Upper Jurassic Oil Shales from European North of Russia

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Summary

The Upper Jurassic oil shales of the northern regions of the European part of Russia were investigated. The structure and composition of their organic matter were studied by spectral and chemical methods. The oil shales under study contain kerogen of II-S type enriched in oxygen that determines their properties.

In the northern regions of the European part of Russia the known oil shale shows are located in the Volga-Pechora shale province (Bushnev, Lyyurov, 2002). Southwestward from the Timan Ridge the Vychegda shale basin is located, which comprises Yarenga and Sysola shale-bearing areas. Northeastward from Timan it is isolated as the Timan-Pechora shale basin including Izhma and Bolshezemelsky shale-bearing areas. The shales represent argillaceous-carbonate varieties enriched by organic matter. The rocks show rather good preservation of the thinnest sentimentogenic horizontal lamination due to bioturbation.

We in detail analyzed the composition of organic matter from shale-bearing deposits of the Sysola shale-bearing area (outcrops along the Vazhyu river (settl.Poinga), Sysola (villages of Yb, Koygorodok) and Kobra (settl. Sinegorye) (Bushnev, Burdelnaya, 2003) and deposits of Izhma shale-bearing area (Ayyuva river). The shales under study represent immature rocks with TOC from 20% and in some locations reaching more than 30% (C_{org} of oil shales from the outcrop at the Vazhyu river is 33.5%). Rock-Eval data show increased HI characterizing a high oil source potential (HI is equal to 630 – 860 mg HC/g TOC), and low values of T_{max} (398 – 426 ^{o}C). The elemental analysis of kerogen showed certain variations in hydrogen content and accordingly in atomic ratio H/C and increased content of heteroelements, at that the first index was greatly affected by terrigenous input. The shales are characterized by a high content of sulfur with the main form as organic sulfur. S_{org}/C_{org} values in the kerogen of high carbonaceous rocks testify to a high sulfurization of the geopolymer and allow its classification as II-S type (Orr, 1986). The oxygen content is also increased that conditions the presence of organic acids, ketons and phenol structures in the kerogen. The solid state ^{13}C NMR spectrum of the studied samples of Middle Volga kerogen supports the presence of carboxyl carbon with the signal at 175 ppm region and signal at 75 ppm characterizing for ether (Fig.). The signal characteristic of carboxyl carbon including carboxyl (ester) group, is too weak to speak about any domination of components in the structure of Upper Jurassic kerogen (Bushnev, Burdelnaya, 2010). The alkaline hydrolysis of kerogen supports a small content of carbonic acid remains in the structure of kerogen.

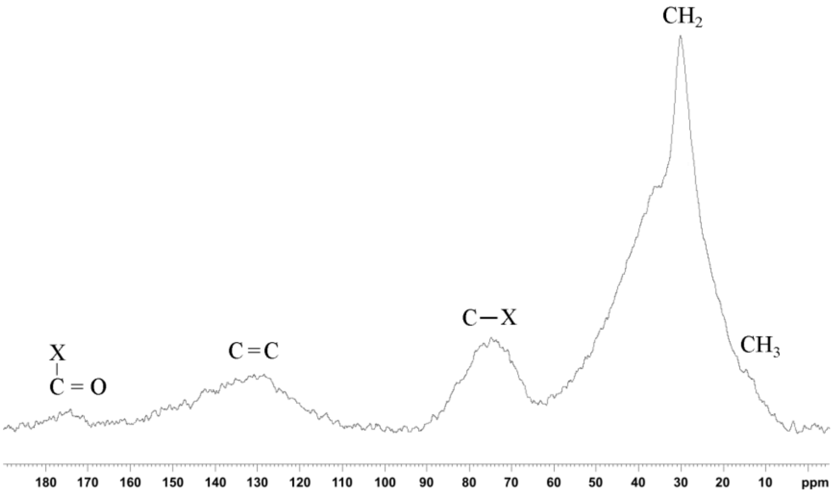

Fig. The solid state ^{13}C NMR spectra of Upper Jurassic kerogen

Further study of OM structure related to detailed analysis of kerogen, particularly off-line pyrolysis, showed a high aliphaticity of kerogen due to generation of n-alkans, n-alkylbenzens, phenilthiophenes and also bisulfurous compounds as n-alkyl substituted thienylthiophenes (Bushnev, Burdelnaya, 2003). At that the latter are dominating among aromatic components of oil shale kerogen pyrolysis products with maximal S/C. All these compounds are structural hydrocarbon fragments of lipid components related to the kerogen matrix via heteroatoms.

The considerable role in shale OM formation is played by carbohydrate components, which presence is supported by high values of “linear” short chain thiophenes in the content of kerogen pyrolysis products (van Kaam-Peters et al., 1998).

As a result, due to early diagenetic sulfurization of initial organic matter, sedimentation in the Volga basin, the kerogen of Jurassic oil shales is characterized by characteristic structure – firstly, due to preservation of the most degradable part of organic structures, secondly, due to sulfur input into the most reactive centers of organic compounds that subsequently results in structural changes of generated products of kerogen.

References

Bushnev D.A., Lyyurov S.V., 2002, Organic Geochemistry of Jurassic Sedimentary Deposits in the Sysola Shale-Bearing Region, Komi Republic: Geochemistry International, №2, Pp.189-195.

Bushnev D.A., Burdelnaya N., 2003, Organic Sulfur Compounds from the Upper Jurassic Shale-Bearing Strata of the Sysola Region: Petroleum Chemistry, Vol. 43, No. 4, pp. 230-239.

Orr W.L., 1985, Kerogen/asphaltene/sulfur relationships in sulfur-rich Monterey oils: In : Leythauser, D., Rullkotter, J. (Eds). Advances in Organic Geochemistry 1985. Pergamon Press, Oxford (Org. Geochem. , 1986. Vol. 10. Pp. 499–516).

Bushnev D.A., Burdel’naya N.S., Mokeev M.V. and Gribanov A.V., 2010, Chemical Structure and ^{13}C NMR Spectra of the Kerogen of Carbonaceous Rock Masses: Doklady Earth Sciences, Vol. 430, Part 2, pp. 210–213.

Van Kaam-Peters H.M.E., Schouten S., Köster J., Sinninghe Damsté J.S., 1998, Controls on the molecular and carbon isotopic composition of organic matter deposited in a Kimmeridgian euxinic shelf sea: Evidence for preservation of carbohydrates through sulfurisation // Geochim. Cosmochim. Acta, Vol. 62. Pp. 3259–3284.