

Some of the Geochemical, Biochemical, and Biotic Consequences of Eustatic Oscillations

Yu. O. Gavrillov* and L. F. Kopaevich**

* *Geological Institute, Russian Academy of Sciences, Pyzhevskii per. 7, 109017 Russia*

** *Moscow State University, Moscow, 119899 Russia*

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Abstract—Regressions and transgressions were caused by short-period sea-level fluctuations that created conditions for more intensive transportation of large amounts of biophilic elements from land to the water basins. This process considerably increased plankton productivity, especially that of shell-less phyto- and bacterioplankton, some of the species of which, under certain conditions, emitted toxins that often stunted or killed the calcareous organisms. Consequently, the sediments accumulated proportionally larger amounts of organic matter with a declining carbonate content. The concentration of numerous toxic elements in sediments, enriched with organic matter, and the diagenetic H₂S generation, sometimes accompanied by the hydrosulfuric poisoning of bottom waters, had a negative effect on benthic fauna. Therefore, in water basins, some of the biotic crises could have been caused by the simultaneous occurrence of interrelated events responsible for the stress effect on plankton and benthic organisms.

Key words: *sea-level oscillations, regression, transgression, sapropelites, biotic events, hydrosulfuric poisoning.*

INTRODUCTION

Changes in Phanerozoic marine biota were often concurrent with eustatic fluctuations that differently affected the ecological niches of various biota representatives, the temperature and salinity of sea water, the oxygen content in it, the circulation system of currents, and other environmental parameters (Kauffman, 1986; *et al.*).

As we know, the state of biota is greatly influenced by anoxic environments during the accumulation of deposits rich in organic matter (OM). This effect becomes particularly apparent, if we correlate the time of anoxic conditions in water basins with the distribution of the number of species of certain organisms in the Cretaceous: the anoxic episodes coincided with a considerable reduction of foraminifer diversity, whereas during the anoxic decline, these organisms flourished and appreciably increased the number of their species (Fig. 1) (Gorbachik and Kopaevich, 1992). In these periods, the geochemical conditions of sedimentation became fundamentally different from those before and after the episodes. The Cenomanian and Turonian boundary layers in the Crimea provide data on the specific geochemical and paleontological features of sediments formed at that time (the Aksudere geological section near Bakhchisarai). These deposits show a sudden change in the content of planktonic and benthic foraminifers and in the concentration of many chemical elements (Fig. 2). A similar pattern is observed in the Cretaceous deposits at other sites (Arthur *et al.*, 1990; Brumsack, 1986; *et al.*). These

kinds of episodes are also typical of certain Phanerozoic time intervals (Jenkyne, 1988; *et al.*).

To understand the nature of these sudden biotic and geochemical anomalies, we have to know the cause-and-effect relations between them and the eustatic oscillations in order to reveal the possible mechanism of sediment enrichment with organic matter, and to find correlations of this phenomenon with the changes in biota.

REGRESSIONS AND TRANSGRESSIONS AS THE POSSIBLE CAUSE OF THE FORMATION OF HORIZONS RICH IN OM

Brockamp (1942) and Strakhov (1947) remarked on the connection between eustatic oscillations and the appearance of certain geochemical anomalies in sedimentary layers, for example, in the form of ferruginous formations. Hallam and Bradshaw (1979), giving no details, arrived at the conclusion that the transgressions, usually associated with short-period eustatic fluctuations of the third order, are often accompanied by the accumulation of sediments rich in OM.

The results of the study of organic matter composition testify that, along with the marine mainly planktonogenic OM, the majority of the Mesozoic and Cenozoic black shales also contain allothigenic OM supplied from land (Simoneit, 1986; *et al.*). These circumstances should be taken into account when studying the possible causes of the black shale-type formation of carbonaceous deposits.

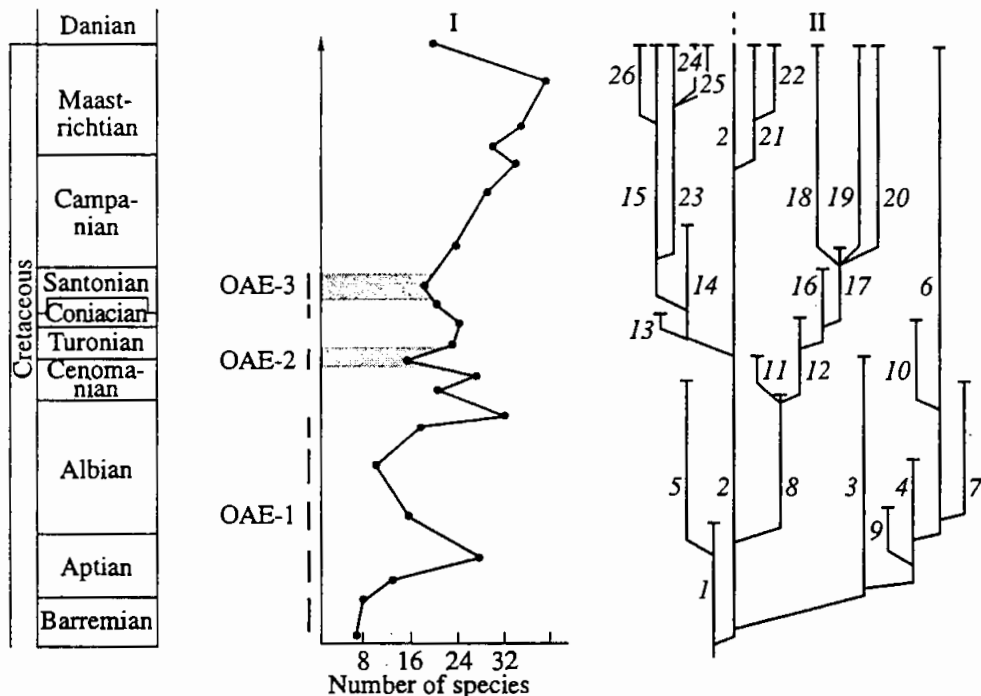


Fig. 1. Schemes of taxonomic diversity of species (I) and phylogenetic evolution of planktonic foraminifer genera (II) in the Cretaceous.

