THE GEOCHEMISTRY OF SAPROPELIC INTERBEDS IN THE PALEOGENE OF THE CENTRAL CAUCASUS

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The geochemistry of beds enriched in organic matter is discussed, taking the Paleogene deposits of the Central Caucasus as an example. They are enriched in a series of elements: S, Ni, Co, Mo, Cu, Pb, Cr, and sometimes Fe and P, with a simultaneous reduction in $CaCO_3$, Mn, and Ti. It is shown that the level of concentration of elements within the beds, together with their distribution, were controlled by various factors, the most important of which were diagenetic processes. A similarity is noted between the geochemistry of the Paleocene—Eocene sapropelic beds and similar Quaternary formations in the Black Sea and the eastern Mediterranean.

The Mesozoic and Cenozoic deposits of the Caucasus and Precaucasus include an interval characterized by an elevated content of organic matter (OM). The accumulation of sediments enriched in OM occurred in specific conditions in each basin, extending over quite long periods of time estimated at hundreds of thousands to millions of years (for example the Kumsk, Maikopian, and Chokrakian-Karaganian successions and others). At the same time there are local (particularly in the Paleogene) thin (several decimeters) dark-colored interbeds which occur within the general mass of the rock and are caused by a sharp increase in the OM enrichment. Despite their thinness, several of these interbeds are known from equivalent stratigraphic levels in outcrops many hundreds or thousands of kilometers from each other. These interbeds must therefore have been formed by some relatively short-lived events which occurred over a wide area, and repeated in a pulsatory fashion. Since these events were accompanied by an elevated bioproductivity in the water column, the sediments were enriched in OM, leading to the creation of geochemical conditions which were in sharp contrast to the conditions which existed in the sediment before and after the accumulation of these interbeds. It is quite possible that the geochemistry of the water column also fluctuated, perhaps leading to waters bearing hydrogen sulfide, especially in the water close to the sediment surface.

We have studied a series of sapropelic* beds, and the surrounding rocks, from the Paleogene of the Central Caucasus in order to investigate the nature of the lithological and geochemical changes which occur when these abrupt depositional fluctuations take place.

The Paleocene and Eocene deposits in the study area have not been buried to any significant depth and show no appreciable signs of catagenic reworking. The rocks are readily saturated in water, and the clays are of mixed-layer hydromuscovite-smectite type with no signs of ordering. In our opinion, catagenesis can therefore be excluded as a possible influence on the geochemistry of the sapropelic interbeds. The geochemistry of the sapropels has resulted primarily from factors operating during sedimentation and early diagenesis.

A continuous Paleogene section along the Kheu River (Kabardina-Balkariya ASSR), 15 km southeast of Nal'chik, has been described, and samples of sapropelic interbeds taken. As shown on the lithostratigraphic column, the succession is composed of various lithologies, but is dominated by marls and marly clays (Fig. 1). The sapropelic interbeds occur at two stratigraphic levels. The lower of these interbeds is isolated within the section, occurring at some distance from the other group of

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*At this stage in the study we have not determined the composition of dispersed organic matter, and therefore use the term "sapropel" for an unlithified sediment enriched in OM, and "sapropelite" for its lithified equivalent, only provisionally. It should be noted that foreign literature (e.g. [17, 28]) uses the term "sapropel" extensively for formations of the type discussed by us, regardless of the type of OM.
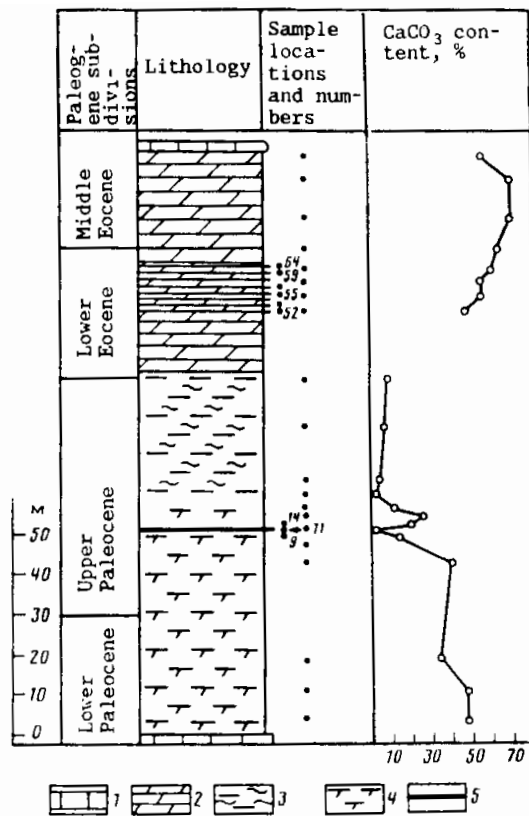

Fig. 1. Lithostratigraphic column of a Paleocene—Eocene section from the Central Caucasus (Kheu River). 1) Limestones; 2) marls; 3) clays with siliceous interbeds; 4) marly clays; 5) sapropelic interbeds.

interbeds, and characterized by a number of distinctive features. This bed occurs within the Upper Paleocene, in an interval corresponding to the *Acarina acarinata* foraminiferal zone (the layer with *Globorotalia aequa*). The stratigraphic position of this interval was formerly placed at the very top part of the *Chiasmolithus bidens* subzone of the *Discoaster multiradiatus* zone, on the basis of nannoplankton [8]. Subsequent study of the nannoplankton using very detailed sampling showed that the sapropelic bed lies precisely on the upper boundary of the *Chiasmolithus bidens* subzone (i.e. the boundary lies within the bed).

