

OIL SHALE FROM CALDERA LAKES OF DIATREMES

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The chemical composition of oil shales from caldera lakes facies, as well as the carbon and oxygen isotope composition of rock-forming carbonates and sulfur isotope composition of pyrite from fine veinlets have been studied. Rocks of clayey, clayey-carbonate and carbonate composition have been differentiated. High P_2O_5 and TiO_2 content of shales should be emphasized. Oil shales are characterized by rather high concentrations of Ni, Co, Cr, V, Cu and Sr, and pyrites – by very high concentrations of As, Mo, Cu and Ag and a light sulfur isotope composition. Rock-forming carbonates show a heavy carbon isotope composition and rather heavy oxygen isotope composition uncommon with non-marine formations. The above geochemical peculiarities are due to the oil shales formation under special conditions of caldera lakes situated over diatremes.

Introduction

Oil shales (OS) from the caldera lake facies were discovered within the Zhlobin saddle (Fig. 1) as a result of searching for diamondiferous diatremes [1]. The diatremes are round or oval in shape and range from a few hundreds to 1,000 m in length. They are formed by xenotuff, tuff and autolith breccias severely changed by postmagmatic and exogenic processes. Calderas are peculiar to the only diatremes breaking through the Sargaievo-Semiluki carbonate deposits, but these latter form a “hillock” over diatremes in sites where Middle-Devonian terrigene deposits are abundant. A number of evidences suggest that alkaline ultrabasic magmatism preceding the early development of the Pripyat paleorift occurred under subaerial conditions within a rather short interval corresponding to the beginning of Rechitsa time [1, 2].

Oil shales and kerogenites (K) occur locally in the Yelenets block where Sargaievo-Semiluki carbonate rocks overlie diatremes with calderas (Asoya, Deniskovichi, Vetochka, Tsuper, Antonovskaya, Yelenets-2,3 diatremes). The most complete volcanogenic-sedimentary sequence of the Rechitsa horizon was found there [3, 4]. The sequence involves three strata: lower or volcanogenic one represented by tuff and xenotuff breccias; middle or vol-

canogenic-sedimentary strata of caldera infilling; and upper strata of sedimentary rocks overlying calderas and being an integral part of deposits of the normal sedimentary sequence of the Pripyat trough formed as a result of the Late Rechitsa sea transgression. Shales are confined to the middle strata showing lens-shaped bedding and a thickness ranging from 10 m along the edges to 40 m in the caldera center. OS and K interlayers are dominant in the upper 5-6 m strata. A thickness of layers unequally enriched with the organic matter (OM) varies between 0.5 and 3.0 m.



Fig. 1. Location of sampling sites

Among the studied OS and K samples rocks of clayey, clayey-carbonate and carbonate composition have been distinguished [3]. A characteristic feature of the OM-containing rocks is the presence of micro-, more seldom macrospores, fragments of fusainized tissues, altered ash material and siliceous substances being parts of the body mass and infilling interlayers and hollows in rocks. The OS combustion heat value is 1,365 kcal/kg of dry fuel with C_{org} of 11.58 %.

A spore complex of the local palynozone and redeposited spores of Middle-Devonian (Polotsk) age [4] have been distinguished in shale deposits. A good safety of both in situ, and redeposited microphyte fossils suggests poor hydrodynamics in shale accumulation water basins and a proximity to vegetation sources. Lithological and geological structural evidences show that

deposits of the shale-bearing part of the Rechitsa horizon sequence had been formed in caldera lakes with moderate and, sometimes, intensive carbonate accumulation, that had appeared above diatremes before the Late Rechitsa transgression advanced over the territory of the Zhlobin saddle.

