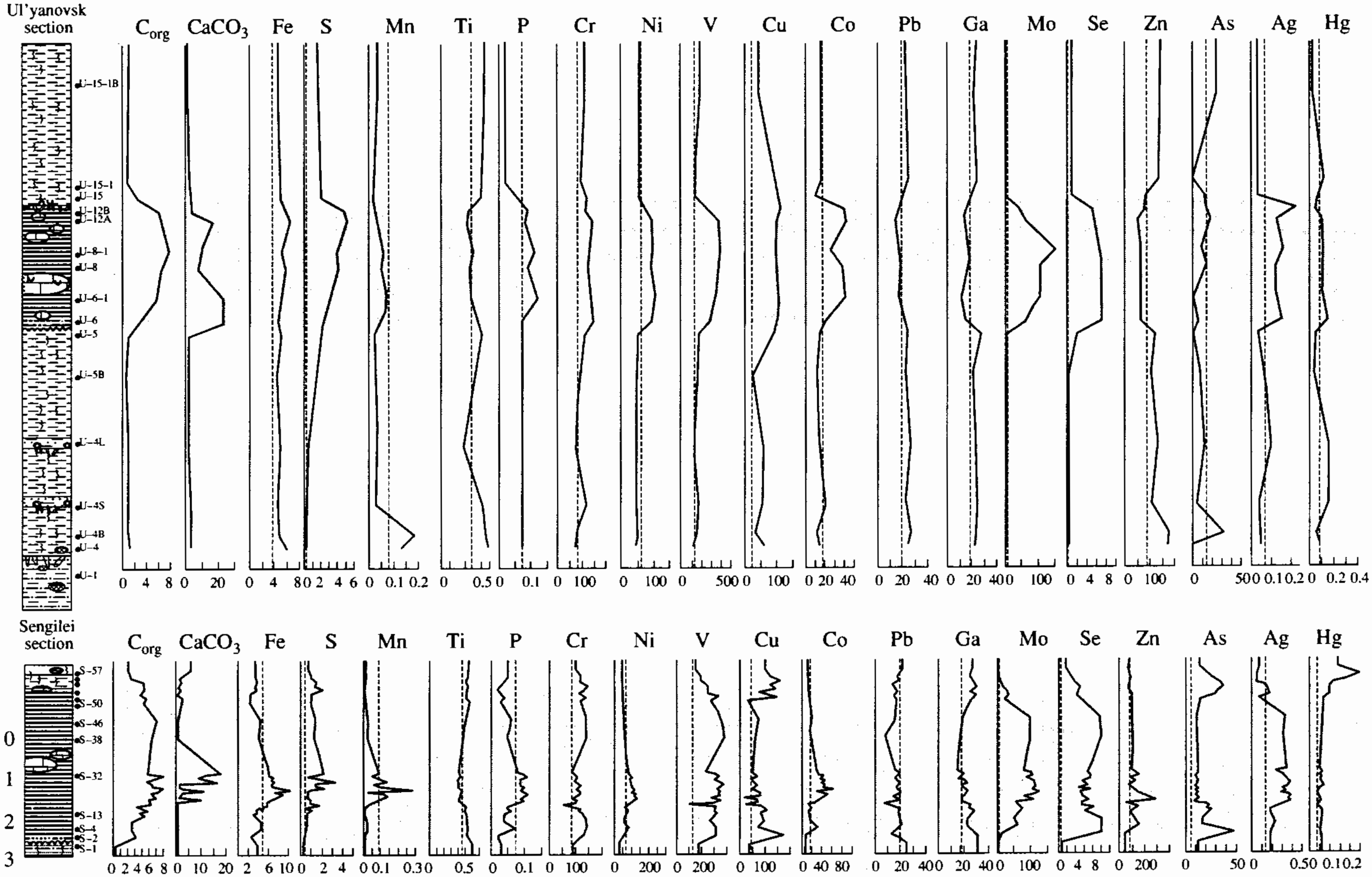

Fig. 5. Distribution of chemical elements in lower Aptian sections (Ul'yanovsk, Sengilei, Fedorovka, and Guselka areas). See Fig. 2 for legend. Dashed lines show mean contents of elements in clayey rocks (based on Turekian and Wedepohl, 1961; Wedepohl, 1991).

