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Geochemistry of the Upper Jurassic-Lower Cretaceous Bazhenov Formation, West Siberia

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Abstract

The Bazhenov Formation (Tithonian to Berriasian) occupies about 1 million km^2 in the central part of the West Siberian plate and is buried by 2,000 to 3,000 m of younger sediments. It was formed in a marine basin connected to the world oceans and is composed primarily of siliceous argillites rich in planktonic organic matter (about 8% of total organic carbon on average). Organic-rich sediments have been accumulating for about 5 to 6 million years; they supposedly formed periodically under anoxic conditions. The aggregate mass of organic matter in the Bazhenov Formation is as high as 18 trillion tons. It is known as one of the largest oil sources in the world. About 500 samples from 39 oil wells throughout the formation were analyzed; it was shown that Bazhenov rocks contain more U, Mo, V, Cu, Zn, and Ni than average black shales; moreover, the concentrations of these elements increase toward the center of the paleobasin. Based on the original data on concentrations of several metals in 500 samples, a representative set of 30 samples was selected and analyzed for 43 chemical elements (using atomic absorption, neutron activation, and X-ray fluorescence analyses) as well as for total organic carbon. Using correlation analysis, the elements determined can be divided into three groups: those associated with organic carbon, with aluminosilicate material, or with carbonates. There is almost complete coincidence between these groups in the Bazhenov rocks and in sapropel from the Black Sea: in both instances total organic cargon is accompanied by Mo, Br, Sb, Cd, V, Cu, S, Ni, As, Ag, U, and Se; for rocks from the Bazhenov Formation, this list also includes Zn. It has been suggested that some of the elements extracted primarily from the seawater by dead planktonic material were later released and that these accumulated in sulfides. By including an enormous amount of elements from the world oceans, the Bazhenov Formation became an important factor in the global geochemical balance of the Jurassic period.

Introduction

THE PERIODIC appearance of giant black shale formations throughout the earth's history has removed great masses of some chemical elements from the geochemical cycle. Among these elements, Krauskopf (1955) listed Mo, Ag, V, Zn, As, and Au. Vine and Tourtelot (1970) added Cu, Ni, and Cr to this list; they also grouped all chemical elements into three associations related to detrital fractionation, organic matter, and carbonates. Holland (1979) emphasized the analogy between metalliferous black shales and sediments from the Black Sea previously proposed by Schneiderhöhn (1955).

In order to detect certain elements in solution, analysts extract them using organic solvents. One can propose that minor elements contained in organic-rich marine planktonogenic sediments reflect their concentrations in ancient seawater, for example, the Upper Jurassic, though Holland (1984) has shown the possible restrictions of this approach. On the other hand, such a unique geologic body as the Bazhenov Formation is an excellent example of a metalliferous black shale deposit whose source is seawater.

Geologic Setting and Organic Geochemical Data

The Jurassic-Lower Cretaceous Bazhenov Formation covers an area of more than 1 million km^2 (Fig. 1). Its thickness ranges from 10 to 60 m, averaging 25 to 30 m. It is buried by 2,000 to 3,000 m of younger sediments and is not exposed at the earth's surface (Bradouchan et al., 1986). The age of the Bazhenov Formation is mainly Volgian (Tithonian) to Berriasian. The lower boundary becomes younger from east to west, from the lower Volgian to the Valanginian.

The Bazhenov Formation is not only one of the world's largest generators of oil but also a unique oil-bearing formation (Nesterov, 1980), which accounts for the many geologic studies that have been done on the area. The principal results have been summarized in several monographs, and schematic maps of organic carbon, distribution of mineral constituents and natural radioactivity, paleogeographical position, and variations in thickness have been published, with special reference to oil and gas geology (Kontorovich, 1974; Kontorovich et al., 1975; Bradouchan et al., 1986). These maps cover only the Bazhenov Formation. Outside the contour of the organic-rich sediments (Fig. 1), formations of the same age have been given other names; moreover, they are thicker and poor in organic matter.

Rocks of the Bazhenov Formation, named bazhenovites by N. Vassoevich (1973, written commun.), are mainly siliceous argillites of black to dark brown color and are either thinly laminated or massive and split into sheets or slabs. Sand and silt grains are very rare, amounting to less than 5 percent. There is a high concentration of biogenous silica (avg 5–20 wt %), accounting for up to 3 percent of total sulfur. Up to 90 percent of the total iron is in the form of sulfides (pyrite and marcasite).

According to Oushatinsky (1984, written commun.), the typical mineral composition is as follows: aluminosilicates + quartz, up to 63 percent; biogenous silica, about 16 but up to 34 percent; organic matter, about 9 but up to 14 percent; carbonate, about 7 but up to 10 percent; pyrite, about 5 percent. The fossils present are mostly pelagic, namely, coccolithophoridae, pterospermaceans, dinoflagellates, radiolarians, ammonites, theutids, and fish. Only two benthonic gen-

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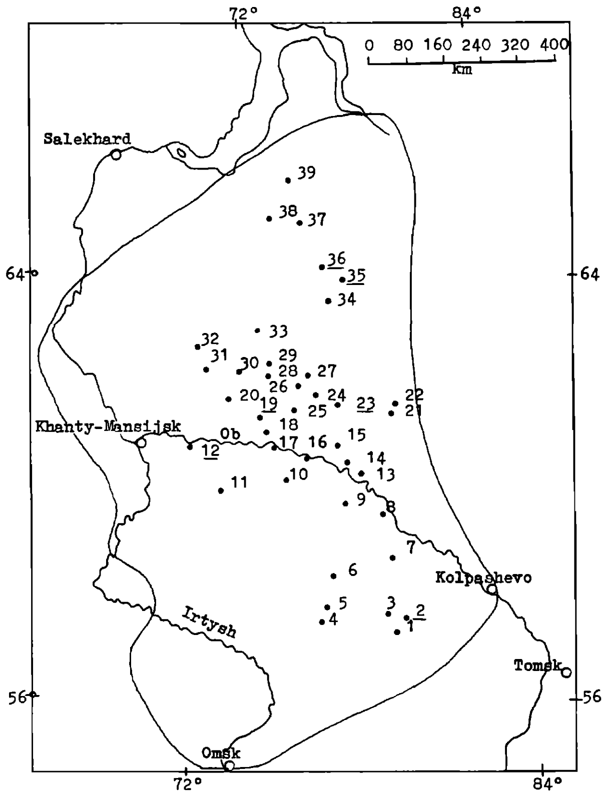

FIG. 1. Locations of the sampled sections of the Bazhenov Formation within the contour of organic-rich sediments distribution, according to Bradouchan et al., (1986). Underlined numbers locate districts where more than one well was sampled.

era are found in the Bazhenov rocks, *Buchia* and *Inoceramus*, the shells of which occur in thin, widely spaced layers. Trace fossils, carnivores, and decomposers have never been observed. There is a distinctive asymmetry in the distribution of fossils in the Bazhenov horizon: more abundant and more diverse assemblages occur along the western and southwestern margin of the West Siberian plate; less diverse assemblages mark the eastern and southern margin. In the northern Urals, in beds of Volgian (Tithonian) age, there are many western European, east Greenland, and central Russian genera and species.

