CAN A MARGINAL MARINE LAGOON ENVIRONMENT BECOME SULFATE-DEPLETED BUT SUPPORT PHOTIC ZONE EUXINA?

Wolfgang Ruebsam[a], Michael E. Böttcher[b], Lorenz Schwark[a,c]

[a]Department of Organic Geochemistry, University of Kiel, Germany
[b]Leibniz-Institute for Baltic Sea Research
[c]WA-OIGC, Curtin University, Australia

Euxinic conditions extending into the photic zone of the water column, termed photic zone euxinia (PZE), played a major role during oceanic anoxic events and have assumed to be a key mechanism driving extinction events in Earth history (Whiteside & Grice, 2016). The presence of sulfidic waters in the photic zone can be inferred from the presence of lipids diagnostic for photoautotrophic sulfur bacteria (e.g. *Chlorobiaceae*). These organisms require free H_2S, originated from bacterial sulfate reduction (BSR). In order to establish PZE, BSR rates must be sufficiently high to shift the redox boundary from the sediment into the water column. In marine environments rates of BSR are commonly controlled by the supply of degradable organic matter, whereas sulfate can be a limiting factor in freshwater environments (Berner & Raiswell, 1984).

Here we present data for an excellently preserved sediment core from the "Gera" lagoon revealing evidence for prolonged euxinic conditions in a restricted but sulfate-depleted depositional system in the southern Kupferschiefer Sea (Ruebsam et al., 2017).

There, the laminated bedding of the Kupferschiefer sediment in combination with the occurrence of small-sized (<10 µm) and finely dispersed framboidal pyrite attested to euxinic conditions, supported by a complete lack of benthic activity. Permanently reducing conditions were further indicated by the excellent preservation of C_{35} hopanes (Peters et al., 2005) and by high concentrations of sedimentary organic matter (TOC up to 5%; $TOC_{carb\text{-}free}$ up to 18%), mainly derived from red algae and cyanobacteria. Moreover, significant abundances of isorenieratane, derived from *Chlorobiaceae*, revealed that euxinic conditions will have expanded into the photic zone of the Kupferschiefer Sea. On the contrary, the sediments investigated revealed a comparably low total sulfur content (TS 0.4 to 2.9%; $TS_{carb\text{-}free}$ up to 13%), resulting in TOC/TS >2.5, with no evidence of later diagenetic sulfur removal. Elevated TOC/TS ratios are considered characteristic for sulfate-poor freshwater environments (Berner & Raiswell, 1984). In the case of the "Gera" lagoon, C/S ratios are explained by freshwater contributions from riverine inflow combined with a strong hydrological restriction of the lagoon, preventing the reflux of sulfate-replete waters from the open Kupferschiefer Sea (Ruebsam et al., 2017). Riverine discharge has been indicated by the occurrence of fossil land plant remains and lipids indicative for terrigenous contributions (long chain *n*-alkanes). Moreover, the freshwater inflow is manifested in low DBT/Phen and TS/Fe_X ratios attesting to the enhanced availability of reactive iron that prevented the incorporation of sulfur into OM.

Results from organic and inorganic geochemistry will be discussed in conjunction with $\delta^{34}S$ data that will further improve our understanding of the "Gera" lagoon sulfur cycle. Combination of these tools will provide detailed and comprehensive information on depositional and environmental conditions in the euxinic freshwater lagoon, emphasizing the benefits of multiproxy investigations. Results further show that the presence of lipids derived from green sulfur bacteria does not imply highly sulfidic waters. In contrast, *Chlorobi* can also contribute to the sedimentary organic matter in sulfate-poor and

potentially weakly sulfidic environments. This contribution will in depth discuss the complexity in the application of isorenieratane in environment reconstruction.

