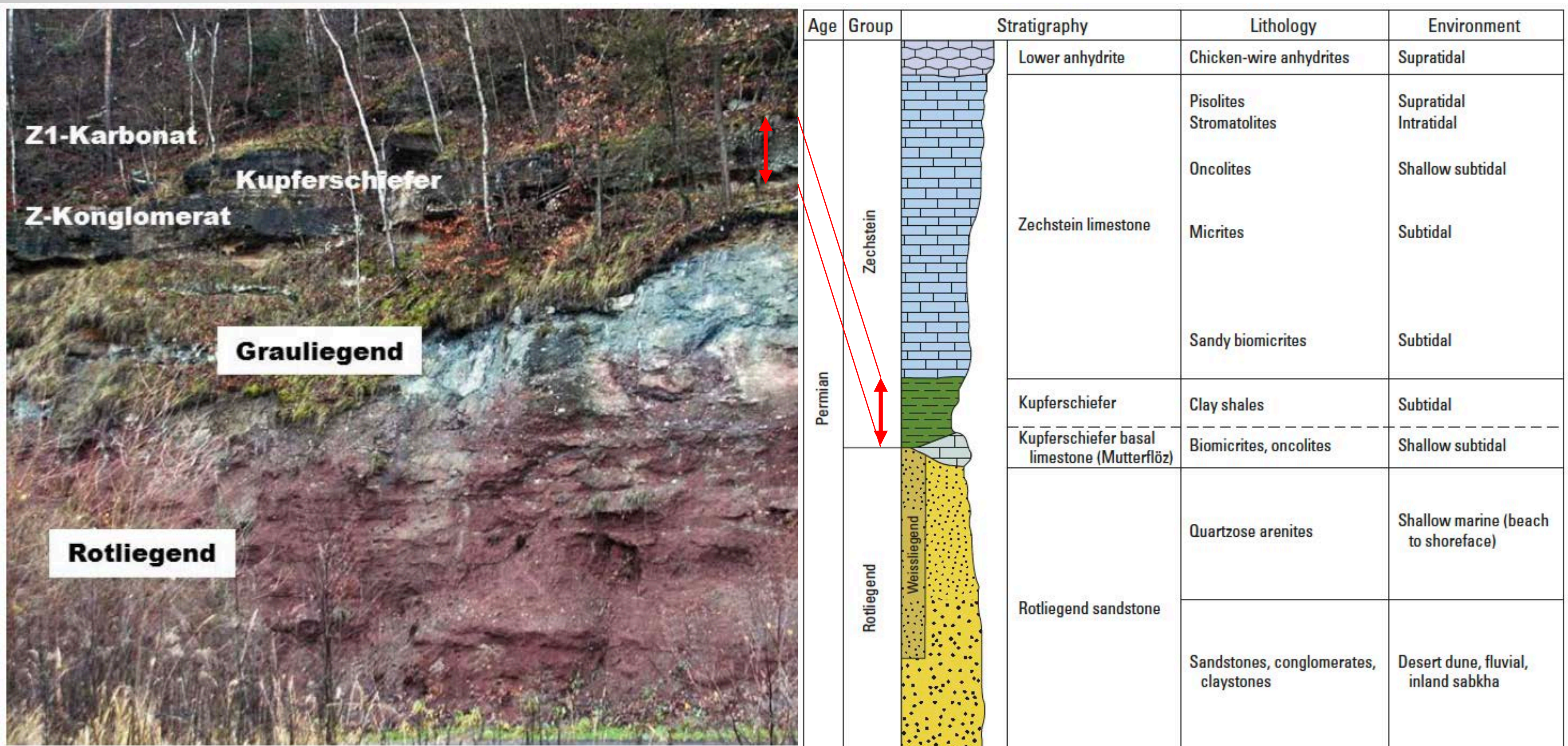
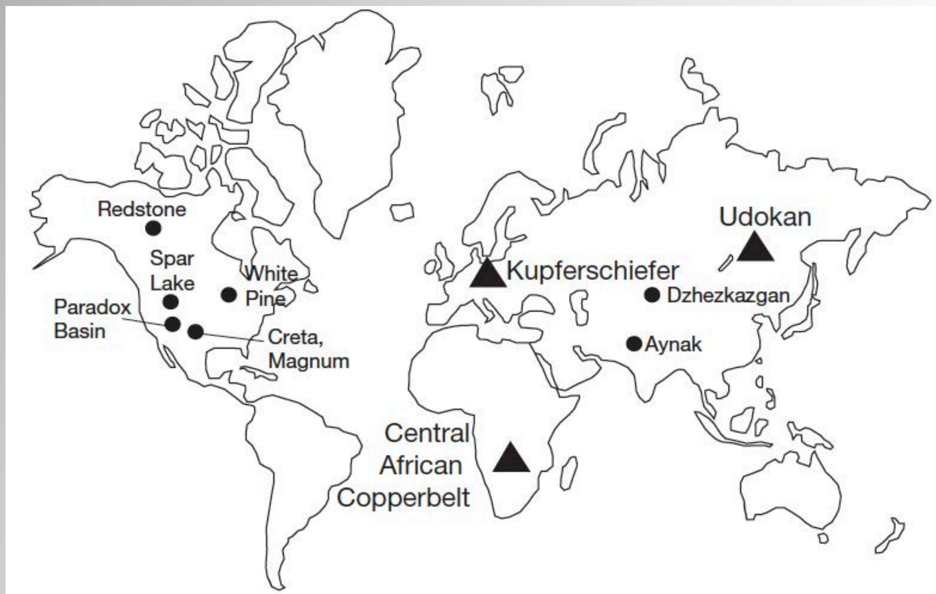
Paleo-ecosystems: upper Permian Kupferschiefer

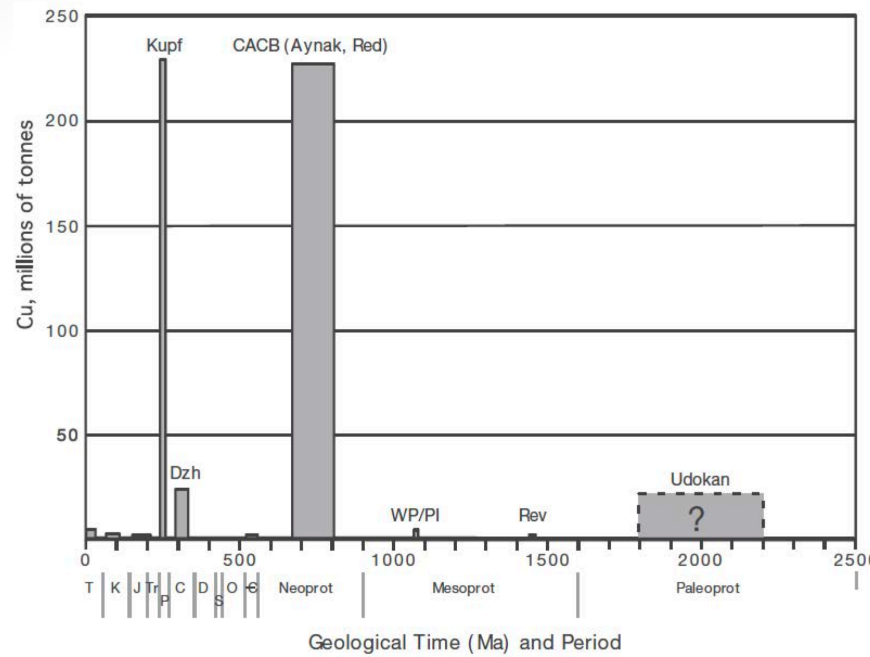
Kupferschiefer:

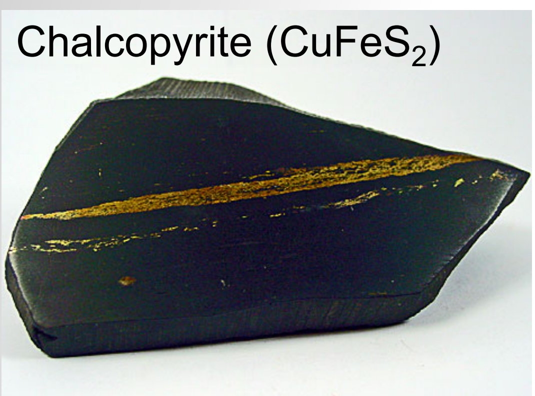
- Upper Permian bituminous and fossilious clay-/marlstone
- Deposited in the Southern Permian European Basin
- Marking the base of the Zechstein
- Thickness mainly between 30 – 60 cm (>1 m at marginal settings)

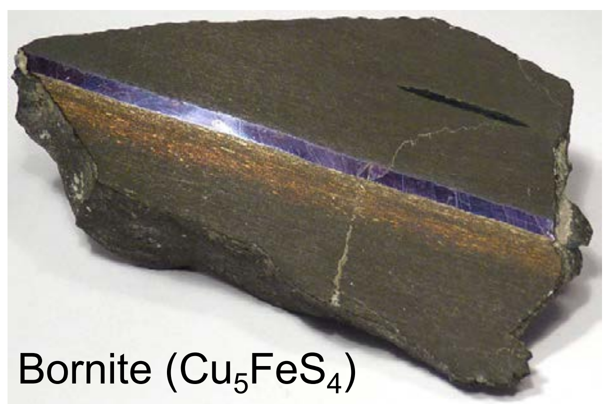


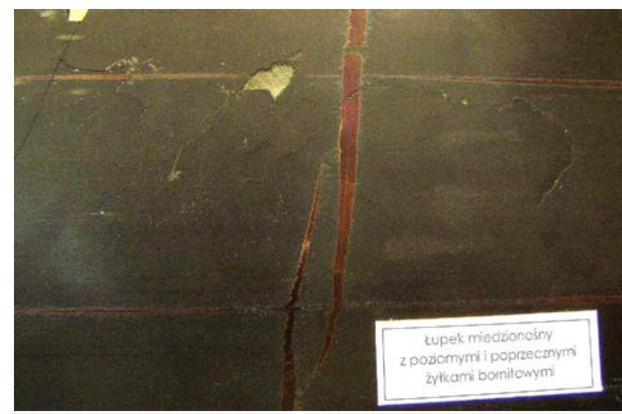
Paleo-ecosystems: upper Permian Kupferschiefer



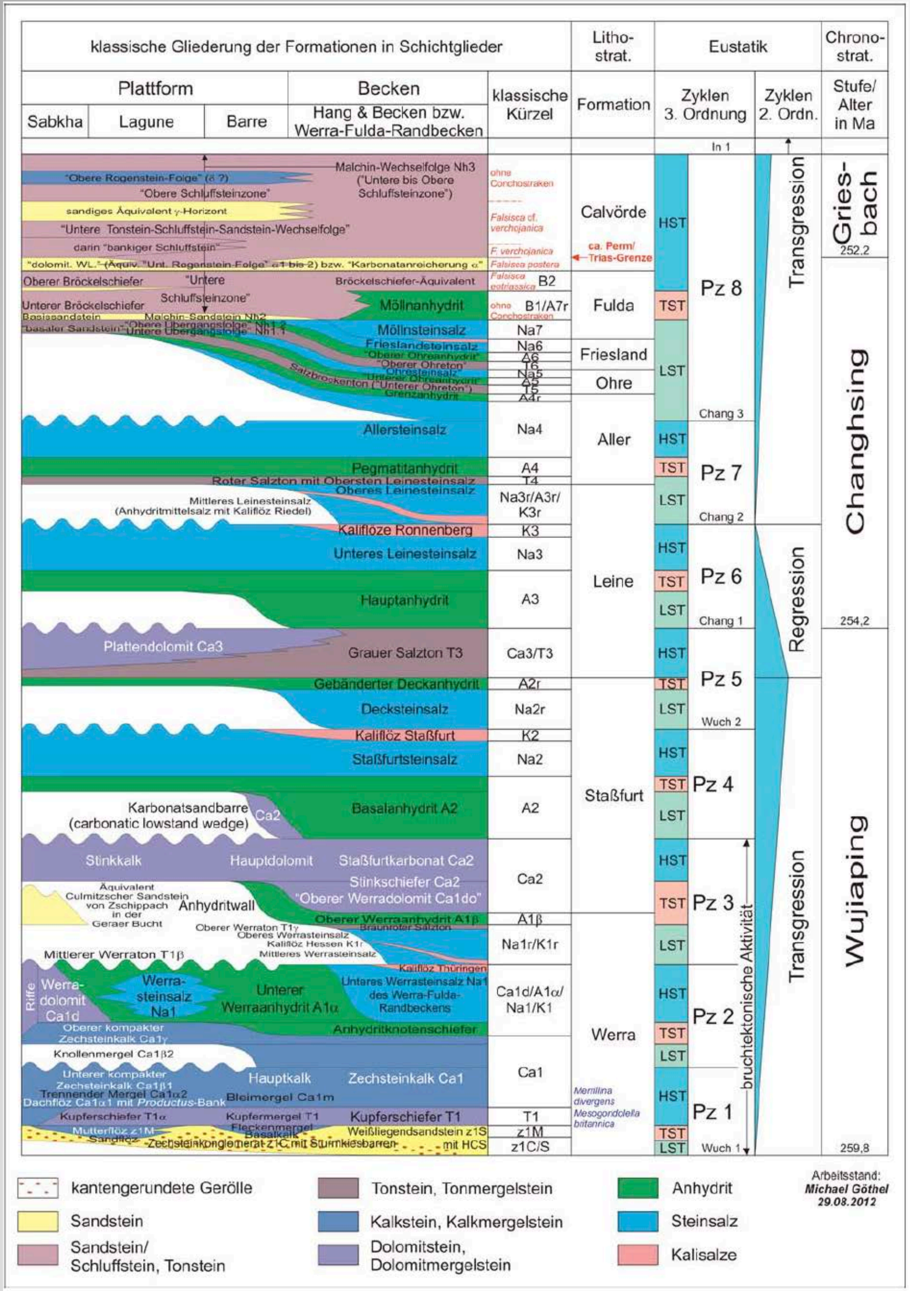



Chalcopyrite ($CuFeS_2$)


Bornite (Cu_5FeS_4)



Sedimentary-rock hosted stratifrom metal deposit: Cu, Pb, Zn (locally >1%); Ni, Co, Ag, Au. Multistage metal enrichment associated with syn- and epigenetic processes.



The Kupferschiefer overlays Rotliegend clastics and marks the base of the Zechstein. The later mainly comprises evaporite and carbonate sequences.

Due to an lack of index fossils (e.g. Conodonts) an exact correlation of the Kupferschiefer with the global Permian timescale is problematic.

However, faunas suggest a Late Permian (Wujiapingian age; about 257 Ma BP) (Legler et al., 2005 and references therein).

The Permian-Triassic boundary can be placed in the lower Buntsandstein Formation, directly overlying Zechstein sediments (e.g. Nawrocki, 2004; Scholze et al., 2016).