A combined sedimentological and paleoecological analysis of 70 cores from oil wells in the Bazhenov Formation was undertaken to gain a better understanding of its characteristics. Based on these studies, one can conclude that:

1. The Bazhenov Sea was a pseudo-oceanic (given its great depth), epicontinental, pear-shaped sea that covered 2.2 million km^2. On the east, south, and west it was surrounded by low plateaus where chemical erosion dominated under a semihumid, subtropical climate.
2. The central deep-water depression occupied about 1 million km^2. Most of the shallow-water sedimentation took place in the eastern and southern part of the basin. The deepest part was on the western side. Thus, the Bazhenov basin was asymmetrical: the western slope was steep, and the eastern slope quite gentle. A certain successive distribution of rich paleobiocoenoses was distinguished: they change their composition from upper to middle and lower sublittoral, indicating depths of 200 to 250 m. Toward the central part of the paleobasin where organic-rich sediments are situated, most of the benthic forms have disappeared (only *Buchia*

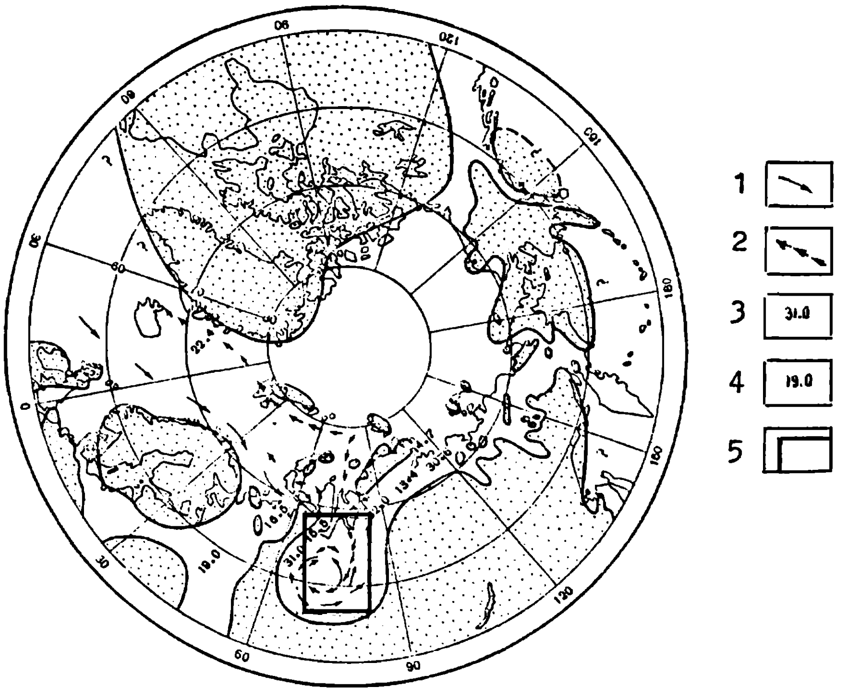

FIG. 2. Schematic paleogeographical map of the Arctic basin and hydrodynamic model of the Bazhenov Sea. From Zakharov and Saks (1983). Dotted areas = land. 1 = warm current; 2 = cold current; 3 = paleosalinity, per mil; 4 = paleotemperature, °C; 5 = contour of Figure 1.

TABLE 1. Rock-Eval Pyrolysis Values (data from Kontorovich et al., 1991)

Depth (m)	TOC (%)	S_1[1] (mg HC/g rock)	S_2[1] (mg HC/g rock)	S_3[1] (mg CO_2/g rock)	T_{max} (°C)	HI (mg HC/g TOC)	OI (mg CO_2/g TOC)
2773–2774.5	13.84	8.46	67.65	2.44	442	489	17

HI = hydrogen index, OI = oxygen index, TOC = total organic carbon

[1] Rock-Eval pyrolysis program from Peters (1986)

and *Inoceramus* are left) and pelagic fauna obviously prevail (radiolaria, ammonites, belemnites, and fish). A water flux from depth to the photic zone was necessary for biotic nutrition. Extrapolations of the change in faunal composition from sublittoral to the central part of the paleobasin give depth estimates of as much as 500 m (Golbert and Kontorovich, 1978; Bradouchan et al., 1986).

3. The Bazhenov basin was connected to the Arctic Sea by two straits, the Yamal strait, which ran in a northerly direction, and the Yenisey-Khatanga strait, in a northeasterly direction (Fig. 2). The warm surface current from the Barents Sea moved through the Yamal strait, flowing along the Ural peninsula, and then turned to the east, thereby producing a counterclockwise gyre. The cold bottom waters flowed in the opposite direction, entering the basin through the Yenisey-Khatanga strait and probably also the Yamal strait. This reconstruction of the currents best explains the asymmetric distribution of the Bazhenov marine biota.

4. Differences in fauna in shallow- and deep-water sediments indicate that surface waters were considerably warmer than bottom waters. Oxygen isotope paleotemperature analyses support this conclusion. They indicate surface water temperatures of 16° to 18°C in the northern part and 20° to 22°C in the southern part; bottom-water temperatures were considerable lower (Bradouchan et al., 1986).

5. Only open-marine stenohaline organisms, such as radiolaria, coccoliths, cephalopods, and bivalves, lived in the Bazhenov Sea.

6. During the period of the Bazhenov Sea (5–6 Ma), 18 trillion tons of organic matter accumulated. The average rate of subsidence was 0.012 to 0.015 mm per year. This is the reason why the Bazhenov Formation is only 25 to 30 m thick, compared to surrounding formations of the same age that are poor in organic matter and 150 to 250 m thick (Oushatinsky and Zaripov, 1978, written commun.).

According to microscopic investigations, between 80 and 100 percent of the organic matter in the Bazhenov Formation is amorphous (Parparova and Nerouchev, 1971), with planktonic algae making up the bulk. This conclusion is strongly supported by organic geochemical data on one sample taken from the central part of the organic-rich area (Kontorovich et al., 1991; Table 1). Additional pyrolytic data give rather similar hydrogen index values (Table 2).

TABLE 2. Organic Geochemical Data (from Gouray et al., 1988)

Sample no.	TOC (%)	EOM	S_1[1]	S_2[1]	HI
9	6.7 ± 1.9	7,700 ± 2,300	4.9 ± 1.5	30.0 ± 9.1	459 ± 58
23	10.2 ± 1.6		5.9 ± 1.0	29.1 ± 5.1	341 ± 116

EOM = chloroform extractable organic matter (ppm to dry rock weight), HI = hydrogen index, TOC = total organic carbon

[1] Rock-Eval pyrolysis program from Peters (1986)

The diagram of the hydrogen index versus oxygen index (Fig. 3) shows that the mudstone of the Bazhenov Formation (Table 1) falls within the same range as that for organic matter in Jurassic sediments from Saudi Arabia and France, referred to as "type II (oil prone) marine organic matter" (Peters, 1986). Using the distribution of biomarkers, Kontorovich et al. (1991) postulated that Bazhenov organic matter is an "aquagenic" (marine) type, which fits in with the fact that type II of the hydrogen index versus oxygen index diagram also contains a significant amount of algal and bacterial material (Clayton et al., 1992). For this type of organic matter, Kontorovich et al. (1985) determined that $\delta^{13}C = 30$ to 31 per mil. The data on chloroform-extractable organic matter (Table 2) and vanadium porphyrin content (up to 6,000–10,000 ppm relative to extractable organic matter; from Kontorovich et al., 1985) are close to other published data, for example, those for Middle Pennsylvanian black shales (Clayton et al., 1992). The present temperature of the Bazhenov Formation is 80° to 100°C (Gouray, 1988). The thermal maturity of organic matter can be estimated by the vitrinite reflectance index: $R^a = 70–86$ per mil, corresponding to $R^o = 0.5$ to 0.9 percent (Kalmykov, 1979, written commun.; Eremin, 1982; Gouray, 1988).