Horizons enriched in OM lie within the same stratigraphic interval in other parts of the southern USSR: the Precaspian, Southern Turkmenia, and the Tadzhik Depression. Sapropelic beds like those discussed can therefore be traced over vast areas.

In the Kheu River section the sapropelic bed lies in the upper part of a uniform succession of marly clays, about 50 m thick. The deposits forming the depression are pale blue-grey, unstratified, and with abundant heterogeneous types of bioturbation. The carbonate content of the rock reaches 40% or more (Fig. 1). The interval containing the sapropelic bed is transitional with the following succession, being marked in particular by a decreasing carbonate content (from 40% to 10-20%). Five meters higher in the section from the sapropelic bed there is a significant change in the nature of the deposits. Clays with a relatively low carbonate content ($CaCO_3 < 10\%$) occur, with beds of siliceous rock.

The thickness of the sapropelic bed is 0.4-0.45 m. Above and below it are 8-12 cm layers which are less dark-colored than the sapropelites, but which have a darker color than the surrounding rocks.

The dark color of the sapropelic bed is due to the elevated OM content, which can clearly be recognized in the section. However the bed is not homogeneous: the intensity of the color varies. It is darkest in the lower part of the bed, and becomes gradually paler upwards, until at the top a bed of quite pale rock can be traced (Fig. 2).

Fish scales are found on smooth bedding surfaces of the clays (several millimeters to 1 cm or more), and sharks' teeth (up to 1 cm). Rare impressions of fragments of fish skeletons are found, sometimes pseudomorphed by pyrite. In the bed itself, and also in the immediately under- and overlying clays, pyrite nodules are found, up to several centimeters in diameter, and with a relatively regular form; lumpy, or botryoidal, with a surface covered in fine pyrite crystals. Inside are clots of fine-grained pyrite
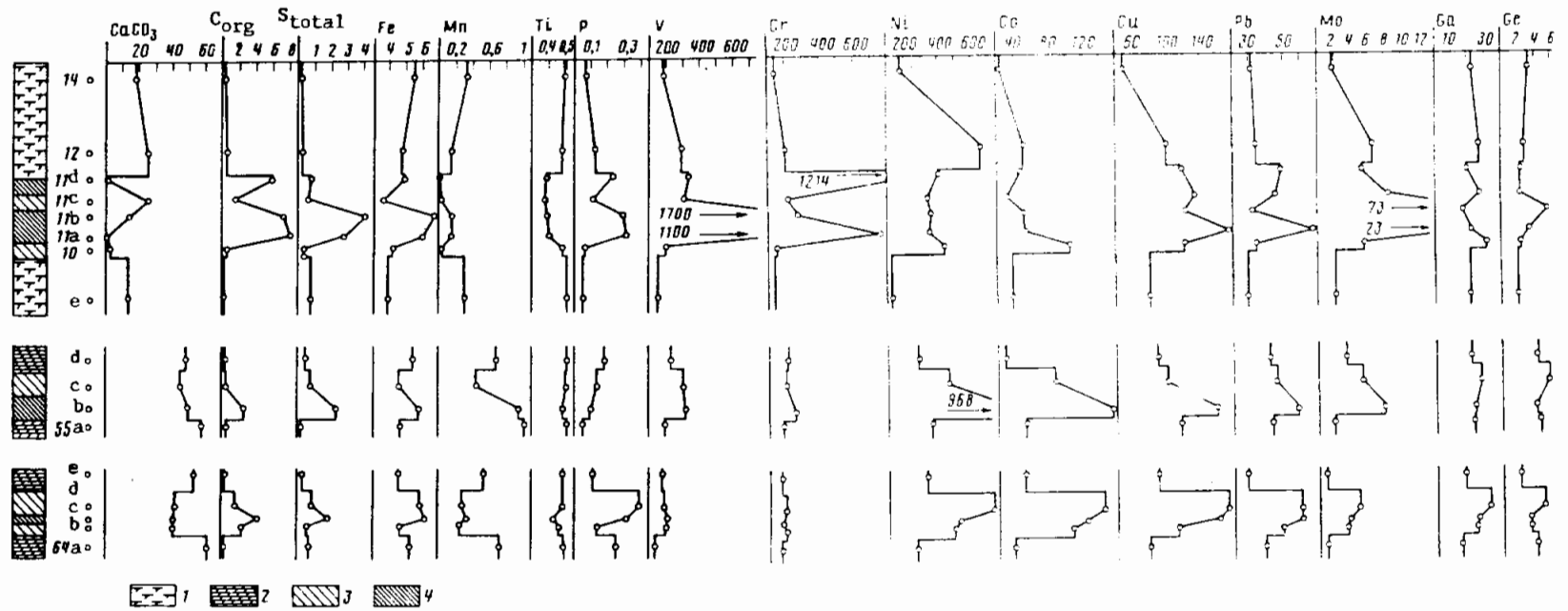
Fig. 2. Distribution of elements in the sapropelic interbed. 1) Marly clays, 2) marls; 3) rock with slight OM enrichment; 4) rock with strong OM enrichment.

alternating with barite segregations. In the lower part of the bed, most enriched in OM, large (up to 10 cm) concretions of radiating sulfide minerals are found.

Among other inclusions in the bed are rare isolated small (1-2 cm) wood fragments, which are pseudomorphed by pyrite.