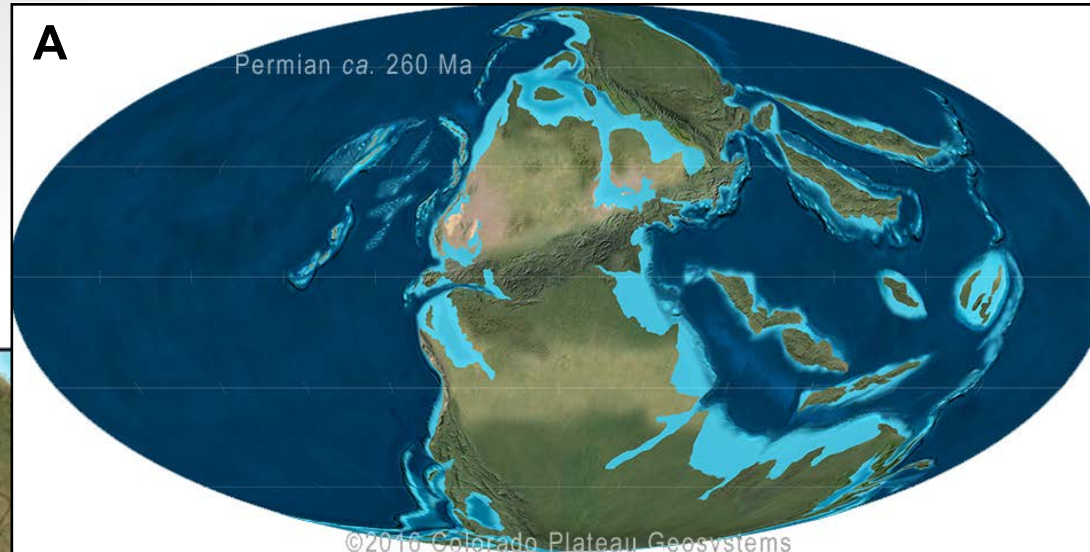
Paleo-ecosystems: upper Permian Kupferschiefer

Distribution of Kupferschiefer and Zechstein sediments, deposited between 257 – 253 Ma BP across present-day Europe.

Paleo-ecosystems: upper Permian Kupferschiefer

A: Global paleogeography upper Permian (260 Ma).

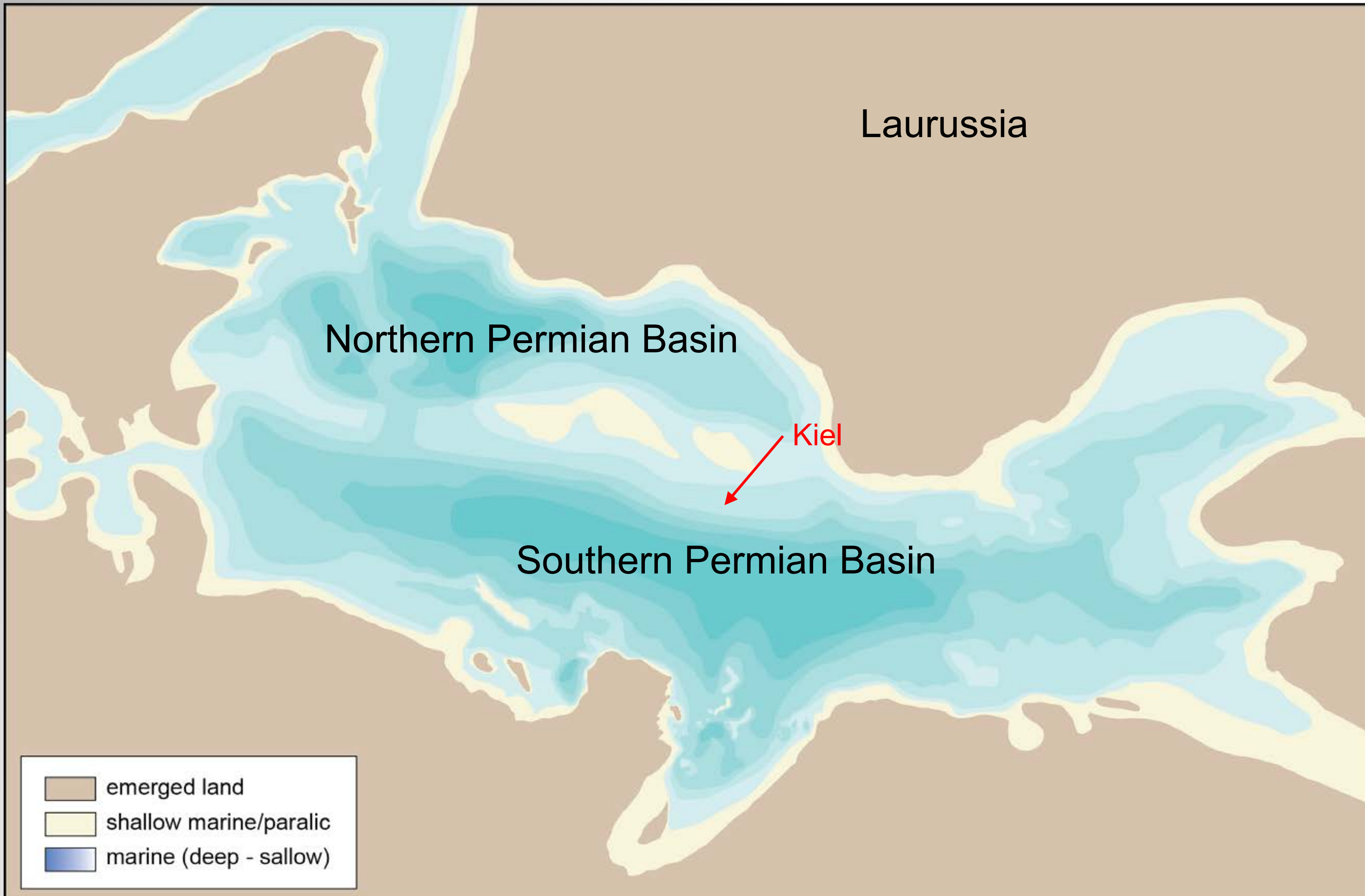
B: Paleogeography of the present-day Europe and adjacent areas.



Blakey

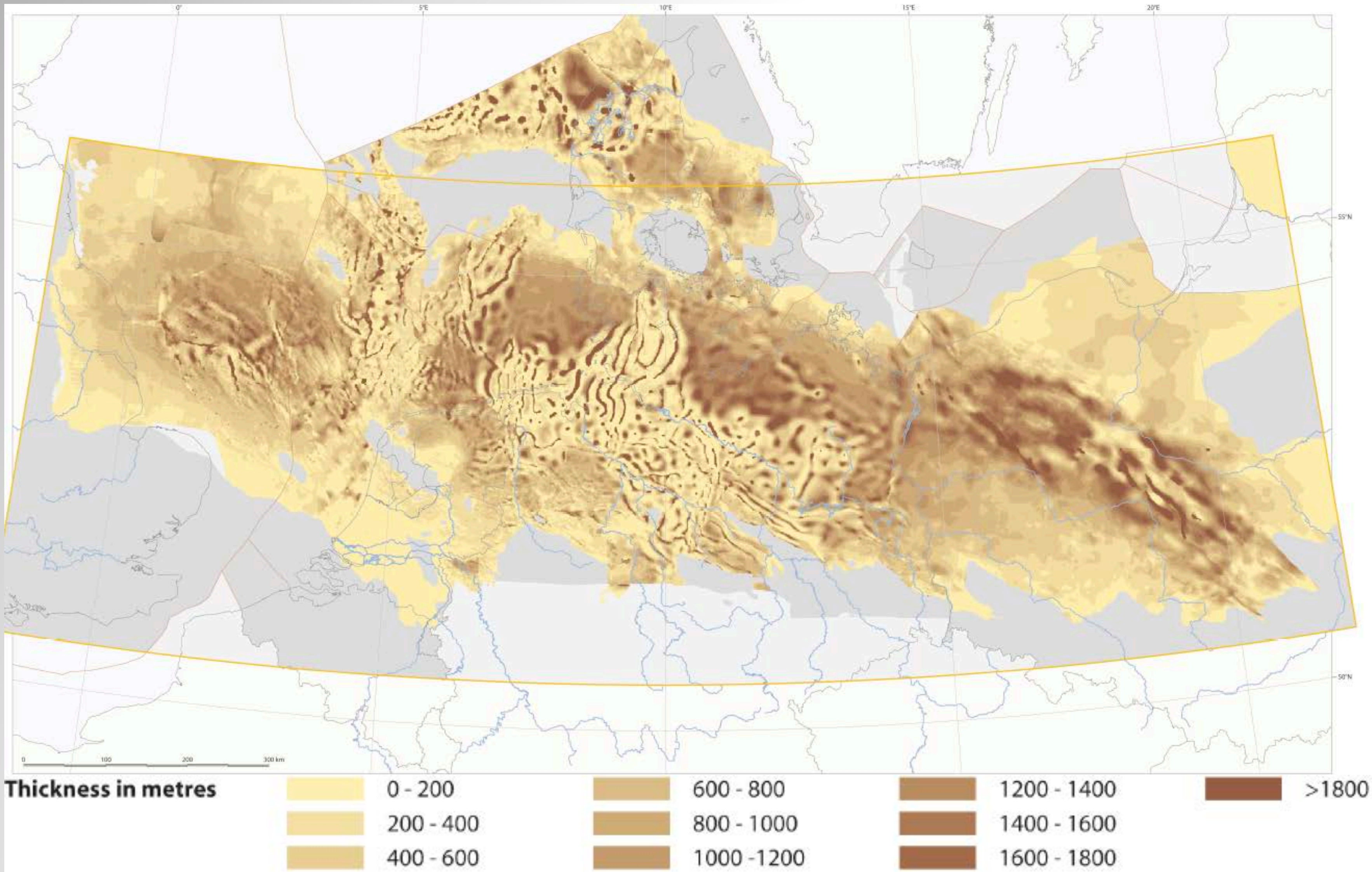
(Paleogeographic maps)

Paleo-ecosystems: upper Permian Kupferschiefer

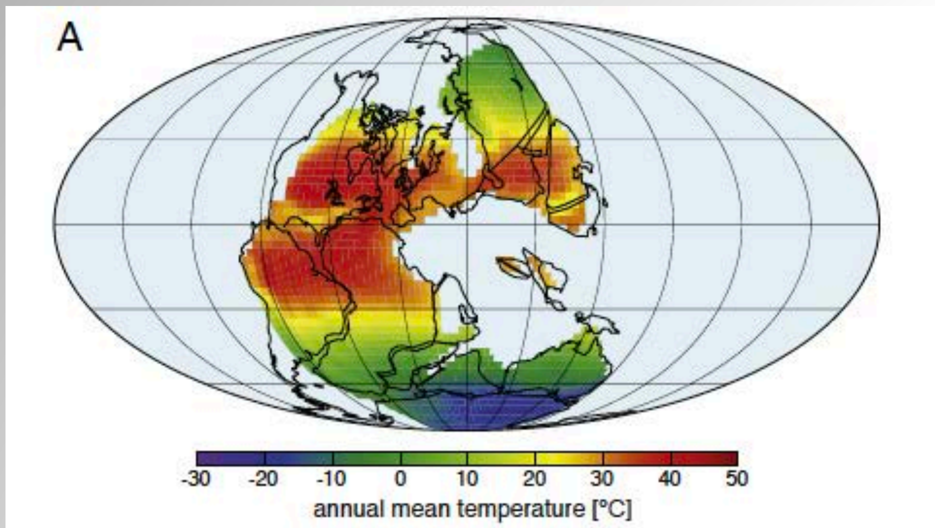


Detailed paleogeographic reconstruction of the southern Permian Basin during deposition of the Kupferschiefer.

Paleo-ecosystems: upper Permian Kupferschiefer



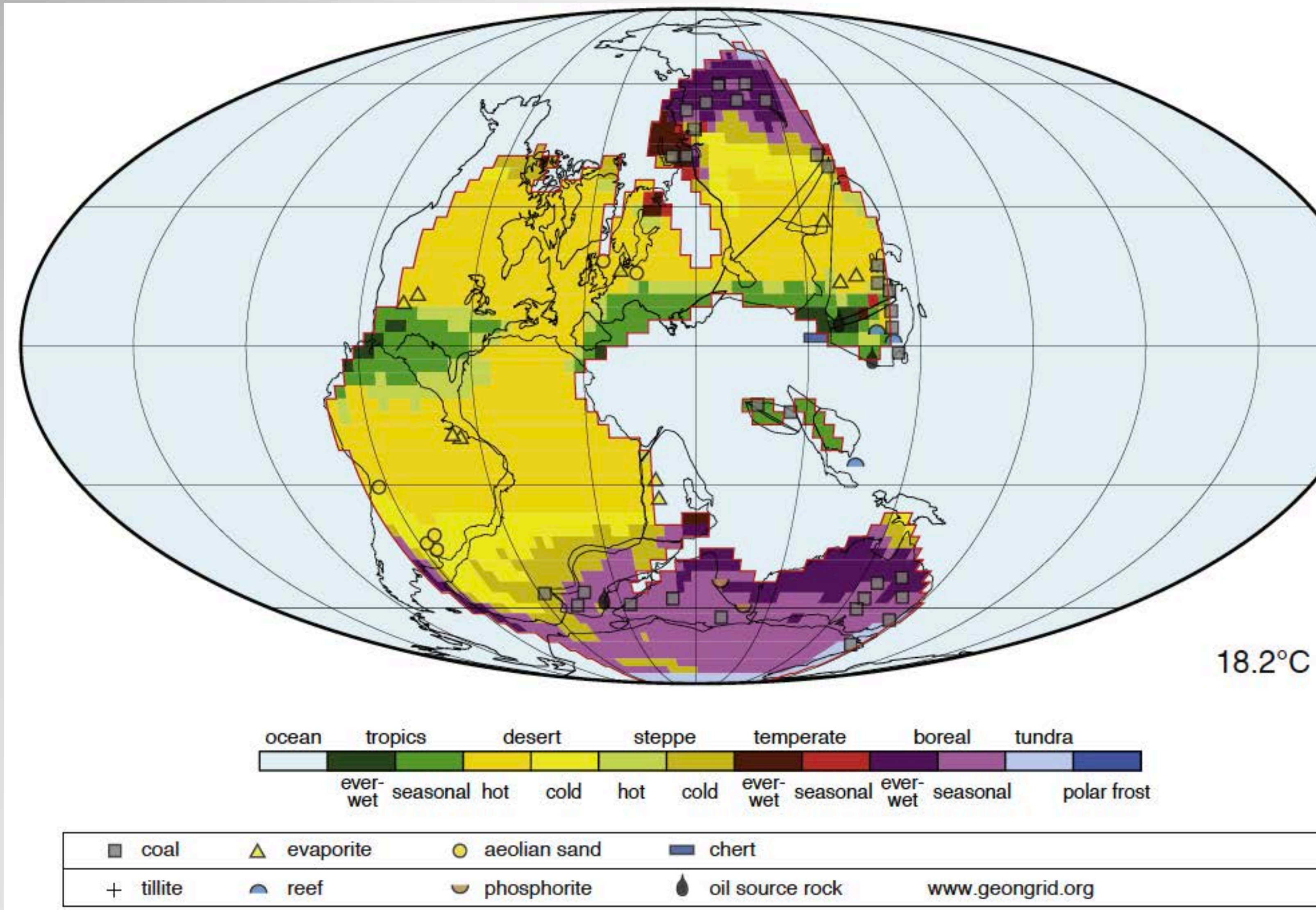
Thickness of Zechstein deposits in the Southern Permian Basins (Peryt et al., 2010). In central parts of the basin more than 1000 m of sediments have been accumulated within 4 – 7 Myr. Spatial variations in the thickness of the deposits can be linked to the basin morphology.



A: Climate models for the Late Permian attested to a strong latitudinal temperature gradient. Hot climates prevailed between 30°S and 30°N, while extreme cold climate conditions has been reconstructed for polar latitudes. On the southern hemisphere ice caps have been formed at polar regions.