Organic matter was primarily of pelagic origin. The first-order consumers were microzooplanktonic and bottom-living mollusks; the second-order, bony fish and cephalopods; and the highest order, ichthyosaurus. The presence of benthos (*Buchia* and *Inoceramus*) in some thin layers within bituminous sediments does not presume the permanent existence of a hydrogen-sulfide-saturated deep-water zone. But the absence of benthic forms between these layers may correspond to euxinic conditions. Resumption of oxygenated conditions

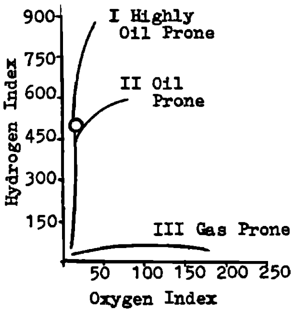

FIG. 3. Plot of whole-rock hydrogen index (HI) vs. oxygen index (OI). From Peters (1986). Circle = data from Kontorovich et al. (1991).

TABLE 3. Statistical Estimates of Minor Elements Content (in ppm, except K) of West Siberian Plate

Location no. (Fig. 1)	No. of cores	Thickness of sampled interval (m)	eU[1]	Mo	V	Cu	Zn	Ni	Co	Mn	Th	K (%)
1	16	14	9.1 ± 1.0	<30	85 ± 25	110 ± 20	190 ± 30	120 ± 10	20 ± 7	230 ± 60	11 ± 2	3.13 ± 0.36
2	17	35	30.3 ± 8.4	90 ± 15	345 ± 45	120 ± 10	470 ± 73	240 ± 40	22 ± 5	195 ± 60	6.6 ± 1.1	1.66 ± 0.51
3	9	11	30.8 ± 6.1	110 ± 20	290 ± 70	120 ± 20	480 ± 140	180 ± 30	17 ± 3	80 ± 70	5.7 ± 0.8	1.09 ± 0.36
4	26	20	35.7 ± 5.6	90 ± 20	300 ± 40	130 ± 15	400 ± 75	200 ± 20	25 ± 5	130 ± 30	6.5 ± 0.6	1.40 ± 0.16
5	29	22	45.0 ± 6.3	120 ± 20	285 ± 30	150 ± 20	460 ± 90	220 ± 25	20 ± 2	55 ± 30	5.6 ± 0.8	1.22 ± 0.14
6	19	15	57.3 ± 11	170 ± 25	340 ± 40	130 ± 10	460 ± 75	220 ± 25	25 ± 5	140 ± 30	3.9 ± 0.8	0.86 ± 0.13
7	13	28		145 ± 55	80 ± 110	120 ± 20	420 ± 165	245 ± 85	25 ± 5	280 ± 10		
8	7	9	66.4 ± 29	160 ± 50	400 ± 140	110 ± 30	420 ± 145	245 ± 75	26 ± 6	140 ± 70	3.2 ± 2.4	0.83 ± 0.54
9	7	13	67.7 ± 32	280 ± 130	590 ± 275	145 ± 45	775 ± 460	280 ± 90	30 ± 9	60 ± 30	1.4 ± 1.8	0.65 ± 0.35
10	4	4		33	397	256 ± 50	850 ± 60	168 ± 59	20 ± 9	147		
11	13	33	39.6 ± 10	130 ± 70	525 ± 160	200 ± 50	600 ± 260	195 ± 55	23 ± 3	190 ± 100	8.7 ± 2.6	1.21 ± 0.85
12	11		50.7 ± 18	227 ± 79	655 ± 160	288 ± 55	1,045 ± 330	230 ± 48	23 ± 4	239 ± 133	2.9 ± 2.9	0.98 ± 0.81
12	21		63.8 ± 11	242 ± 42	837 ± 95	240 ± 48	1,188 ± 214	327 ± 35	25 ± 3	116 ± 28	5.0 ± 1.1	0.55 ± 0.20
12	27		40.2 ± 7.4	221 ± 45	1,013 ± 183	258 ± 39	1,035 ± 219	305 ± 36	28 ± 4	158 ± 68	4.2 ± 1.0	0.92 ± 0.17
13	18	23	39.3 ± 16	140 ± 40	350 ± 90	115 ± 20	450 ± 115	215 ± 55	25 ± 5	210 ± 70	6.2 ± 1.4	1.50 ± 0.95
14	6	6	57.8	235	540	150	1,045	390	37	112	6.0	0.95
15	5	7		250 ± 50	460 ± 115	180 ± 70	790 ± 330	620	48	255		
16	3	2		161	641	188	698	261	26	468		
17	14	17		270 ± 55	720 ± 160	165 ± 25	1,035 ± 275	310 ± 40	23 ± 3	100 ± 20		
18	26	15	104 ± 28	205 ± 40	715 ± 145	185 ± 25	990 ± 140	325 ± 45	26 ± 4	85 ± 10		
19	22	34		210 ± 30	735 ± 115	220 ± 30	1,040 ± 200	320 ± 60	29 ± 8	110 ± 20		
20	7	9		140 ± 80	470 ± 170	145 ± 25	900 ± 30	225 ± 100	21 ± 9	436		
21	19	9	9.4 ± 6.4	<30	190 ± 45	120 ± 20	260 ± 85	70 ± 15	15 ± 3	255 ± 25	8.9 ± 2.0	2.59 ± 0.43
22	3	5		80 ± 25	250 ± 60	117	460 ± 100	170 ± 25	19 ± 2	250		
23	23	22		190 ± 95	745 ± 225	170 ± 30	1,095 ± 270	310 ± 50	30 ± 7	130 ± 45		
24	5	5			394	150 ± 70	620	155 ± 75	29	185 ± 100		
25	33	20		230 ± 40	780 ± 120	200 ± 35	960 ± 165	325 ± 40	31 ± 5	120 ± 30		
26	2	2		103	505	230	728	171	22	297		
27	11	13		160 ± 60	590 ± 70	135 ± 35	1,080 ± 580	290 ± 115	23 ± 8	160		
28	9	14		135 ± 85	880 ± 470	140 ± 55	980 ± 435	270 ± 160	19 ± 7	90 ± 15		
29	6	24		87	685 ± 350	200 ± 100	695	185	15	150 ± 95		
30	4	4		299	890 ± 420	350 ± 140	940 ± 320	360	37	195		
31	13	13		15 ± 12	230 ± 100	220 ± 45	550 ± 215	160 ± 30	12 ± 5	75 ± 20		
32	23	18		235	837	200	1,155 ± 860	395	31	120 ± 50		
33	5	6		285 ± 85	1,015 ± 290	295 ± 135	840 ± 180	370 ± 60	35 ± 5	90 ± 3		
34	8	8		90 ± 20	600 ± 150	190 ± 65	1,050 ± 410	170 ± 20	20 ± 3	310 ± 145		
35	2		16.5	60	370	75	500	180	25	280	11.5	2.58
36	1		56.0	270	2,450	220	2,350	725	35	105	3.8	1.98
37	2	14			87	25	88	60	19	483		
38	4	12			284	115	171	111	24	263		
39	3	8		153	576	138	596	566	54	161		
Average black shales												
	a		15.2 (U)[2]	65	500		310		16.9	383	11.6	2.99
	b		12 ± 1 (U)[2]		200 ± 10	70 ± 3	130 ± 10	70 ± 2	19 ± 1	400 ± 200		

Average values: a, from Yudovich and Ketris (1990, written commun.); b, from Quinby-Hunt et al. (1989), means for the low calcic black shales

[1] eU = equiv uranium (estimate of uranium content through the activity of its decay products)