Against the dark background of clay are seen small (several millimeters) tubular structures infilled with green-grey clays, and in the upper part of the bed (close to the top) are lenslike marks (0.3-1 × 0.5-4 cm), representing the traces of mud-living organisms.

Studies of the mineral composition of the clays in the OM-enriched bed, and from the over- and underlying deposits, do not show marked differences between them. The main rock-forming minerals are mixed-layer hydromicas and smectites, with subordinate chlorite.

In the same section, in the upper part of the Early Eocene succession, lies a group of eight beds which are enriched in OM relative to the surrounding rocks (Fig. 1), containing up to several percent of organic carbon. These beds are less enriched in OM than the Paleocene bed. The stratigraphic interval over which these beds lie can be defined quite precisely by foraminifera. It corresponds to the *Globorotalia aragonesis* zone and the very base of the *Acarinina bullbrooki* zone. According to the nannoplankton it occupies the middle and upper parts of the *Mathasterithes tribrachiatus* zone and the *Discoaster lodoensis* zone. We note that sapropelic beds corresponding to the same stratigraphic interval outcrop in a number of sections in the Precaspian [8].

In the Kheu River section the interbeds lie within a 13-15 m interval, and lie several decimeters to meters apart from one another. Moreover the nature of the surrounding rocks over the whole interval in which the sapropelic beds are developed is in general uniformly calcareous, with a carbonate content reaching 70% (Fig. 1). The sapropelic beds are 0.1-0.25 m thick, and they vary in their OM concentrations. The base and top of the beds are not usually sharp. In the upper part, and sometimes over the whole thickness of a bed, there are traces of fossil organisms which are clearly distinguished by their pale-grey color against the background of the brown sapropelite. Amongst the inclusions it is possible to note rare small (several millimeters) fish scales, and individual fine wood fragments. Large concretions are usually absent, but in thin sections clots of sulfide minerals can be seen.

The silicate phase both within the interbeds and between them is identical. Argillaceous minerals are represented by mixed-layer smectites and hydromicas, with subordinate kaolinite which is absent in the Paleocene bed. Traces of chlorite are noted.

COMPOSITION AND DISTRIBUTION OF CHEMICAL ELEMENTS IN THE SAPROPELITE BEDS

Within the sapropelite beds and the surrounding deposits the distribution of a number of components has been studied. C_{org}, CO_2, S, P, Fe, Mn, and Ti have been determined chemically, and V, Cr, Ni, Co, Cu, Pb, Ga, Ge, and Mo have been determined by quantitative spectral analysis. Analyses were undertaken in the chemical laboratories of the Geological Institute of the Academy of Sciences of the USSR. Figure 2 illustrates three of the interbeds studied, and shows the distribution of samples. The samples were selected as much as possible to ensure that different parts of the sapropelite beds, differing from one another in the level of OM enrichment, were represented. The overlying and underlying rocks were also sampled.

Quite high concentrations of carbonate material were established in the large majority of samples. This was mostly in the form of $CaCO_3$, the quantity of which varied markedly between the samples. In order to avoid this factor influencing the picture of the distribution of the elements, their contents were recalculated in terms of the noncarbonate fraction (Table 1). In order to compare the different elements, their relative concentration coefficients were calculated, taking the content of each element in the underlying bed as unity (Fig. 3). It should be noted that for a number that for a number of the elements in the rocks surrounding the sapropelites the background values are quite high. For example, values for Cr, Ni, V, Cu, Co, and Pb exceed the Clark abundances by 1.5-3 times for argillaceous and especially for carbonate rocks (Table 1). Because of this, the coefficients of relative concentrations do not reach high values, although the absolute values of the elemental composition of the sapropelite beds are substantial. The relatively high concentration of manganese in the deposits surrounding the sapropelites (0.31%) attracts attention (Table 1, samples 9, 14, 55a, 55d, 59a, 64c, 68a).

In comparing the behavior of elements in the various beds we note that two groups can be distinguished: in one group there is an increase within beds enriched in OM, and in the other group there is a decrease.

One group comprises those elements, such as Mo, V, Ni, Co, Cr, Cu, Pb, Ge, and S, which in most cases show a tendency to become concentrated within sapropelites.

TABLE 1. Contents of Chemical Elements in the Sapropelite Beds and in the Surrounding Rocks