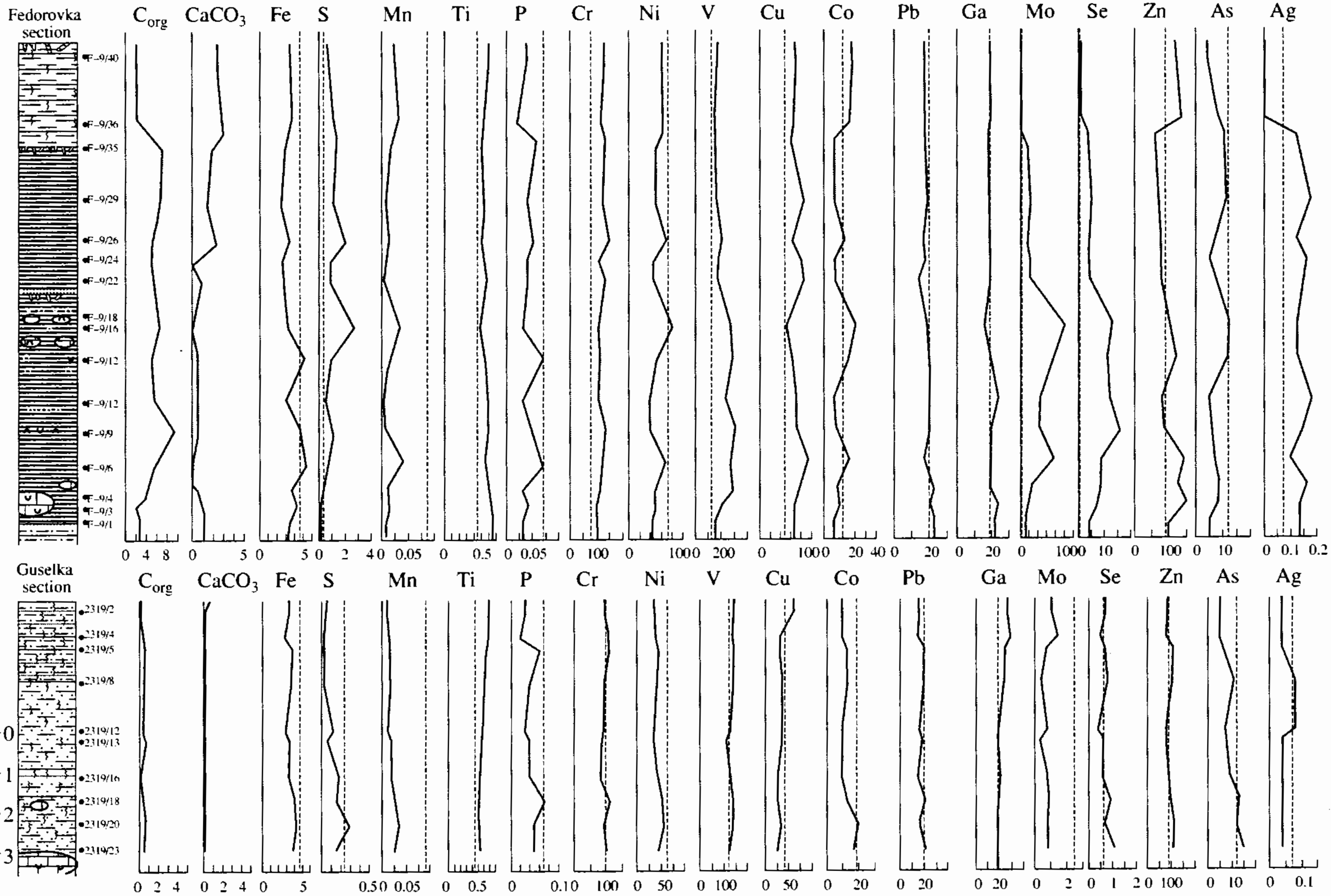
Fedorovka section
C org
CaCO3
Fe
S
Mn
Ti
P
Cr
Ni
V
Cu
Co
Pb
Ga
Mo
Se
Zn
As
Ag
F-9/40
F-9/36
F-9/35
F-9/29
F-9/26
F-9/24
F-9/22
F-9/18
F-9/16
F-9/12
F-9/12
F-9/9
F-9/6
F-9/4
F-9/3
F-9/1
Guselka section
2319/2
2319/4
2319/5
2319/8
2319/12
2319/13
2319/16
2319/16
2319/18
2319/20
2319/23
0
1
2
3

Fig. 5. (Contd.)