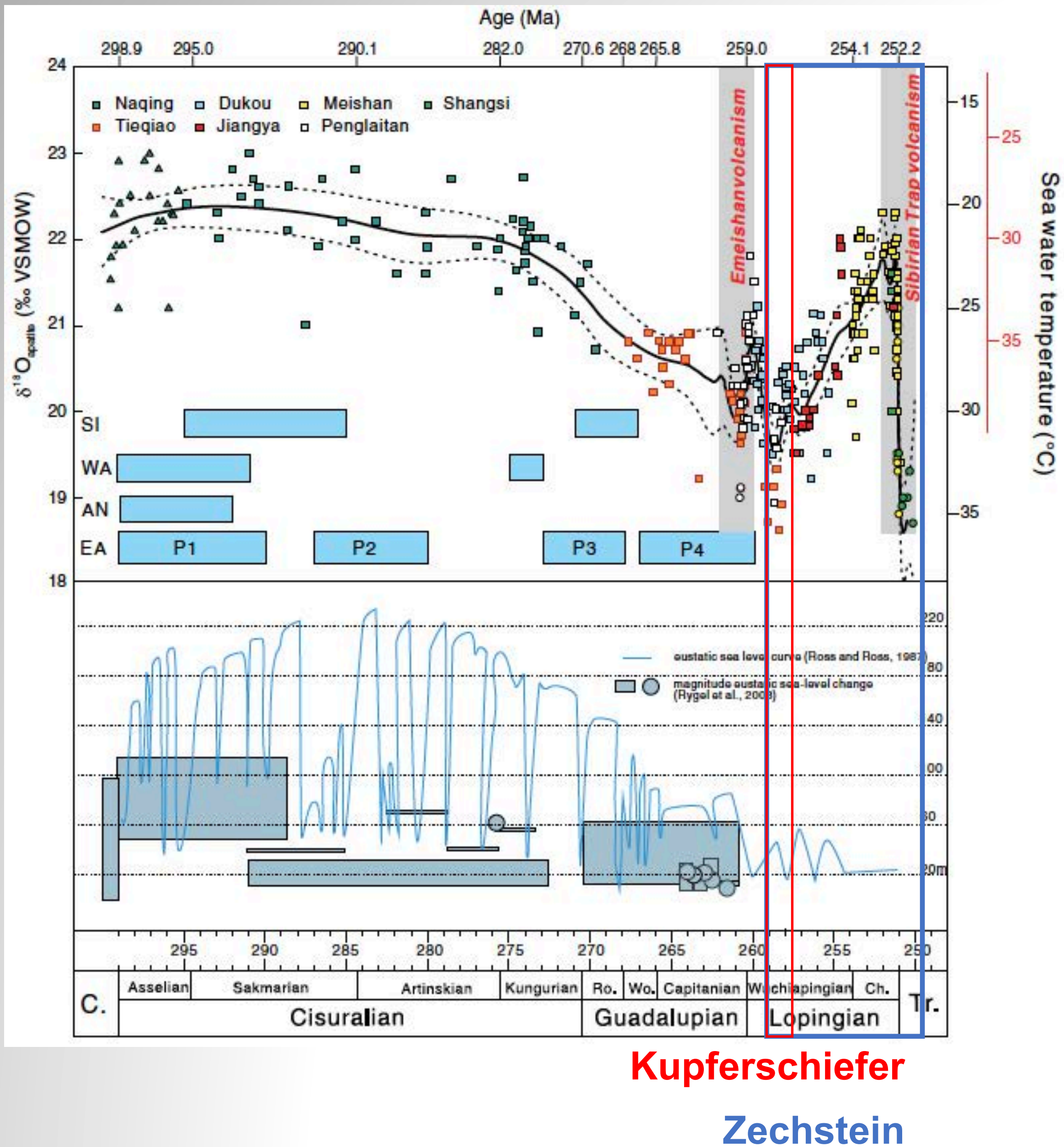
B: Huge continental areas of Pangea controlled the global distribution of rainfall. Central areas of Pangaea were characterized by extreme low precipitation rates. Figures from Roscher et al. (2011).

Paleo-ecosystems: upper Permian Kupferschiefer



Late Permian climate zones (Roscher et al., 2011). Arid climates prevailed in central parts of Gondwana as well as between 15 – 40°N.

Paleo-ecosystems: upper Permian Kupferschiefer



Permian climate evolution and glacial history after Chen et al. (2013).

The upper Permian is marked by a long-term global warming. Rising SSS has been inferred from apatite oxygen isotope values and could be associated with enhanced volcanic activity.

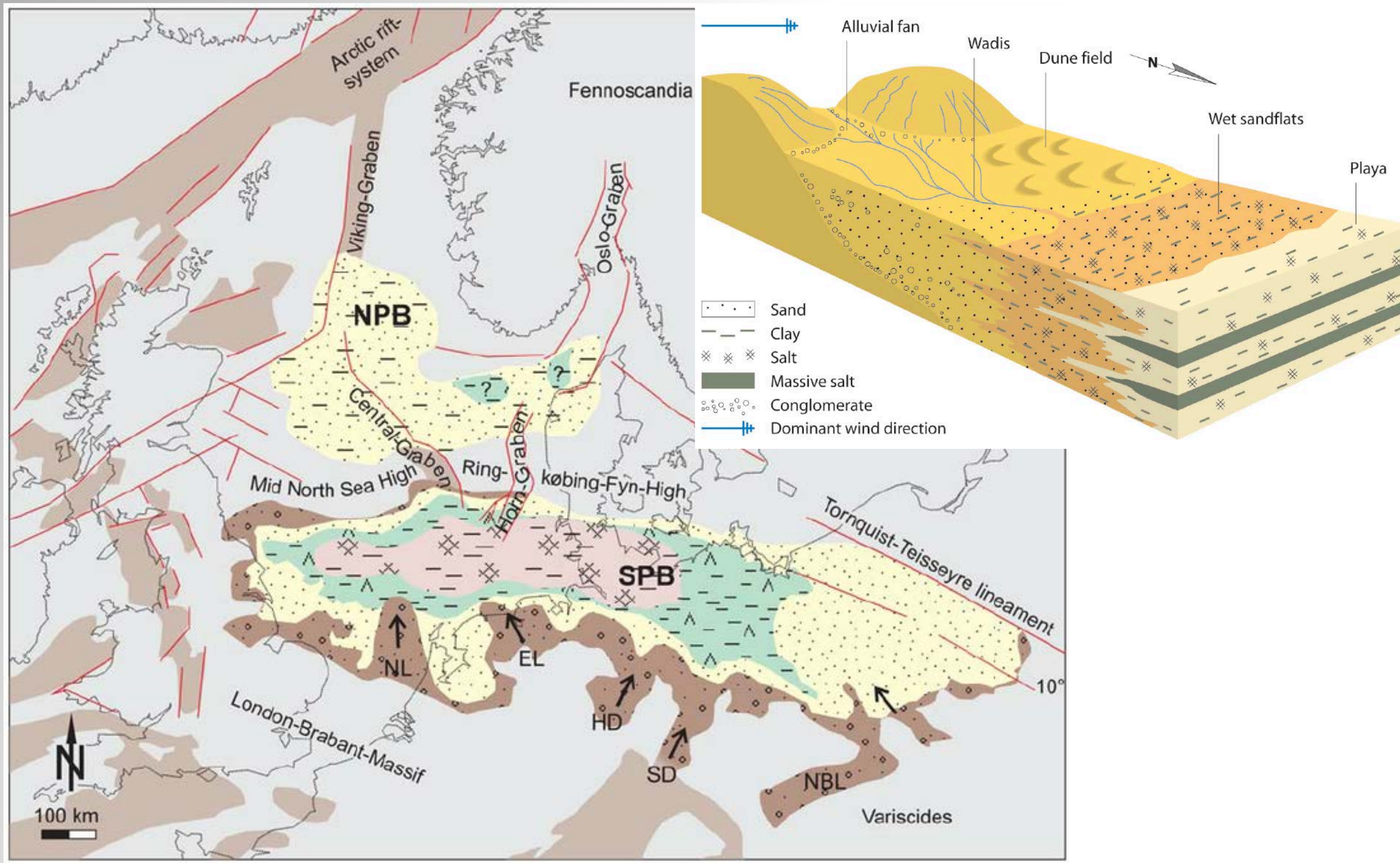
Warming was accompanied by a demise of polar ice caps, initiating a high-amplitude glacio-eustatic sea level changes.

Global warming culminated in the Permian-Triassic mass extinction, one of the most severe extinctions in Earth's history.

The European Permian Basins

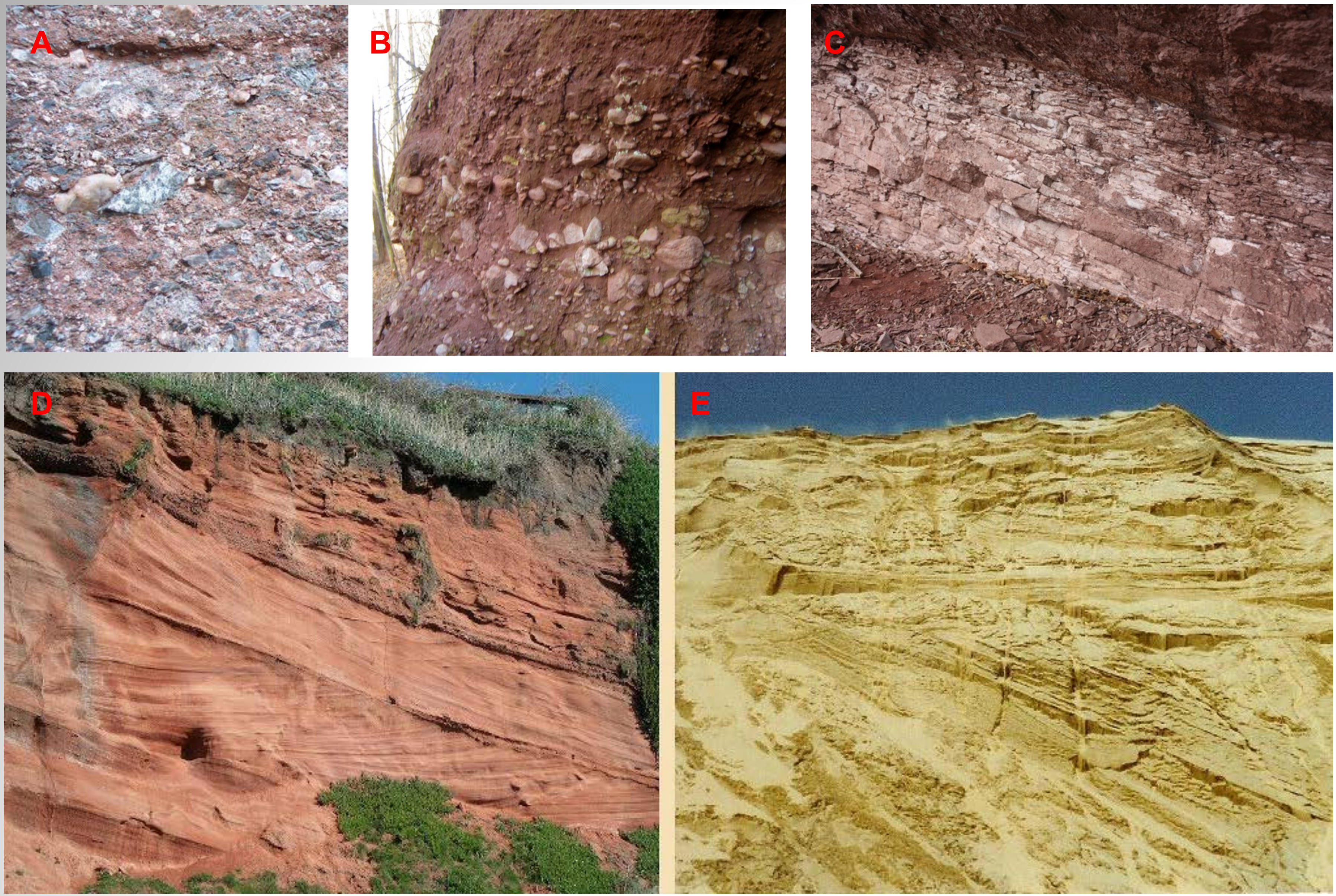
prior to the formation of the Kupferschiefer/Zechstein Sea

Paleo-ecosystems: upper Permian Kupferschiefer



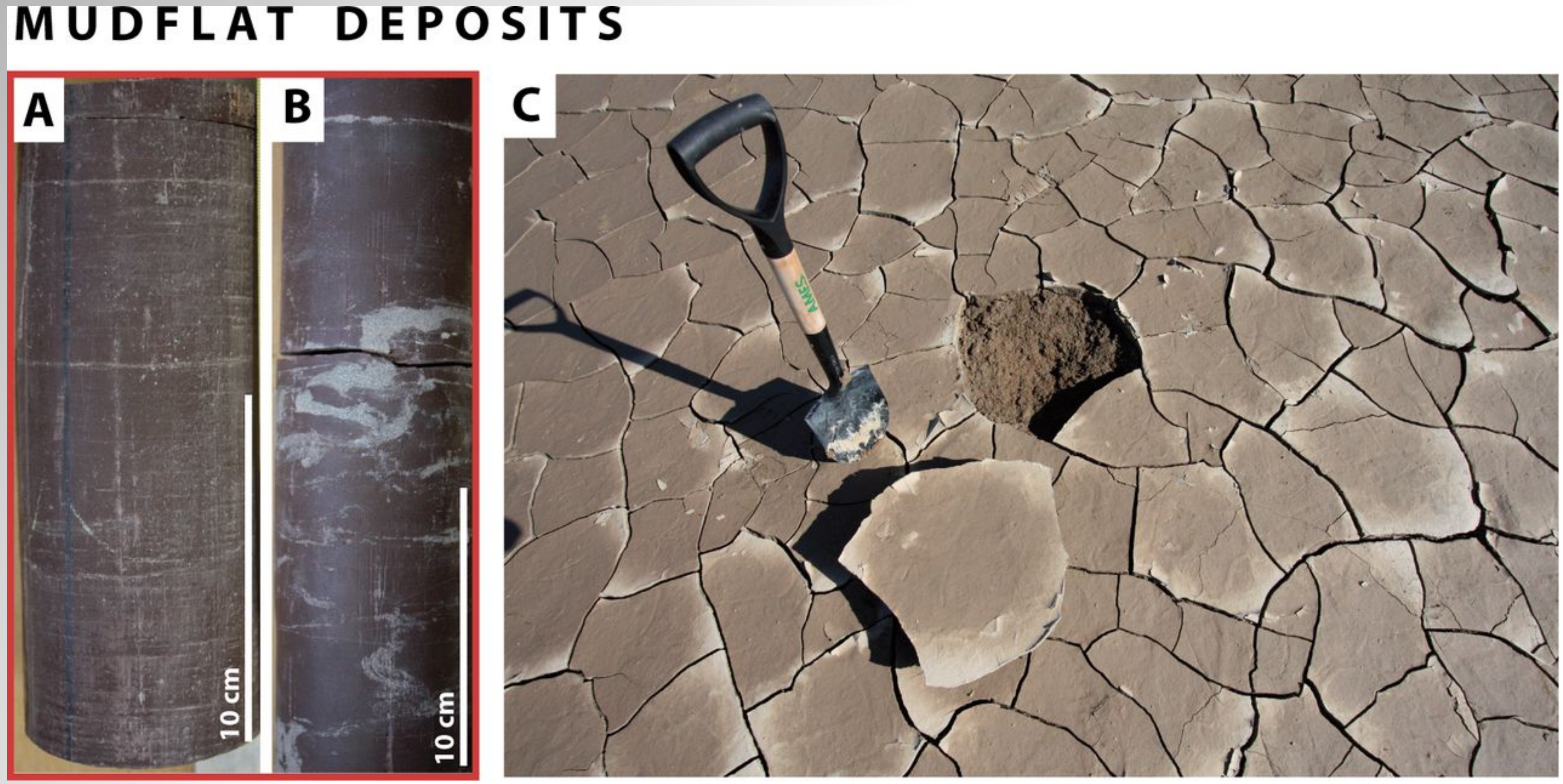
Upper Rotliegend paleopgeography of the European Permian Basins, a huge depression that has been formed north of the Variscian Mountains. The basin was situated a few hundreds of meters below the sea level (e.g. Ziegler, 1990).