Bed	Sample number	CaCO$_3$	C$_{org}$	S$_{val}$	Fe	Mn	Ti	P	Cr	Ni	V	Cu	Co	Pb	Mo	Ga	Ge
	9	13.6	Trace	0.78	3.89	0.30	0.51	0.06	141	112	162	79	38	30	2.3	22	2.3
	10	1.6	0.52	0.26	4.25	0.02	0.48	0.07	152	430	208	122	106	34	5.48	32	2.5
	11a	Zero	8.0	2.73	5.95	0.16	0.41	0.31	740	338	1100	172	53	69	23.1	21	3.5
I	11b	12.9	7.2	3.99	6.69	0.16	0.38	0.30	270	356	1700	122	52	32	73	18	6.1
	11c	25.8	1.29	0.73	3.63	0.07	0.36	0.11	213	332	315	131	32	46	8.4	28	2.6
	11d	1.1	6.05	0.82	4.74	0.007	0.38	0.24	1214	400	342	119	47	49	5.3	21	2.8
	12	26.1	0.30	0.47	4.68	0.16	0.47	0.13	196	701	304	104	51	34	6.6	27	3.0
	14	17.8	0.17	0.23	5.56	0.32	0.50	0.08	140	182	179	49	26	32	1.9	23	3.3
	55a	56.5	0.44	0.16	4.67	1.03	0.53	0.06	182	356	202	117	55	44	2	23	4.6
II	55b	48.9	2.57	2.27	5.67	0.95	0.48	0.10	254	968	323	160	156	59	7.8	23.5	5.9
	55c	43.5	0.25	0.71	4.57	0.44	0.51	0.14	204	455	314	103	87	46	5.5	28	4.3
	55d	48.4	Trace	0.35	5.43	0.68	0.52	0.19	215	275	233	89	31	43	3.5	23	4.7
	59a	56.2	"	0.43	5.23	0.75	0.52	0.27	205	267	173	132	32	52	3.2	18	4.6
III	59b	27.5	3.37	0.93	3.66	0.13	0.36	0.11	269	455	242	141	51	63	3.8	36	5.4
	59c	35.9	Trace	0.40	5.16	0.34	0.45	0.18	203	814	374	154	134	85	5.0	28	4.2
	64a	61.0	"	0.62	5.27	0.72	0.49	0.25	182	266	131	77	38	39	1.1	15	4.1
	64b	40.5	2.15	0.45	4.61	0.25	0.47	0.13	202	491	205	113	109	49	3.4	25	3.4
IV	64c	41.3	4.02	1.82	6.10	0.34	0.44	0.32	191	520	216	164	124	61	3.6	26	3.4
	64d	42.2	1.42	0.97	5.73	0.28	0.48	0.41	199	718	185	173	142	60	4.8	33	5.2
	64e	54.0	Trace	0.30	4.52	0.54	0.48	0.11	183	326	176	89	50	28	1.1	17	2.3
	68a	63.9	"	Not det.	4.35	0.80	0.47	0.17	172	305	158	144	80	30	1.2	~15	~2
V	68b	49.5	2.41	"	3.94	0.28	0.46	0.06	208	722	317	170	257	67	4.4	30	~2
					Clark abundances of elements in argillaceous rocks												
					3.33	0.067	0.45	0.077	100	95	130	57	20	20	2	30	2
					4.72	0.085	0.46	0.07	98	68	130	45	19	20	2.6	19	1.6

Notes: Contents of CaCO$_3$, C$_{org}$, S$_{val}$, Fe, Mn, Ti, and P are given in %; remainder in 10^{-4} %
Clark abundance coefficients given: in numerator according to A. P. Vinogradov; in denominator according to K. K. Turek'yan and K. Kh. Velepol'.
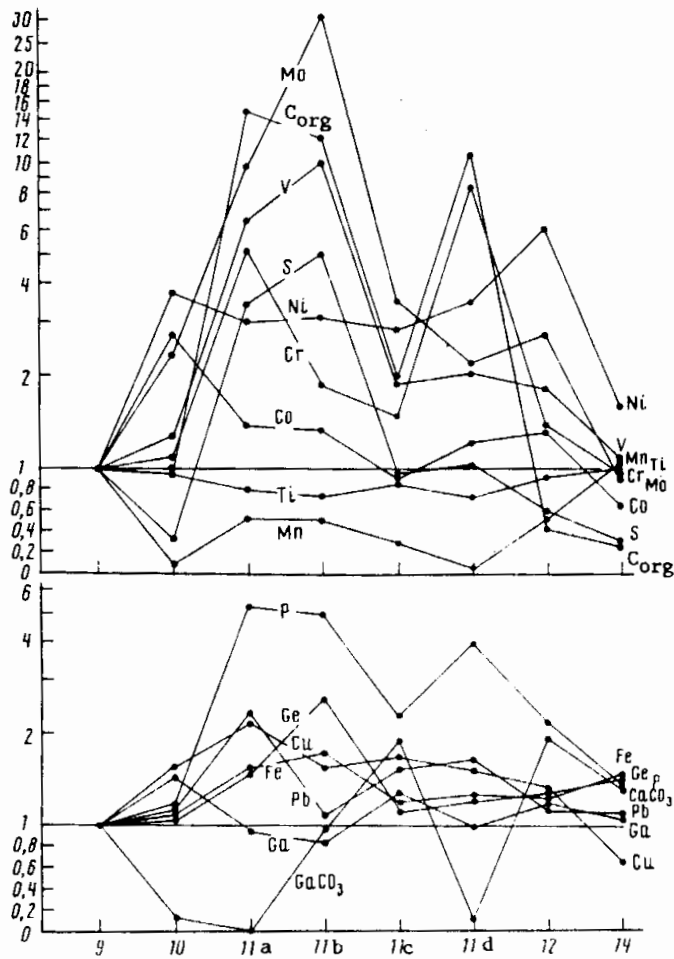
Fig. 3

The other group of components, which show a definite trend of reduced concentrations in the interbeds, includes $CaCO_3$, Mn, and Ti.

Fe and P display a less well-defined trend. In the majority of cases they are enriched (even if only by a negligible amount) in the sapropelite beds, but in two of the Eocene beds their concentration shows a marked decrease in comparison with the surrounding rocks.

The lower (Paleocene) bed is distinctive compared to the others in being the most enriched in OM and in having a relatively complex structure. First we shall discuss the geochemical characteristics of this bed.

As shown by the data given in Fig. 2 and Table 1, the OM content within the bed varies significantly from 8% C_{org} at the base to 1.3% in the pale layer in the upper half. Virtually all of the elements studied, and $CaCO_3$, display corresponding fluctuations.

