Geochemical study of Upper Jurassic (Volgian) black shales from the Russian Platform

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A geochemical study of Upper Jurassic black shales from the Russian Platform is presented. Samples were collected from Gorodische section, which is the type-section of the Russian 'Volgian' stage, located near Ulyanovsk along the Volga river. This section displays a 6 m thick series of black shales of Middle Volgian age (= Late Tithonian) which is a lateral equivalent of the so-called "Bazhenova Formation", the main source rock of the West Siberian giant oil fields.

Firstly, a bulk study by Rock-Eval pyrolysis of these black shales was performed, indicating TOC values ranging from 1 to 45% and HI between 25 and 700 mg HC/g TOC (Fig. 1) with slightly higher TOC and HI values in the higher part of the series. Such a wide range of TOC and HI reveals important differences in the quality of the organic matter (OM) in these black shales.

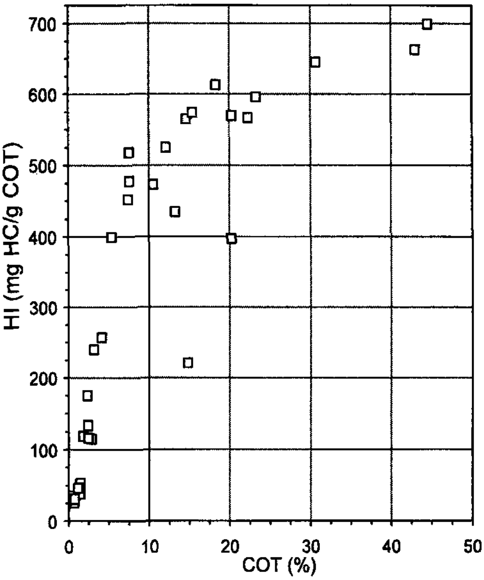

FIG. 1. TOC *vs* HI diagram for the set of black shale samples.

The presented results are a part of a more general study which aimed at (i) determining the controlling factors that led to the preservation and accumulation of the OM and (ii) explaining the above variations in bulk geochemical parameters.

Elemental analyses and FTIR spectrometry were performed on the kerogen isolated from 10 selected samples of various TOC and HI values. In agreement with the HI values, a relatively wide range is noted for the H/C ratios (0.89 to 1.39). Moreover, and a strong contribution of organic sulphur, with S_{org}/C ratios ranging from 0.026 to 0.068 is observed in all the samples. FTIR spectra do not reveal major differences between the samples, showing intense bands around 2920 and 1370 cm^{-1} (CH_2), and 2850 and 1440 cm^{-1} (CH_3) reflecting the presence of abundant aliphatic chains, absorptions at 1700 cm^{-1} (C=O) and 1630 cm^{-1} (C=C) and a band at *c.* 750 cm^{-1} which may be due to C-S bondings. The only differences observed via FTIR are concerned with the relative intensity of the C=C and C=O bands.

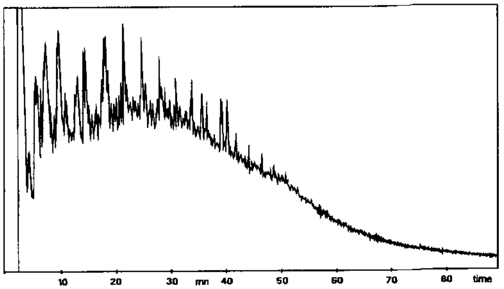

FIG. 2. GC trace of the total pyrolysate of the kerogen isolated from the OM richest sample.

Solid state ^{13}C NMR and pyrolysis of the kerogen from the OM richest sample (TOC = 45%) revealed that the main pathway involved in OM preservation was the so-called natural sulphuration one. Indeed, the ^{13}C NMR spectrum is dominated by a strong peak at 30 ppm, assigned to long aliphatic chains, with significant shoulders between 30 and 60 ppm attributed to C-S bondings and a weak shoulder at 15 ppm (CH_3). Large peaks centred at 75 ppm (C-O), at 130 ppm (C=C) and 175 ppm (C=O) are also present in the spectrum.

The GC trace of the pyrolysate appears very complex due to numerous coelutions of released products (Fig. 2). However, selective ion detection allows the identification of a number of sulphur-containing series such as thiophenes and benzothiophenes. The hydrocarbon skeleton of the sulphur-containing pyrolysis products were identified by GC-MS analysis of the Raney Ni desulphurized pyrolysate.

A pyrolytic study of a relatively poor sample of the series is under progress for comparative purpose.