Oceanic anoxic events: (OAE-1) Barremian—Albian; (OAE-2) Cenomanian—Turonian; (OAE-3) Coniacian—Santonian (?). Taxa: (1) *Globuligerina*; (2) *Hedbergella*; (3) *Clavihedbergella*; (4) *Blowiella*; (5) *Favusella*; (6) *Globigerinelloides*; (7) *Planomalina*; (8) *Ticinella*; (9) *Leopoldina*; (10) *Hastigerinoides*; (11) *Rotalipora*; (12) *Praeglobotruncana*; (13) *Helvetoglobotruncana*; (14) *Whiteinella*; (15) *Archaeoglobigerina*; (16) *Dicarinella*; (17) *Marginotruncana*; (18) *Globotruncana*; (19) *Contusotruncana*; (20) *Globotruncana*; (21) *Globotruncanella*; (22) *Abathomphalus*; (23) *Rugoglobigerina*; (24) *Rugotruncana*; (25) *Kuglerina*; (26) *Bucherina*.

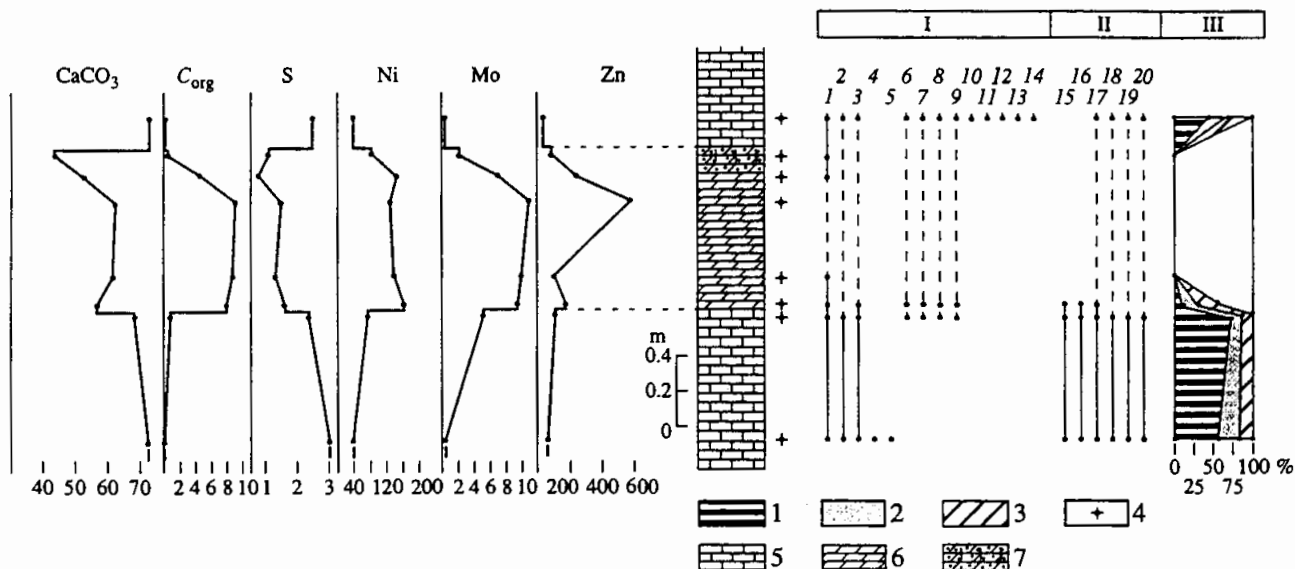


Fig. 2. Lithological column of Cenomanian—Turonian boundary layers (Crimea, Aksu-Dere locality) and distribution of chemical elements and various foraminifer species.

CaCO_3 , C_{org} , and S contents are given in wt %; Ni, Mo, Zn in ppm (recalculated for carbonate-free matrix); I, planktonic foraminifers: (1) *Hedbergella* spp., (2) *Dicarinella* cf. *algeriana*, (3) *Whiteinella* *brittonensis*, (4) *Rotalipora* *greenhornensis*, (5) *R. cushmani/deecke*, (6) *Whiteinella* *baltica*, (7) *Wh. archaeocretacea*, (8) *Wh. aumalensis*, (9) *Wh. holzli*, (10) *Wh. paradubia*, (11) *Dicarinella* *hagni*, (12) *Praeglobotruncana* *oraviensis*, (13) *Pr. imbricata*, (14) *Pr. cf. praehevetica*; II, benthic foraminifers: (15) *Gaudryina* *filiformis*, (16) *Arenobulimina* spp., (17) *Lenticulina* spp., (18) *Brotzenalla* *berthelini*, (19) *Lingulogavelinella* *globosa*, (20) *Gyroidina* *turgida*; III, planktonic to benthic form ratios. Key 1, 2, planktonic foraminifers (1, ratites, 2, keeled taxa); 3, benthic foraminifers; 4, localities of samples; 5, limestones; 6, bituminous shales; 7, silty shales with bioturbation marks.