Paleo-ecosystems: upper Permian Kupferschiefer



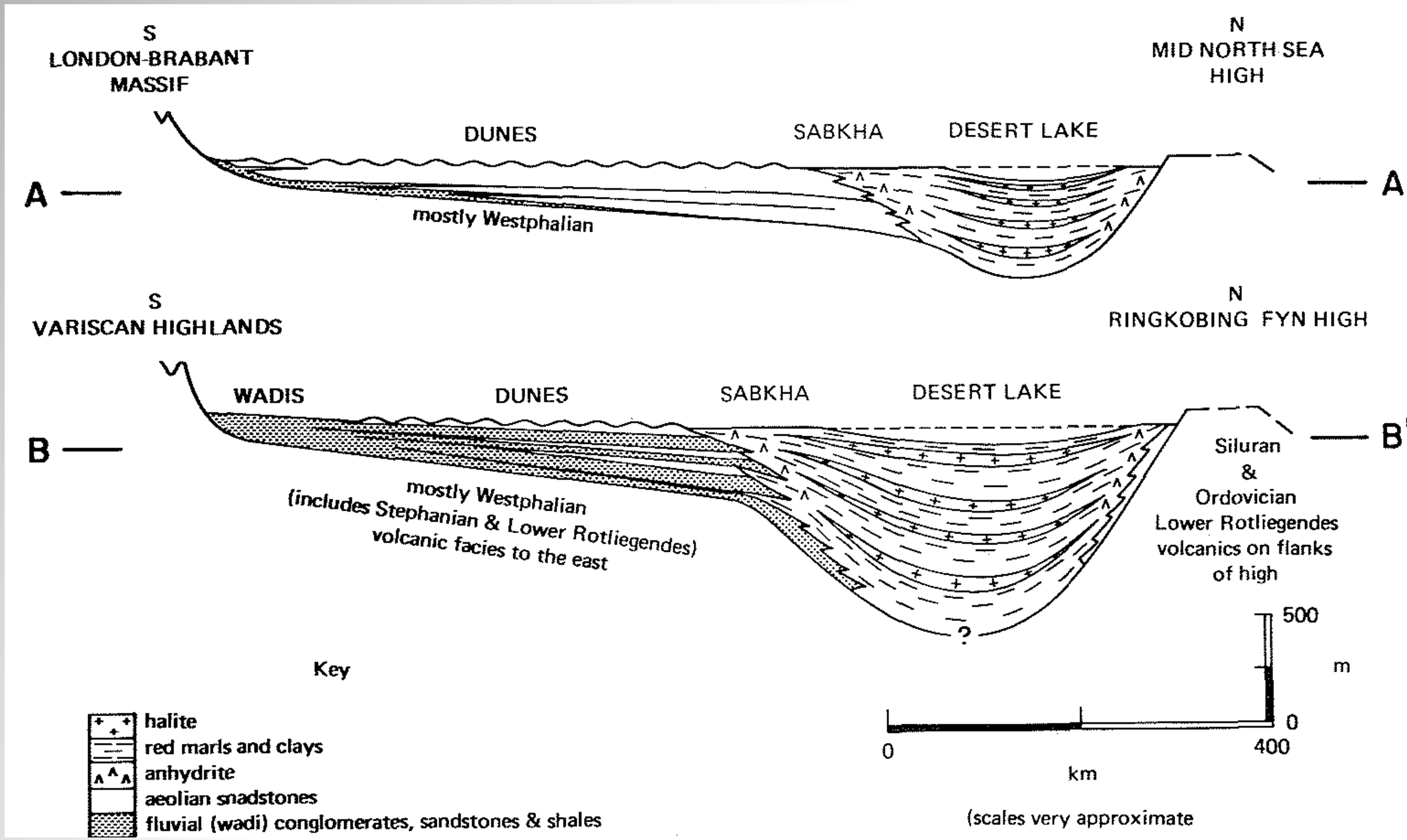
A, B, C: Rotliegend conglomerates and sandstones.

D, E: Permian cross-bedded dune sands exposed at the Dawlish Bay (UK) (West & West, 2008).



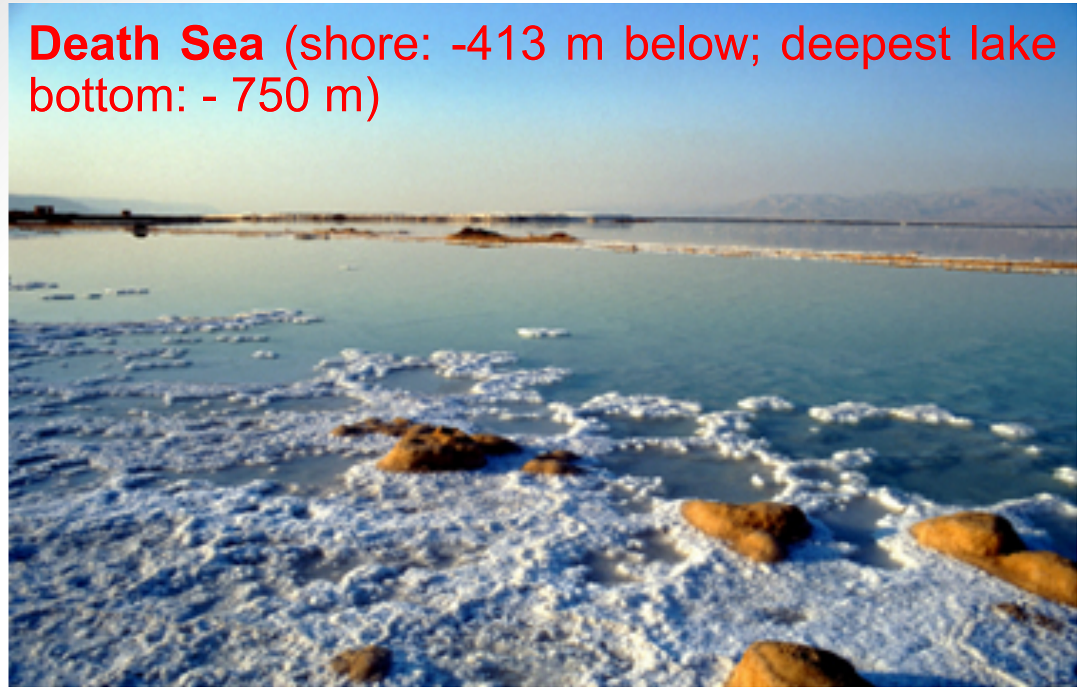
In the central part of the European Permian Basin Sabkha/Mudflat sediments have been deposited during Rotliegend times. Lacustrine sediments have been deposited in palaeolake systems that were sourced by rivers and eventually by periodic minor marine ingressions (Legler & Schneider, 2008).

Paleo-ecosystems: upper Permian Kupferschiefer



Transect through the Southern Permian Basin Systems during upper Rotliegend times (Glennie, 1972).

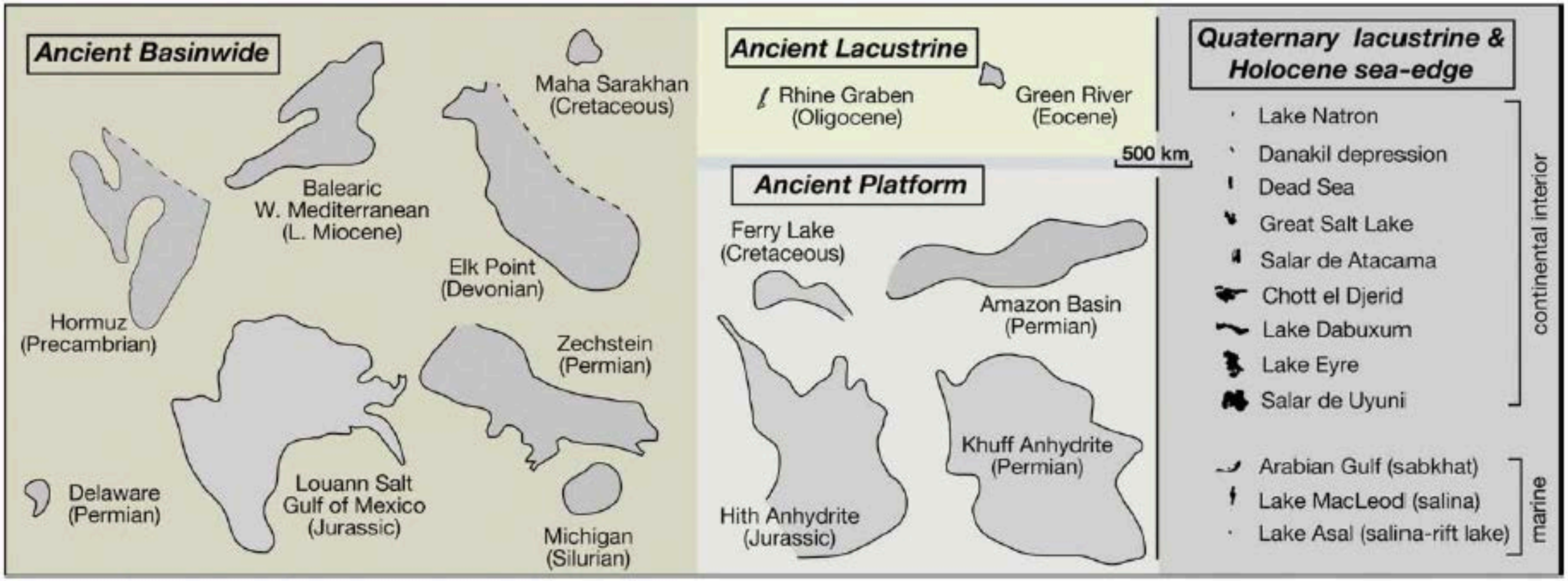
Paleo-ecosystems: upper Permian Kupferschiefer



Death Sea (shore: -413 m below; deepest lake bottom: - 750 m)

Salten Trough (-76 m)

Paleo-ecosystems: upper Permian Kupferschiefer

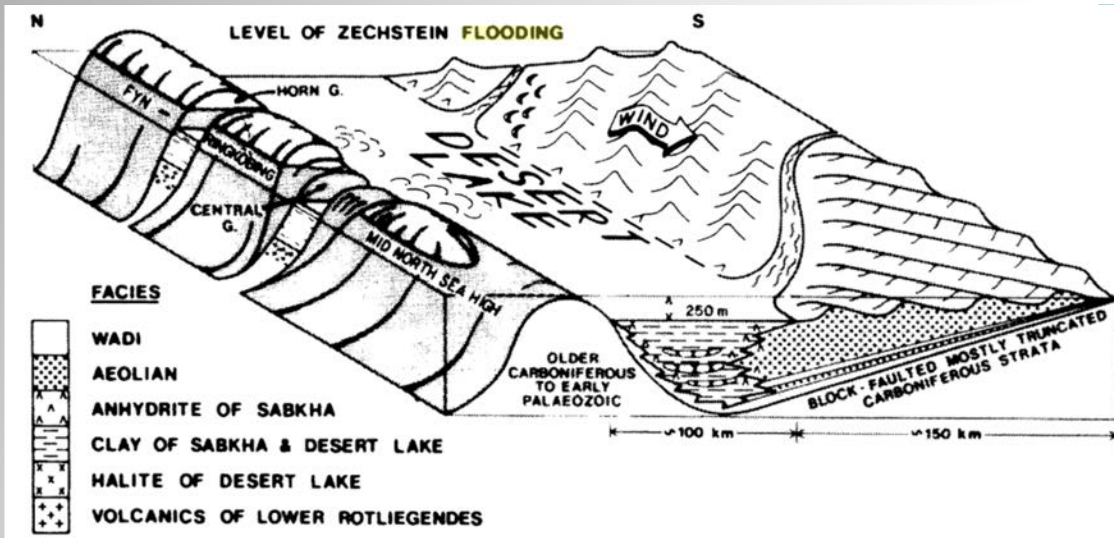


Extent of ancient and recent evaporite basins (Warren, 2010)

