Environment of Upper Paleocene black shale deposition in Southern Russia and adjacent regions as revealed by isotope and biomarker study

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INTRODUCTION

In addition to the global changes that affect marine depositional environments and control eventually the carbon isotope composition of sediments, there are local fluctuations of environmental conditions controlling availability and $\delta^{13}C$ value of CO_2 and (or) photosynthetic carbon isotope fractionation in restricted marine depositional environments (Kuspert, 1982; Moldovan *et al.*, 1985; Chung *et al.*, 1992).

This paper aims at studying carbon isotopic and biomarker peculiarities of the local environment favorable to sedimentation of marine black shales containing organic matter depleted in ^{13}C. Samples from two outcrops were investigated: one along the Kheu-river in Central Caucasus near Nalchik town and the other an outcrop at Kurpayi in the Tadzhikskaja Depression (Middle Asia).

RESULTS AND DISCUSSION

Sea level fluctuations in the U. Paleocene basin which extended into Southern Russia and adjacent regions are well represented in different parts of the basin by dramatic changes of facies in the sedimentary column. Sea transgressions are marked by deposition of organic-rich shales. The stratigraphic position of the shale horizon throughout the territory corresponds to the foraminiferal zone of *Acarina acarinata*. The thickness of shale interbeds does not exceed 0.5 m, C_{org} content in samples of Kheu-river outcrop reaches 8-10%, in samples of Kurpayi outcrop it ranges from 3 to 20% (e.g., Table 1). The maturity of the most organic-enriched sample (Kurpayi) corresponds to R_0 value of 0.3%.

Rock-Eval pyrolysis revealed highly bituminous, hydrogen-rich organic matter (HI=520-550 mgHC/g·Corg) in black shale samples of Kurpayi outcrop. A marine source (algal and bacterial) of organic matter throughout the Kurpayi sequence is inferred from the predominance of short-chain *n*-alkanes maximizing at C_{17}-C_{19}, abundant steranes C_{27}-C_{29} dominated by ααα-20R-cholestane, high abundance of hopanes with prevailing 17α(H), 21β(H)-hopanes with 22R-configuration and the presence of 4-methylsteranes and 2α- & 3β-methylhopanes. Khey-river black shales may contain some terrestrial input and show lower HI-values (310 mgHC/g·Corg) and *n*-alkane maxima at C_{25}.

Diaryl isoprenoids derived from isorenieratene with ^{13}C-values ranging from -22.9 to -17.8‰ are present in Kurpayi black shales (Fig.1) along with isotopically light compounds notably *n*-alkanes (-34.0 to -29.4‰), pristane (-31.2‰), phytane (-29.8‰) and chroman (-32.7‰), steranes (-29.9 to -32.9‰) and hopanes (-27.9 to -32.1‰). The absence of hopanes highly depleted in ^{13}C indicates that methane cycle did not operate actively at the time of deposition.

Redox conditions throughout the both sequences investigated were contrasting with being highly reducing in the black shale interbeds. It is shown by the low pristane/phytane ratio (0.6, contrasting the higher values (1.0-1.5) in organic-lean marls), the presence of Ni-porphyrins and pyrite as well as extremely high concentrations of V, Ni, Mo, Cu, Cr and low concentrations of Mn, Ti, $CaCO_3$ in the both sets of shaly samples. The biomarker assemblage of the black shales displays an absence of diasteranes, but high T_m/T_s and moretane/hopane ratios as opposite to marly sediments (Table 1).

Table 1. Some geochemical parameters of black shale against marly clays examplified by Kurpayi outcrop samples

Sample	Lithology	TOC %	$CaCO_3$ %	Bitumen %	Pr/Ph	Tm Ts	Moretane Hopane	V $n\cdot10^{-4}$	Ni $n\cdot10^{-4}$	Mo $n\cdot10^{-4}$
317	Marly clay	1.2	7.3	0.3	1.0	1.46	0.33	300	90	30
319	Black shale	17.0	1.0	3.0	0.6	4.11	1.43	800	380	230

Table 2. Organic and carbonate carbon isotope composition throughout the U. Paleocene succession of Kheu-river outcrop (Central Caucasus).

Sample No	Lithology	TOC %	$CaCO_3$ %	$\delta^{13}C_{org}$ ‰	$\delta^{13}C_{carb}$ ‰
2314	marly clay	0.2	17.8	-27.4	0.5
2312	marly clay	0.3	26.1	-27.9	-0.2
2311d	black shale	9.2	1.1	-30.8	-1.7
2311c	marly clay	1.6	25.8	-27.3	-0.6
2311b	black shale	8.5	12.9	-30.3	-1.6
2311a	black shale	10.6	0.1	-30.5	-1.8
2309	marly clay	0.1	13.6	-27.2	0.3

Anaerobic conditions, with the presence of H_2S in the photic zone of the sedimentary basin, can be deduced from the occurence in the Kurpayi black shales of diaryl isoprenoids with isotopic compositions (-22.9 to -17.8‰, Fig.1) and 1-alkyl-2,3,6-trimethylbenzenes derived from anaerobic photosynthetic green sulphur bacteria *Chlorobium* (Summons and Powell, 1986; Damste et al., 1993). The paleoenvironment must therefore have included an anaerobic photic zone, as is the case in the modern Black Sea (Damste et al., 1993). The regularities of carbon isotope distribution throughout the sequence investigated support this suggestion. The organic carbon isotope composition of marly sediments in both outcrops is about -27.5‰, which is typical for Tertiary-Eocene marine sediments (Dean et al., 1986). It is remarkable that the organic-rich shaly interbeds are impoverished in the ^{13}C-isotope as much as -2.5 to -3‰ relative to embedding marls (Table 2). A ^{13}C depletion of about -1.5‰ for individual *n*-alkanes was revealed in the black shale samples of Kurpayi outcrop (sample 319), compared to the marly background (sample 313). The depletion of carbonate carbon in the ^{13}C-isotope ($^{13}C_{carb}$=-1.8‰, against 0.5-1.0‰ in marly rocks) is another characteristic feature of the black shale interbeds (the Kheu-river outcrop, Table 2). This suggests that the inorganic and organic carbon cycles were coupled in the Paleocene Basin during the periods of organic-rich sedimentation.