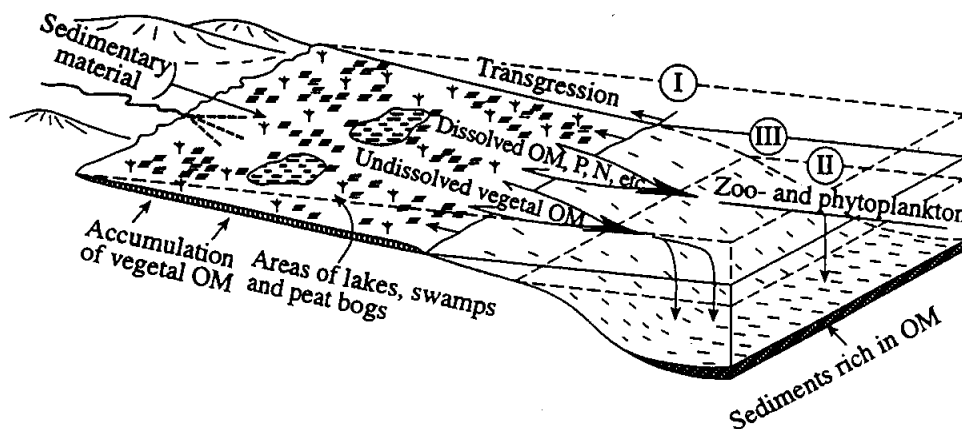


Fig. 3. Schematic model of interaction between the transgressing sea and coastal lacustrine-swamp landscapes (after Gavrilov, 1994). I-III. Position of sea level: I, before regression, II, during maximal regression, III, during developing transgression.

A comparison of the Mesozoic-Cenozoic eustatic oscillation curve (Haq *et al.*, 1987) with the distribution of deposits containing OM shows that not all transgressions caused the formation of black shales. Obviously, certain conditions should have been present to somehow regulate this kind of sedimentation. Normally, the transgressions, associated with the formation of horizons rich in OM, were preceded by more or less developed regressive episodes that initiated specific paleogeographic environments. The regressions exposed great areas of sea floor in relatively shallow epicontinental seas or on the shelves of basins (Fig. 3). Geomorphologically, they were lowlands flattened out by sea erosion and sedimentation. In predominantly warm and humid climates, the vast newly formed coastal plains were favorable for the development of the limnetic-swamp and adjoining lagoon landscapes. The former probably appeared very quickly: as the data on recent peat accumulations indicate, the impressive peat bogs, many meters thick, were formed during several hundreds or a few thousand years (Blaine, 1989; *et al.*). Therefore, the regressions, initiated by eustatic fluctuations, caused the appearance of vast swamped territories on the earth's surface, so that the sea basins were banded on their perimeters by coastal plains, where considerable amounts of vegetal OM accumulated.

After a certain time period, however, at least in the case of the short-period eustatic fluctuations, it was usually after a few tens of thousands of years that a regressive stage changed to a rapidly developing transgression. During this latter stage, the advancing sea actively interacted with the coastal limnetic-swamp landscapes. The process of erosion of the accumulated vegetal OM into the sea basins was not limited by the mechanical transportation from the coastal landscapes. In addition to the solid OM, the swampy basins stored large amounts of the dissolved OM, the product of disintegration of the available OM mass. Moreover, the process of OM accumulation and partial dissolution was persistently maintained during the entire time of exist-

ence of these landscapes. The transgressing sea advanced over the swamped basins and reduced the run-off distance of the drainage waters, thus providing an easy supply of dissolved OM into the sea basin, where it was partially buried in sediments and increased their C_{org} content; the other part, most likely the dissolved OM, was involved in a new biological cycle being utilized by plankton, thus raising its bioproductivity (Fig. 3).

An analysis of mineralogical-geochemical environments in modern swamp systems indicates that the process of peat formation creates conditions favorable for the chemical activity of phosphorus, an important element in the biological cycle. The swamp evolution process, on the whole, can be regarded as one of the typical means of geochemical migration of phosphorus in the hypergenesis zones (Kovalev, 1985). Even if the territory was not swamped, the accumulations and deposits of phosphates were actually formed under hypergenic weathering, especially in the tropical areas. For example, the phosphate eluvium is one of the frequent formations in outcrops of the Cretaceous carbonate deposits in central Russia (Mikhailov, 1986). We, therefore, suggest that the interaction between the sea and the coastal landscapes provided the means for carrying off significant amounts of phosphorus compounds into the sea basin. A supply of these substances to the sea could have greatly increased its bioproductivity and, given certain conditions, could have enriched its sediments with OM.

The aggressive environment of swampy systems was favorable for the reworking of alluvial sediments, when these systems interacted with the underlying rocks. Quite a number of terrigenous minerals, normally known to be resistant to weathering, were dissolved in a peat bog environment and enriched waters with many microelements. These latter were carried off by the drainage network to the water basins and were involved into the biological cycle. Therefore, the peat bogs served as a sort of filter and as a reworking system

of the sedimentary material supplied from the inner parts of the continents. It should also be taken into account that the coastal lacustrine–swamp landscapes primarily developed not on ancient rocks, but also on poorly lithified or nonlithified deposits, the former shelf sediments. That is why they were so easily affected by reworking in the aggressive peat bog environment.