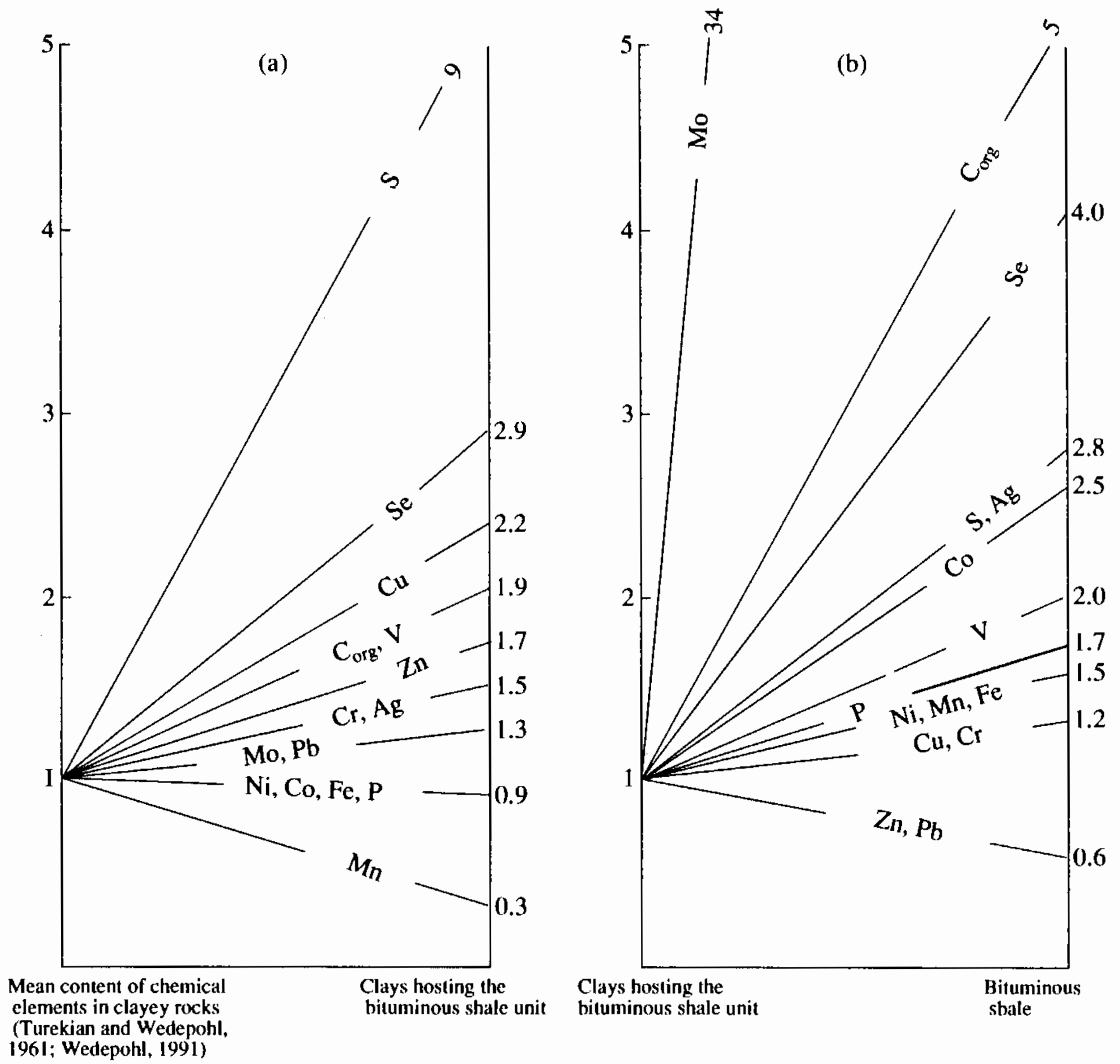

Fig. 6. Coefficients of concentration of chemical elements in lower Aptian rocks of the Russian Plate. (a) In clays hosting the bituminous shale unit relative to mean contents of elements in clayey rocks (based on Turekian and Wedepohl, 1961; Wedepohl, 1991); (b) in bituminous shale relative to the host clay.