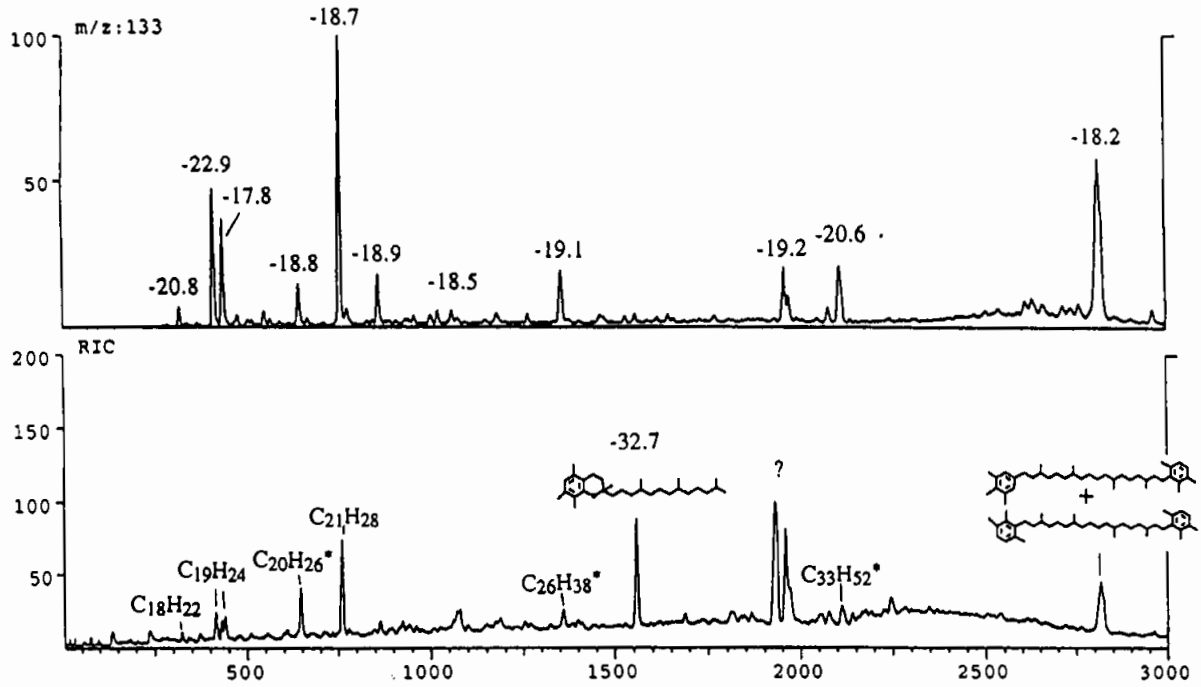

Fig. 1. GC-MS trace of the "diaromatic fraction" from Kurpayi black shale 319 separated by silver nitrate TLC. The diaryl isoprenoids are shown as molecular formula and are enhanced in m/z 133 mass fragmentogram (*=peaks with m/z 134 as base peak). The negative numbers on top of each peak denote their carbon isotopic compositions (‰ vs PDB).

CONCLUSIONS

(1). A dynamic euxinic system with short-period sea level fluctuations in the U. Paleocene basin in Southern Russia was identified by the synchronous ^{13}C depletion of -2.5‰ in carbonate and organic (bulk and *n*-alkanes) carbon in black shale horizons relative to embedding marly clay. The phenomenon implies that isotopically light organic-derived CO_2 is assimilated by planktonic organisms, with consequential local deposition of isotopically light organic matter and carbonates.

(2). Special features characteristic of highly reducing conditions in sediments during early diagenesis were revealed by the presence of Ni-porphyrins and pyrite, high prevalence of T_m over T_s and of moretane over hopane in the black shales, as well as the absence of diasteranes.

(3). The development euxinic conditions in the photic zone of the basin during the periods of organic-rich sedimentation was deduced from the presence of aryl isoprenoids of specific isotopic signature.

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REFERENCES

Chung H.M., Rooney M.A., Toon M.B. and Claypool G.E. (1992). Carbon isotope composition of marine crude oils. Bull. Am. Assoc. Pet. Geol. 76, 1000-1007.

Damsté J.S.S., Wakeham S.G., Kohnen M.E.L., Hayes J.M. and de Leeuw J.W. (1993). A 6.000-year sedimentary molecular record of chemocline excursions in the Black Sea. Nature 362, 827-829.

Dean W.E., Arthur M.A. and Claypool G.E. (1986). Depletion of ^{13}C in Cretaceous marine organic matter: source, diagenetic, or environmental signal? Mar.Geol. 70, 119-157.

Kuspert W. (1982). Environmental changes during oil shale deposition as deduced from stable isotope ratios. In: Cyclic and Event Stratification (Edited by Einsele G. & Seilacher A.), 482•501, Heidelberg, Springer.

Moldovan J.M., Sundraraman P. and Schoell M. (1985). Sensitivity of biomarker parameters to depositional environment and /or source input in the Lower Toarcian of SW Germany. Org. Geochem. 10, 915-926.

Summons R.E. and Powell T. (1986). Chlorobiaceae in Paleozoic seas revealed by bioligical markers, isotopes and geology. Nature 362, 827-829.

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