Accordingly, we believe that the interaction between the advancing sea and the lacustrine–swamp landscapes that appeared on the coastal plains as a result of the previous regression was the mechanism, on the one hand, supplying the water basins with considerable amounts of vegetal material and, on the other hand, promoting the flourishing of zoo- and phytoplakton mainly owing to the run-off of the dissolved biophilic elements into the water basin (Gavrilov, 1994). This mechanism was responsible for the formation of rock horizons enriched in OM of either vegetal (land) or planktonogenic origin in accordance with the conditions of sedimentation in that, or another setting in the basin; as a rule, the two processes were concurrent.

Furthermore, the lacustrine–swamp landscapes, particularly the peat bogs, are rather unstable systems, and the wave erosion during transgression often completely demolished them, leaving almost no trace in the geological records except in the regions with an active coal accumulation and specific tectonic regime. That is why the sedimentary sections rarely show direct marks of the interaction between marine and continental coastal landscapes. There are certain indirect evidence, among them geochemical (Gavrilov, 1992), that seem to generally confirm our conclusion. The observation data on artificial reservoirs during their filling also imply this, because such basins are miniature models of a developing transgression. It was noted, that during the first years of filling, an extremely intensive burst of phytoplakton productivity was caused by the growth of concentration of biogenic elements washed out of the inundated soils (Petrova, 1990; Tseeb, 1962). In essence, this phenomenon is an analogue to the processes that took place during the full-scale sea transgressions.

We should bear in mind, though, that providing the supply of biogenic matter and raising the productivity of the basins, the interaction of sea transgressions with the coastal landscapes could be favorable for the formation of OM rich sediments, whereas the realization of this process depended on the combination of different factors. For example, in the basin with a dominant biogenic carbonate sedimentation, the growth of bioproductivity along with preservation of the organic forms traditional for the basin can simply result in the growth of the sedimentation rate, and, in this case, the geological section of sediments will not show any appreciable changes in the character of sedimentation. Consequently, the impression that transgression has no effect on sedimentation can be wrong. A different pattern

appeared in cases when the burst of bioproductivity was followed more or less apparent change in the plankton composition and sudden increase of shell-less forms (dinoflagellates, bacterial plankton, etc.); as a result, the sediments were enriched with OM, if the background sedimentation rates were relatively low.

Further, we shall analyze the consequences of such bursts of bioproductivity accompanied by the structural reconstruction of plankton assemblages and accumulation of excessive amounts of OM in sediments.

STRESS EFFECT OF GEO- AND BIOCHEMICAL FACTORS ON BIOTA

Toxic chemical elements. The high OM content in sediments causes intensive diagenetic processes that determine the geochemical environment not only in sediments, but, to a certain extent, in bottom water as well. The abundance of OM in sediments also affects the character of mainly the anaerobic type of diagenesis throughout the entire sedimentary sequence. The absence of the oxidizing film at the sedimentary surface encourages a considerable supply of certain chemical elements and their compounds from the bottom water into sediments (Volkov, 1980; *et al.*). Owing to this and the sufficiently high absorption capacity of the dead plankton tissues at the sedimentation stage, the silts become enriched in many heavy metals: Cu, Pb, Ni, Hg, Co, Mo, Ag, Cd, Zn, As, and others. According to the degree of their toxicity, the elements can be divided into three groups (Wood, 1984): nontoxic (Na, K, Mg, Ca, H, O, N, C, P, Fe, S, Cl, Br, F, Li, Rb, Sr, Ba, Al, Si); highly toxic and easily absorbed by organisms (Be, Co, Ni, Cu, Zn, Sn, As, Se, Te, Pd, Ag, Cd, Pt, Au, Hg, Tl, Pb, Sb, Bi); and toxic, either very rare or occurring in hardly soluble compounds (Ti, Hf, Zr, W, Nb, Ta, Re, Ga, La, Os, Rh, Ir, Ru). Most of the elements accumulating in sediments rich in OM are those of the highly toxic group. The data on the geochemistry of black shales indicate that they generally contain large amounts of toxic trace elements (Yudovich and Ketris, 1991). The toxicity of metals in these groups is different for individual organisms. Somers (1959) compared the relative toxicity of metals for some of the groups of organisms and suggested the following toxicity sequence that corresponds well to the electronegativity values of elements: Hg > Cu > Pb > Pd > Ni > Co > Be > Zn > Mn > Sr > Mg > Ca > Ba. The sapropelic horizons often lack correlation between pyritic sulfur and heavy metals. This implies that heavy metals in sediments occur in forms more mobile than sulfides and may exercise their toxic properties. The diagenetic (as well as sedimentary and biogenic) enrichment of silts with toxic heavy metals has a negative effect on benthic fauna, particularly on the burrowing species.

The studied influence of microelements in the habitat environments on microorganisms (Letunova and Koval'skii, 1978) reveals that high concentrations of

Co, Mo, Cu, V, U, Sc, in most cases, inhibit biota growth. The degree of this influence is different for similar forms in different biochemical provinces. Letunova and Koval'skii remarked that, in a population, the presence of organisms, which are variably adapted to geochemical factors and show an inherited fixed threshold sensitivity to various concentrations of chemical elements, triggers the process of natural selection that becomes more vigorous under extreme conditions.

