

## ORGANIC GEOCHEMISTRY OF THE DEVONIAN BITUMINOUS SHALES AND LIPTOBIOLITHE COALS OF THE KUZNETSK BASIN

A.E. Kontorovich, I.D. Timoshina, A.N. Fomin, V.N. Melenevsky

Institute of Petroleum Geology and Geophysics SB RAS, Russia

### Introduction

The paper is devoted to comparative study of the Dmitrievka-Pereboy Formation bituminous shales from the Dmitriyevskoye field and the Barzas Formation liptobiolithe coals from the Barzasskoye field in Kuzbass. To determine the type, catagenesis, and hydrocarbon generation potential, concentration and pyrolytic characteristics of organic matter (OM), and total organic carbon (TOC) isotopic composition of samples from these fields have been identified (Table) using conventional techniques [1-4].

### Results

The liptobiolithe coals of the Barzasskoye field are significantly more enriched in TOC (48.2-73.3 %) than the bituminous shales of the Dmitriyevskoye field (2.7-16.6 %). S<sub>2</sub> values ("kerogen" component) in the Dmitriyevskoye shales comprise 17-123 mg HC / g rock and 197-450 mg HC / g rock the Barzas coals. Fluctuations in the S<sub>2</sub> values precisely replicate the profile of TOC, and similar variations are marked for S<sub>1</sub> values ("bitumoid" component). In the Dmitriyevskoye shales, very high values of the hydrogen index (HI) have been recorded (488-879 mg HC / g TOC), and OM falls in the region of lake sapropel (type I kerogen), with the exception of four samples, which belong to sapropelic marine OM (type II kerogen). In the Barzas coals, HI is slightly lower, though is very high for coals only (343-654 mg HC / g TOC). A third of the Barzas samples can be attributed to type I kerogen and the rest to type II kerogen. Carbon isotope composition of the Dmitriyevskoye shales OM match pyrolysis data.  $\delta^{13}\text{C}$  values [(-37.7 ‰) – (-32.0 ‰)] indicate marine (or lake) OM and Barzas coals are isotopically notable for heavier carbon –  $\delta^{13}\text{C}$  values [(-21.4 ‰) – (-17.8 ‰)], which is peculiar to terrestrial OM. The Barzas coals consist of residues of higher plants – Lycopodiaceae Barsassia ornata Zal. [5], as well as Orestovia and Petzia plants, that Z.V. Yergolskaya [6] defined as the higher terrestrial plants (psilophytes) and proposed to refer the Barzas coals not to sapromixite, but to cuticle liptobiolithes. Perhaps the presence of both terrestrial and sapropelic marine (or lake) OM signs just due to the specifics of these ancient plants preserved features of the aquatic life with hydrogen compounds predominance. The presence of type I and II kerogens in the Devonian shales and coals suggests an existence of marine and large lakes facies with sapropel accumulation along with running-water peatlands and lagoon environments [7, 8] in the Middle Devonian of the studied area. Both in the Dmitriyevskoye shales and Barzas coals catagenesis by pyrolysis analysis ( $T_{\text{max}}$  ranges 439-448°C and 430-449°C respectively) corresponds to protocatenesis (immature) and early mesocatenesis (early oil window). The vitrinite reflectance data confirm by Dmitriyevskoye shales pyrolysis data ( $R^{\text{vt}} = 0.46\text{-}0.60\%$ ). In the Barzas coals,  $R^{\text{vt}}$  values range from 0.48% to 0.49%, i.e. OM is immature and completely preserved its hydrocarbon generation potential.

## Conclusions

Therefore, based on pyrolysis data, the Middle Devonian OM of the Dmitrievskoye bituminous shales and Barzas liptobiolithe coals refer to type I (lake) and II (marine) kerogens, altered within protocatagenesis (immature) and early mesocatagenesis (early oil window), and largely or completely saved its high generation potential. The organic carbon isotopic composition of the Dmitrievskoye bituminous shales corresponds to type I and II kerogens. In the Barzas coals, discordance in the organic carbon isotopic composition (terrestrial, with high  $\delta^{13}\text{C}$  values) and pyrolytic characteristics (type II and I kerogens) probably due to the specificity of the original biota – the oldest higher plants in the Earth's history.

Table. Concentrations, pyrolysis characteristics, isotope composition and vitrinite reflectance of the Devonian organic matter in the Kuznetsk Basin

| Characteristics                  |                       | Liptobiolithe coals of the Barzasskoye field (22 samples) |            | Bituminous shales of the Dmitriyevskoye field (67 samples) |            |
|----------------------------------|-----------------------|---|------------|--|------------|
|                                  |                       | spread of values  | mean value | spread of values   | mean value |
| TOC, %                           |                       | 48.2-73.3   | 60.1       | 2.7-16.6   | 10.4       |
| Pyrolysis                        | S1, m HC / g rock     | 0.2-8.5   | 2.3        | 0.1-2.5  | 1.0        |
|                                  | S2, mg HC / g rock    | 197-450   | 292        | 17-123   | 76         |
|                                  | HI, mg HC / g TOC     | 343-654   | 484        | 488-879  | 725        |
|                                  | T <sub>max</sub> , °C | 430-449   | 443        | 439-448  | 445        |
| $\delta^{13}\text{C}$ , ‰        |                       | (-21.4) – (-17.8)   | -19.5      | (-37.7) – (-32.0)  | -33.8      |
| R <sup>o</sup> <sub>vt</sub> , % |                       | 0.45-0.50   | 0.48       | 0.46-0.60  | 0.52       |

## References

1. Korchagina, Yu.I., Chetverikova, O.P., 1980. Methods of interpretation of analytical data on the composition of dispersed organic matter. Moscow: Nedra (in Russian).
2. Lopatin, N.V., Yemets, T.P., 1987. Pyrolysis in petroleum geochemistry. Moscow: Nauka (in Russian).
3. Matthews, D.E., Hayes, J.M., 1978. Isotope-ratio-monitoring gas chromatography-mass spectrometry. *Anal.Chem.* 50 (11) 1465–1473.
4. Werner, R.A., Brand, W.A., 2001. Referencing strategies and techniques in stable isotope ratio analysis. *Rapid Commun. Mass Spectrom.* 15 (7) 501–519.
5. Zalessky, M.D., 1931. On the genesis of the Barzas sapromixite. *Math. AN SSSR, Ser. Dep. Mat. and Natur. Sciences VII* (3) 401-402 (in Russian).
6. Yergolskaya, Z.V., 1936. Petrographic study of the Barzas coals. Leningrad: ONTI NKTP, (*Math.TsNIGRI*, issue 70), 5-54 (in Russian).
7. Tyzhnov, A.V., 1938. Geological sketch of the Barzas region of the Kuznetsk Basin. *Materials on geology of Western Siberia. Tomsk, N 3(45)*, 91-131 (in Russian).
8. Gritsko, G.I., Kashirtsev, V.A., Kuznetsov, B.N., Kochetkov, V.N., Moskvina, V.I., Parmon, V.N., Startsev, A.N., Fedorin, V.A., 2011. Sapropelites of the Barzasskoye field in Kuzbass. Novosibirsk: IPGGSB RAS (in Russian).