Flooding of the European Permian Basins

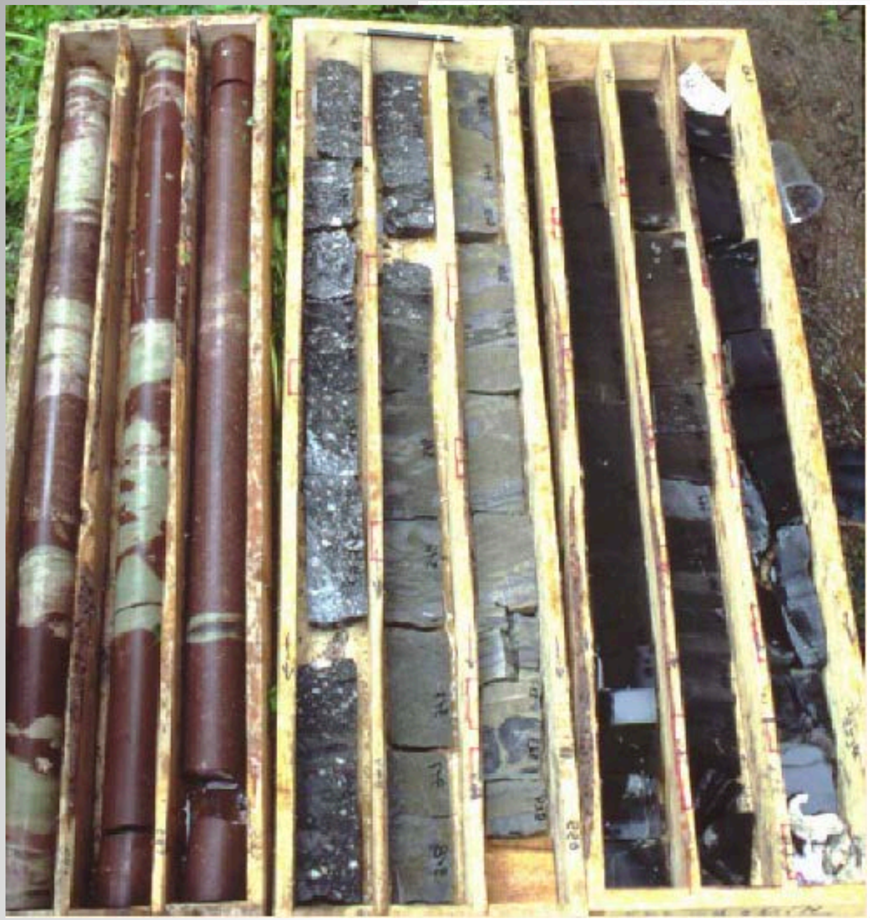
and formation of the Kupferschiefer Sea

Paleo-ecosystems: upper Permian Kupferschiefer



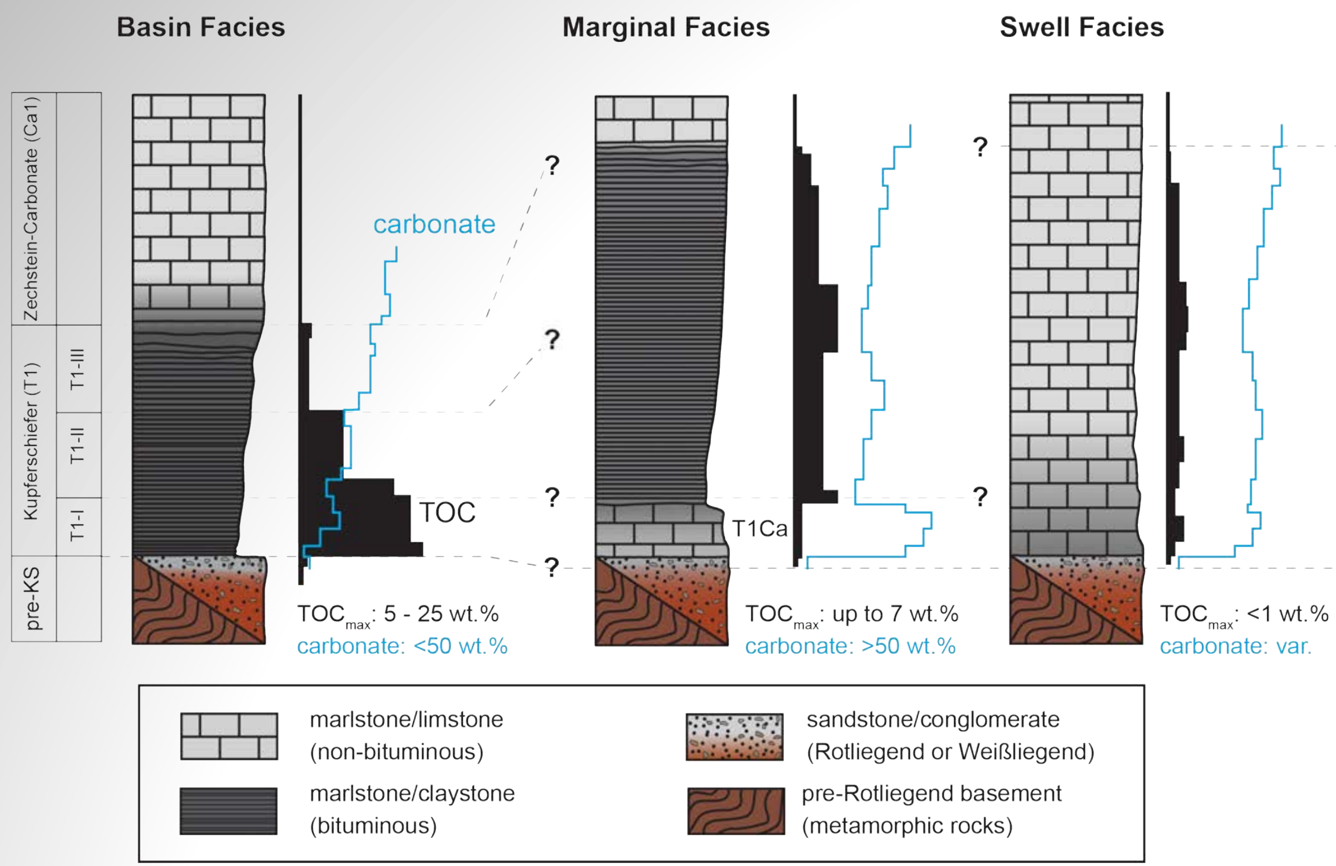
- The Kupferschiefer Sea was formed by the rapid flooding of the European Permian Basin.
- Flooding was caused by the combined effect of rifiting between Greenland and Norwegian and a glacio-eustatic sea level rise (e.g. Glennie & Buller, 1983).
- Flooding of the basin within a few 10th of years (Glennie & Buttler, 1983).
- In dependency of the basin depth Sea level rise about 30 cm/day can be assumed.
- Flooding had a loading effect on the lithosphere and caused a regional subsidence, causing further deepening of the basin (e.g. Ziegler, 1990; Geluk, 1999).

Paleo-ecosystems: upper Permian Kupferschiefer



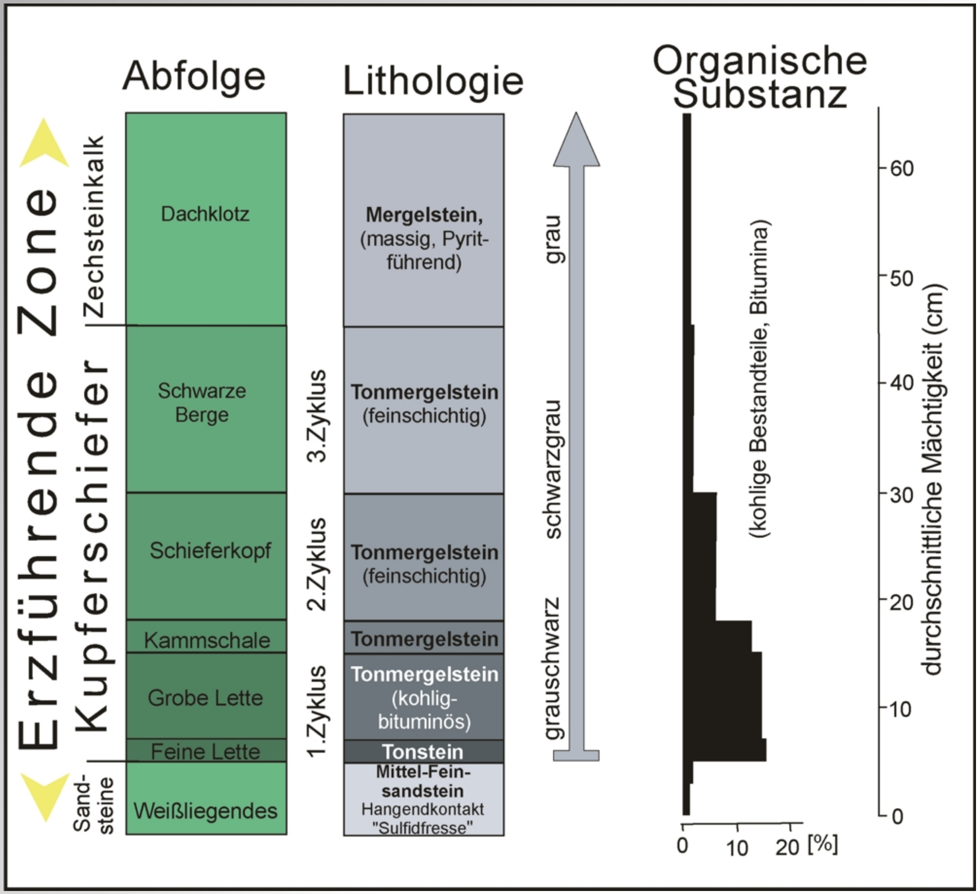
- During marine ingression, the topmost parts of the Rotliegend deposits were reworked to form the so-called Weissliegend (bleached Rotliegend clastics).
- In their uppermost part, bioturbation and a marine fauna indicate that the sandstones originated in a shallow-marine environment.
- The initial ingression also resulted in the local deposition of a basal conglomerate (transgressive conglomerate).

Paleo-ecosystems: upper Permian Kupferschiefer



- Three major Kupferschiefer facies types can be distinguished and were associated with different depositional settings (e.g. Vaughan et al., 1989; Paul, 2006).
- In central basin parts Weissliegend clastics are directly overlain by bituminous Kupferschiefer sediments attesting to the rapid development of oxygen-deficient conditions.
- Delayed onset of anoxia at more shallow marginal settings is indicated by the so-called Mutterflöz, a organic matter lean limestone underlying the Kupferschiefer.
- At shallow swell settings the Kupferschiefer is represented by bioturbated marlstones.

Paleo-ecosystems: upper Permian Kupferschiefer



At basin settings the Kupferschiefer shows distinct geochemical gradients and trends.

Those are nicely expressed in the organic matter (OM) content, but are also associated with lithological features (e.g. bedding style of the sediments).

Highest OM abundances were seen in the lower part of the Kupfershiefer. A steady decline in the OM content is seen in the upper Kupferschiefer.

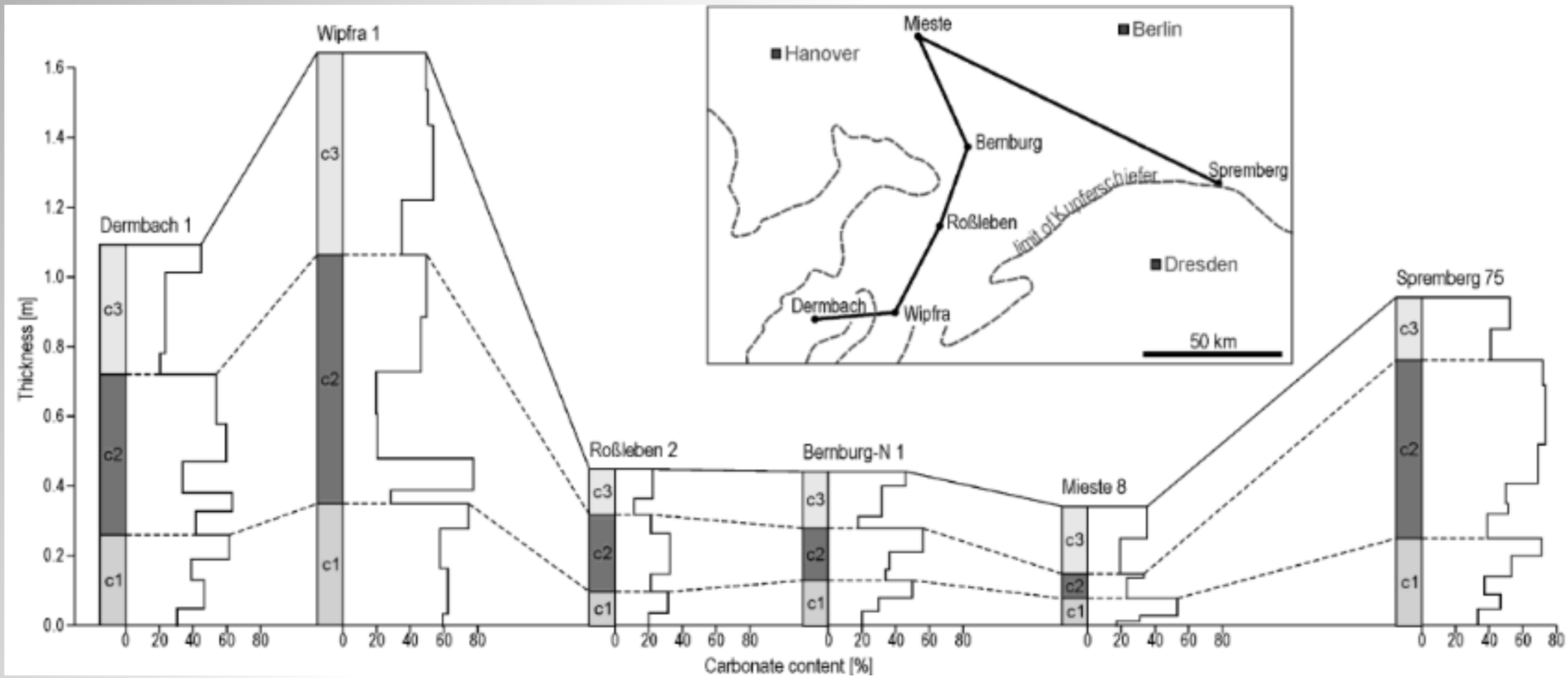
Geochemical trends can be linked to changes in depositional conditions.

Long-term trend seen throughout the Kupferschiefer were superimposed by a internal cyclicity.

This cyclicity is expressed by systematic variations in clay and carbonate contents.

Three cycles can be distinguished. Each cycle starts with a carbonate-poor and clay-rich interval. Throughout each cycle an increase in the carbonate ontent has been seen.

Paleo-ecosystems: upper Permian Kupferschiefer



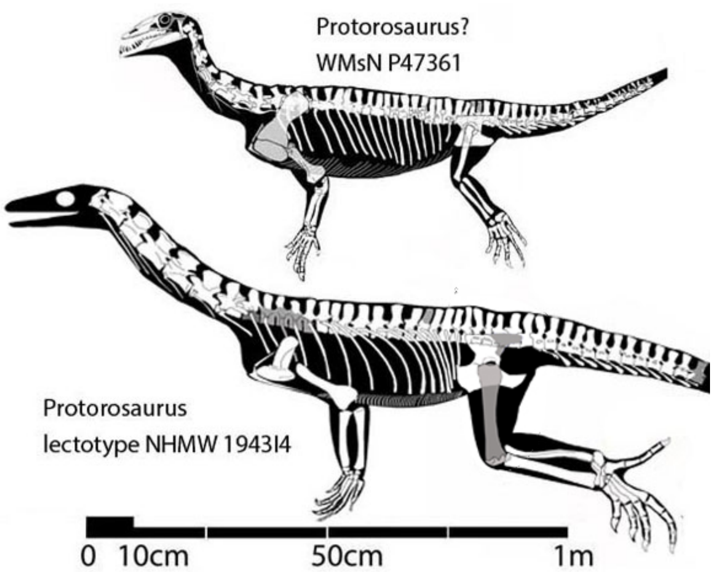
The cyclicity of the Kupferschiefer Formation (clay-carbonate cycles) can be traced throughout the basin (Rentsch, 1965; Legler & Schneider, 2013).

The origin of the sedimentary cycles remains speculative, but might be associated with e.g. climate cycles and/or sea level fluctuations.

It is also no clear whether this cycles match astronomical periods (e.g. Milanokovitch cycles). Thus, also the time span, represented by the Kupferschiefer Fm, is unknown.

