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GEOCHEMISTRY

Role of Endogenous Fluids in the Formation of Carbon-Bearing Rocks in the Geological Section of the Oil-and-Gas Provinces

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The base of practically all oil-and-gas basins is composed of rocks with anomalous geochemical characteristics: elevated contents of organic matter (OM) and metals. Most researchers suggest that periodical accumulation of such specific sequences was caused by large-scale global basaltic volcanism [1–3], which led to catastrophes in the history of organic life and simultaneous accumulation of significant amounts of trace elements in sediments [4, 5].

The aim of this study was to establish the contribution of deep-seated emanations in the formation of the Frasnian (Upper Devonian) domanik carbon-bearing rocks within the South Tatar dome of the Russian Plate.

We studied trace element distribution in rocks, bitumens, and kerogens; carbon isotope composition in carbonates; Sr and Nd isotope ratios in rocks and bitumens; the uranium distribution in thin sections; and the petrographic composition of rocks. Samples were analyzed with neutron-activation, ICP-MS, *f*-radiography, and laboratory and borehole gamma-spectrometry. Numerous diagrams of radioactive logging were also studied. The Sr and Nd isotope composition was determined on a multichannel Finnigan MAT-262 mass spectrometer. The element contents were analyzed with isotope dilution. The ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd ratios are reported relative to Eimer and Amend (0.70800) and La Jolla (0.51184) standards, respectively.

The studied samples are composed of clayey–siliceous–carbonate rocks with a variable OM content. In terms of physical properties, they differ from the under- and overlying rocks in the higher radioactivity related to the high U content (up to 35 ppm) and low contents of Th (up to 2 ppm) and K (up to 0.5–0.6%). In addition, the considered rocks show higher concentrations of one to two orders of magnitude of Ti, V, Mn, Ni, Cu, Zn, As, Se, Y, Mo, Ag, Cd, Cs, REE, Re, and Sc relative to the clarke values for the upper crust. These features are typomorphic of practically all black shales [6]. In general, the metal content has a positive correlation with the U concentration, which is most expressed in the carbonaceous–siliceous–carbonate varieties (Fig. 1). Therefore, the U content can be considered an indicator of geochemical difference between sedimentation settings.

The *f*-radiography showed extremely uneven U distribution in the carbonate rocks. Fine-grained limestones contain up to 4–5 ppm U and up to 35–50 ppm in the bacterially enriched domains. The diagenetic and catagenetic recrystallization of the rocks led to the redistribution of matter, which was expressed in the coarsening of calcite grains, dolomitization of matrix, and segregation of bacterial mats with the formation of individual beds. Simultaneously, U was redistributed to form U-rich organogenic intercalations containing up to 200 ppm U. The amount of such beds and content of U in them define its present-day content in the rocks (Fig. 2). The correlation between U and other elements suggests that U accumulation is a rather universal process.

The data obtained showed that the initial rocks and their chloroform extracts have similar geochemical features. In particular, the bitumens show elevated contents of V, Ni, Se, Mo, Re, Au, Ag, and Pb, i.e., elements that determine the geochemical specialization of rocks. We also recorded significant contents of Ru and Pd, which were not analyzed in the rocks. The concentration of these elements in extracts suggests that most of

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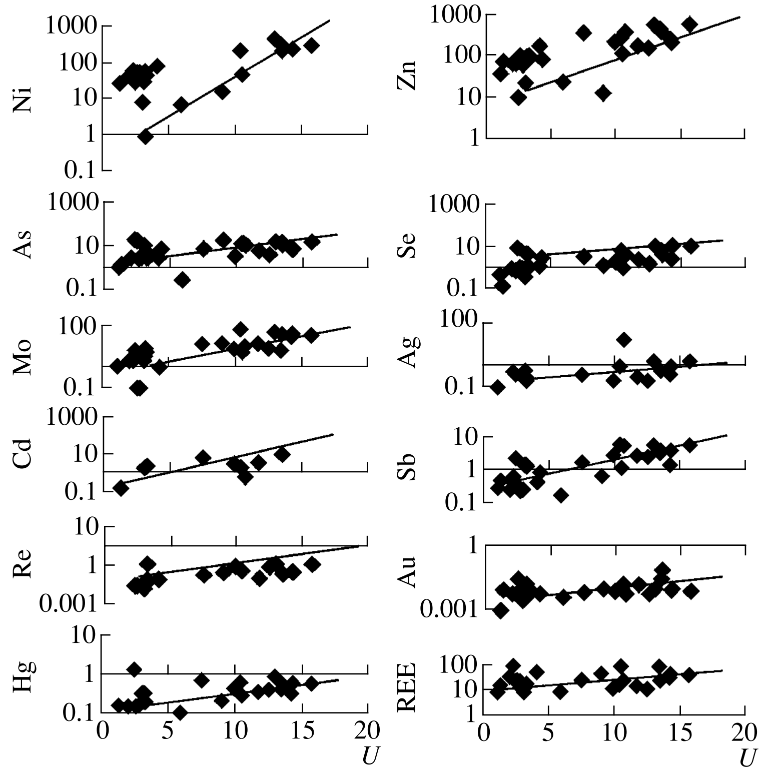