The behavior of $CaCO_3$ is particularly noteworthy as a component which plays a rock-forming role. The content of OM generally has an inverse relationship to that of carbonate material in the rocks. An increase in the amount of C_{org} is invariably accompanied by a decrease in $CaCO_3$, and furthermore where C_{org} reaches a maximum, $CaCO_3$ is always absent.

Manganese displays a clear tendency to decrease in concentration within the sapropelite horizons, and to vary with the C_{org} content to a lesser degree in the other parts of the bed.

The Ti concentration also shows a uniform tendency to reduce somewhat in the sapropelite, although the difference between its background concentration and that in the sapropelite is, compared to other elements, much less distinct.
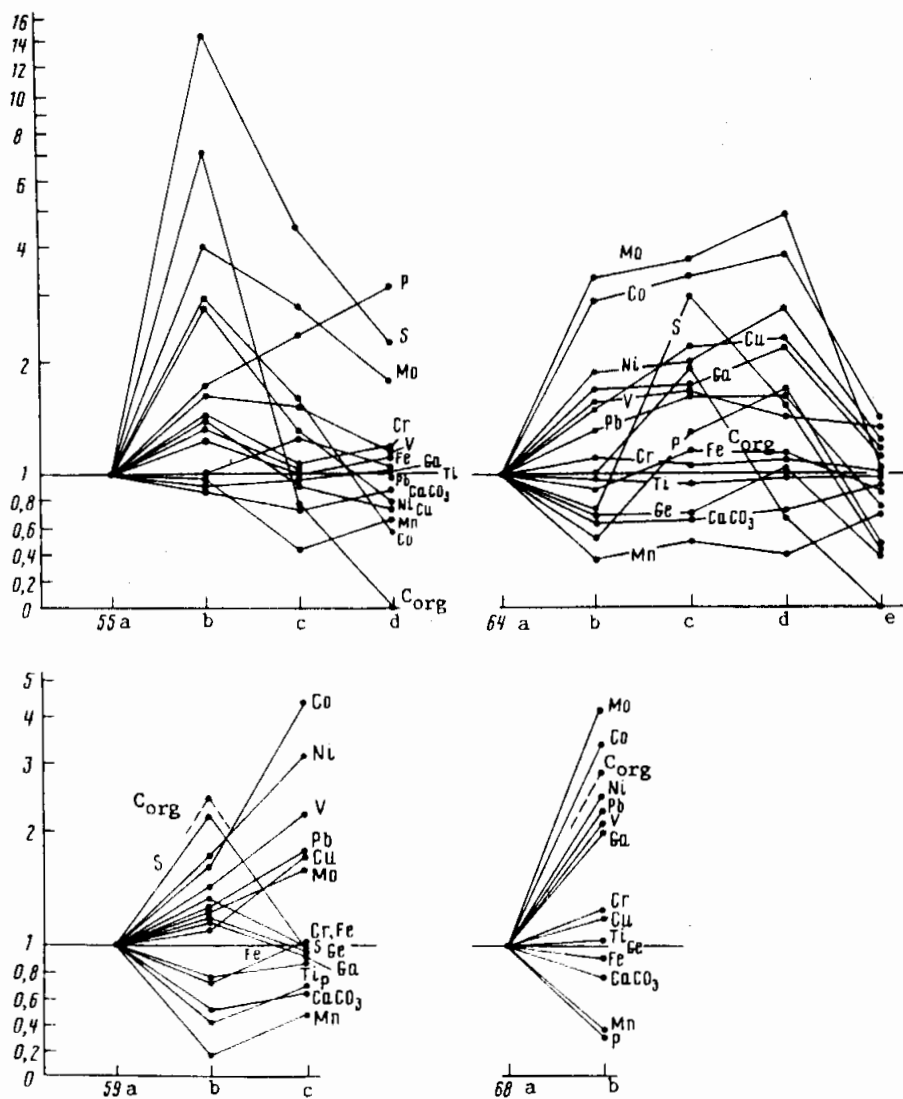
Fig. 3. Diagrams of concentration coefficients of chemical elements in the sapropelite beds. The concentrations in the underlying beds are taken to be one; the scale is logarithmic, but linear from 0 to 1. On the diagrams, sample points are plotted on the x-axis, corresponding to sample numbers on Figs. 1 and 2 and Table 1. Because of its complexity, the diagram of the Paleocene bed is shown in two parts.

Quite a large group of elements — Fe, S, P, Co, Ni, V, Mo, Cr, Cu, and Ge — is characterized by an increased concentration in the sapropelite bed, and the increase is sometimes quite substantial. In individual samples, for example, the concentrations reach ($10^{-4}\%$): Cr, 1200; V, 1700; Ni, 700; Mo, 60-70. These values exceed background concentrations by more that 5-10 times, and 30 times for Mo; and the Clark concentrations are exceeded even more.

It should however be noted that, despite the general tendency for these elements to accumulate in the sapropelite, within the bed they are distributed irregularly and the different elements behave differently. As shown on Figs. 2 and 3, the most stable relationship with OM is displayed by chromium. The maximum and minimum concentrations of this element correspond to those of C_{org}. The same may be said, with less certainty, of P and Cu.

Other elements which accumulate in the sapropelite (Fe, Mo, V, Ni, Co, Pb, and Ge) are distributed so that their maximum concentrations are quite out of phase with the C_{org} maxima. The Ga content of this bed is rather poorly defined.