DISCUSSION

The first question, which arises in the discussion on formation conditions of the Aptian bituminous unit, concerns the causes that were responsible for the deposition of organic-rich sediments. There are different views on the contribution of various factors to the deposition of carbonaceous sediments. Some researchers suppose that the burial of a considerable amount of OM in sediments was caused by anoxic conditions, which hamper the OM decomposition, in water reservoirs (see, for example, Demaison and Moore, 1980, 1991). Other researchers attribute it to the bioproductivity of basin (Pedersen and Calvert, 1990, 1991). Based on the study of the Holocene history of the Black Sea, Strakhov (1937, 1976) showed that the hydrosulfuric contamination does not play a crucial role in the burial of considerable OM amount in sediments, although this factor can control the OM composition. The increase in bioproductivity of paleobasin is the major factor providing the enrichment of sediments in OM.

We also regard the formation of Aptian organic-rich sedimentary rocks in the Russian Plate as a result of increased bioproductivity of the early Aptian basin. In particular, this interpretation is favored by the OM geochemistry that records an abrupt increase in basinal OM during the deposition of carbonaceous sediments in comparison with the preceding stage when the terrestrial OM was predominant. However, this brings up the question concerning the causes that led to the outbreak of phytoplankton and bacterioplankton bioproductivity and the accumulation of considerable OM mass in sediments.

It is known that the upwelling is the most effective modern mechanism of biophile element supply to the

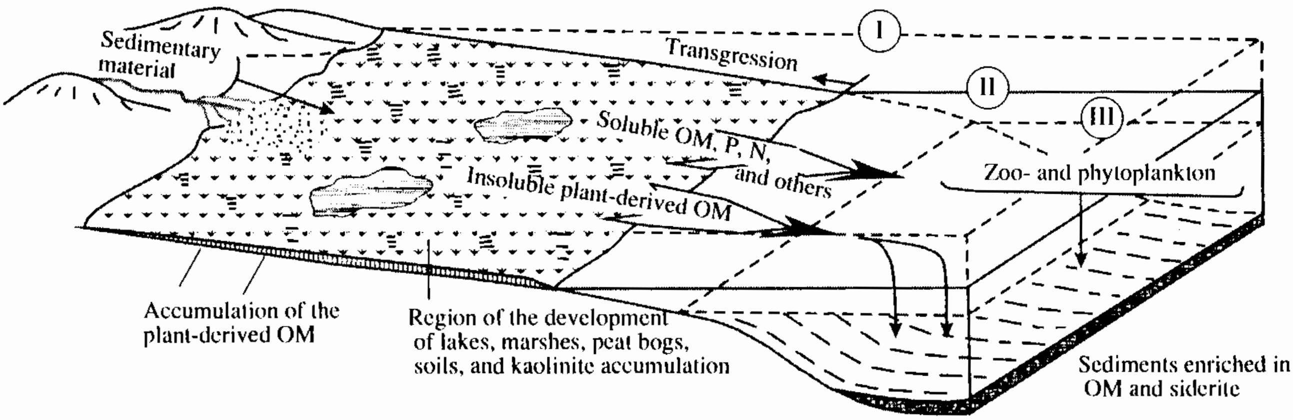

Fig. 7. Model of organic-rich sediment deposition during the sea transgression, after Gavrilov (1994). Sealevel: (I) before the regression, (II) during the transgression, (III) during the maximal regression.

zones of high productivity of marine organisms. However, this mechanism could not be realized in the paleogeographic environment of the deposition of bituminous sediments. In addition, it is difficult to imagine that the upwelling functioned only during a relatively short period of bituminous sediment accumulation and did not work before and after this time.

