

Pyrite framboid diameter distribution in the Lower Oligocene black shales of the Vrancea Nappe as an indicator of changes in redox conditions, Eastern Outer Carpathians, Romania

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Studies of recent and ancient sediments revealed that the diameter distribution of pyrite framboids may be reliably used to characterise oxygen-restricted environments and distinguish ancient euxinic conditions (water column hydrogen sulphide bearing thus oxygen-free) from anoxic, non-sulfidic or dysoxic (oxygen-poor) conditions. Such diagnoses are of great importance when reconstructing palaeoenvironments in ancient basins and the processes of source rocks formation. During Oligocene to early Miocene time an extensive accumulation of organic matter (OM)-rich sediments occurred in the entire Paratethys including the Carpathian Foredeep, which was closed forming fold-thrust belt of the Outer Carpathians. These OM-rich black shales are represented by so-called Menilite shales, widely considered as hydrocarbon source rocks, which constitute as well a detailed archive for palaeoenvironmental changes. The purpose of this preliminary study is to characterise the depositional environment of the Lower Oligocene black shales basing on the pyrite framboid diameter distribution.

Five samples of finely laminated black shales were selected from the Nechit section outcropping in the Bistrica half-window of the Vrancea Nappe in the Eastern Outer Carpathians, E Romania. At least 100 framboid diameters were measured on polished blocks using scanning electron microscope in a back-scattered electron mode.

Framboids from four samples starting from the lowermost part of the section exhibit a narrow range of diameters from 1.0 to 11.5 μm ; mean value ranges from 3.65 to 4.85 μm . Small-sized framboids ($< 6 \mu\text{m}$) account for 70% up to 91% of all framboids, while large framboids ($> 10 \mu\text{m}$) are absent or rare (max. 2%). Within the sample from the uppermost part of the section framboids reveal more variable sizes, 2 – 25 μm , with mean value of 6.63 μm . Small framboids are still numerous (54%), however the amount of framboids $> 10 \mu\text{m}$ increases to 15%.

The domination of small framboids with narrow size range in analysed samples, as well as lamination of rocks, suggest domination of anoxic / euxinic conditions during sedimentation of the Menilite shales. The transition into dysoxic bottom-water conditions can be evidenced by increased amount of larger framboids (up to 25 μm) in the upper part of the section.

It has been concluded that framboids growing at interface of oxic/euxinic water column are in general smaller and less variable in size than framboids from sediments overlain by oxic or dysoxic water column. In the presented case, the prevalence of small framboids indicates that the water column euxinia could have developed, at least temporarily, during the deposition. Although the euxinia did not reached the photic zone as it reconstructed based on the occurrence of isorenieratane and its derivatives, e.g. C19 aryl isoprenoid in equivalent rocks from many locations of the Outer Carpathians. These biomarkers are derived from carotenoids biosynthesised by the photosynthetic green sulphur bacteria (Chlorobiaceae), anaerobic organisms requiring light and hydrogen sulphide for growth.