The Early Eocene sapropelite interbeds differ from the Paleocene bed primarily in the reduced content of OM (Table 1). However, despite this, the geochemical characteristics of the bed are similar in many respects to those of the bed discussed above. In all of the Eocene beds, $CaCO_3$, Mn, and Ti also display a fixed tendency to decrease in content. In contrast, Ni, Co, Mo, Pb, Cu, and S show a marked concentration in the sapropelites. Chromium also belongs to this group but, in the first place,

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its relative concentrations are substantially lower than in the Paleocene bed and, in the second place, its correlation with OM is not marked. An irregular distribution is displayed by Fe and P. In some sapropelite beds their concentration increases, and in others it decreases. The same may be said of Ga and Ge.

In the Eocene beds (samples 59 and 64) a number of elements (Co, Ni, V, Cu, and P) display the same characteristic as in the Paleocene bed, that their greatest concentrations are found not within the layer of the sapropelite containing the highest C_{org}, but in the layer immediately above in which the OM concentration has decreased somewhat. Therefore, this distinctive shift of the maximum concentration of some elements seems to be characteristic of these sapropelite beds. Variations in the nature of the curves of elemental distribution are to a large degree an effect of the sampling within the sapropelite bed and the surrounding deposits, i.e. of the distribution of sample points.

DISCUSSION OF RESULTS

In describing the general features of the environment existing within the basin during deposition of the sapropels we note the following. The geological information on the structure of the Paleogene succession in the area shows that the formation of the Paleocene sapropelite took place against the background of a short-lived and quite rapid transgression. According to data provided in [24], the time interval corresponding to the accumulation of the Paleocene bed was a transgressive period which can be recognized on a global scale. Data presented by Shackleton [26] are of interest in this respect. They resulted from a carbon isotopic study of carbonates from deposits of the South Atlantic, and concluded that there was a reduction in the oxygen content of the ocean waters at the end of the Paleocene. This phenomenon is probably directly related to the widespread increase in the C_{org} content of marine sediments at this time. It should be emphasized here that the accumulation of sediments enriched in OM is a process which occurs extensively during transgressive episodes [23].

The generalized curve of eustatic fluctuations in sea level for the Early Eocene [24] shows several partial and small transgressive—regressive episodes which, as also with the Paleocene horizon, may have been responsible for the formation of the series of Eocene sapropelite beds. An increase in bioproductivity in the marine basins was probably also related to the additional supply of biophilic chemical substances which led to the rapid development of several forms of planktonic organism.

The increase in bioproductivity was not simply a growth in the number of organisms, but was accompanied by the introduction of different organisms compared to the preceding period. For example, the number of foraminifera within the sapropelite beds fall, and benthonic forms disappear completely. Simultaneously, quite numerous dinoflagellates appear, which may be regarded as one of the sources of OM within the sapropelite beds. As noted above, scraps of terrestrial plant material are found within these beds, although compared with the amounts of organic material of basinal origin they occur only in subordinate amounts, and the OM is therefore of mixed origin: basinal and terrestrial. The disappearance of benthonic foraminifera is probably related to the establishment of an environment during sapropel accumulation in which they could not survive. This may have been due to hydrogen sulfide within the water column close to the sediment—water interface because of the diffusive flow of H_2S out of the sediments. Quite high concentrations of toxic metals, such as Cu, Ni, Co, and others, within the sapropel pore fluids may have been a further cause [14].

Since the accumulation of carbonate material within the sediments was mainly a result of biogenic deposits, the decrease in the proportion of foraminifera and the flourishing of dinoflagellates and other forms of phytoplankton which are not dominated by carbonate-bearing species, must have had an effect on the amount of $CaCO_3$ buried within the sediments. This was one of the reasons for the decrease in the carbonate content of the sapropelite beds. The diagenetic dissolution of $CaCO_3$ within the OM-rich muds also contributed to its reduction and removal from the sediments. We believe that the decrease in carbonate within the sapropelite beds was due to a combination of these factors, although it is not clear which was the more important.

The geochemistry of the sapropelite beds was affected by various influences: the accumulation of elements within the tissues of living organisms during metabolism; the sorption of elements by the remains of the same organisms during deposition; and diagenetic processes, which led to the accumulation of some and the removal of other elements from the sediments.

Numerous studies have been undertaken which have determined the elemental composition of living organisms and, in particular, of planktonic forms [2, 10, 18, 20, 21, 27, etc.]. It has been shown that almost all of the elements which we have considered are contained within the tissues of various species of phyto- and zooplankton. However, in general, only one or two elements tend to show a marked concentration in any particular planktonic form, and not in such large amounts that they could subsequently enrich the sediments significantly.

The process of sorption of a number of elements from the marine waters by the remains of organisms before they are buried within the sediment is an entirely plausible reason for the enrichment of sapropelites by these elements [5, etc.]. Hydroxides of Fe and Mn may also act as sorbents. However the complex and nonuniform relationship between them and other elements concentrated in the sapropelites prevents us from assessing the contribution of this mechanism in the accumulation of the elements observed.

A number of other factors may have had an influence on the geochemistry of the sediments. Volkov [3] considered the distribution of elements in the sediments of the Black Sea and noted that their behavior depended to a certain extent on the geochemical evolution of the basin, and was controlled by, for example, variations in the hydrodynamic regime of the basin, and related variations in the rate of sediment accumulation; the hydrogen sulfide content of the water column; or the supply to the basin of waters of a contrasting composition (i.e. in terms of salinity or dissolved elements).