The genetic model of the Aptian bituminous unit should take into account the following conditions. The sedimentation proceeded in a vast and relatively shallow-water epicontinental basin during the rapid transgression caused by the eustatic sealevel rise in the early Aptian. The transgression was preceded by a regressive episode, which is proved by an onlap of Aptian bituminous shales on the eroded surface of underlying rocks. An outbreak of bioproductivity of diverse bacterioplankton and organic-walled phytoplankton served as the main cause of OM-enrichment of sediments. In other words, organic matter was mainly derived from the basin; however, the terrestrial OM also played a certain role in the total budget.

The formation of the bituminous shale unit is best agreed with the model of organic-rich sediment deposition controlled by the supply of biophile elements into the basin from the coastal landscapes during the rapid eustatic transgression as shown in Fig. 7 (Gavrilov, 1994; Gavrilov and Kopaevich, 1996; Gavrilov *et al.*, 1997).

An important role in the formation of Aptian bituminous sediments was played not only by the transgression, when the organic-rich sediments were deposited, but also by the previous regressive stage of the basin evolution, when the related sediments accumulated along the basin margins and at internal uplifts. The regression resulted in the emergence of vast territories along margins of a shallow-water sea and around island archipelagoes. These territories existed as lowlands flattened by marine erosion and sedimentation. Therefore, even insignificant sealevel fluctuations gave rise to a substantial shift of the coastal line. The area exposed after regression was covered by friable nonlithified marine sediments. Thus, specific coastal landscapes were created. The nonlithified and generally reduced sediments, which contained sulfides and occasional authigenic phosphate minerals, underwent a subaerial weathering. Sulfides were oxidized to produce sulfuric and sulfonic acids that readily interacted with sediments and enhanced the weathering.

Yasamanov (1978) pointed to an important consequence of the sea recession under a humid climate: lakes and coastal marshes were developed on the newly formed coastal plains. Judging from the modern counterparts, the peat bogs were formed with a high rate. The mineralogical and geochemical environments in the present-day bog systems indicate that the peat formation promotes the geochemical activity of phosphorus, which is an important element for the biological cycle. In general, the swamp-forming process may be regarded as one of the characteristic processes that favored phosphorus migration in the supergene zone (Kovalev, 1985). The aggressive medium of bog systems provided the reworking of sedimentary material supplied into the basin and affected the underlying rocks. Many terrigenous minerals, which are commonly stable during weathering, were dissolved in peat bogs. Thus, the water was enriched in microelements. It is important to note that the swamped basins contained not only solid OM but also abundant dissolved OM produced as a result of the breakdown of permanently regenerated plant materials. The gain in OM and its conversion into dissolved state continuously proceeded over the whole period of the existence of such landscapes. The plant-derived OM accumulated in this environment was characterized by an enrichment in the light carbon isotope, which is generally typical of the land vegetation.

The soil was undoubtedly formed over vast territories of coastal-marine plains. Various chemical elements (including the biophile ones) inherited from underlying nonlithified or slightly lithified sediments were absorbed by soils.

Thus, we can suppose with a strong probability that the landscapes, which were formed on coastal lowlands during the regression, served as a place of active and diverse geochemical transformations related to eluvial and soil- and bog-forming processes. They provided the accumulation of various (first of all, biophile) chemical elements and their conversion into the labile state.

The area of the early Aptian basin on the Russian Plate was very large (Fig. 1). Therefore, different regions of coastal landscapes were characterized by special features. The geomorphological factor played a critical role in the development (or absence) of vast coastal plains. In regions with a steep slope of seafloor, even a substantial sealevel fall could not result in the emergence of wide coastal zone, whereas a gentle slope (most typical situation) was favorable for such an emergence.

The regression was succeeded by a rapid transgression and deposition of organic-rich sediments. The sealevel rise was not less than several tens of meters. A similar estimate was given by Haq *et al.* (1987).