Fig. 1. Variations of trace elements in the domanik carbon–siliceous–carbonate rocks (in ppm).

them are present either as elementoorganic compounds easily extracted by organic solvents or as complexes with organic ligands formed during extraction.

Although the content of REEs in the domanik rocks is below the clarke value for the upper crust, their accumulation in carbonate material is seen from the REE/Th ratio, which can be accepted as the terrigenous index of the rocks. This ratio in the "pure" limestones (Th < 1.0 ppm) is ~15. The same value was obtained for the Kynovian mudstones underlying domanik sediments, which contain 122.5 ppm REE and 8.10 ppm Th. With increasing OM content in the rocks, this ratio increases to ~50 in carbonaceous–carbonate rocks, which indicates elevated contents of REEs in seawater and the decisive role of OM in their accumulation.

REEs serve as indicators of rock composition in the provenance and provide insight into sedimentation conditions in carbonates [7]. Different carbonate rocks have similar REE distribution patterns characterized by low-angle curves with an insignificant LREE enrichment relative to HREE (Fig. 3). If we take the REE distribution pattern in mudstones as the background, the La_N/Yb_N ratio is lower in carbonate rocks and minimal in carbonaceous–siliceous–carbonate rocks (3.8 versus 11.7). The HREE enrichment is also expressed in Sm_N/Yb_N values (1.3 versus 2.3). These facts indicate that the share of HREE in the total REE budget is higher in carbon-bearing carbonates than in the rocks dominated by terrigenous material. Limestones are characterized by distinct Eu and Ce minimums. The Eu_N/Eu_N^* and Ce_N/Ce_N^* ratios are 0.62–0.66 and 0.36–0.45, respectively (1.0 in argillites).

The REE distribution pattern in the bitumens differs from that in the rocks. The reduced character of the extract was responsible for the virtually complete disappearance of the Ce minimum, while the Eu anomaly was preserved only in bitumens extracted from mudstone. As compared to mudstone, extracts from carbonate rocks are drastically enriched in HREE. Consequently, the La_N/Yb_N ratio decreases from 21.1 to 9.2 in the Verkhnee Suleevo area (Table 1, Fig. 3). These data attest to the presence of different REE sources in the Frasnian (Upper Devonian) terrigenous and carbon-bearing carbonate rocks, which were formed under the influence of deep-seated fluids (products of the degassing from mafic magmas).

The presence of U in fluids and its decisive role in the natural radioactivity of domanik rocks allowed us to apply the maps of variations in the gamma field of Upper Devonian rocks compiled on the basis of radioactive logging data to reveal the possible pathways of deep-seated fluxes both for the regional plan and within individual objects (deposits).

The discrepancy in the gamma field parameter is as high as 20–25γ. The distribution of high-γ fields is correlated with tectonic disruptions in the crystalline base-