[2] U = uranium content directly determined

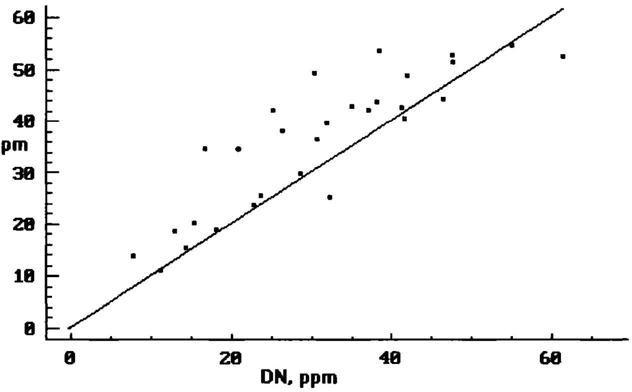

FIG. 4. Gamma-ray spectrometric data (eU) vs. delayed neutron (DN) uranium determinations plot.

depended upon the sill depth in the Yamal strait. At times of shallowing of the sill depth, the exchange of Arctic and Bazhenov seawaters was reduced. During such periods the deepest parts of the Bazhenov Sea would be anoxic (the validity of euxinic condition criteria will be discussed later). With an increase in the sill depth, more oxygen could reach the deep parts of the basin. It was during these periods that Arctic mollusks migrated to the deep parts.

Low rates of sedimentation, high biological productivity, connection with the world oceans as a source of chemical elements, intensive chemical weathering on surrounding plateaus, active circulation currents, periodical anoxic conditions--all these features facilitate the enrichment of deep-water sediments in particular elements, primarily metals.

Sampling and Analytical Methods

In order to outline the distribution of minor elements inside an area of maximum organic matter content, certain sections containing oil wells were sampled. The cores (from 1 to 33), representing thicknesses ranging from several meters up to 35 m, were taken from 39 districts (Table 3). The network of sampling was not complete but permitted some conclusions concerning the distribution of several minor elements throughout the area investigated (Fig. 1). The uranium content given in Table 3 was determined by gamma-ray spectrometry; the accuracy of these data was proved by comparison with delayed neutron analysis (Fig. 4).

Thirty cores with an average total organic carbon content of about 8 percent were then chosen from the entire set of 500 cores: 17 cores were taken from four wells within district 2, and the other 13 cores from several wells in districts 12, 19, 23, 36, and 37 (Fig. 1). The above value of 8 percent is close to the average value given for the Bazhenov Formation

TABLE 4. Results of the Standard Samples Analyses (ppm)

Elements	SGD-1A, gabbro		SDO-1, black shale	
	This study	Reference	This study	Reference
Li	15 ± 0.8 a	14 ± 3	21 ± 4 a	28.6 ± 5.5
Rb	74 ± 2	73 ± 4	116 ± 2 a	126 ± 3.9
Cs	3.8 ± 0.2	3.8 ± 0.4	5.5 ± 1.2	6.9 ± 1.2
Be	2.4 ± 0.2 a	2.0 ± 0.4	2.2 a	3.3 ± 0.6
Sr	2,251 ± 104	2,300 ± 200	58 ± 12 a	75.1 ± 11.0
Ba	1,300 ± 46	1,300 ± 100	400 a	397 ± 38
Sc	26.7 ± 0.4	27 ± 3	18	13.2 ± 1.5
La	77 ± 1.5	80 ± 2	39 ± 1	38.5 ± 5.5
Ce	153 ± 4	150 ± 10	79 ± 3	79.3 ± 7.8
Sm	19.1 ± 1.0	17 ± 1	7.5 ± 0.3	7.7 ± 0.81
Eu	3.98 ± 0.12	5 ± 1	1.9 ± 0.2	1.6 ± 0.22
Tb	1.44 ± 0.06	1.4 ± 0.2	1.17 ± 0.16	1.2 ± 0.24
Yb	2.03 ± 0.13	2.9 ± 0.5	3.8 ± 0.4	3.4 ± 0.46
U	2.2 ± 0.3	2.0 ± 0.5	52	48.8 ± 6.5
Th	8.4 ± 0.5	9 ± 1	10.9 ± 0.6	10.5 ± 0.55
Hf	5.8 ± 0.3		5.1 ± 0.3	4.7 ± 0.75
V	223 ± 7 a	240 ± 20	148 a	160 ± 21
As	1.8 ± 0.4	1.8 ± 0.2	67 ± 5	68.5 ± 8.6
Sb	0.26 ± 0.04		4.3	4.1–4.8
Ta	0.61 ± 0.10	1.1 ± 0.4	1.3 ± 0.2	1.1 ± 0.13
Cr	50 ± 4	55 ± 4	67	66.4 ± 7.6
Mo			153 ± 30 a	134 ± 21
Mn	1,192 ± 30 a	1,300 ± 100	310 ± 127 a	324 ± 39
Co	39.8 ± 1.6	40 ± 5	42 ± 8 a	46.8 ± 6.3
Ni	40 ± 2 a	50 ± 5	86 ± 14 a	99.5 ± 9.9
Cu	67 ± 2 a	68 ± 7	49 ± 8 a	60.2 ± 9.6
Zn	126 ± 3	120 ± 10	57 ± 9 a	64.1 ± 6.9
Pb	23 ± 2	17 ± 2	34 a	27.9 ± 5.2
Ag			0.029 a	0.092–0.17
Cd			0.06 a	<10
Se			1.4 a	3–6.8

Analytical methods: a = atomic absorption (analyst, L.N. Boukreeva), other = neutron activation analysis (analyst, V.S. Parkhomenko)
Reference values: for SGD-1A, from Govindaraju (1984) and other sources; for SDO-1A, from Kane et al. (1990)

TABLE 5. Statistical Estimates of the Bazhenov Formation Chemical Elemental Composition: A Comparison with Global Means