However in our case, in the Paleogene succession, it is almost impossible to estimate the rate of accumulation of the sapropelite beds compared to the surrounding sediments since the absolute chronology cannot be determined with sufficient accuracy; and since the deposits were laid down quite rapidly there is insufficient variation in the composition of index fossils in the beds under- and overlying the sapropelites. Furthermore, the amount of hydrogen sulfide within the water column in the Paleogene at the time of the accumulation of the sapropel muds cannot be determined unambiguously: did it affect only the bottom waters, or the entire water column?

Diagenetic processes played a significant role in the geochemistry of the sapropelite beds. Studies of modern sediments have shown that muds enriched in OM undergo transformations caused by the migration of a series of elements out of the bottom waters into the reduced sediments. This is due primarily to the substantial contrast in the oxidizing conditions of the bottom waters compared to the sediments, in which an anaerobic environment is generated. Secondly, sulfate-reducing processes take place within the sediment, leading to sulfide formation. The combination of these conditions leads to elements migrating from the bottom waters into the pore waters within the sediments, and several of them combining with sulfides, usually in the form of authigenic pyrite [1, 6, etc.].

This process requires sulfur, which displays a marked tendency to concentrate within the sapropelite beds (Figs. 2 and 3). It is interesting that, as has been noted, the amount of Fe increases in one bed and decreases in another. It is clear that the great bulk of S in the sapropelite beds goes to form pyrite. A clear correlation would be expected between Fe and S in the interbeds, although this is not always observed. This anomalous behavior of these elements may easily be explained if it is considered that they entered the sediments by different mechanisms. Almost all of the Fe was buried with the sediment during deposition, whereas the overwhelming majority of the S did not enter the sediment until after deposition, during early diagenesis (in the active zone of [11]) as a result of diffusion from the bottom waters. A direct relationship may exist between S and Fe in pyrite, but not with total iron.

Elements such as Mo, Cu, Pb, Ni, and Co are also observed to be enriched in the sapropels, mainly as a result of diffusion into the sediments from the marine bottom waters. However, for the diffusion of these elements to work successfully there must be no oxidizing surface layer of sediments, otherwise the elements will be unable to pass into the sediment pile [4, 12]. Therefore, it must be supposed that with other conditions remaining unaltered the sapropel layer, which remained for longer without a cover of oxidized sediments, was able to become more enriched with elements from the bottom waters. This may explain the different degrees to which different parts of the Paleocene sapropelite layer have been enriched by these elements (Figs. 2 and 3). The relatively thick lower part (sample 11a) is more strongly enriched in Cu and, particularly, Mo than the thinner upper part (sample 11d) which accumulated far faster.

The elements which are introduced to the sediments during diagenesis may enter the sulfide phase. For example, elements such as Cu, Pb, Co, Ni, Mo, and others were observed to have been concentrated within the sulfides of sapropelite beds in the Black Sea [1, 6]. The presence of macroscopic and microscopic pyrite segregations in the Paleogene sapropelites suggests that a number of elements may in this case have combined with sulfides. One sulfide concretion (about 4 cm across) was found to contain the following metal concentrations (in $10^{-4}\%$): Pb, 50; Ni, 370; Co, 44; Zn, 100; Cu, <100; Mo, 10; As, 320; Sb, ~200. If the concentrations of these elements in the concretions are compared with those in the surrounding rocks (Table 1), it is apparent that if the sulfides are enriched in several elements it is only slightly. In general, the concentrations are close to one another. Some proportion of the elements undoubtedly passed into the sulfides, but at the same time the absence of a clear correlation between S and a number of other elements, including chalcophile elements (e.g. in beds 59 and 64; Fig. 3), demonstrates that these elements occur in the sapropelites in a form other than just sulfides.

Diagenetic processes are not only largely responsible for the enrichment of a number of elements in the sapropel muds during deposition, but also for the subsequent marked redistribution of elements within beds. This in particular is associated with the shift note above in the position of the maximum concentrations of some elements relative to the C_{org} maxima, into the upper layer containing less OM enrichment (Figs. 2 and 3). This type of distribution of elements is in some ways similar to the well-known phenomenon where beds of oxidized muds overlying reduced beds are enriched in elements [4, 12]. This is due to the migration of mobile reduced forms of the elements upwards, where they are oxidized and reprecipitated as less mobile compounds.

Elements also migrate in response to the compaction of sapropelite beds, the thicknesses of which reduce to a larger extent during diagenesis than do those of the surrounding sediments. This is because the carbonate content of the sapropel beds is lower that the background values, and the increased OM content of the sapropelites means that they contain more water and are more friable, and consequently have a higher primary porosity. A subsequent higher level of reduction in the thickness of the sapropel interbeds led to pore waters being forced upwards, carrying soluble organic matter [9] and elements which were able to be reprecipitated in the upper parts of the beds, and even in the overlying sediments.

Diagenesis may also be associated with the process of "self-enrichment" by several elements due to a loss of a proportion of the reactive OM and of carbonates, the mechanism for which was proposed by Kholodov and Nedumov [13].

Various diagenetic processes took place simultaneously, and the present distribution of elements is to a large extent the result of these combined processes.