Methods

The texture and components of oil shales have been studied by optical methods using petrographic and scanning electron microscopes, and the phase composition and absence of other mineral admixtures have been controlled by X-ray diffraction analysis. The ash-forming elements have been determined by X-ray fluorescence analysis, concentrations of elements – by spectral emission analysis (spectral response is 10^{-3} – 10^{-4} %). The calcite and dolomite content have been calculated from the results of CO_2 determination in carbonates using V. N. Scherbina's method, and the organic carbon (C_{org} , %) – by I. I. Tiurin's method. The carbon and oxygen isotope composition have been measured by mass-spectrometry without preliminary heat treatment, instrument precision was 0.3‰. The $\delta^{13}\text{C}$ values are cited relative to the PDB standard, and $\delta^{18}\text{O}$ values – relative to the SMOW standard. Analytical tests have been performed at the laboratories of physical and chemical analyses and lithohydrogeochemistry of the Institute of Geological Sciences of the National Academy of Sciences of Belarus.

Results and Discussion

The mineral base of most of the studied samples is represented by limestone with a small admixture of clay material. In some samples the dolomite content is great enough. Composition of shales at X-ray phase usually includes calcite, quartz, feldspar, more seldom hydromica, dolomite and pyrite.

In conformity with the results of petrographic and X-ray diffraction studies, the X-ray fluorescence analysis of samples has shown a prevalence of CaO (21–45 %) in the shale composition, which corresponds to the calcite content in a series of lithological rock types from marl to limestone. The MgO amount varies within two percents increasing to as high as 3.5–13.8 % in dolomite marl. The SiO_2 content ranges from 1.2 % in pure limestones to 45 % in clay marls and carbonate clays. High SiO_2 amounts relative to small Al_2O_3 and K_2O values that do not correspond to a quantity of fragmental quartz in samples are due to silica presence in rocks of the amorphous phase. Rather high P_2O_5 content, sometimes near to 2 %, is probably due to some amounts of phosphorus-bearing minerals of tuffaceous rocks (apatite, phlogopite) and supplied to the sedimentary environment, which is supported by a close correlation between this element concentration distribution and sodium occurrence uncommon in the case of this type of deposits.

Variations of the Fe_2O_3 and S_{total} content in shale reflect to some extent the abundance of pyrite framboids on fusainized plant remains and pyrite which infills fine veinlets together with calcite. The variation of the Fe/S value between 0.6 and 7.0 shows that Rechitsa shales include non-pyritic iron and non-sulfide forms of sulfur in its total amount. Rather high S_{total} content uncommon with "non-marine" formations (as we think of the Rechitsa horizon shales from geological and geochemical evidences) may be explained by several factors. Among the most probable causes of a rather high sulfur content of shales are a short duration of continental conditions within the territory that were replaced by marine conditions in Late-Rechitsa time; abundance of spores in shale OM that are the most rich in sulfur as compared with the other microcomponents; possible sulfur supply to caldera lake water due to fumarolic activities, as well as to dissolution of sulfate rocks of the Narova horizon broken as a result of explosion, which xenoliths and sulfate cement are peculiar to tuff breccias infilling diatremes.

A high TiO_2 content (0.5–1.5 %) of carbonate-rich shales deserves a special attention. CaCO_3 in the Rechitsa horizon shales is a carrier of mobile (dissolved) Ti acting as a sorbent or bioassimilator, like as in basins where hydrogenic accumulation makes much greater contribution (as compared with the terrigenous one) to the total Ti of sediments, which depends on this element migration with the organic suspension of surface water. Not denying a probability of Ti supply with allochthonous OM, we believe that the major source of dissolved Ti in hydrochemical medium of caldera lakes was most likely the tuff material, which provided the bottom and muddy water with mobile Na, P, Ti and other elements as a result of halmyrolysis. This assumption is supported by high (up to 1 %) Ti concentrations determined in secondary carbonates from the fissures in tuffaceous rocks infilling diatremes*. The average content of main components is given in Table 1.

Table 1. Average Content of Main Components of the Rechitsa Horizon Oil Shale, %

Object	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	CaO	MgO	P_2O_5	S_{total}
Elenets	24.91	4.43	3.52	0.53	3.64	24.33	3.25	0.75	1.14
Zhlobin	12.07	2.42	2.28	0.27	2.40	35.50	1.21	0.83	1.83
In whole	16.80	3.15	2.74	0.36	2.86	31.38	1.96	0.80	1.57

The trace element composition of shales is typically described by V and Cr amounts higher than their clarke values, Ni, Co, Cu and Sr 1.5–3 times exceeding the clarke values and rather low Pb, Zr, Ba, Nb, Be, Y, Yb, La, Ga and B not characteristic of rocks rich in the organic matter. This may be attributed to a high carbonate content (and a low clay content) of the OS mineral substrate. The average content of trace elements is given in Table 2.