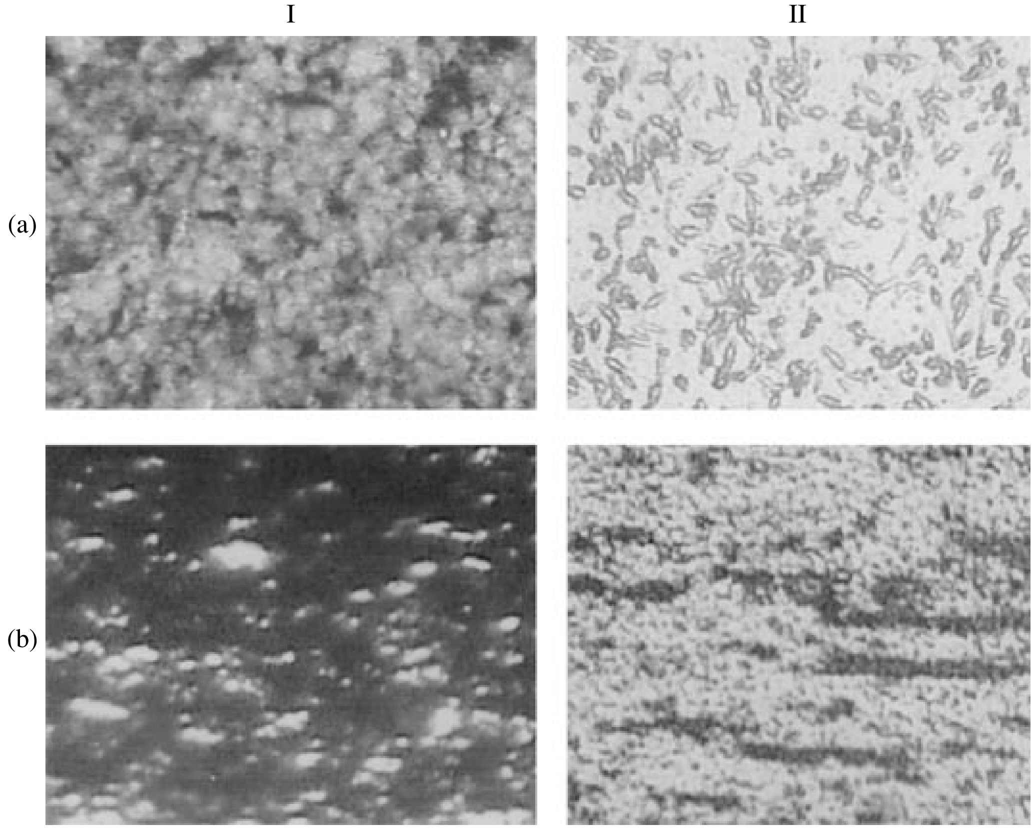

Fig. 2. Distribution of U in (a) the fine-grained limestone and (b) bacterial mats. (I) Thin section; (II) detector.

ment, which indicates the spatiotemporal conjugation of endogenous and exogenic processes. The presence of a wide range of other elements, in addition to uranium, in the fluid promoted the formation of geochemically anomalous metalliferous carbonaceous–siliceous–carbonate rocks atypical of sedimentary cover. Thus, the crystalline basement and sedimentary rocks are interrelated components of a common fluid–dynamic system [9].

The contribution of deep-seated fluids to the formation of domanik rocks also follows from the lighter carbon isotope composition of limestones relative to marine carbonates. The depletion in carbon isotope composition is most distinctly expressed in the rocks with a high U content, in which $\delta^{13}C$ decreases to –13.2‰, indicating both a general influx of "light" carbon with gas emanations into the sedimentation basin and its more significant contribution to the formation of carbonates in gas injection zones. Input of fluids with isotopically light carbon into the Upper Devonain sedimentary basins is also supported by data on vein calcite sampled from the crystalline basement recovered by the Novo-Elkhov superdeep borehole ($\delta^{13}C$ from –13.9 to –16.9‰) (Table 2).

Data on the isotopic characteristics of rocks and bitumens were used to determine the source of metals delivered to the sedimentary basin.

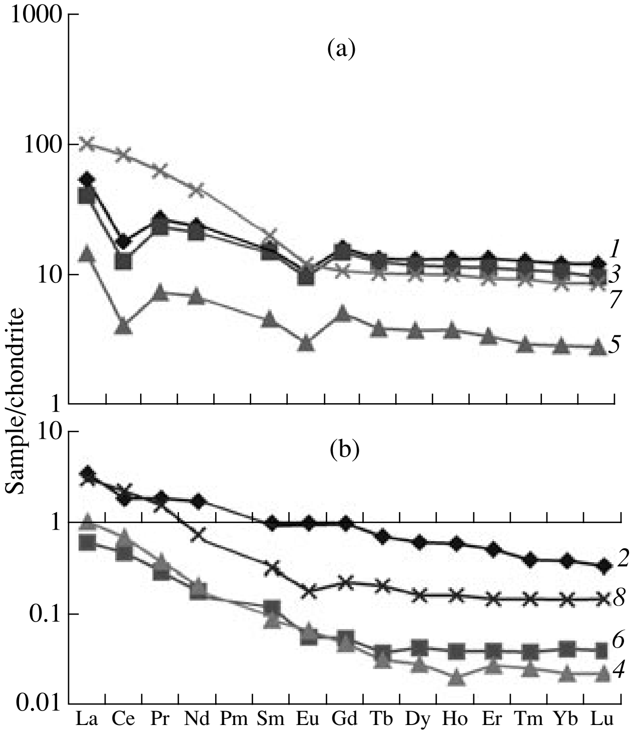

Fig. 3. REE distribution in (a) domanik rocks and (b) bitumens.