The invading sea readily interacted with coastal-marine landscapes. On the flat coastal plain, even a relatively small rise of the water level led to flooding of large territories, and the organic matter accumulated in peat bogs and soils were transported to the sea. The solid OM was eroded and redeposited in marine mud. Thus, the mud was enriched in C_{org}. The dissolved organic matter, which was abundant in peat bogs, entered a new biological cycle as a result of utilization by plankton and fostered the bioproductivity. In addition to OM, biophile elements (first of all, phosphorus) were supplied into the basin from the coastal landscapes. As was shown above, most of the studied sections are characterized by elevated phosphorus contents in comparison with host rocks. The supply of phosphorus into the basin provoked a burst of bioproductivity of organic-walled phytoplankton and bacterioplankton, which was the main source of OM in sediments (see above).

Observations during the filling of artificial water reservoirs, which serves as a reduced model of transgression, support the reality of the proposed model of Aptian bituminous shale formation. In particular, the initial period of filling is marked by an extremely vigorous phytoplankton productivity due to enrichment in biophile elements washed out from the flooded soil (Petrova, 1990, etc.). In its essence, this phenomenon is similar to processes during the large-scale marine transgressions.

The important role of swamps in the supply of biophile matter into the invading sea and the respective growth of marine algae productivity was emphasized by Wenger and Baker (1986) in the discussion concerning the origin of Pennsylvanian black shales in Kansas and Oklahoma.

The Aptian bituminous shale is often enriched in Fe. In this connection, it should be mentioned that experiments in the Pacific Ocean (Martin *et al.*, 1994; Coale *et al.*, 1996; Frost, 1996) have recorded an increase in phytoplankton bioproductivity after the introduction of this element into the surface water layer owing to the participation of Fe in the chlorophyll structure. Thus, Fe can behave as a biophile element in certain cases. In the situation under discussion, the existence of the Early Cretaceous lacustrine–bog system could strongly stimulate the supergene migration of Fe and its supply into the marine basin (Strakhov, 1962) with its subsequent involvement into the biological cycle and increase in phytoplankton bioproductivity.

The mechanism of biophile element supply to the sea and the growth of phytoplankton bioproductivity acted in a similar way in different parts of basin, except for some distinctions in particular facies environments. Therefore, regional specific features of sedimentation within a paleobasin were responsible for some discrepancies in the geochemical signature of lower Aptian sediments from different sections.

The accumulation of a considerable amount of OM was responsible for the generation of significant masses of H_2S that diffused into the bottom water layer giving rise to the hydrosulfuric contamination of certain basin sectors. Since the basin was relatively shallow, the contamination first embraced the bottom water column and occasionally rose up to the euphotic zone. This is indicated by traces of large-scale death of young ammonites of the plankton ontogenetic stage.

The lack or oppressed state of the benthic fauna is related to the development of anoxic environments in the basin. The degree of anoxia could be markedly variable. The low anoxia was accompanied by an appearance of some benthic organisms (bivalves *Nuculana* and *Neocomiceramus*) that can survive under unfavorable anoxic environments.

After the transgression and termination of the supply of biophile elements into basin, the intense bloom of various plankton forms stopped and the OM-enrichment of mud ceased. Due to the conservative character of the basin system and the gradual cessation of transgression, the final stage of carbonaceous sedimentation was not so abrupt as its onset. The relatively shallow-water character of the basin, the termination of intense H_2S generation in sediments, and its diffusion in the bottom water—all this provided a rather fast oxidation of hydrogen sulfide contained in seawater and cessation of anoxic environments. It is not ruled out that in some basin sectors situated close to river deltas, the density stratification could arise due to the partial freshening of surface water layers. The presence of fresh-water green algae in sediments evidences in favor of this suggestion (Baraboshkin and Smirnova, 2002).

From our point of view, the enrichment of bituminous shale unit in kaolinite is consistent with the model of interaction between marine and coastal landscapes against the background of sealevel fluctuations. Indeed, the coastal landscapes with a rapidly forming soil cover and swamp systems under a stable humid climate were favorable for the kaolinite formation. The kaolinite-rich soil was eroded along with other continental sediments during the transgression. Thus, kaolinite was removed into the sea to enrich the carbonaceous sediments in comparison with underlying units.