* N. D. Mikhailov, personal communication.

Table 2. Average Content of Trace Elements of the Rechitsa Horizon Oil Shale, g/t

Object	No	Pb	Ni	Co	Cr	V	Mn	Ti	Zr	Cu	Sr
Elenets	7	8	94	19	151	186	589	4743	83	104	1000
Zhlobin	12	11	49	16	78	229	518	3191	71	49	742
In whole	19	10	66	17	105	213	544	3763	75	69	837
Object	Ba	Mo	Nb	Sc	Be	Y	Yb	Ga	B		
Elenets	167	0.5	13	15	1.8	14	1.4	10	69		
Zhlobin	175	3.3	11	10	1.4	12	1.1	11	45		
In whole	172	2.2	11	12	1.5	12	1.2	11	54		

Geochemical features of the environments in which OS accumulation and postsedimentary processes occurred are most evident in the trace element composition of pyrites (Table 3) located in fine veinlets and hollows of shales. The concentrations of As (up to 300 g/t), Mo (up to 380 g/t), Cu (up to 370 g/t) and Ag (up to 57 g/t) in pyrites from fissures are so high that only a predominance of Ni over Co peculiar to pyrites from sedimentary strata, and the light sulfur isotope composition of pyrites ($\delta^{34}\text{S} = -30\text{‰}$) prevent us from relating them to proper hydrothermal formations. There is no doubt about a volcanogenic origin of the metal supply source associated with the pyroclastics decomposition and products of fumarolic activities at the sedimentary stage and hydrothermal reworking at the post-sedimentary stage.

Table 3. Trace Element Content (g/t) and Sulfur Isotope Composition of Pyrites from Fine Veinlets in the Rechitsa Horizon Oil Shale (Vetochka-562)

No.	Pb	Ag	Ni	Co	V	Mn	Ti	Cu	Mo	As	$\delta^{34}\text{S}, \text{‰}$
1	230	14	60	44	45	15	500	370	120	300	-29.1
2	15	57	18	12	10	10	480	270	380	200	
3	80	2	70	15	30	150	1400	180	1	200	
4	60	1	13	11	17	60	1500	140	35	300	-30.3

A study of the carbon and oxygen isotope composition of rock-forming carbonates from OS (Table 4) has shown high values of $\delta^{13}\text{C}$ (ranging from -0.9 to $+3.9\text{‰}$) and a small variation of $\delta^{18}\text{O}$ values (from $+25.2$ to $+28.8\text{‰}$). The dominant participation of $\delta^{13}\text{C}$ -enriched CO_2 in their formation is most likely one of the causes of the heavy carbon isotope composition of rock-forming carbonates. Such CO_2 could be produced under considered conditions both at the sedimentary stage and during diagenesis. In the first case, in the upper water layers (carbonate formation zone) CO_2 and carbonates formed with its participation could be enriched with the heavy carbon

isotope as a result of active photosynthesis accompanied by $\delta^{12}\text{C}$ release into the created OM. On the bottom of the lake basin and in the upper sedimentary layers (carbonate accumulation zone) an environment favourable for methane generation with decreased CO_2 production could be created under anaerobic conditions of sapropel diagenesis. As reported in [5, 6], the carbon isotope distribution between CH_4 and CO_2 in equilibrium results in the formation of the isotopically light methane and enrichment of CO_2 and resulting carbonates in the heavy carbon isotopes. The paper [6] cites the similar explanation of the isotopically heavy carbon associated with the heavy oxygen isotope composition of carbonate deposits and attributes it to the organic matter of sapropel influencing the carbonate formation under intensive water evaporation in closed water reservoirs.