Table 1. Comparative metal potential (ppm) of rocks and bitumens

Element	Verkhnee Suleevo borehole 30075		Minnibaevo borehole 20355		Bukhara borehole 750		Stepnoe Ozero borehole 1001	
	1	2	3	4	5	6	7	8
Ti	748.17	30.81	202.92	25.31	134.46	2.95	4366.92	60.83
V	576.47	226.55	1258.47	805.55	227.76	322.63	156.72	24.04
Cr	100.32	2.16	31.93	4.14	11.21	4.23	124.52	3.26
Mn	931.66	26.43	221.99	212.38	11.30	1.75	249.37	6.13
Co	4.07	0.83	2.06	0.85	0.92	0.17	21.22	2.01
Ni	465.20	115.63	241.89	412.20	75.64	380.95	61.40	268.36
Cu	326.02	211.02	147.04	105.61	15.03	50.67	13.21	42.90
Zn	561.31	550.9	251.51	105.90	83.83	50.67	66.95	43.00
Ga	3.94	2.32	1.36	0.67	0.61	0.12	30.56	0.33
As	16.40	0.62	18.80	0.41	5.10	0.21	20.62	0.06
Se	11.80	8.32	12.90	10.81	5.10	1.62	0.80	0.82
Rb	22.66	10.46	6.49	0.17	3.16	0.08	140.95	0.99
Sr	97.28	21.57	549.41	1.91	14.41	1.21	72.51	4.55
Y	37.44	1.53	27.95	0.96	11.18	0.10	14.66	0.23
Zr	40.03	3.48	29.68	1.30	9.34	3.48	218.89	3.02
Nb	2.15	0.071	1.43	0.045	0.30	0.007	15.10	0.11
Mo	48.31	45.49	40.99	17.96	7.91	1.01	2.06	0.25
Ru	n.d.	0.0036	n.d.	0.002	n.d.	0.001	n.d.	–
Rd	n.d.	0.023	n.d.	0.016	n.d.	0.008	n.d.	–
Ag	0.74	0.263	0.63	0.164	0.23	0.15	0.54	0.086
Cd	2.58	0.560	2.02	0.411	0.82	0.31	n.d.	0.084
Sb	5.95	1.100	4.15	0.186	1.50	0.086	0.66	0.051
Cs	1.02	0.021	0.29	0.005	0.19	0.003	11.73	0.051
La	13.53	0.857	10.17	0.250	3.72	0.149	25.60	0.748
Ce	11.99	1.187	8.45	0.440	2.67	0.299	54.59	1.441
Pr	2.69	0.179	2.36	0.036	0.73	0.008	6.26	0.152
Nd	11.76	0.819	10.47	0.097	3.37	0.385	21.69	0.349
Sm	2.54	0.153	2.41	0.013	0.76	0.018	3.20	0.050
Eu	0.64	0.057	0.58	0.004	0.18	0.003	0.58	0.010
Gd	3.41	0.201	3.18	0.009	1.07	0.011	2.27	0.045
Tb	0.52	0.026	0.49	0.001	0.15	0.001	0.40	0.007
Dy	3.47	0.155	3.12	0.007	0.98	0.011	2.66	0.041
Ho	0.78	0.033	0.68	0.001	0.22	0.002	0.59	0.009
Er	2.30	0.084	1.96	0.004	0.58	0.006	1.62	0.024
Tm	0.34	0.009	0.29	0.0006	0.07	0.001	0.24	0.003
Yb	2.09	0.061	1.80	0.004	0.38	0.007	1.47	0.024
Lu	0.32	0.007	0.25	0.0006	0.07	0.001	0.22	0.004
Hf	0.95	0.048	0.77	0.025	0.23	0.005	6.11	0.075
Ta	0.18	–	0.08	–	0.05	–	1.08	0.009
W	0.57	0.458	0.37	0.195	0.15	0.03	1.23	0.082
Re	0.15	2.50	0.05	0.192	0.02	0.07	0.01	0.009
Au	0.03	0.09	0.01	0.012	0.02	0.002	–	0.001
Hg	0.92	3.24	0.63	1.32	0.35	3.43	–	0.38
Tl	0.71	0.041	0.42	0.014	0.20	0.010	1.17	0.009
Pb	20.75	31.75	14.97	31.24	2.15	4.38	23.89	2.71
Bi	0.20	0.02	0.13	–	0.05	0.03	0.39	0.17
Th	1.99	0.063	0.80	0.030	0.39	0.005	8.10	0.090
U	14.28	0.661	12.96	0.290	3.23	0.109	2.29	0.076

Note: Rocks: (1) carbonaceous–clayey–siliceous–carbonate; (3) carbonaceous–siliceous–carbonate; (5) carbonate; (7) mudstone; (2, 4, 6, 8) bitumens. (n.d.) Not detected.

