PALEONTOLOGICAL AND GEOCHEMICAL SIGNALS OF PALEOPRODUCTIVITY FROM BLACK SHALES AND CARBONATE/PHOSPHATE CONCRETIONS: CASE STUDY FROM THE MIDDLE JURASSIC OF THE CARPATHIANS (POLAND AND SLOVAKIA)

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Various paleo-tracers for marine primary paleoproductivity have been proposed in the last decade. They can be, considering available methods we use, separated into two groups: (1) paleontological, such as palynofacies, various ratios of dinoflagellate groups, specific taxa or groups of benthic and planktonic microfossils, intensity of macrofaunal bioturbation; and (2) geochemical like $CaCO_3$ variations, total organic carbon (TOC) content, hydrogen index (HI), biomarkers, isotope composition (^{13}C), trace elements etc. It is evident that application of these paleo-proxies are subject to various limitations. For example, it is known that early diagenetic processes may considerably alter the primary paleoproductivity signal. Geochemical parameters are especially sensitive to such secondary alteration. Close-correlation with organic fossil parameters is therefore required to help to avoid misleading interpretation.

Diagenetic overprints are strongly pronounced within black shale anoxic and dysoxic facies. Higher fluxes of organic matter usually cause steep geochemical gradients bringing about dissolution, precipitation, up- and downward diffusion of various compounds within the uppermost portion of the sedimentary column. Much of information is usually lost, but at least part of it may be „frozen" in early diagenetically formed concretions, which are relatively common within black shale facies. Perfectly preserved macrofossils are known from such concretions. Such concretions can provide more information when compared with the background signals of the black shales.

This case study was undertaken in the Upper Aalenian-Lower Bajocian black and dark grey claystones and mudstones of the Skrzypny Shale Formation in the Polish and Slovak parts of the Pieniny Klippen Belt (Western Carpathians). The sequence includes common concretions which were collected together with shale samples.

The analyses of foraminiferal assemblages has indicated lower primary productivity and/or suboxic conditions during deposition of the lower part of the black shales and higher primary productivity for the upper part. Low primary productivity is suggested by low foraminiferal abundances and dominance by epibenthic forms. High productivity (higher nutrient supply and utilization) is supported by high numbers of foraminifers per gram of sediment, increased numbers of endobenthic forms, and the appearance of flood abundances of epibenthic epistominids (primarily weed fauna). The expected strong difference in organic carbon influx has been examined by determining the TOC level. Surprising, both parts of the black shale sequence appears to contain relatively low concentrations of organic matter (0.5-1.1 wt.%; overmatured organic matter). This contrasts with the foraminiferal palaeoproductivity interpretations. Palynofacies analysis of the shales has revealed slighly more meaningful information showing an increase in amorphous organic matter within the more productive interval.

The change of palynofacies is much more distinctive in the concretions. Comparison of palynofacies between shales and concretions has revealed a strong increase in „marine" components, such as dinoflagellates and amorphous organic matter. Thus, concretions appear to be an early diagenetic trap for more reactive, marine organic matter, showing a better relationship with the original character of the sedimentary organic mater.

Further studies have revealed that foraminiferal assemblages are strongly correlated with the type of sedimentary concretions. Carbonate (sideroplesite and calcareous) concretions occur in the low productivity interval and phosphatic concretions are present within the highly productive interval. Moreover, phosphatic nodules are distinctly enriched in barium, which has been suggested to be a good paleo-proxy for primary productivity.

Comparison of paleontological and geochemical signals of primary productivity has revealed the utility of paleontological indicators, especially in diagenetically altered deposits.