Hydrosulfuric poisoning of bottom waters. The effect of toxic trace elements on biota is often eclipsed by the action of another product of anaerobic diagenesis, the hydrogen sulfide. The toxic properties of H_2S and its effect on organisms are well known. The hydrosulfuric poisoning of water in basins with more or less stable anoxic environments mainly results from the H_2S migration from OM-rich sediments to bottom waters, as in the Black Sea. The amount of H_2S escaping from sediments depends, however, on the intensity of sulfate reduction and the capacity of sediments to fix the resultant hydrogen sulfide. The latter process is determined by the content of the reacting forms of metals, primarily iron, in sediments. As long as the content of reacting iron is greater than that of H_2S , the released hydrogen sulfide is completely absorbed in the sediments for the formation of Fe sulfide (Volkov, 1984). The dynamics of the process definitely implies that the accumulation of either the terrigenous or carbonate sediments rich in OM (as the extreme members of the continuous clay-limestone series) differently affects the commencement of hydrosulfuric poisoning of a basin. In fact, the average Fe content in clays is almost an order higher than in limestone, i.e., 4.72% versus 0.38%, respectively (Turekian and Wedepohl, 1961). Therefore, if the OM content in deposits is the same, then the clays have a much higher H_2S fixing potential than the carbonate sediments. We should keep in mind, of course, that not all the iron in sediments possesses the same reactive ability and is involved in sulfide formation; however, this does not alter the process in general.

In basins with mostly terrigenous sedimentation, the OM enrichment may be unable to provoke hydrosulfuric poisoning. The process starts only when the OM accumulation becomes much more intensive than the Fe concentration, though somewhat later than the initial enrichment of sediments with OM, when the reacting Fe reserves would run out. On the other hand, the OM enrichment of carbonate sediments with a low Fe content can almost instantly launch the evacuation of diagenetic H_2S from sediments and the hydrosulfuric poisoning. The thickness of the poisoned water layer is primarily controlled by the intensity of diagenetic processes in sediments, the hydrodynamic regime in the basin, and water stratification.

In the Cenomanian-Turonian boundary layers of Crimea (Fig. 2), the sulfur content in rocks with OM is 1.5–2% lower than in the rocks upsection or downsection, i.e., almost twice as less.¹ We believe that this kind

of sulfur distribution resulted from intensive reduction processes and evacuation of a large share of generated H_2S from the sediments. The hydrosulfuric poisoning of the basin was one of the principal factors responsible for the distribution of organisms in the section (Fig. 2). The sulfide formation in these OM-rich deposits, however, was insignificant due to their low iron content.

The toxic element accumulation in silts with higher OM and hydrogen sulfide contents was the leading factor that negatively affected the benthic fauna. However, many plankton forms, such as foraminifers, concurrently disappear from the sediments, which accumulated during the anoxic events (Fig. 2). The biological cycle of foraminifers did not necessarily involve sinking to the deeper water levels that could have been poisoned by hydrogen sulfide. For instance, some of the taxa were visibly affected by stress processes in the upper water layers, where mainly the cosmopolitan *Hedbergella* forms were likely to survive. The absence of carbonate shells in black shales could have been partly caused by their diagenetic dissolution. Nevertheless, this circumstance alone cannot account for the actual distribution patterns of fauna in the geological sections. For example, in the Cenomanian-Turonian boundary deposits (Fig. 2), the bituminous marls show a general decline in the carbonate content that, apparently, reflects the reduction of $CaCO_3$ accumulation in sediments caused by the lower productivity of certain planktonic calcareous forms. The rise of the OM content in sediments, however, is the result of the flourishing of carbonateless phytoplankton and, perhaps, also of the bacterial mass. Let us assume, that the formation of an OM-rich horizon was connected not with the planktonic assemblage reorganization, but only with the bioproductivity growth in a basin with an intact former biotic structure; then, as noted above, there would have been a simple increase in sedimentation rate without the growth of OM content in sediments, and no sharp lithological-geochemical differences in the section units.

There is evidence that during the anoxic events, the phytoplankton assemblages essentially changed; thus,

¹ The manuscript was already submitted for publication when the paper by Naidin and Kiyashko (1994) was published. The authors also presented data on the distribution of some chemical elements in the Cenomanian-Turonian boundary units from the Aksu-Dere section in Crimea. Unlike the pattern shown in Fig. 2, these elements show considerable scattering of their concentration values inside the OM-rich layer. We believe that the discrepancies between the results cited and our results are caused by the different way of sampling: the cited authors have, apparently, collected all of the rock varieties conspicuous within the layer, including those from the light-colored lenslike interbeds, where the contents of C_{org} and other elements are much lower. We think that the formation of light-colored lenslike patches inside the black shales was caused by hypergenic processes, i.e., by oxidation of occasional diagenetic pyrite concretion during the weathering. The subsequent action of the resultant sulfuric and sulfanilic acids on rocks changed them, particularly, by bleaching and lowering their $CaCO_3$ content (Perel'man, 1972). For our analyses, we used rocks mainly unaltered by hypergenic processes.

the data on the distribution of palynomorphic groups in the lower Toarcian Posidonia shales shows that some forms of the phytoplankton disappear, whereas other forms are particularly abundant (Wille, 1985; Riegel *et al.*, 1986). Therefore, the accumulation of OM-rich sediments was concurrent with the stress effect on biota, both in the bottom and upper water strata of the basin. However, it is hardly probable that the stress effect was the result of hydrosulfuric poisoning of waters on such a large scale, in some cases almost global.

Red tides and their effect on biota. One of the possible causes of the sudden bioproductivity increase in the surface water layers and of the stunted state, if not complete extinction, of the numerous planktonic forms inhabiting marine basins was the active bloom of phytoplankton, or the so-called red tides. The oceanographic studies of red tides indicate that they are quite common in nature; they are observed off the coasts of nearly all continents and in the inner seas (Tumantseva, 1985; Anderson *et al.*, 1982; Bodeanu and Usurelu, 1979; Correto *et al.*, 1986; Kat, 1983; Maclean, 1979; Murphy *et al.*, 1975; Sukhanova *et al.*, 1988; Watras *et al.*, 1985). The contemporary occurrences of this phenomenon were considered by a number of researchers to account for certain peculiarities in biota development in the seas in the geologic past. Naidin was the most persevering advocate of the relationship between the Late Cretaceous biotic events and red tides (Naidin, 1985, 1986; Naidin *et al.*, 1986).