		Set of 30 cores				Average black shale	
Element	Method	Average	Range	39 cores	21 cores	a	b
Li	A	27 ± 10	17–46			31 ± 2	
Na	A, N	0.95 ± 0.11	0.51–1.39				0.53
K	A	1.81 ± 0.21	0.80–2.67	0.93 ± 0.15	0.55 ± 0.20		2.99
Rb	N	90 ± 12	40–60			74 ± 4	131
Cs		9.1 ± 1.3	3.8–15.2			4.7 ± 0.4	8.6
Be	A	3.4 ± 1.0	1.1–7.7			2.0 ± 0.1	
Mg	A	0.80 ± 0.18	0.22–2.56				1.04
Ca	A	1.58 ± 0.68	0.34–8.74				1.71
Sr	X	248 ± 37	142–1577			190 ± 10	310
Ba	A	320 ± 100	84–1,436			500 ± 20	1120
Al	A	5.92 ± 0.60	3.23–9.50				8.21
Sc	N	16.4 ± 1.2	10.2–21.0			12 ± 1	15.6
Y	X	24 ± 4	10.3–67.7			26 ± 1	
La	N	27 ± 3.4	12–52			29 ± 1	44
Ce	N	53 ± 5.6	29–92			44 ± 4	80
Sm	N	6.3 ± 0.7	3.1–10.0			3.7 ± 0.3	6.2
Eu	N	1.34 ± 0.16	0.92–2.98			1.1 ± 0.03	1.27
Tb	N	0.89 ± 0.10	0.50–1.71			0.64 ± 0.04	0.95
Yb	N	3.23 ± 0.35	1.66–5.69			2.6 ± 0.1	3.10
Si		26.00[1]					
Ti	A, N	0.32 ± 0.03	0.14–0.53			0.30 ± 0.01	0.43
Zr	X	148 ± 15	87–284			120 ± 5	230
Hf	N	3.13 ± 0.42	1.2–5.7			4.2 ± 0.3	4.3
Th	N	6.3 ± 0.8	2.7–12.5	3.5 ± 0.8	5.0 ± 1.1		11.6
U	N	35.7 ± 7.0	12–97	59.4 ± 1.2	63.8 ± 11.4		15.2
Cr	N	80 ± 10				96 ± 3	111
Mn	A	202 ± 66	70–1,016			400 ± 200	383
Fe	A, N	3.83 ± 0.63	1.52–9.17				3.68
Co	A, N	23 ± 3	11–46	24 ± 3	25 ± 3	19 ± 1	16.9
Ni	A	192 ± 27	101–422	235 ± 24	327 ± 35	70 ± 2	
Cu	A	136 ± 18	74–287	143 ± 15	240 ± 48	70 ± 3	
Ag	A	1.2 ± 0.7	0.33–9.55			1.0 ± 0.1	
Au	A	4.2 ± 1.5				7	23
Zn	A	659 ± 185	255–2,142	561 ± 97	1,188 ± 214	130 ± 10	310
Cd	A	14 ± 4	1.8–49.0			5.0 ± 0.6	
Hg	A	2.6 ± 0.7	0.08–7.5			0.27 ± 0.03	
Pb	A	16 ± 4	7–66			21 ± 1	
P		0.11[1]					
V	A	461 ± 149	150–2,227	421 ± 70	837 ± 95	200 ± 10	500
S		2.83[1]					
Se	A	27 ± 8	9.5–108.4			8.7 ± 1.4	5.6
As	N	45 ± 10	18–136			30 ± 3	28.8
Sb	N	6.9 ± 2.6	1.5–26.0			4.9 ± 0.5	5.7
Nb	X	7.3 ± 1.2	1.9–13.8			12 ± 1	
Ta	N	0.55 ± 0.07	0.22–0.88			0.7 ± 0.1	0.9
Mo	A	123 ± 27	16–268	168 ± 31	242 ± 42	20 ± 1	65
Sol.		9.7 ± 2.2	2.0–31.0	8.1 ± 1.7	9.8 ± 0.4		
TOC		8.0 ± 1.3	3.20–18.16	10.1 ± 1.1	12.5 ± 1.5		

Data in ppm, Au in ppb, Na, K, Mg, Ca, Al, Si, Ti, Fe, P, S, Sol., and TOC in percent

Methods: A = atomic absorption, N = neutron activation, X = X-ray fluorescence

Data in columns: set of 30 cores = Bazhenov Formation, representative set with average TOC about 8%; set of 39 cores = six districts in central part of West Siberian plate (5, 6, 8, 9, 11, and 18 in Fig. 1); set of 21 cores = a single oil well, Salym area, point 2 in Figure 1; average values for black shales: a, from Yudovich and Ketris (1990, written commun.); b, from Quinby-Hunt et al. (1989), means for the low calcic black shales

[1] Data from Oushatinsky (1981), averages of 793 cores

Sol. = HCl-soluble material, TOC = total organic carbon

by Kontorovich et al. (1971), Khabarov et al. (1980, written commun.), and Oushatinsky (1984, written commun.). All 30 samples were analyzed using X-ray fluorescence (XRF), atomic absorption spectrometry (AAS), and instrumental neutron activation (INA) techniques. The reproducibility and accuracy of analytical results can be estimated from Table 4, which gives analytical data for two reference samples being analyzed.

The statistical treatment procedure included the estimates of arithmetic mean values at a 0.05 confidence level: $\bar{x} \pm \Delta\bar{x} = \bar{x} \pm s \times t\ (P,f)/n$, where $\bar{x}$ = arithmetic mean, $\Delta\bar{x}$ = confidence interval, s = standard deviation, t = Student's

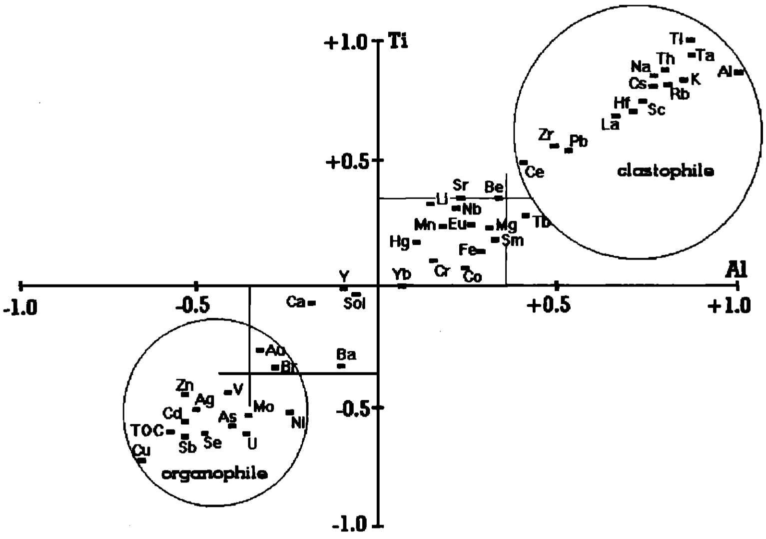

FIG. 5. Correlation coefficients of chemical elements with Al (x axis) vs. Ti (y axis).

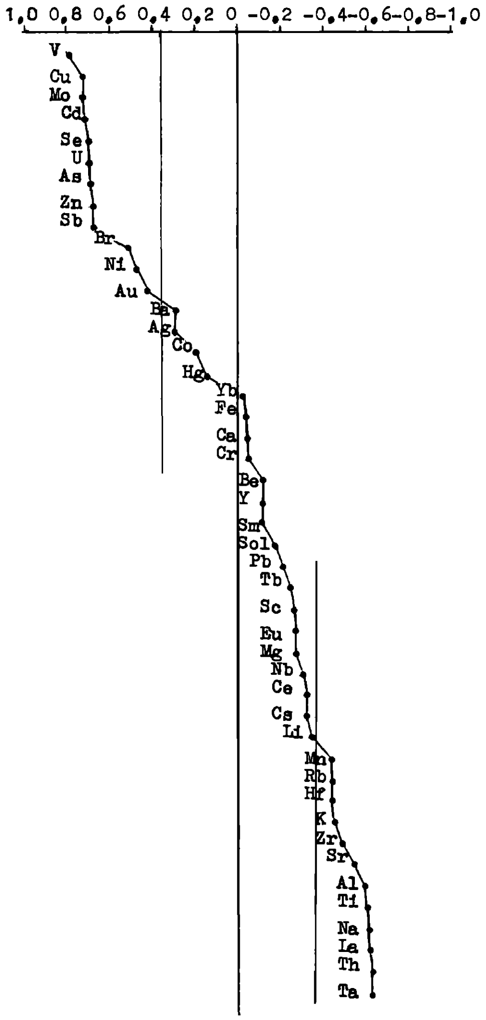

FIG. 6. Range of the chemical elements according to their correlation with total organic carbon; 0.05 confidence level: $r = 0.35$.

criterion, n = number of samples, P = accepted probability, $f = n - 1$. This treatment is recommended for the cases of normal distribution of analytical data. However, using the partial means method (Vasilenko et al., 1978, written commun.), it was demonstrated that statistical deviations only weakly depend on the distribution pattern of the analytical results.

Owing to the similarity of the organic matter content in our set of samples and the Bazhenov Formation as a whole, it is proposed that the minor element content computed from our set of samples is also representative of the Bazhenov Formation in general. In addition we have attempted to select the elements that accompany the organic matter in sediments using correlation analysis.