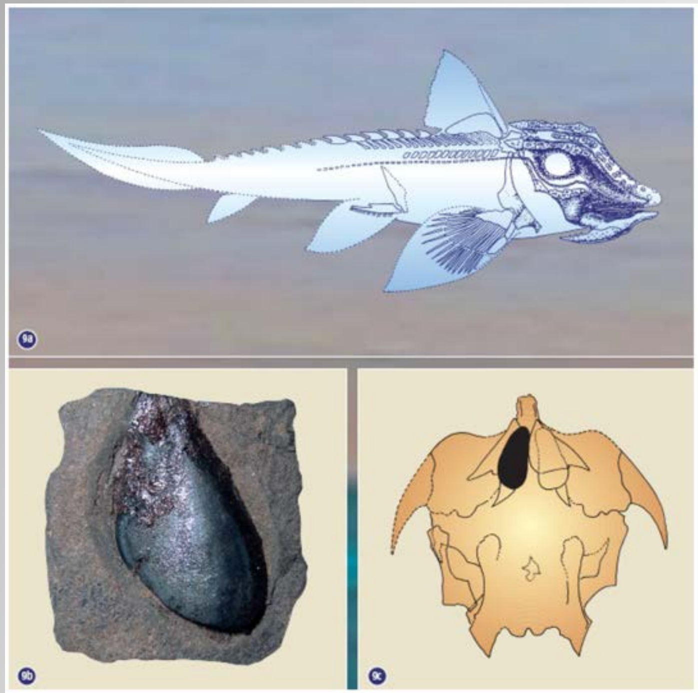
Common fossils of the Kupferschiefer Formation

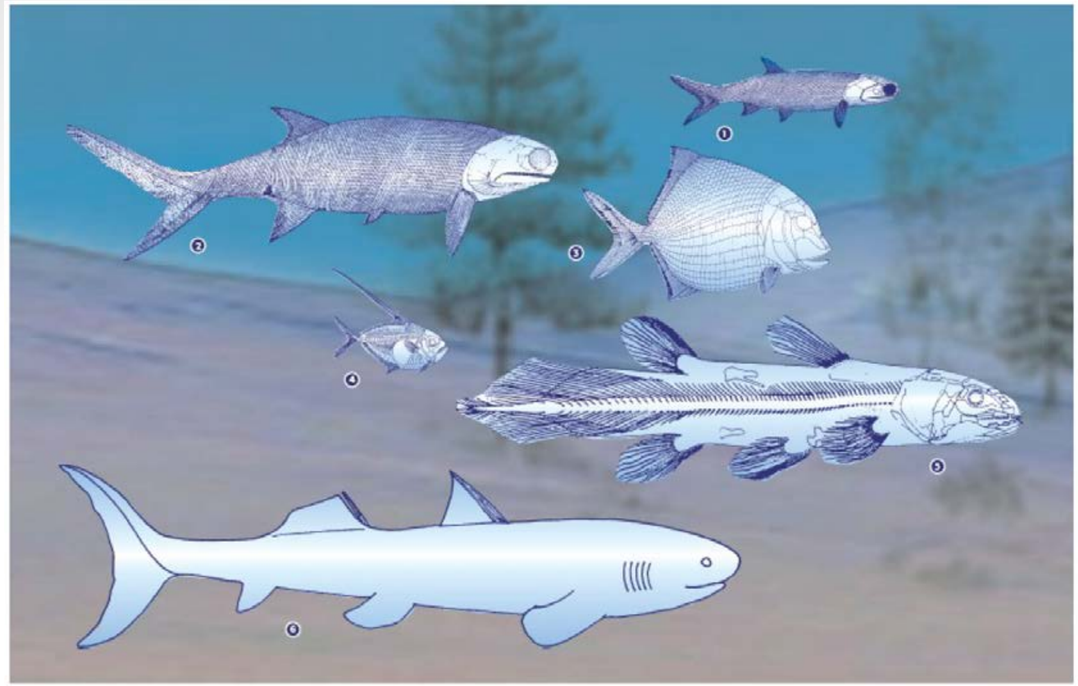
Paleo-ecosystems: upper Permian Kupferschiefer

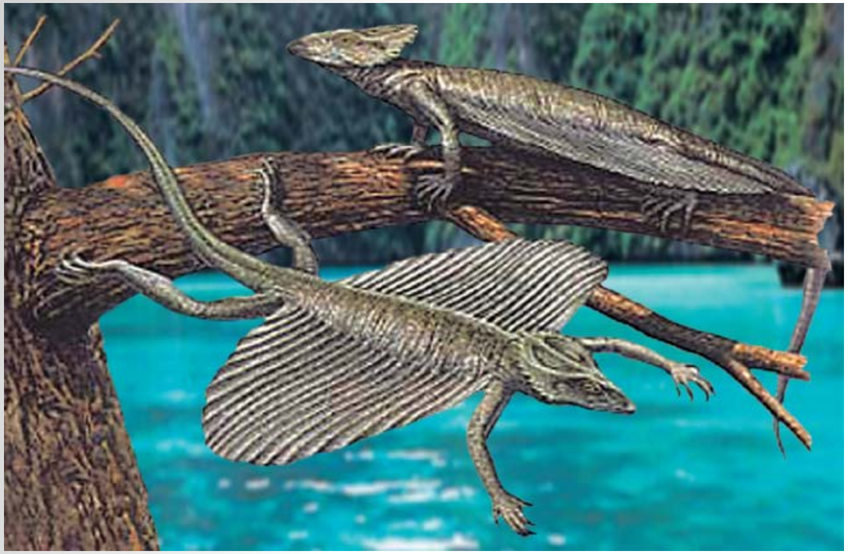


Depositional conditions that prevailed during Kupferschiefer formation were associated with an excellent preservation of fossils (e.g. invertebrates, fishes, reptiles, archosauromorph reptile, land plants).

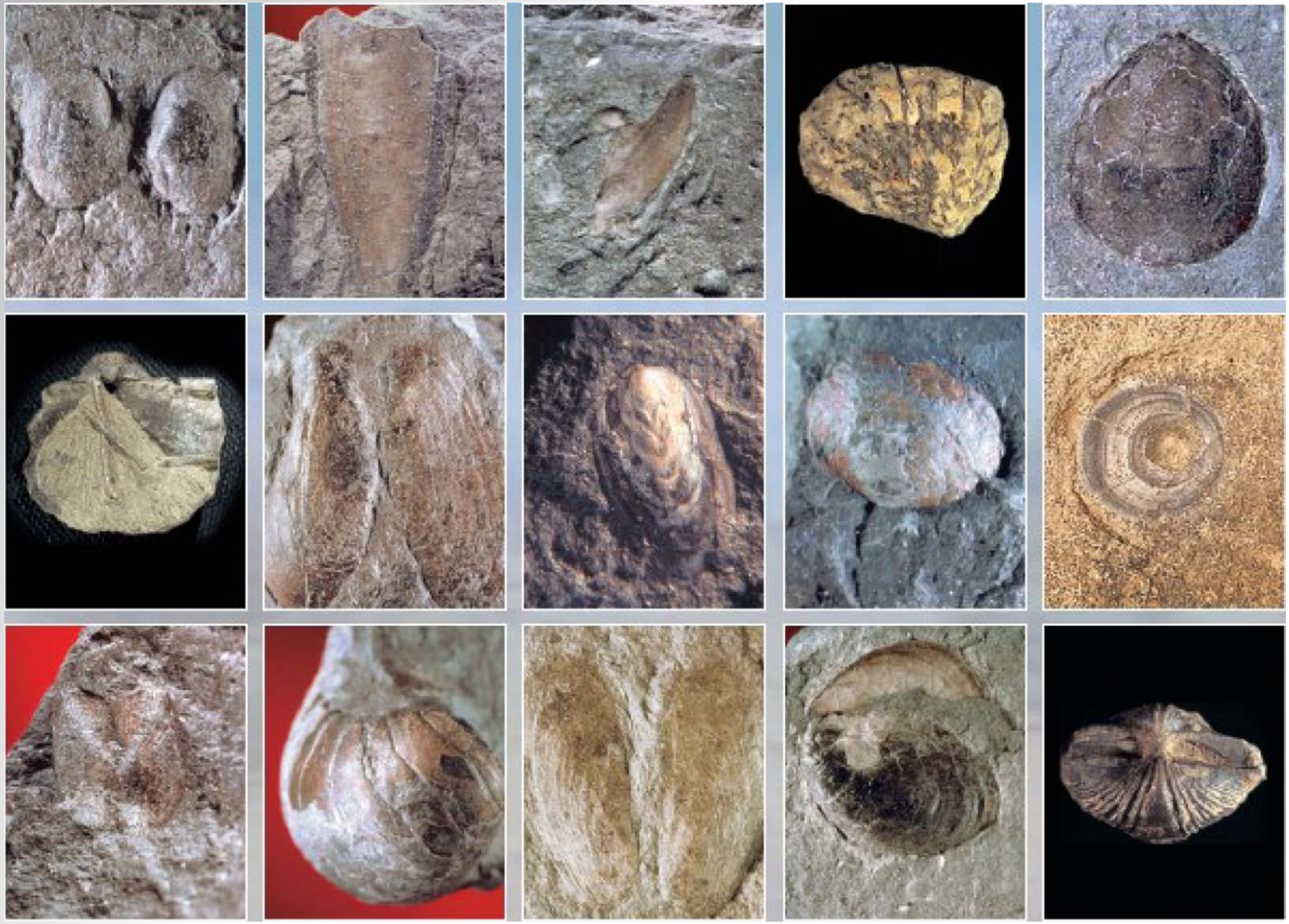
Paleo-ecosystems: upper Permian Kupferschiefer





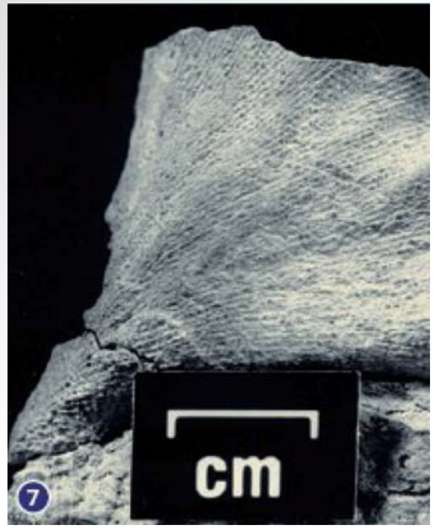


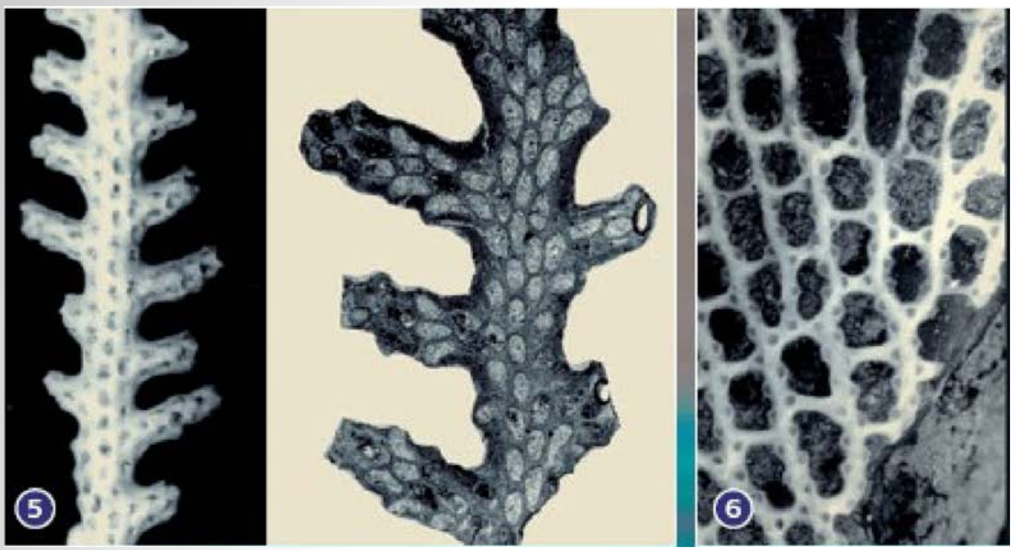
Paleo-ecosystems: upper Permian Kupferschiefer



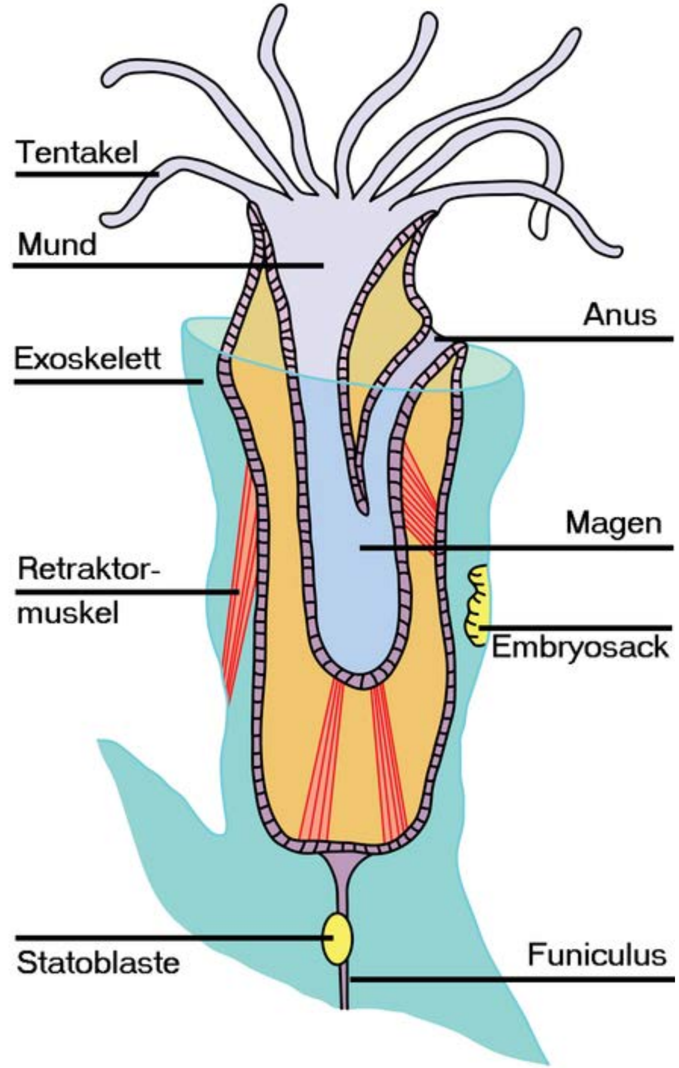
Brachiopodes documented in sediments coeval to the Kupferschiefer.

Paleo-ecosystems: upper Permian Kupferschiefer





Bryozoa – reef builders in the Zechstein Sea



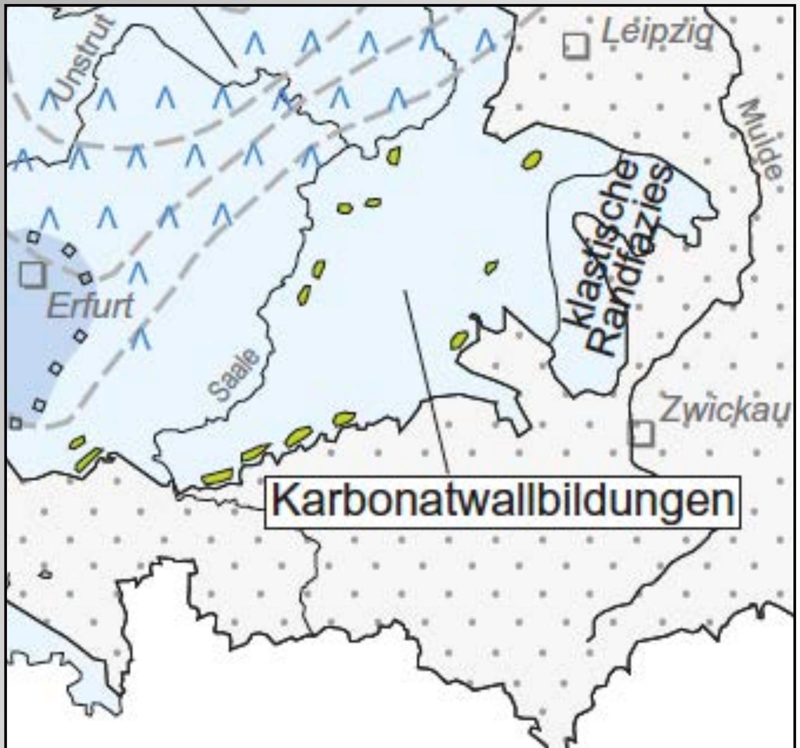
Recent bryozoa

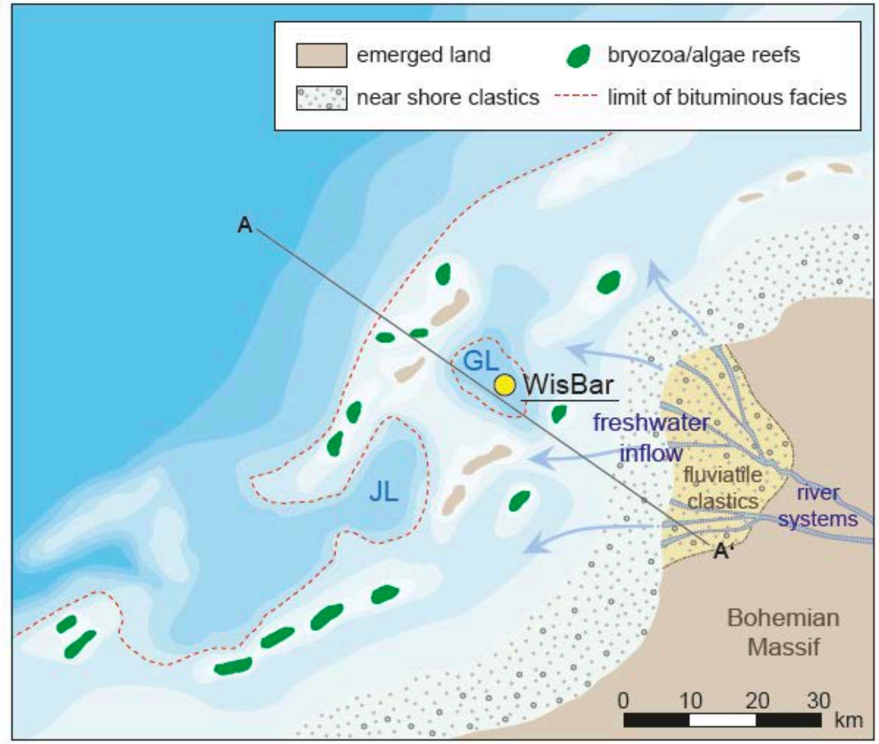
Paleo-ecosystems: upper Permian Kupferschiefer