The effect of red tides on ecology could be drastic (Dale and Yentsch, 1978; Ray and Aldrich, 1965; White, 1981; *et al.*). For example, the red tide off the eastern coast of England, in May 1968, was responsible for the extermination of mollusks, eels, and sea birds, mainly cormorants (Adams *et al.*, 1968); eighty people were poisoned from eating mollusks. This red tide was associated primarily with the dinoflagellate bloom, particularly of the *Gonyaulax tamarensis* Lebour (Robinson, 1968). The zone of toxic dinoflagellates stretched along the coast for almost 500 km, and was more than 10 km wide (Indham *et al.*, 1968). The ecosystem received additional stress from the decay of a mass of dead algae that caused a decrease in the oxygen content of the sea.

The mass mortality of marine fauna, including numerous fish, was periodically recorded in the areas of oceanic upwelling. This phenomenon can be caused by an oxygen deficit and hydrogen sulfide formation (Copenhagen, 1953). In the Walvis Bay, however, fish mortalities almost invariably coincided with red tides and, at the time, the *Gonyaulax tamarensis* Lebour (Pieterse and Van der Post, 1967) was one of the four dominant dinoflagellate species.

The red tides are provoked by blooms of both toxic and nontoxic algae. There are toxic diatoms, and up to 200 dinoflagellate species are toxic (Zernova, 1992; Abbott and White, 1979; Loeblich and Loeblich, 1979;

Shimizu, 1978; Steidinger and Baden, 1984); the blue-green algae and bacteria can also be neuro-, hepato-, and, apparently, dermatotoxic (Petrova and Chernaenko, 1993; Jackim and Gentile, 1968). Moreover, the emission of toxins by some phytoplankton species under certain conditions becomes a part of more extensive events, for instance, in the interaction of plant assemblages followed by the formation of various chemical compounds and their extraction into the environment (Grodzinski, 1965; Rice, 1978; Khailov, 1971; Lucas, 1947; Sounders, 1957; Whittaker and Feeny, 1971; *et al.*). Numerous experiments confirmed this kind of phytoplankton interaction (Rice, 1978; *et al.*).

It is important to note, that some of the phytoplankton forms are inherently toxic, whereas other forms extract toxins under adverse conditions; e.g., under low concentrations of biophilic elements in their environment, or by an impaired balance between these elements. The observed development of one of the red tides off the eastern coasts of the North Sea in 1989 (Zernova, 1992) shows that its appearance was caused by a combination of conditions that set in after the run-off of excessive amounts of phosphorus and nitrogen from the continent into the sea. It was established that a certain plankton species, e.g., the flagellate alga *Chrysochromulina polylepis* responsible for the red tide, started emitting the toxin during the early stages of its mass development under low phosphorus and high nitrogen contents. This toxin, at a certain stage of its concentration in the environment, caused the mortality of other plankton forms. There were even cases of large fish kills. When the supply of nutrient was exhausted, the growth of the phytoplankton population ceased, and all the dead biomass sank to the sea bottom, essentially altering the geochemistry of the bottom waters and the habitat conditions of benthic fauna and certain fish species. There are numerous examples of similar effects of red tides on the environment (Aubert, 1990; Brongersma-Sanders, 1957; *et al.*).

The situation described above was caused by a combination of several climatic factors in Europe in 1989 that instigated the run-off of considerable quantities of phosphoric and nitric compounds into the sea, and to a lesser extent, by constant anthropogenic eutrophication. In the geologic past, however, analogous situations could have been created in the periods of rapid sea-level fluctuations, when transgressions carried off excessive amounts of biophilic elements from land into the sea, and thus caused productivity bursts in plankton and toxic phytoplankton. The fine lamination in numerous horizons rich in OM testify to the cyclic character of these surges of bloom. We can be fairly positive that these periods were favorable for the development of phenomena analogous to the recent toxic red tides. The phytoplankton bloom, greatly increasing the biomass and, consequently, saturating the silts with organic matter, stunted or killed the leading plankton forms, including the zooplankton with a carbonate shell that inhabited the basin. The annual occurrences of intensive phy-

Content of chemical components in interbeds with different content of organic matter*

Sample no.	C _{org}	CaCO ₃	Fe	Mn	Ti	P	Cr	Ni	V	Cu	Co	Pb	Mo	Ag	Stratigraphic and geographic locality of samples
18/1	0.5	74.1	0.89	0.04	0.15	0.05	40	20	60	47	12	10	1.8	0.05	Kuma Formation (Bartonian), Rubaschai River (Dagestan)
18/2	10.6	7.9	3.66	0.02	0.45	0.13	210	105	400	220	30	30	8.8	2.35	"
25	1.53	88.3	3.91	1.46	0.25	0.20	76	21	48	28	5	5	2.4	0.27	Kuma Formation, Kheu River (Kabardino-Balkariya)
26	7.50	54.0	3.25	0.36	0.30	0.27	240	102	1600	220	10	14	14	0.19	"
9	traces	13.6	3.89	0.30	0.51	0.06	141	112	162	79	38	30	2.3	0.08	Upper Paleocene, Kheu River
11a	8.0	traces	5.95	0.16	0.41	0.31	740	338	1100	172	53	69	23.1	6.50	"
11b	7.2	12.9	6.69	0.16	0.38	0.30	270	356	1700	122	52	32	73	2.70	"

* Contents of C_{org}, CaCO₃, Fe, Mn, Ti, P, in wt %; other elements in ppm.

toplankton blooms persisted as long as the ample supply of phosphorus, nitrogen, and other elements was maintained. With the termination of transgression, this process gradually attenuated, the bioproductivity of phytoplankton was reduced, and those forms of organisms that survived or escaped to more beneficial environments during the adverse period returned to the areas of their previous habitat (Fig. 2).