The elevated OM content in accumulating sediments of the early Aptian basin induced a high intensity of diagenesis therein. As was mentioned above, silty interlayers cemented by pyrite occur within the bituminous shale unit; the dispersed pyrite is also abundant. This points to the extensive sulfide formation, and hence, to the active sulfate reduction and generation of a considerable mass of H_2S. Additionally, the above processes provided a substantial redistribution of the carbonate material in sediments. In particular, diagenetic processes were responsible for the formation of several levels of carbonate concretions within the bituminous shale unit including giant lenticular concretions of the Aptian plate (Fig. 2).

In principle, interlayers enriched in biogenic carbonate material can be formed in sites subsequently occupied by lenticular concretions during the sedimentation, for example, owing to the periodically enhanced bioproductivity of the calcareous plankton. However, the obligatory similar distribution of concretion layers in different sectors is not observed in our case. We suppose that both the concretions and host interlayers appeared in Aptian carbonaceous sediments as a result of the intense diagenetic redistribution of the biogenic carbonate material, which was initially dispersed in sediments much more uniformly.

The formation of interlayers of carbonate concretions followed the model proposed for the diagenetic origin of carbonate layers and rhythms (Gavrilov, 1979). This is supported by the following facts. The dissolution of carbonate shells of marine organisms, including numerous ammonite conchs and nannoplankton, was very intense. Therefore, one can now observe only nacreous remains of ammonite conchs. Moreover, only casts of dissolved conchs are often found in bituminous shales. At some levels, the nannoplankton is completely dissolved. In places where it is retained, the signs of corrosion are observed. Bicarbonate compounds formed as a result of biogenic $CaCO_3$ dissolution could diffuse and precipitate in near-surface sedimentary layers due to lower concentrations of diagenetic CO_2 in the mud water. As a result, the $CaCO_3$-rich sedimentary layer was formed. With the deposition of next portions of sediment, this process was resumed to produce several concretion levels.

As was shown above, the deposition of organic-rich sediments was accompanied by their enrichment in many chemical elements. It is important to note that the coefficients of concentration vary from 1.5 to 3.0 for most of these elements. However, the relative concentration of Se and especially Mo may increase by one or even two orders of magnitude in some samples. The main mechanisms of sediment enrichment in V, Ni, Co, Cr, and other elements were the sorption, first of all, on particles of dead OM and the diagenetic diffusion of elements into the sediment from the bottom water. The sorption on clay particles was of subordinate importance, because the bituminous unit-hosting rocks are also composed of clayey sediments but lack an appreciable enrichment in minor elements.

Some elements probably concentrated in still living organisms. However, the anomalously high Mo and Se contents (relative to other elements) in bituminous sediments indicate that other enrichment mechanisms also existed. Most likely, the high concentration of these elements was additionally created by the hydrosulfuric contamination of the bottom water in the basin. Indeed, a very high Mo content (up to 130 ppm) is recorded in all of the sections probably marked by a rather strong hydrosulfuric contamination of the bottom water. In the sections where Se was determined, its content in bituminous shales is more than one order of magnitude higher than in host rocks. The specific feature of Mo and Se consists in their ability to precipitate as insoluble sulfides from the water contaminated by hydrogen sulfide along with other sedimentary materials (Volkov and Sokolova, 1976). It is evident that just this mechanism provided anomalous contents of these elements in sediments.

We compared our geochemical data with the results obtained for Lower Cretaceous C_{org}-rich sediments in the northern Atlantic and northern Germany (Brumsack, 1980; Hild and Brumsack, 1998) showed that both spectra of elements accumulated in anoxic basins of that age and the sequence of concentration are generally similar.

It is important to emphasize that the deposition of lower Aptian carbonaceous shales on the Russian Plate was a regional manifestation of the Early Cretaceous Oceanic Anoxic Event-1 (OAE-1), which was accompanied by the accumulation of organic-rich sediments, more precisely, an expression of its early Aptian episode defined as Oceanic Anoxic Subevent-1a (OASE-1a), in different parts of the Earth. Deposits corresponding to this event were found in the Pacific, Italy, Germany, and elsewhere (Arthur *et al.*, 1988).