Permian reef communities:

- Bryozoa (a-d)
- Brachiopodes (d-h)
- Moluscs (i-k)

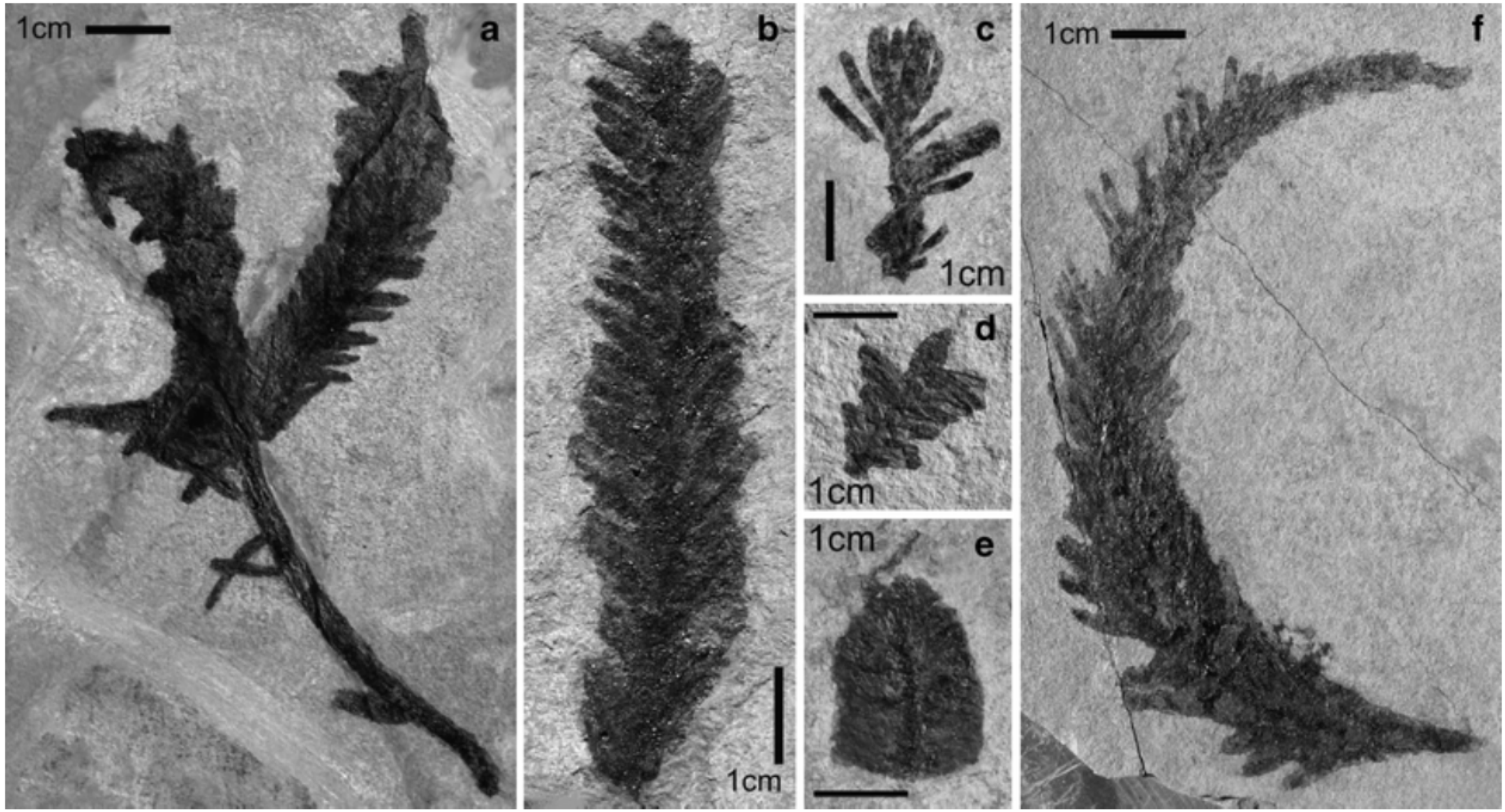
Paleo-ecosystems: upper Permian Kupferschiefer





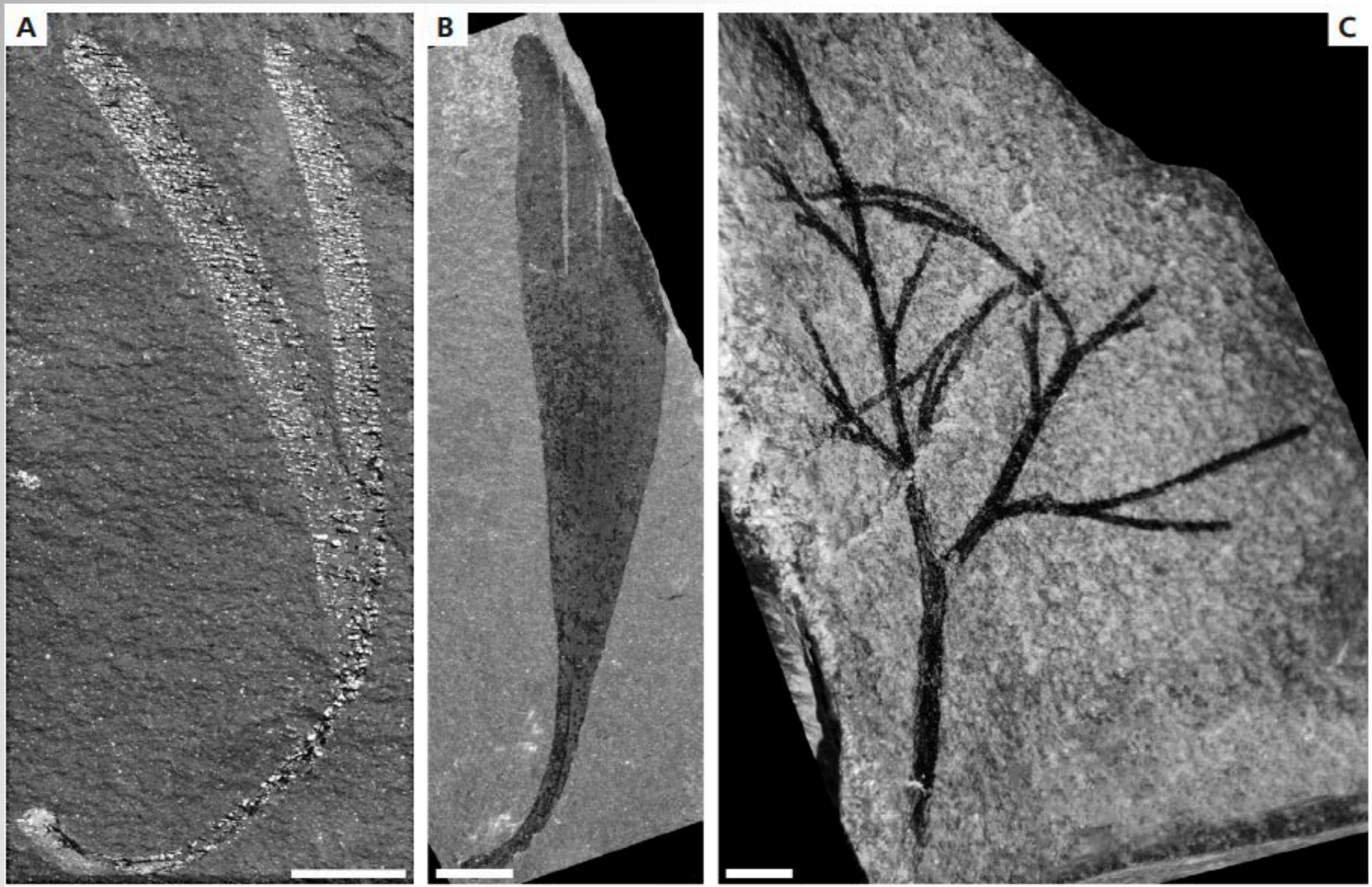
Zechstein reefs occur widespread in the south-eastern Kupferschiefer Sea. In the eastern Thuringian Basin they occurred in from of barrier reefs that have formed a belt parallel to the coastline.

Paleo-ecosystems: upper Permian Kupferschiefer



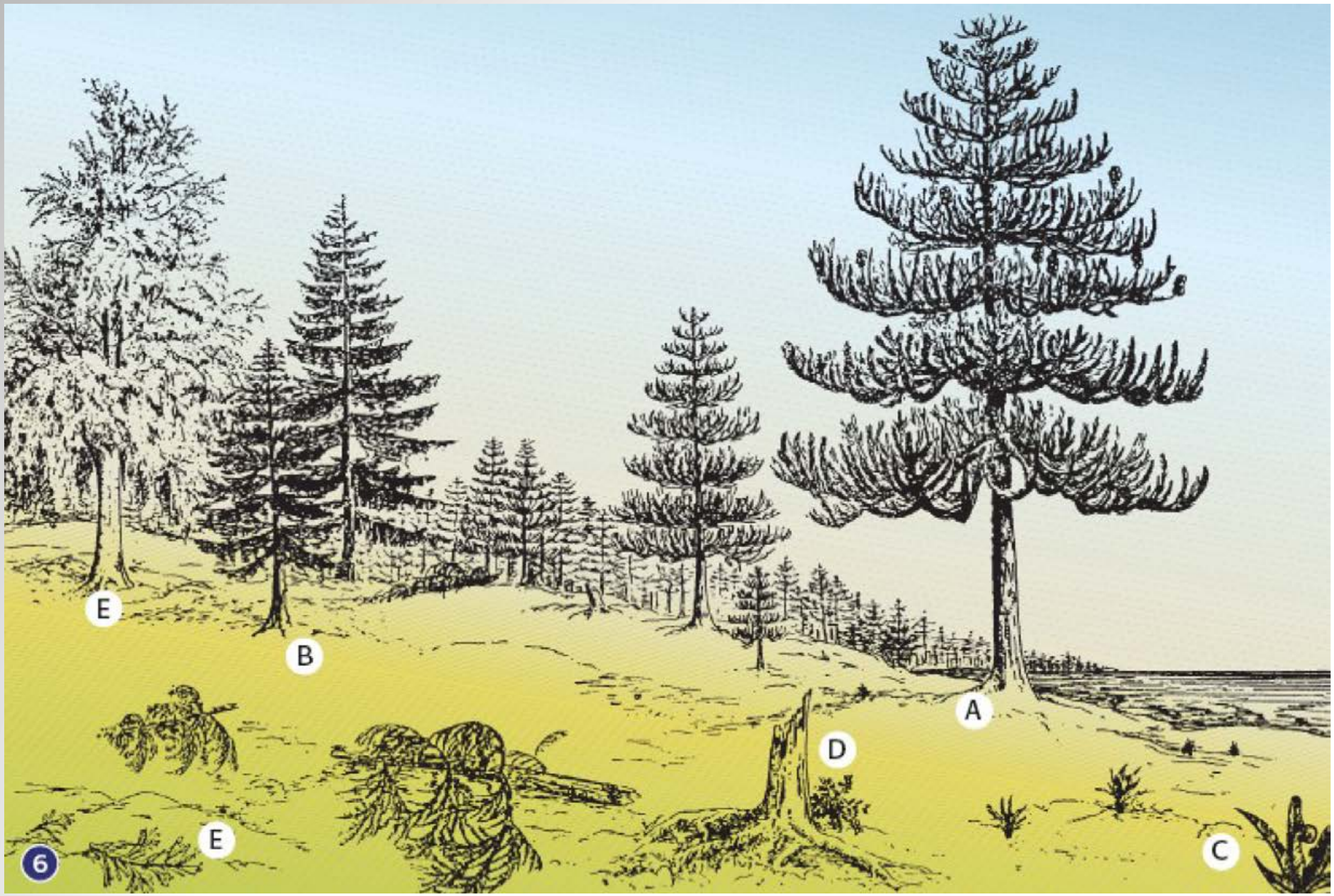
Plant remains from the upper Permian Kupferschiefer of Hasbergen: **a)** Pseudovoltzia liebeana (Geinitz); **b)** Ullmannia frumentaria (Schlotheim); **c)** Quadrocladus solmsii (Gothan and Nagelhard); **d)** Conifera indet.; **e)** Conifer cone; **f)** Conifer Pseudovoltzia liebeana (Dietrich, 2009).

Paleo-ecosystems: upper Permian Kupferschiefer



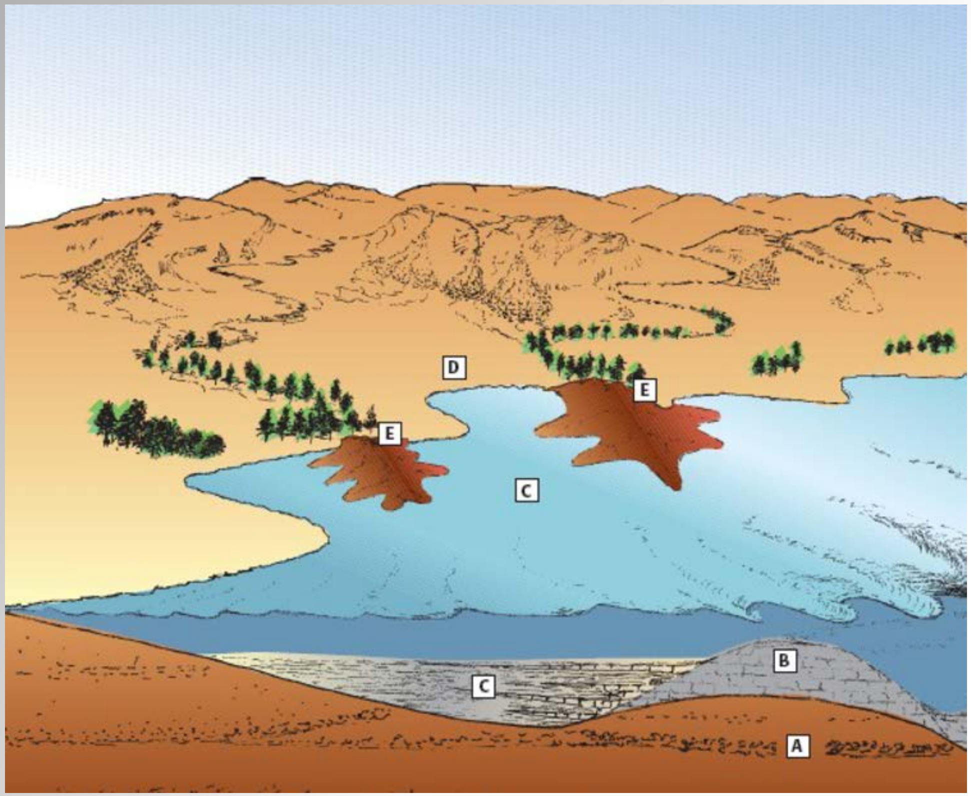
Plant remains from the upper Permian Kupferschiefer of Hasbergen: **A)** Baiera mansfeldensis sp. nov., Mansfeld; **B)** Baiera mansfeldensis, Eisleben; **C)** Esterella gracilis, Eisleben (Bauer et al., 2012).