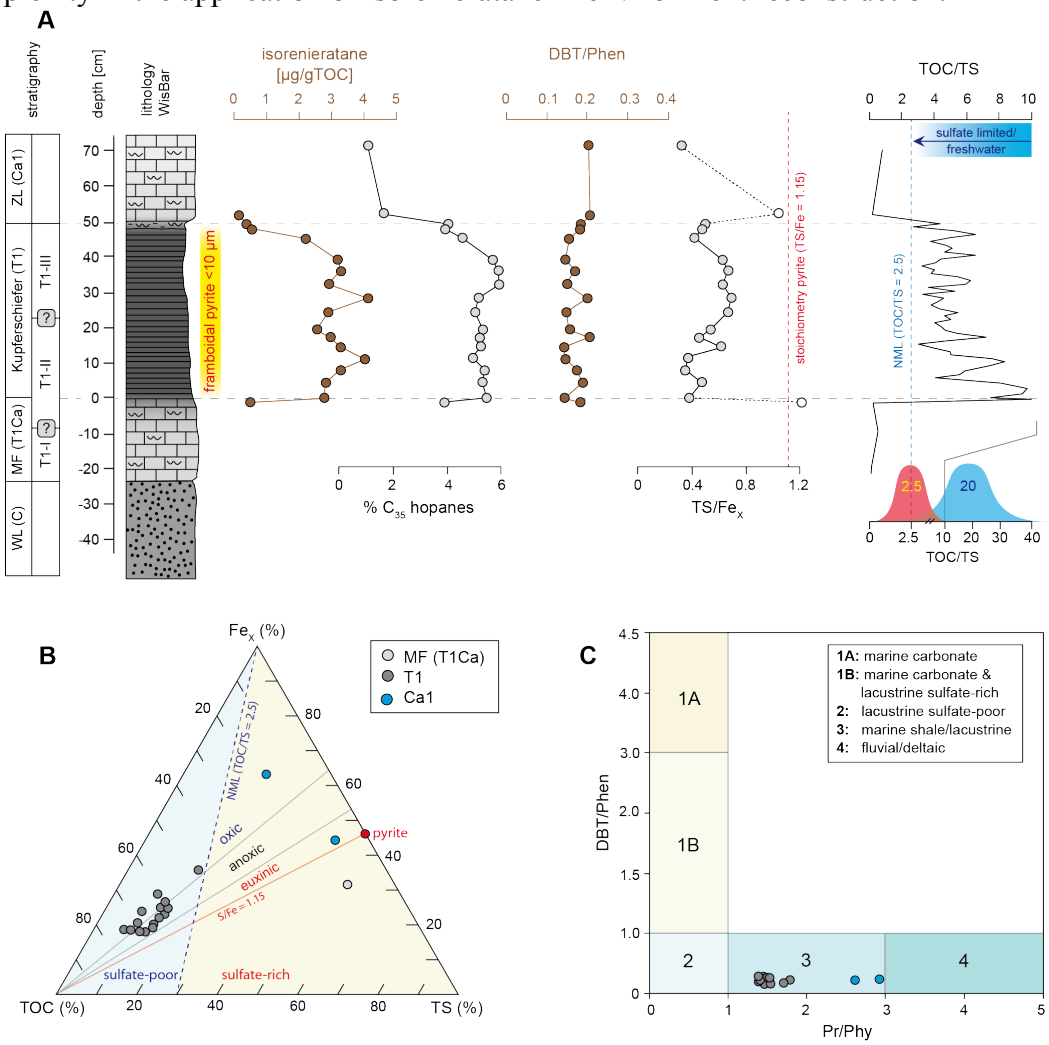

Figure 1 A) *Kupferschiefer section from the "Gera" lagoon showing lithology and stratigraphic evolution of selected redox proxies. The excellent preservation of C_{35} hopanes attests to reducing conditions, whereby the presence of isorenieratane revealed that euxinic conditions have extended into the photic zone. Low DBT/Phen in combination moderate TS/Fe_X ratios point to Fe-replete waters, limiting the formation of organosulfur compounds. High TOC/TS ratios indicate sulfate-poor waters controlling bacterial sulfate reduction and, thus, pyrite formation in the freshwater-affected lagoon. Ranges of TOC/TS data for marine (red) and lacustrine settings (blue) are shown for comparison (Berner & Raiswell, 1984).* ***B)*** *Position of the data points within the TOC-TS-Fe_X ternary diagram attests to a sulfate-poor freshwater environment, in which pyrite formation was controlled rather by the availability of sulfate than by the availability of organic matter or iron (NML = normal marine line).* ***C)*** *Low sulfate concentrations in combination with Fe-replete waters resulted in low rates of organosulfur compound formation, indicated by low DBT/Phen ratios.*

References

Berner, R.A., Raiswell, R., 1984. C/S method for distinguishing freshwater from marine sedimentary rocks. Geology 12, 365 – 368.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide: Volume 2, Biomarkers and Isotopes in Petroleum Systems and Earth. Cambridge University Press, 1132 pp.

Ruebsam, W., Dickson, A.J., Hoyer, E.M., Schwark, L., 2017. Multiproxy reconstruction of oceanographic conditions in the southern epeiric Kupferschiefer Sea (Late Permian) based on redox-sensitive trace elements, molybdenum isotopes and biomarkers. Gondwana Research 44, 205 – 218.

Whiteside, J.H., Grice, K., 2016. Biomarker Records Associated with Mass Extinction Events. Annual Review of Earth and Planetary Sciences 44, 581 – 612.