Results

As shown in Table 3, the U, Mo, V, Cu, Zn, and Ni contents in Bazhenov sediments enriched in organic carbon are similar to those reported for some black shales, for example, the Cambrian alum shale in Sweden and Appalachian Devonian shales in the United States (Armands, 1972–1973; Leventhal, 1991).

The concentrations of all the above elements together with organic carbon decrease from the center of the area investigated toward the north, south, and east, whereas thorium and potassium concentrations grow markedly from the center toward the periphery (Fig. 1, Table 3). Owing to the irregularity of sampling, however, it is not worthwhile to show this tendency by isolines.

In addition to U, Mo, V, Cu, Zn, and Ni, the more complete list of elements accompanying the organic carbon includes Ag, Au, Cd, As, Sb, Se, and Br (Table 5). The last element is not included in the tables because its content was estimated after INA in values of radioactivity only; this nonetheless allowed calculation of the correlation coefficient between Br and total organic carbon ($r = 0.52$). We shall discuss the ratio of total organic carbon to sulfur later.

Correlations between chemical elements show two alternative geochemical associations: "clastophile," elements related

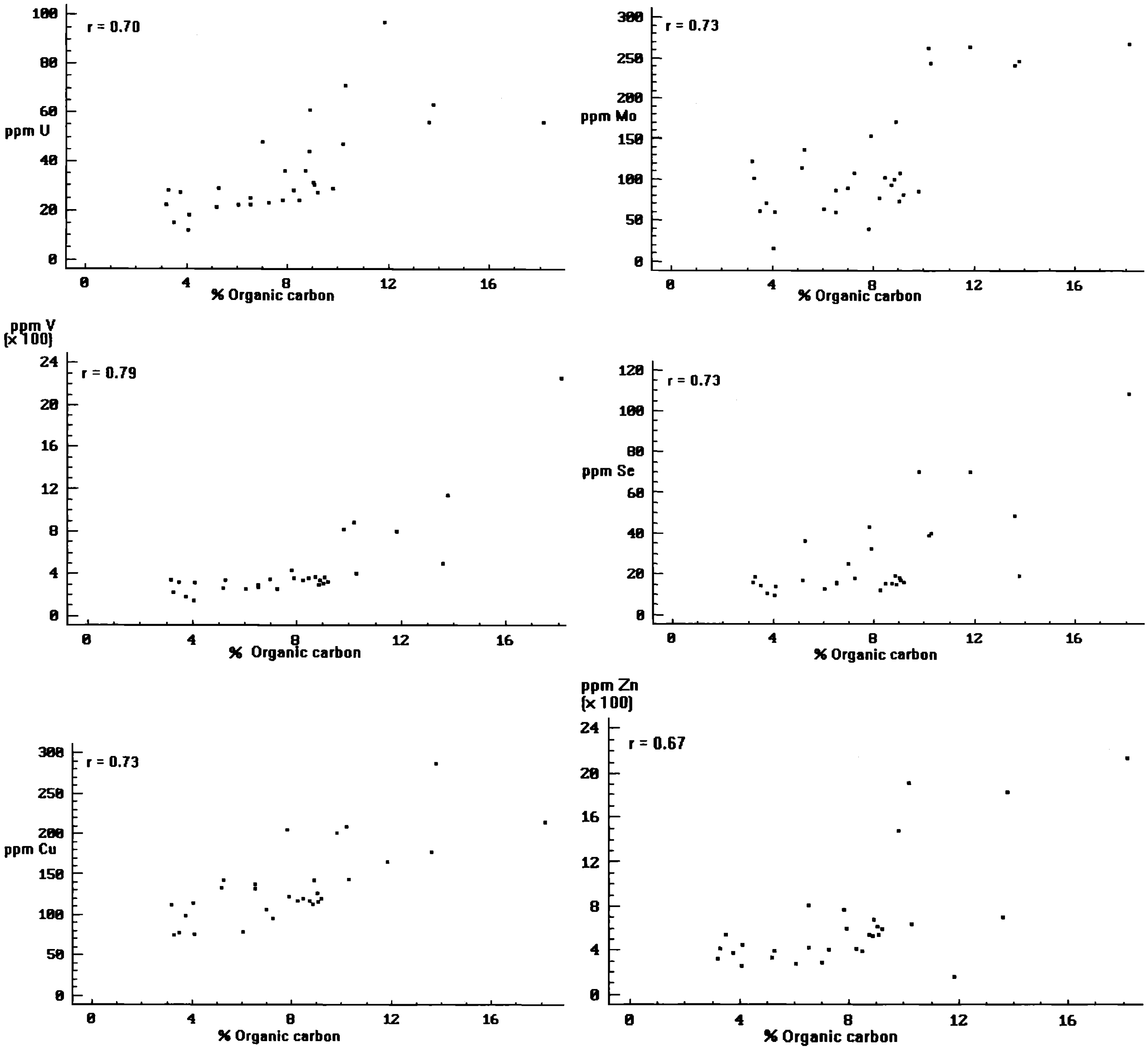

FIG. 7. Plots of some organophile elements vs. organic carbon for 30 cores of Bazhenov Formation rocks.

to aluminum and titanium (the usual components of terrigenous mineral fraction), and "organophile," elements related to the organic matter and accompanying sulfur (Fig. 5); several elements placed in Figure 5 between the two associations were probably influenced by both of these as well as by other factors; the correlation coefficients to aluminum and titanium are beneath the confidence levels shown. Organophile does not necessarily imply a chemical bond between metals and organic matter but rather only the coexistence of metals and organic matter in sediments. Another approach based on correlation of the elements with total organic carbon also clearly demonstrates the existence of two opposite geochemical associations (Fig. 6).

The distribution of clastophile elements is characterized by coefficients of variation between 19 and 36 percent; for organophile elements, with the exception of Cu and Ni, these values are higher than 50 percent and can be as high as 80 to 90 percent, whereas for total organic carbon, the coefficient of variation is 42 percent. Correlation coefficients of U, Cu, Ag, Zn, Cd, As, Sb, Se, and Mo with total organic carbon range from 0.67 to 0.73, with a confidence level of 95 percent (Fig. 7). Because of these correlations, the pattern of distribution of organophile elements shows a good coincidence with previously published maps of organic carbon content (Bradouchan et al., 1986). The dilution of organic matter by terrestrial aluminosilicate material decreases the amount of all organophile elements.

The consistent correlation of organophile elements with

TABLE 6. Content of Some Elements in Pyrite Grains

Grain	Fe	S (%)	Total	Ni	Cu (ppm)	Zn
1	45.74	54.42	100.96	1,650	690	240
2	45.66	54.65	101.40	1,770	1,110	140
3	46.11	53.16	100.09	100	480	200
4	46.45	54.13	101.43	180	170	260
5	46.39	53.48	99.98	400	420	310
6	45.60	53.24	99.23	1,750	1,620	560
7	46.66	54.39	101.18	350	580	430
8	46.20	53.38	99.73	310	470	740
9	46.17	54.09	100.34	190	290	310
10	43.18	51.05	94.47	810	730	810
11	45.49	53.42	98.99	190	620	n.d.
12	41.83	48.08	90.31	3,800	260	n.d.
13	41.31	45.06	86.77	2,240	750	920
14	40.17	48.12	89.07	5,610	2,180	n.d.
15	35.07	41.47	77.10	2,670	3,000	n.d.
16	40.61	47.49	88.71	4,190	1,580	410
17	43.66	48.83	92.59	490	370	260
18	44.13	52.20	96.43	240	480	240

One sample, core from district 2 in Figure 1
Grains 13–18 are too small to recognize optically
n.d. = not determined

organic carbon suggests the sorption or chemical linkage between these elements and organic matter at the early stages of the sedimentation process. However, electron microprobe analysis shows that a significant part of some elements is at present bonded to the framboidal and xenomorphic grains of substoichiometric pyrite dispersed through the organomineral matrix. Some sulfide grains are too small to be recognized by optical observation, but they are found owing to the high sulfur content corresponding to high values of Ni, Cu, Zn, As, and Mo (Table 6).