Red tides in the geologic past. An analysis of the causes of the formation of "fish cemeteries" in the Oligocene deposits of Ciscaucasia implies that red tides affected biota in the geologic past as well (Mstislavskii and Kochenov, 1960). The Lower Cretaceous deposits in Denmark contain accumulations of bivalve mollusks, the mass mortality of which was associated with the toxic dinoflagellate bloom (Noe-Nygaard *et al.*, 1987).

The finds of marine fauna mass mortality (fishes, mollusks, and others) in ancient geological sections are few, but the red tides were, apparently, rather frequent. There is no direct evidence of toxic red tides, as the toxins in rocks were not discovered, as can now be done, by studying the forms responsible for the bloom in water basins (Carmichael *et al.*, 1993). Moreover, it is not yet clear, whether the toxins can be stored in ancient deposits, at least after the diagenesis stage. Probably, in the course of evolution, the susceptibility of organisms to toxins changed, and the substances that were then poisonous to them are now harmless. Therefore, to establish connections between the formation of certain layers and the toxic red tides, we have to rely on indirect evidence. A sudden replacement of organisms traditional to the basin by other organisms, or even considerable changes in their relative quantities may serve as such evidence. The bursts of dinoflagellate, blue-green algae or, probably, bacteria blooms enrich the sediments with OM, and noticeably alter the geochemistry

of deposits. The occurrences of toxic diatom blooms are evidently specifically recorded in the sediments.

In southern Russia and the adjoining areas, the Mesozoic and Cenozoic deposits, at different stratigraphic levels, have layers of different thickness and extent that can be associated with the red tide events.

The middle Eocene marls of the Kuma Formation in Ciscaucasia show a higher background C_{org} content than that in the upsection or downsection deposits. The formation lacks benthic fauna, probably owing to the H₂S poisoning of the bottom waters, but the plankton forms, foraminifers included, are abundant and constitute one of the groups of rock-forming organisms. These deposits have thin intercalations (less than one to few cm thick), with considerably higher C_{org} and reduced CaCO₃ contents. This is evident from the comparison of data of chemical analyses of sample pairs from these intercalations (table, Samples 18/2, 26) and a few decimeters apart from them (Samples 18/1, 25). One of the interbeds is particularly interesting (Sample 18/2), because the C_{org} content in it grows from 0.5 to 10%, while the CaCO₃ amount is reduced from 74 to 8%. The interbeds either completely lack foraminifers, or contain very rare specimens. Concurrently, as shown in the table, the geochemical features of the deposits are largely changed. The dissolution was not responsible for the lack of foraminifers, because the same interbeds have large amounts of well-preserved coccoliths without a trace of dissolution. These kinds of intercalations were formed during a vigorous reconstruction of the ecosystem in the upper water layer caused, as we believe, by a burst of toxic phytoplankton bloom that stunted the other plankton forms and foraminifers. In the Kumian time, the red tide periods were short and, evidently, affected rather small areas, because as soon as they terminated, the traditional plankton of the basin recovered its habitat.

This problem also concerns the upper Paleocene sapropelic horizon stretching over a large territory, from the Caucasus to Central Asia (Muzylev *et al.*, 1989); it was formed under conditions of a rather short and rapid transgression. In Ciscaucasia (Kabardino-Balkariya), the base of the inhomogeneous sapropelic layer, about 0.4–0.45 m thick, includes a 4- to 5-cm-thick band with C_{org} content up to 8%; the band lacks $CaCO_3$ (table, Sample 11a) and calcareous plankton remains. In the middle of the horizon, the plankton remains appear, the carbonate content rises (table, Sample 11b) (Gavrilov and Muzylev, 1991), and the C_{org} content is still rather high. Among the two beds of the sapropelic horizon with similar C_{org} contents, one contains intact calcareous shells, while they are absent in the other; this indicates that the differences in the degrees of diagenetic reworking of the sediments were not the main cause of shell distribution, and that these differences appeared at the sedimentation stage. We consider it realistic to associate the formation of the interbed at the base of the sapropelic layer with the toxic phytoplankton bloom. This latter process is responsible for the absence of the coccolithoforid and foraminifer skeletons in the sediments. In a later period, during the accumulation of the rest of the horizon, the environment in the basin, perhaps, somewhat changed, the phytoplankton bloom ceased to encourage toxin extraction, and other plankton forms, including zooplankton, returned to this part of the basin and participated in the formation of sapropelic sediments. An intensive phytoplankton bloom at the end of the late Paleocene developed concurrently with the rapid global transgression and, evidently, was one of the forms of biota reaction to the changing environment in the basins; in other regions, this event could have occurred and been recorded in sediments differently. It is obvious, however, that in most localities, the stress effect of the bloom on the marine ecosystem was dramatic. Thus, according to Muzylev's data (Gavrilov and Muzylev, 1991), the boundary between the nannoplankton subzones lies inside the sapropelic layer, as evident from nannoplankton distribution.