Table 4. Carbon and Oxygen Isotope Composition of Oil Shale Rock-Forming Carbonates

Borehole	Depth, m	$\delta^{13}\text{C}$ (PDB), ‰	$\delta^{18}\text{O}$ (MOW), ‰
Elenets			
Tsuper 485	161.8	+1.5	+25.4
	172.0	+2.7	+26.8
	174.0	+1.4	+26.5
Zhlobin			
Asoya 503	159.0	-0.2	+28.0
Deniskovichi 555	142.0	+1.4	+28.3
	143.0	-0.3	+27.5
Vetochka 561	146.1	+3.1	+25.6
	148.2	+3.0	+25.2
	151.0	+3.9	+27.9
Vetochka 562	159.5	-0.9	+28.8

The caldera lake water concentration and positive carbonate-calcium balance could be sustained by the evaporation (under conditions of arid climate and possible deep heat inflows at the posteruptive stage) and a supply of carbonate-calcium material due to Sargaevo-Semiluki carbonate rocks ($\delta^{13}\text{C}$ is about -1‰) broken by explosion and building up the caldera borders, as well as to volcanic products.

Assuming the non-marine origin of water in caldera lakes, it is reasonable to expect the lighter oxygen isotope composition of OS rock-forming carbonates, the more so as the Sargaevo-Semiluki marine carbonate rocks building up the caldera borders have the lighter oxygen isotope composition ($\delta^{18}\text{O}$ from $+23.2$ to $+25.2\text{‰}$) (Fig. 2). A cause of the heavier oxygen isotope composition of carbonates of the oil shale facies from caldera lakes could be the evaporation process, which resulted in the lake water enrichment in ^{18}O . Carbonates precipitated from such water show much heavier oxygen isotope composition. There is no reason to judge about an extent of

possible variations of the carbonate isotope compositions from samples that do not show the recrystallization evidences.

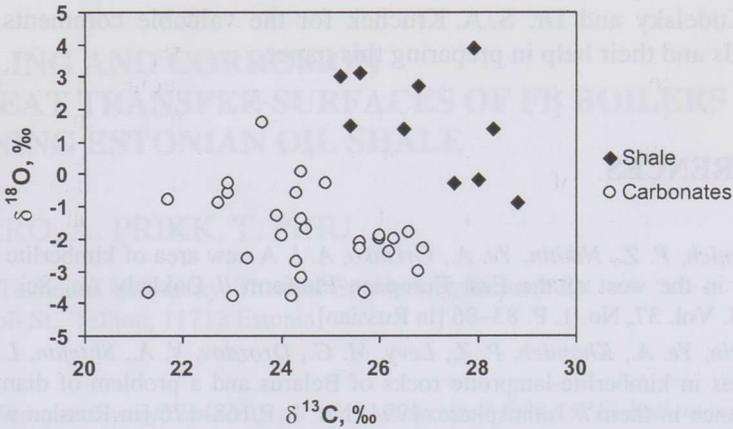


Fig. 2. Oxygen and carbon isotope composition of rock-forming carbonates from Upper Devonian deposits of the Zhlobin saddle

Conclusions

Mode of occurrence, structure and texture characteristics, variations of the mineral composition of shales, abundance of micro- and macrospores, as well as a good safety of in situ and derived microphyte fossils suggest these shales accumulation in local water reservoirs with a poor water dynamics and a close proximity to vegetation material sources. Caldera lakes that had appeared above diatremes before the Late Rechitsa transgression advanced over the territory of the Zhlobin saddle could be such water reservoirs.

High P_2O_5 , TiO_2 and S_{total} content of shales together with their rather high concentrations of Cr, Ni, Co, V, Cu and Sr, as well as very high concentrations of As, Mo, Ag and Cu in veinlet pyrites are indicative of a volcanogenic source of element supply, associated with the decomposition of pyroclastics and products of fumarolic activity at the sedimentation stage and with hydrothermal reworking at the postsedimentation stage.

The carbon and oxygen isotope composition of rock-forming carbonates is due to a considerable influence of the sapropel OM upon the carbonate formation under intense evaporation in closed water reservoirs.

The promises of commercial utilization of the Rechitsa horizon oil shales, which are rather rich in OM, are not very good because of their local occurrence and unevenness of their beds in strike and thickness.

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