Discussion

One of the key questions concerning the problem of metalliferous black shales is whether we can consider seawater a source of metals. To answer this question, it is necessary to see which elements are concentrated in the organic-rich abyssal sediments of the Black Sea presently being deposited from water with a well-known chemical composition. A triangle diagram (based on statistical estimates: Gavshin, 1991) shows the remarkable concentration of Mo, Br, Sb, Cd, V, Cu, S, Ni, Ba, As, Ag, U, and P in sapropelic mud.

A triangle diagram can also be drawn for bazhenovites after dividing the 17 selected samples into three groups--those with Al > 7 percent, those with total carbon >10 percent, and those with Ca >4 percent--and then computing the mean values of the chemical element content for each group. The three sets of data in Figure 8 show nearly the same distribution pattern for elements as the one for sapropelic mud (Gavshin, 1991). This similarity suggests that the processes of planktonogenic sediment enrichment by metals in the Recent Black Sea and Jurassic Sea of the West Siberian plate were rather similar. Both triangle diagrams also reflect the dilution effect of terrigenous and carbonate materials on organophile element content. What appears enigmatic in the differences between the two diagrams is the absence of zinc in the Black Sea's organophile association, since it is one of the most characteristic elements in bazhenovites. It is noteworthy that the

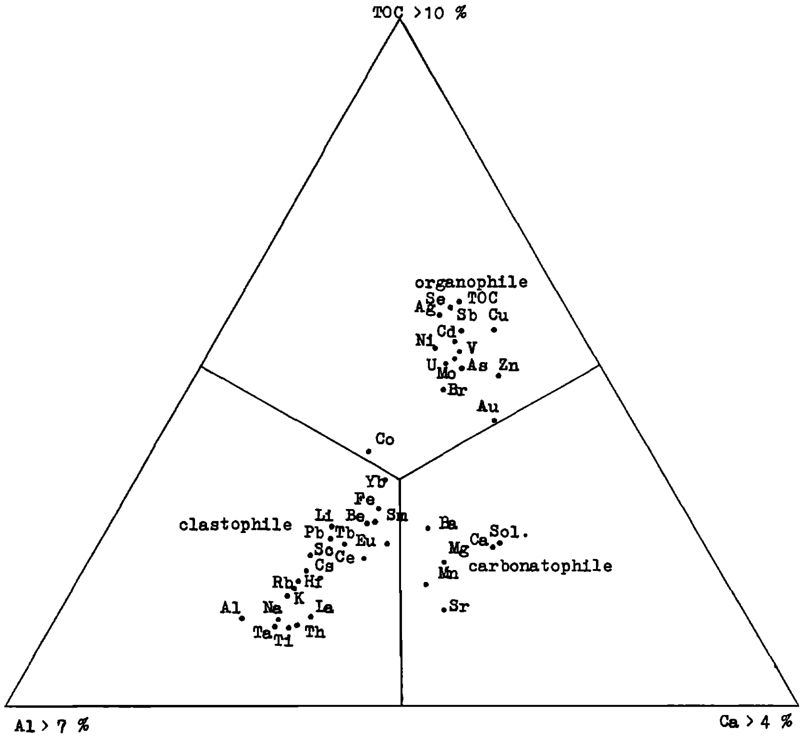

FIG. 8. Chemical element associations in organic-rich sediments of the Bazhenov Formation.

concentration of the majority of organophile elements in bazhenovites is much higher than the averages for black shales given by Vine and Tourtelot (1970), Quinby-Hunt et al. (1989), and Yudovich and Ketris (1990, written commun.; Tables 3 and 5).

The next problem is related to the time of concentration of minor elements in planktonogenic material. It has been shown that living planktonic organisms do not contain metals (except zinc) in concentrations comparable to those in sapropelic mud or black shales (Loukashin and Shiganova, 1987). The most probable assumption is that minor elements are extracted from the seawater by dead planktonic material. Among the products of planktonic organism decomposition, "humic substances" of a melanoidine type are formed by the reaction between amino acids and carbohydrates (Manskaya and Drozdova, 1964; Ouspensky et al., 1977, written commun.). Melanoidine and humic acid possess certain similar properties (Hoering, 1973). Both melanoidines and humic acids have in their structure sites favorable for fixation of some cations--Fe, Al, U, Cu, Zn, Mo, Co, and other elements--through ion exchange and chelation (Manskaya and Drozdova, 1964; Leventhal, 1985). The extraction processes could occur during the fall of organic matter particles through the water column and somewhat later, in the early stages of diagenesis. This is one way to explain the strong correlation between organic carbon and certain metals in sediments.

One can estimate the quantitative ratios of total organic carbon and sulfur from published statistical data (Kontorovich et al., 1971; Oushatinsky, 1981). These data do not allow us to see the scatter of individual values, but they do show the main tendency: the majority of points in Figure 9a are close to the normal marine line given, for example, by Leventhal (1983). The general Fe to S ratio poorly satisfies the FeS_2 stoichiometry that Leventhal (1993) considers to be the evidence of iron deficiency, resulting in the release of hydrogen sulfide from sediments. There are several exceptions--e.g., the samples low in total organic carbon where sulfate reduction was limited by the deficiency of organic carbon (Fig. 9b). A similar tendency in Cambrian alum shale from Sweden was presented as evidence of deposition under a euxinic environment (Leventhal, 1991). This suggestion does not contradict the above assumption of periodic anoxic conditions based on paleobiological data.

Further decomposition of organic matter and hydrogen sulfide generation in sediments during diagenesis led to the partial translation of metals into pyrite, but under euxinic conditions some quantity of metals could combine with sulfides still in the water column. Electron microprobe profiles demonstrate the enrichment of sulfides by Ni, Cu, and Zn and to some extent by As and Mo (Fig. 10). Besides the rather large grains, there are also micrograins enriched in iron, sulfur, and accompanying metals in the matrix of the shale; in some cases the micrograins contain more Ni and Cu than the relatively large grains. The amount of metals found by electron microprobe analysis is comparable to that reported by Volkov and Smertina (1984, written commun.) on the basis of heavy fractions investigation; they concluded that only a certain part of bulk metal concentrations is related to pyrite (up to 30% of Ni, 50% of Cu, 25% of Zn); the remaining quantities are probably contained directly in the organo-mineral matrix. According to results of INA analysis, pyrite is enriched in arsenic, antimony, and to some extent, gold (Table 7). Electron microprobe analysis shows also that part of the total uranium is contained in the calcium phosphate of fish scales and that large fragments of scales (>0.1 mm) contain less uranium than small ones (Table 8). Concentration of planktonic matter under conditions of slow sedimentation with minor quantities of allochthonous terrigenous material resulted in extraction of the enormous amounts of organophile elements from the seawater.