An analysis of Cretaceous fauna reveals that in many localities, the Cenomanian–Turonian anoxic event was associated with the formation of C_{org} -rich deposits, and was followed by the extinction of highly specific "deep-water" taxa. To complete their life cycle, they must have sunk to the lower water layers. The hydrosulfuric poisoning of the bottom waters drastically reduced the reproductive processes in the euphotic zone. In a number of cases, however, the "shallow-water" taxa, whose life cycle is confined to the euphotic zone, disappeared from the geological units. These taxa seem to exemplify another type of selection with numerous quickly maturing offspring and a high competition between the young and adult specimens (r-selection). The regulating function for this group of fossil organisms was exercised, evidently, by the processes in the euphotic zone itself. Leary *et al.*

(1989) suggested a rather attractive scheme, though not always accurate in its second part (C, D, and E). The mortality of planktonic foraminifers of the *Hedbergella* and *Whiteinella* genera was, apparently, caused by stress events in the surface water layers. The most resistant to this process were the small forms of cosmopolitan taxa with little shells and globular chambers of the *Hedbergella* type. The oligotaxic period in the development of planktonic foraminifers of the Globotruncanidae family coincided with the period of the highest level of the World Ocean. The variations in the oceanographic parameters could have acted as powerful controlling factors in the phylogenetic development of foraminifers; e.g., a deficit in O_2 in the bottom waters often caused the appearance of H_2S and concurrent considerable amounts of toxins in the euphotic zone as a result of bacterial or phytoplankton blooms. These events not only destroyed the highly specific morphotypes of the *Rotalipora* and *Thalmaninella* genera, but also caused the formation of new morphological characteristics promoting higher degrees of specialization of organisms (Fig. 1).

In this respect, the Cretaceous–Paleogene boundary is of particular interest. In some regions, the Maastrichtian–Danian boundary corresponds to a small hiatus and, in other regions, to a clayey layer of few decimeters thick, often brown and located between carbonate rocks upsection and downsection. In some localities, the Cretaceous–Paleogene boundary deposits were formed in anoxic environments (Kajiwara and Kaiho, 1992). The sea-level fluctuations, the anoxic environments, and a sudden decline in the productivity of calcareous plankton were also typical of the Cenomanian–Turonian and late Paleocene events mentioned above. It is quite probable, that during the Maastrichtian–Danian event, the calcareous plankton suffered strong stresses due to the development of toxic red tides that could have led to biotic crises in a number of regions of the World Ocean. In several publications, Naidin suggests that red tides were one of the causes of the biotic crises at the Cretaceous–Paleogene boundary (Naidin, 1985, 1986; Naidin *et al.*, 1986).

The opponents of the idea that red tides essentially influence biotic life usually refer to the fact that the modern red tides are local and brief and, therefore, cannot cause global events. We should bear in mind, however, that environments in the past geological epochs could be quite different from those we have today. Thus, during the Cretaceous, there was the so-called "sluggish ocean," with an extremely slow circulation and lacking active contour currents. In this ocean, the red tides, stimulated by a developing transgression, could cover vast territories and, once started, could continue for a rather long period. Consequently, they could cause the extinction of certain specific groups of organisms, and further, the rapid expansion of other groups.

The problem of red tides in the geological past, their effect on biota, and the definition of criteria for their identification are, as yet, insufficiently elaborated. But this phenomenon occurs in our time, and we can hardly overlook the fact that it could have occurred in ancient epochs, though in a somewhat altered form. We assign red tides, or similar phenomena, to factors that produce the strongest stress effect on biota, both in marine and freshwater basins, and, therefore, should allow them due consideration in paleoecological and lithological reconstructions.

CONCLUSION

In sum, the scheme of biota evolution under factors responsible for the accumulation of black shales can be as follows. Rapid sea-level fluctuations created conditions for a more intensive supply of higher amounts of biophilic elements from land to water basins and caused sudden bursts of plankton productivity, particularly the shell-less phytoplankton. Under certain conditions, e.g., in the case of an unbalanced supply of nutrient, certain phytoplankton species secreted toxins that stunted or even killed other forms of organisms, in particular, the calcareous plankton. As a consequence, the sediments accumulated OM derived from shell-less algae and other organisms, and were concurrently depleted in CaCO₃ due to a smaller share of foraminifera, coccolithophorids, and other carbonate fossils in the sediments.

The abundance of OM in silts caused an intensive development of diagenetic processes, which (a) were primarily responsible for the accumulation of numerous toxic heavy metals in silts, and (b) generated a large amount of H₂S. Both the toxic elements and H₂S had a negative effect on bottom organisms. Under the conditions of anaerobic diagenesis, the H₂S migration was largely controlled by the intensity of processes of diagenetic sulfide formation. Provided that all other factors are equal, the basins where sediments had a lower Fe content were more favorable for hydrosulfuric poisoning than the basins that accumulated sediments relatively rich in Fe. Since in carbonate sediments the Fe content, as a rule, is much lower than in clayey sediments, the hydrosulfuric poisoning of water in the basins with carbonate sedimentation, apparently, developed more intensively than in those with terrigenous sedimentation.

Therefore, as the OM-rich horizons accumulated, different factors, including geo- and biochemical, affected both the benthic and planktonic biota. The mechanisms of these stresses were different, but the results were similar: throughout the basin system, from its bottom to surface layers, the conditions adverse to the existence of organisms could be generated more or less synchronously. This combined stress on biota by the stated factors could take place together with other effects that accompanied the sharp oscillations of the ocean level, such as the changes in the area, salinity (?)

and temperature of a basin, the greater stratification of its waters, etc. All of these factors were obviously essential to biota reorganization, i.e., the extinction of the old and the flourishing of the new forms.

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