The so-called fish shale (Fischschiefer) in northwestern Germany (Kemper and Zimmerle, 1978; Mutterlose and Böckel, 1998) is among the sediments closest in facies environments to the Aptian rocks of the Russian Plate. The fish shale unit, which varies in thickness from a few decimeters to 8 m and covers a considerable area, is composed of thin-bedded carbonaceous sediments (3.6–7.0% C_{org}). Up to 90–95% of OM in the fish shale is of marine origin (Littke *et al.*, 1998). This rock exhibits the highest degree of enrichment in the autochthonous basinal OM in comparison to other Lower Cretaceous rocks in northwestern Germany. The spectrum of chemical elements and C_{org} distribution in this rock are very close to that established for lower Aptian sediments of the Russian Plate. Investigators of the fish shale came to a unanimous opinion that the deposition of organic-rich sediments in Germany was accompanied by the development of anoxic environments in the paleobasin water (Mutterlose and Böckel, 1998; Hild and Brumsack, 1998; Littke *et al.*, 1998). As can be seen, lower Aptian sediments of the Russian Plate and northwestern Germany are very similar in sedimentological and geochemical aspects. Hence, formation mechanisms considered above can be applied to both regions.

Relatively thin (usually a few meters thick, occasionally >10 m) organic-rich units, commonly extending over a great distance as a continuous strip (or a discontinuous zone confined to the same stratigraphic interval, were formed in the Phanerozoic many times. In addition to the early Aptian episode, early Toarcian (Jenkyns, 1988), Senomanian/Turonian (Jenkyns, 1980), late Thanetian (Gavrilov *et al.*, 1997), and some other episodes also correspond to the anoxic events. Despite the fact that regional factors strongly affected the lithology and geochemistry of these rocks, they also reveal the general typical features. The synchronism of these rocks in different regions of the Earth and their common sedimentological and geochemical characteristics should be controlled by some universal constraints of their formation. All of the black shale units mentioned above were formed during eustatic transgressions that provided the conditions needed for the deposition of organic-rich sediments. However, not all transgressions resulted in the deposition of such sediments. It required the combination of certain conditions, such as high rate of transgression preceded by regressive episodes, favorable climatic conditions, appropriate topography of paleobasin and surrounding land, and so on.

CONCLUSIONS

(1) The stratigraphic setting of lower Aptian bituminous shales of the Russian Plate indicates that they are a regional manifestation of the global geological episode defined as Oceanic Anoxic Subevent-1a (OASE-1a).

(2) Based on petrography and geochemistry of organic matter, the rocks hosting the bituminous shale unit contain mainly terrestrial OM, whereas the basinal OM is predominant in the bituminous unit. The enrichment in OM was caused by a bloom of bioproductivity of various marine plankton species including the bacterioplankton and phytoplankton. The contribution of terrestrial OM to the total OM budget was very insignificant.

(3) Many chemical elements, in particular, biophile elements (C, P, and Fe) and elements typical of anoxic environments (Mo, Se, S, and other) are concentrated in bituminous shales.

(4) The clay mineral assemblage in the Aptian sedimentation basin in the Russian Plate was composed of mixed-layered smectite–mica, hydromica, chlorite, and kaolinite, which tends to be more abundant toward the paleocoast. The kaolinite content is also somewhat higher in the bituminous shale than in host sediments.

(5) The abundance of authigenic minerals serves as evidence for a high intensity of diagenetic processes in lower Aptian carbonaceous sediments.

(6) The thin lamination of bituminous shales without signs of bioturbation, the lack or extremely rare occurrence of high-tolerant benthic fauna, and the geochemical signature testify to the sedimentation in an anoxic marine basin.

(7) The bituminous shale unit was formed during the fast eustatic transgression (Haq *et al.*, 1987) that followed the regressive episode. Geological, mineralogical, and geochemical characteristics of bituminous shales are consistent with a model that supposes the deposition of carbonaceous sediments as a consequence of interaction between the invading sea and coastal landscapes (Gavrilov and Kopaevich, 1996; Gavrilov *et al.*, 1997).

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