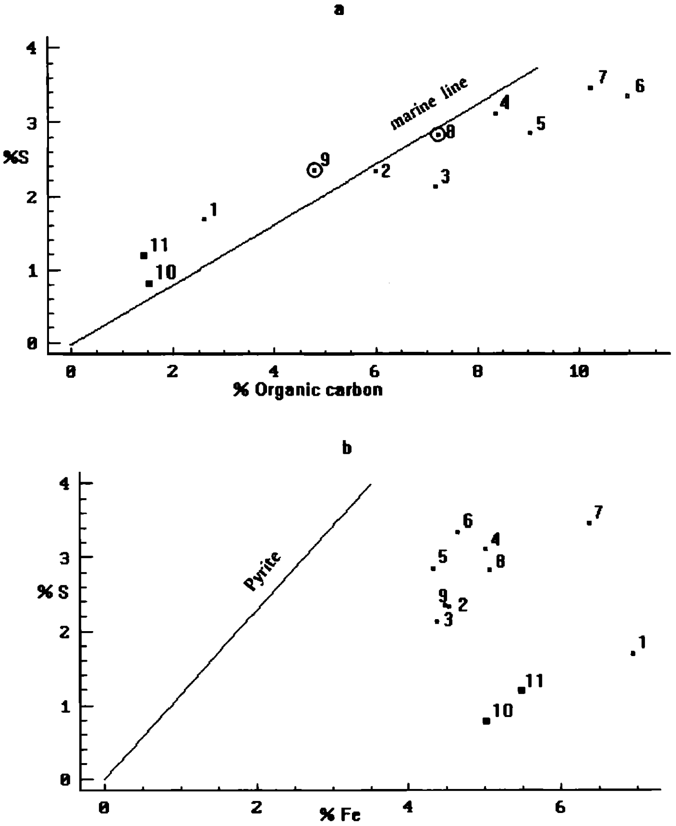

FIG. 9. Sulfur vs. (a) organic carbon and (b) iron plots, Bazhenov Formation. Data from Oushatinsky (1981). Averages for districts: 1 = northeastern, 25 samples; 2 = eastern, 64 samples; 3 = southeastern, 96 samples; 4, 5, 6 = central, 39, 78, and 136 samples, respectively; 7 = western, 65 samples. Total averages for the Bazhenov Formation (circles): 8 = data from Oushatinsky (1981), 793 samples; 9 = data from Kontorovich et al. (1971), 167 samples. Sediments from Oushatinsky (1984, written commun.): 10 = above the Bazhenov Formation; 11 = below the Bazhenov Formation.

If we accept the total quantity of organic matter in the Bazhenov Formation to be as high as 18×10^{12} t, the total organic carbon in organic matter to be 77 percent, the mean uranium concentration to be 35 ppm, and the total organic carbon in Bazhenov rocks to be 8 percent, our estimate of the total uranium in the Bazhenov Formation will be as high as 6×10^9 t. This is more than the quantity of uranium in the recent ocean (about 4×10^9 t). Assuming the continuous accumulation of Bazhenov sediments for 6×10^6 years, we calculate an annual input of 10^3 tons of uranium to the bottom. This value is equal to 1/18 of the annual riverine input of uranium to the recent ocean (Baturin, 1975). Hence, the suggestion of seawater uranium reserve replenishment by riv-

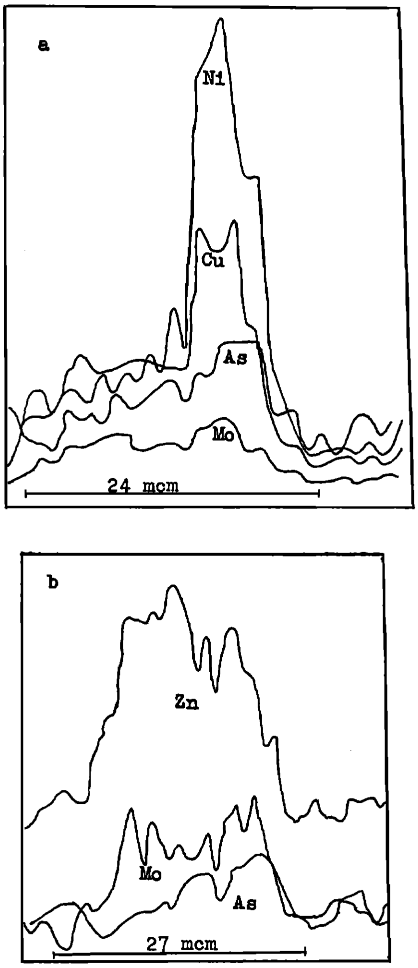

FIG. 10. Electron microprobe scans across the pyrite grain tabulated in Table 6. Covariation of As and Mo with Ni and Cu (a) and Zn (b). WDS-microprobe, eV = 20 keV, carbon coating.

erine flux is rather realistic, and it is not necessary to seek any other sources of uranium without strict evidence of their existence. If we assume for the Bazhenov Sea a mean depth of 150 m and a surface area of 2×10^6 km^2, the volume of water would be estimated at 0.3×10^6 km^3, which is close to the volume of the Black Sea. Using the residence time of uranium calculated for the Black Sea (4,000 years; from Baturin, 1975), one arrives at an estimate of 1,000-fold water renewal during the existence of the the Bazhenov Sea. This riverine input supplied seawater with organophile elements found in organic-rich sediments together with uranium.

TABLE 7. Gold, Arsenic, and Antimonium Content in Pyrite

Core	Au (ppb)	As (ppm)	Sb (ppm)
1	4.8 ± 1.3	285 ± 27	20 ± 1
2	15 ± 3	82 ± 8	2.2 ± 0.3
3	8 ± 2	843 ± 82	53 ± 5

Three cores from the central part of the region
Neutron activation analysis by V. Parkhomenko

TABLE 8. Uranium Content in Phosphatic Fish Fragments

Fragments	CaO (%)	P_2O_5	U (%)
1	46.85	32.65	0.11
2	38.28	26.26	0.16
3	36.34	24.84	0.17
4	35.48	25.14	0.20
5	35.16	24.88	0.14
6	35.16	24.18	0.17
7	24.46	17.87	0.31
8	20.07	12.71	0.60
9	16.96	11.44	0.53
10	16.35	10.49	0.69

One sample, core from district 2 in Fig 1

But the Upper Jurassic-Lower Cretaceous planktonogenic sediments are not restricted to the Bazhenov Formation only. They have also been found, for example, under the Barents Sea, though their distribution there has not yet been completely traced (Gavshin and Zakharov, 1991), and they are also known in some regions to the west of the Urals (Yudovich and Ketris, 1988).

A comparison of the Bazhenov Formation with some other well-known metalliferous black shales shows common as well as distinguishing features. Nonetheless, all these formations have intrinsic characteristics: slow rates of sedimentation, high organic carbon content, and evidence of anoxic conditions in paleobasins. Like the Cambrian alum shale, the Bazhenov Formation is composed of marine organic matter, though it was deposited at greater depths and contains benthic fauna in some places. On the other hand, according to Rock-Eval pyrolysis and carbon isotope data, the Bazhenov Formation is comparable to the shallowly buried Appalachian Devonian shales, although these contain terrestrially derived organic matter in some places (Leventhal, 1991, 1993), and to the Pennsylvanian shale composed of either terrestrial or sapropelic-marine organic matter (Coveney et al., 1987; Hatch and Leventhal, 1992).

Conclusions

The Bazhenov Formation, occupying about 1 million km^2, was formed in an open marine basin under low sedimentation conditions that resulted in the concentration of great masses of organic matter, primarily of phytoplanktonic origin. This giant geologic body is enriched in U, Mo, V, Cu, Ni, Zn, Cd, As, Ag, Sb, Se, Br, and to some extent, Au, relative to most shales. The majority of these elements were extracted from seawater by organic compounds or sulfides, and some elements later bound in pyrite. The fact that the amounts of elements extracted from an aquatic environment are much greater than their content in the recent ocean is of great importance for estimates of global geochemical balance: the Bazhenov Formation was a trap that concentrated certain metals and thereby controlled their content in Jurassic-Cretaceous seawater.

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