As has already been noted in relation to the discussion on the distribution of $CaCO_3$ in the sediments, diagenetic transformations of the muds may have been responsible for the removal of several components of the sediment. In this case, this relates primarily to Mn, the concentration of which within the sapropelite interbeds decreases markedly in comparison with that of the surrounding sediments. Furthermore the absence of an oxidized layer on the sediment—water interface played an important role both in supplying elements from the bottom waters from into the muds, and also in allowing several elements to migrate out of the muds, and particularly Mn. We consider that removal of Mn during diagenesis is most probable, although the possibility of the original sedimentary material being depleted in Mn should also of course be considered, perhaps due to the hydrogen sulfide content of the water. This has been observed to occur where there is quite a thick column of water containing hydrogen sulfide, in which Mn remains in solution and therefore is not buried with the sediment (for example in the Black Sea [3, 12, etc.]).

In assessing whether the waters of the Paleocene basin were hydrogen sulfide-bearing during accumulation of the sapropel, the following should be considered. The disappearance of benthonic organisms from the sapropelites shows that H_2S was present. But the question of the scale of its occurrence arises, since the interpretation of several geochemical processes taking place in the water column is dependent on this. Within the beds over- and underlying the Paleocene sapropelite there are numerous crawling and burrowing traces of benthonic fauna. The degree of bioturbation in the muds was quite high. The water depth must therefore have been several hundred meters or less. The column of water containing hydrogen sulfide, even at its maximum development, could therefore not have been more than several tens of meters thick, and was probably restricted to the water immediately above the sediment—water interface. But in any case the sedimentary material, including Mn, may on deposition have passed rapidly through the zone of H_2S, and have been little affected by it. In contrast, even if the H_2S was restricted to the layer immediately above the sediment—water interface, it would have created a favorable environment for soluble Mn compounds to have been mobilized, removed from the sediment and dispersed. Subsequently, after the bottom waters became free of hydrogen sulfide, the Mn may have been precipitated and may have enriched the sediment. This may in part explain the quite high Mn content of the surrounding sediments.

A comparison of the Paleogene sapropelite beds with similar beds from other times shows that they have many features in common. For example, the Drevnechernomorsk ("Ancient Black Sea") deposits of the Black Sea include beds which are highly enriched in OM compared to the underlying Novoevksinsk deposits, and they also show an enrichment in certain elements (Mo, Co, Ni, Cu, and V), and a reduction in others (Mn, Ti, and also $CaCO_3$) [3]. However, a comparison of the actual concentrations of the elements shows that the Paleogene beds are richer in Ni, Co, Cu, and V. Only Cr behaved differently in the two locations. Its concentration within the Drevnechernomorsk muds decreased, whereas it accumulated more intensely in the Paleogene beds. A number of papers have reported a tendency for this element to accumulate in reducing environments, although to a much lesser extent than is observed in our case [15 etc.]. Moreover, studies of modern marine basins have shown that Cr can form organic complexes within pore fluids [19]. There is a marked correlation between dissolved OM and Cr (together with Mo and V) in pore waters, which suggests that OM plays an important role in mobilizing these elements [16]. It has been established

that in a number of ancient successions, for example in the oil shales of the Randal—Condor Formation in Australia, an increased Cr concentration is associated with OM, and in particular with the humic acid fraction [22]. So a connection between Cr and OM has been recognized both in modern and ancient deposits. However, this relationship does not hold everywhere, as is shown clearly by the example of the Drevnechernomorsk sapropels [3]. Specialist studies of OM (and particularly humic acids) are needed to confirm the controls on Cr concentrations in the Paleocene sapropelite. Furthermore, a study of the geochemistry of the synchronous Paleocene beds which occur over a wide area will allow the influence of local factors on the geochemistry of chromium to be assessed. The possibility of a local influence is shown by the following. It is known that the sources of chromium-bearing minerals which formed in several Mesozoic successions with very high concentrations were the Paleozoic serpentinite-bearing massifs which are common in the North Caucasus. For example, sandstones from the base of the Liassic deposits in the Northwest Caucasus contain up to 0.28% Cr as the result of enrichment from the breakdown products of serpentinite massifs [7]. It is quite possible that in the period immediately preceding the Paleocene transgression, several serpentinite massifs underwent weathering and subsequently supplied Cr which was incorporated into the sediments. This did not, however, involve simple redeposition of minerals, but the incorporation of Cr into more complex geochemical relationships. In particular, as recent studies have shown, bacteria have a marked influence on the behavior of chromium [25]. The activity of bacteria causes Cr complexes to dissolve and to combine with long-lived polysaccharides. If a similar mechanism operated in the case being examined here, it is quite probable that these polysaccharides were utilized by marine organisms, and subsequently enriched the bottom sediments. During diagenetic redistribution of the sedimentary components, chromium must have participated to a much lesser degree than elements such as Ni and Co, and therefore a clear correlation between Cr and C_{org} was retained.

Apart from the Black Sea sapropels, the Pleistocene sapropel horizons from the sediments of the eastern part of the Mediterranean Sea also display great similarities to the Paleogene beds [17, 28]. On the whole the same groups of components are enriched (C_{org}, S, Fe, Mo, Ni, Pb, Zn, Cu), and impoverished ($CaCO_3$, Mn) The fact that marine sapropelites of different ages, accumulating in dissimilar environments, are generally characterized by similar geochemistries, shows that similar mechanisms must have operated for the enrichment of elements in beds with elevated OM contents. The differences which are observed between them are due to the activity of specific factors related to the particular local conditions of deposition and diagenesis.

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CONTENTS

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