Table 2. Uranium content and carbon isotope composition of bitumens from the domanik rocks and vein calcite in the basement rocks

Area borehole	Rock	U, ppm	$\delta^{13}C$ of carbonate, ‰	$\delta^{13}C$ of bitumens, ‰
Minnibaevo 20355	Limestone	2.0	−4.7	−28.1
		10.5	−10.4	−29.4
		18.5	−13.2	−27.4
Novo-Elkhov 8113	The same	1.0	0.1	−27.9
		6.2	−8.6	−25.3
Bukhara 750	"	5.9	−8.6	−29.2
		13.3	−12.6	
V. Leninogorsk 28 955	"	1.3	−5.5	−29.4
		10.7	−12.2	−28.1
Novo-Elkhov 20009, int. 3986m	Vein calcite		−14.3	
4153–4155	The same		−13.9	
4360–4363	"		−16.4	
4827–4829	"		−16.9	

Table 3. Rb–Sr isotope data on rocks and bitumens

Ordinal no.	Material	Content, ppm		$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$ (meas)	$^{87}Sr/^{86}Sr$	ε_{Sr}^{T}
		Sr	Rb				
1	Limestone	385	1.59	0.012 ± 1	0.70833 ± 6	0.70827	115
2	Marl	285	30.1	0.3050 ± 12	0.71001 ± 3	0.70842	115.8
3	Mudstone	14.5	257	0.510 ± 3	0.71130 ± 5	0.70865	120.5
4	Bitumoid	0.16	1.55	0.296 ± 19	0.70973 ± 10	0.70833	115.9
5		3.77	0.808	0.621 ± 1	0.711593 ± 14	0.70859	119.6
6		1.81	0.17	0.2692 ± 18	0.70934 ± 6	0.70794	110
7		12	2.39	0.578 ± 1	0.709764 ± 13	0.70676	93.5

The Sr isotope composition of Paleozoic seawaters is known and governed by the geodynamic regime of the regions, i.e., relations between exogenic and endogenic factors. We studied the Sr isotope composition in pure limestone, marl, and mudstone, as well as in the bitumens from the rocks with different U contents. As follows from Table 3, the initial $^{87}Sr/^{86}Sr$ values in the rocks were 0.70827–0.70865, which correspond to those in the Upper Devonain water. Data on two bitumens are also plotted in this field, attesting to relative equilibrium between mineral and organic components of the sediment. At the same time, the $^{87}Sr/^{86}Sr$ ratio (0.7079 and 0.7068) in two bitumens proved to be less than that in seawater. Such low initial Sr ratios in the bitumens from Devonian rocks could be caused by the contribution of endogenous emanations.

The results of the Sm–Nd isotope study (Table 4) showed that the marls, silicified clayey–carbonate rocks, and bitumens in them have similar Nd isotope compositions ($\varepsilon_{Nd}^{T} = -4.8, -4.9$, and -4.3, respectively). However, fine-grained carbon-bearing limestone has an elevated value of $\varepsilon_{Nd}^{T} = -3.9$, while bitumens from the carbon-bearing rocks with the U content of 35.8 ppm, and hence, elevated contents of hydrogenic REE, show depleted mantle signatures ($\varepsilon_{Nd}^{T} = 8.2$). The source model age (T^{DM}) determined for this sample is 411 Ma, which corresponds to the time of tectonomagmatic activation in the East European Platform [10].

The obtained data allowed us to draw the following conclusions: (1) the domanik rocks formed in the study

Table 4. Sm–Nd isotope data on rocks and bitumens

Ordinal no.	Material	Content, ppm		$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	ε_{Nd}^{T}
		Nd	Sm			
1	Silicified limestone	4.41	0.966	0.132	0.512230 ± 7	−7.96 (−4.9)
2	Marl	24.1	4.9	0.123	0.512210 ± 10	−8.3 (−4.9)
3	Limestone	4.16	0.852	0.124	0.512261 ± 10	−7.4 (−3.9)
4	Bitumoid	0.471	0.086	0.1105	0.512212 ± 10	−8.3 (−4.3)
5		2.302	0.153	0.0402	0.512681 ± 10	0.84 (8.2)

area with the contribution of an endogenous component; (2) deep-seated gas emanations in the sedimentary basin had a reduced character, while their source was represented by conduits of cooling mafic magmas derived from the depleted mantle reservoir in the Middle Devonian.

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