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Geochemical evidences for photic zone euxinia during the end - Ordovician mass extinction event from the black shales of Poland

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The end-Ordovician (Hirnantian) extinction belongs to so called “big five” Phanerozoic mass extinctions and, along with end-Permian and end-Cretaceous to three globally distinct extinction events (Bambach et al. [1]). Knowledge about redox conditions during deposition of the end-Ordovician and lowermost Silurian sedimentary rocks are still insufficient to define the impact of anoxia/euxinia on mass extinction. Here we report the multi-proxy record of redox condition changes during end-Ordovician and early-Silurian deposition in the deep shelf basin from the Holy Cross Mountains and shallow epeiric sea from the E part of Pomerania Basin. Because of relatively low maturation, what is rare to such old sedimentary rocks, it was possible to apply organic indicators of photic zone euxinia supported by inorganic proxies and pyrite framboid diameter study. The 47 samples were collected from the boreholes Zbrza PIG-1 and Gołdap IG-1, which are represented by different kind of claystones and black shales. The shale samples from the Zbrza well (Holy Cross Mountains) are characterized by significant variations in TOC, ranging from c.a. 0.2% to 8.3% at the Ordovician - Silurian boundary (O-S). The TOC values of the two Rhuddanian samples from the Gołdap IG-1 borehole (Pomerania Basin) are around 6% TOC. TOC content pattern across the Zbrza section corresponds generally to the inorganic proxies values, as well as to total sulphur content, reflecting variable redox conditions. For the Zbrza PIG-1 profile, relatively low values of trace metals proxies, such as U/Th, Mo (ppm), $U_{authig.}/V/Cr$, have been noted in Katian and are being continued through the Hirnantian. The gradual increase of the values has been recorded just before the O-S boundary. The U/Mo ratio has recorded quite high values, through the Katian to Hirnantian with the mean value 3.6, while O-S is characterized by the mean 1.2. In the case of Gołdap IG-1 well, the results of trace metals content are in accordance as well. Pyrite framboids are common in almost all samples. Lower part of Wolka Formation (Katian) contains large populations of small framboids (mean diameters around 5 μm), with low standard deviations, while the younger part of the formation (Hirnantian) does not contain framboids at all. The end of Hirnantian is the beginning of change in redox conditions with large population of small framboid pyrites, what continues through the whole Rhuddanian. The set of organic indicator has been elaborated for Ordovician and Silurian rock samples. The most restricted redox conditions at the O-S boundary indicated by inorganic proxies have been confirmed by elevated concentration of aryl isoprenoids, as well as isorenieratane in the case of the samples from the Pomerania Basin. The ratio of steranes to hopanes is low through the Hirnantian, while increasing during the O-S boundary indicating increase of algal blooms. Maleimides (1H-pyrrole-2,5-diones), products of bacteriochlorophyll pigments degradation related to autotrophic sulphur

bacteria (Chlorobiaceae), were identified in samples from both regions. The Katian and the Rhuddanian are the two intervals with Me,*i*-Bu maleimides enrichment. In contrast, for the Hirnantian sedimentary rocks absence of maleimides has been noted.

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References:

[1] Bambach, R.K., Knoll, A.J., & Wang, S.C., 2004. Origination, extinction, and mass depletions of marine diversity: *Paleobiology* 30, 522–542.

