

Oxygen depletion events in the Paleogene of the northeastern Peri-Tethys

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In the vast Paleogene basin of the NE Peri-Thetys, sporadic changes from normal oxic to disoxic/anoxic environments occurred. The first anoxic event took place at the Paleocene/Eocene boundary (NP9/NP10), when organic-rich sediments (up to 10–20% TOC) accumulated during a rapid eustatic transgression. These sediments show considerable changes in nannofossil assemblages (including appearance of short-lived species) and significant fluctuations in species proportion. Generation of the appreciable amounts of early diagenetic H₂S and its diffusion into bottom water resulted in temporary hydrosulfuric contamination in many parts of the basin and ensuing benthic fauna disappearance. However, this environment lasted shortly (several tens of thousand years), and after organic-rich sedimentation had ceased, anoxic conditions gave way rapidly to oxic ones (Gavrilov et al., 2003). A negative excursion of $\delta^{13}\text{C}$ in both organic matter and carbonates and a negative $\delta^{18}\text{O}$ shift are recorded.

A number of sapropelitic beds were formed in the late Ypresian (NP12-NP13). TOC is 2–3.5% (Gavrilov and Muzylov, 1991); isotopic shifts of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are irregular, but increase of heavy oxygen isotope at the base of some sapropelite beds led to suggest episodic fresh water input (Oberhansli and Beniamovskii, 2000). Nannofossil assemblages show no significant changes, becoming somewhat poorer within sapropelitic interbeds but retaining many species of normal salinity preference (*Discoaster*, *Chiasmolithus*, a.o.). The abundance of benthic forams and geochemical signals indicate lack of apparent anoxic conditions and high probability of disoxic environments. Each sapropelitic bed took no more than several thousand years to have accumulated, and the entire sapropelitic sequence, some 70 ± 15 k.y.

In the Bartonian (NP16-NP17), a new anoxic basin (Kuma Fm.) took shape, to persist much longer (several m.y.) than the preceding ones. Initially, as evidenced by oppressed benthic forams (Beniamovskii pers. comm), disoxic conditions prevailed, and anoxia occurred sporadically. At the same time, an excellent nannoplankton assemblage survived in the surface water layer, to reach maximum abundance and diversity in Paleogene. At a later stage, anoxic environment developed. Benthic forams disappeared, and nannofossils show very poor monospecific assemblages of *Reticulofenestra* spp. in isolated intervals corresponded to TOC maxima likely suggestive of short-lived fresh water inputs. A negative $\delta^{13}\text{C}$ shift is detected. In the late Eocene, normal oxic environment recovered.

The Eocene/Oligocene boundary is marked by a sharp change from carbonatic/terrigenous to clayey sediments (Maykop Fm.). Biotic and geochemical signals suggest anoxic environment that persisted from the Oligocene to early Miocene (ca. 17 m. y.) with sporadic interruptions by short oxic/suboxic events.

Each particular change from oxic to anoxic conditions significantly affected the behavior of redox-sensitive elements. Anoxic sediments have high TOC and remarkably increased concentrations of Mo, Se, Cu, Zn, Re, etc., and extremely low Mn contents. Although anoxic sediments retained similar sedimentologic and geochemical features through time, a variety of factors were responsible for the formation of oxygen-depleted basins. The short-lived anoxic basin that came into being at the Paleocene/Eocene boundary resulted from productivity outburst and accumulation of considerable masses of organic-rich sediments,

caused by massive input of land-derived biophile elements during a rapid eustatic transgression. The long-lived Bartonian and, especially, Oligocene–early Miocene basins ensued from (i) deterioration of connection with the ocean due to tectonic pulses in the Mediterranean foldbelt and eustatic fluctuations, (ii) sluggish hydrodynamic conditions and water stratification resulting in stagnant conditions, (iii) recycling of biophile elements and high productivity, and (iv) gradual climatic cooling and sporadic humidity changes. This set of changes features the steps in transition from greenhouse to icehouse world.

This research was supported by RFBR Projects no. 03-05-64840 and 01-05-64805.

IUGS – International Union of Geological Sciences
ICS – International Commission on Stratigraphy

**International Subcommittee
on Paleogene Stratigraphy**



SYMPOSIUM ON THE PALEOGENE

Preparing for Modern Life and Climate

25 – 30 August 2003, Leuven, Belgium

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PROGRAM BOOK**

WITH THE FINANCIAL SUPPORT OF THE F.W.O. – Vlaanderen ,
THE F.N.R.S , THE I.S.P.S.