Paleo-ecosystems: upper Permian Kupferschiefer



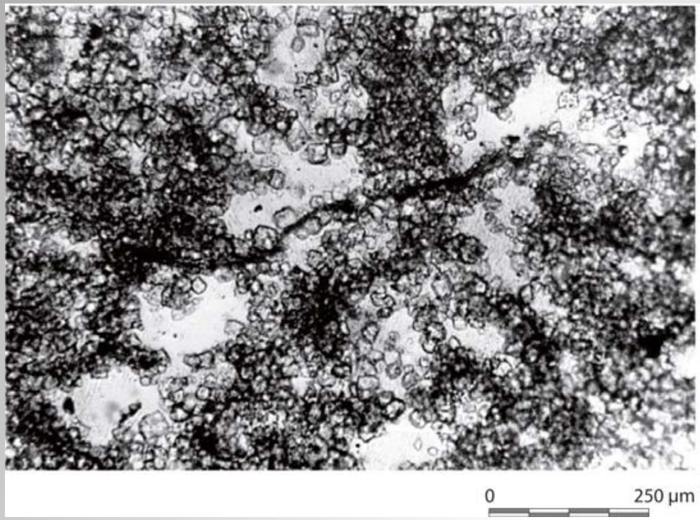
Reconstruction of terrestrial vegetation at the shore of the Kupferschiefer Sea (after Mägdefrau, 1952). A: Ullmannia frumentaria, B: Pseudovoltzia liebeana, C: Taeniopteris eckardtii, D: Peltaspermum martinsii, E: Sphenobaiera digitata.

Paleo-ecosystems: upper Permian Kupferschiefer

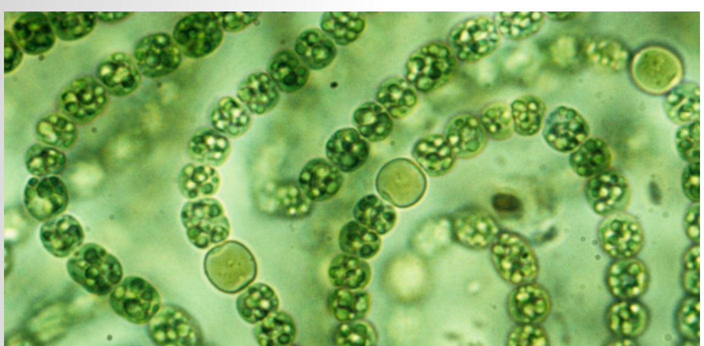


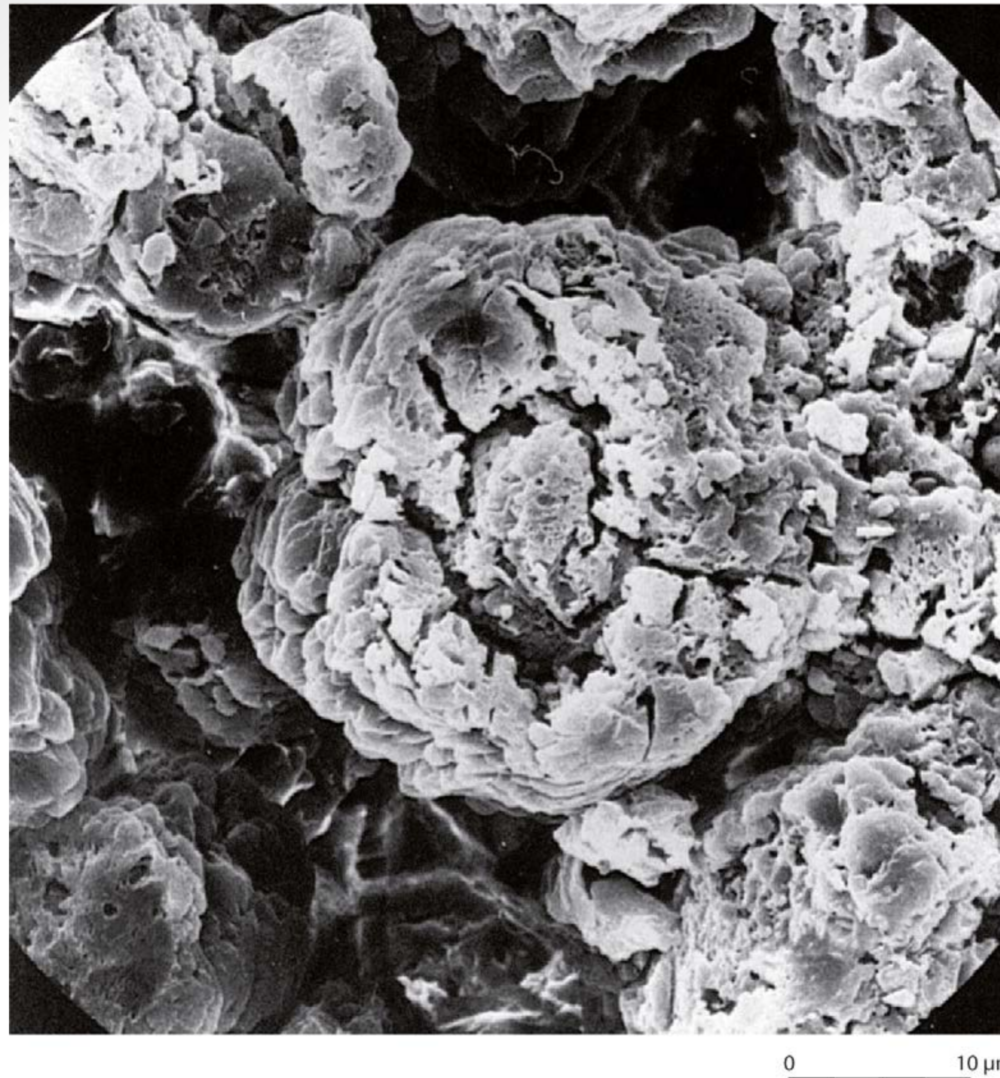
The Kupferschiefer Sea was located at latitudes of between 20 – 30°N, where arid climate conditions prevailed. Humidity might have increased after flooding of the Permian Basin. However, vegetation was mainly bound to river systems.

Paleo-ecosystems: upper Permian Kupferschiefer



Thin section showing biolaminoid with preserved microfossil interpreted as the remains of filamentous cyanobacteria encrusted by fine-grained dolomite crystals.

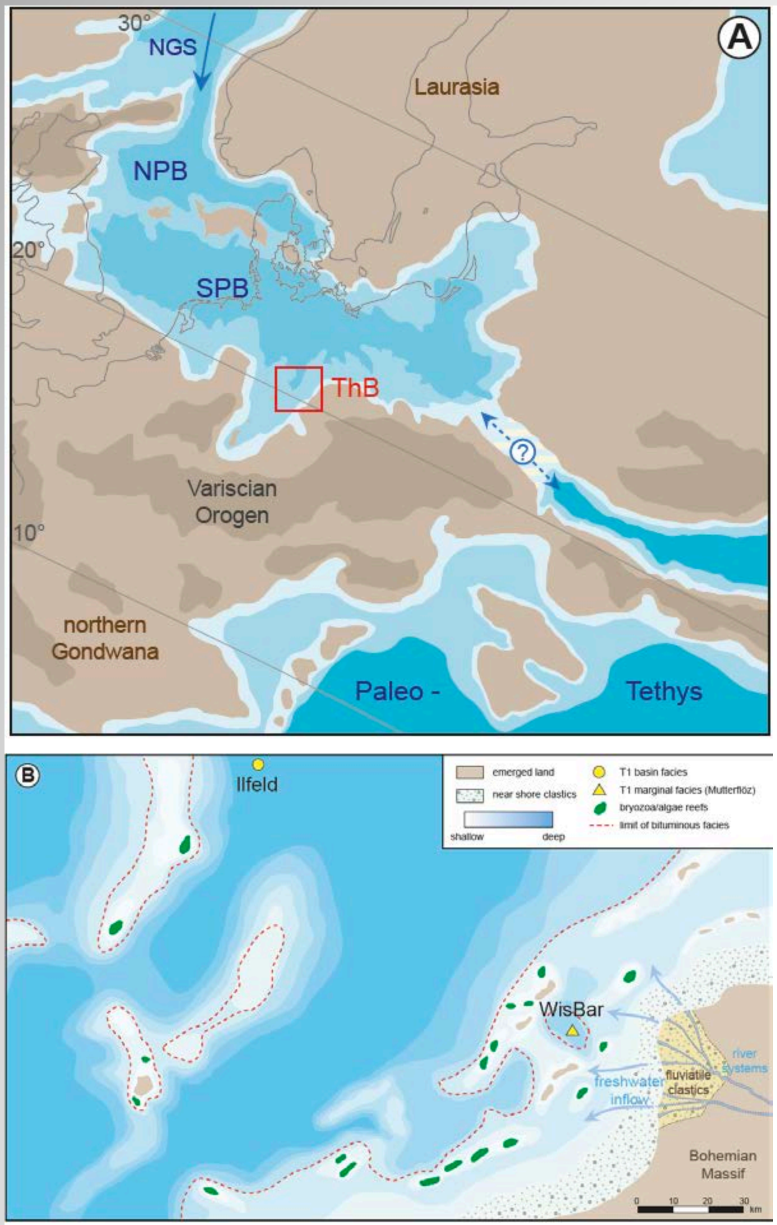


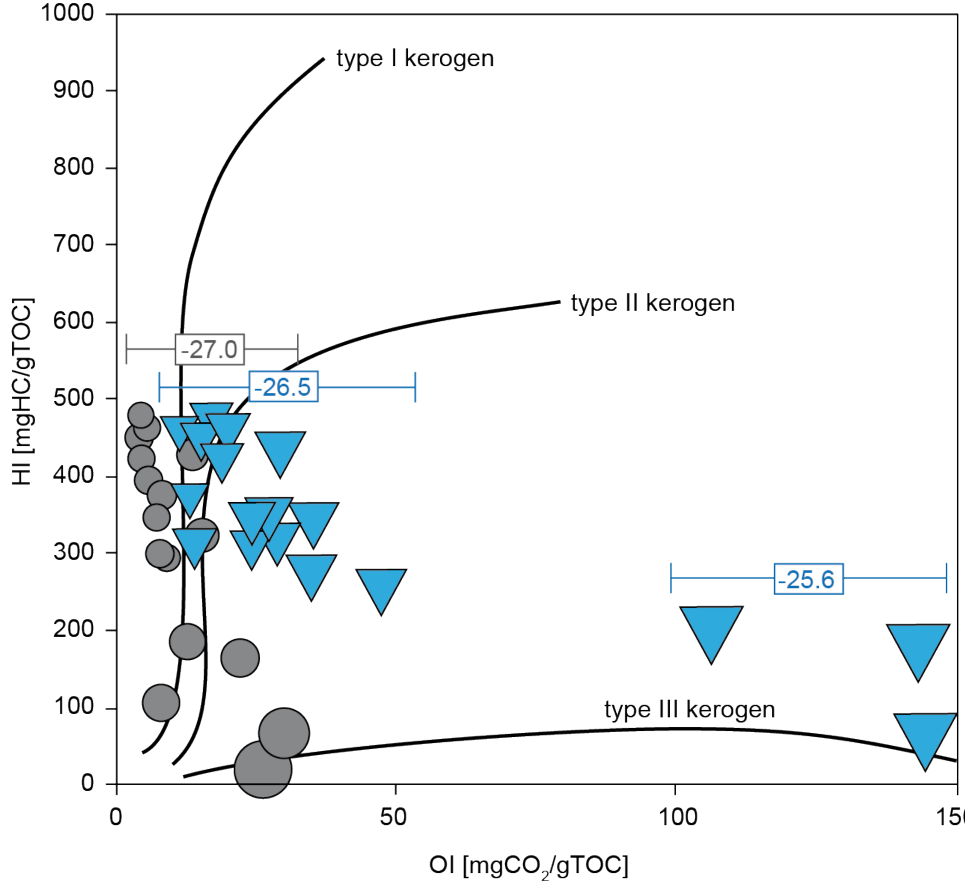


Scanning electron micrograph (SEM) of biolaminoid with fine-scale microfossils interpreted as the remains of coccoid cyanobacteria.

Organic geochemistry of the Kupferschiefer and organic matter characterisation

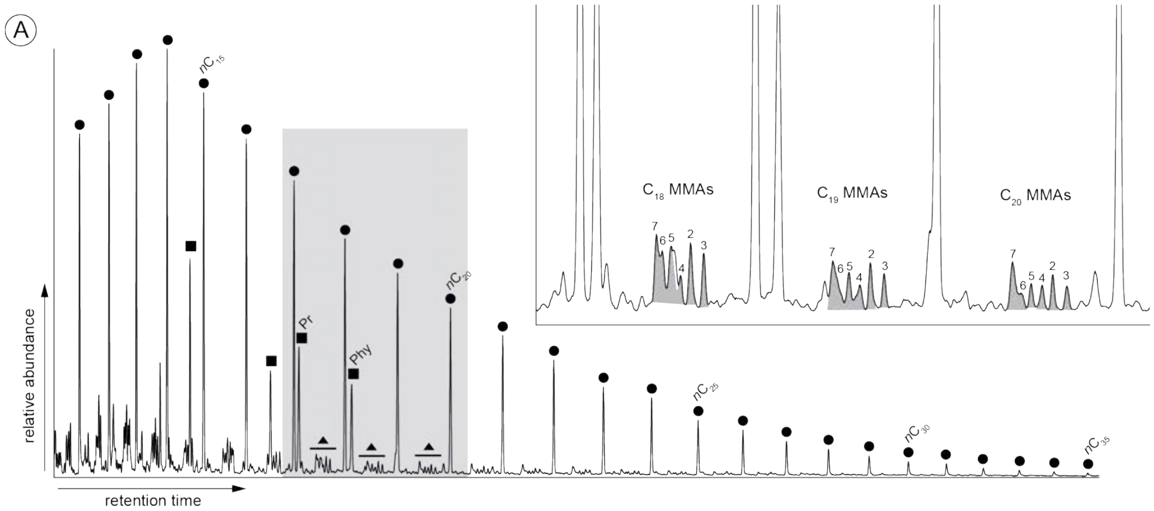
Paleo-ecosystems: upper Permian Kupferschiefer



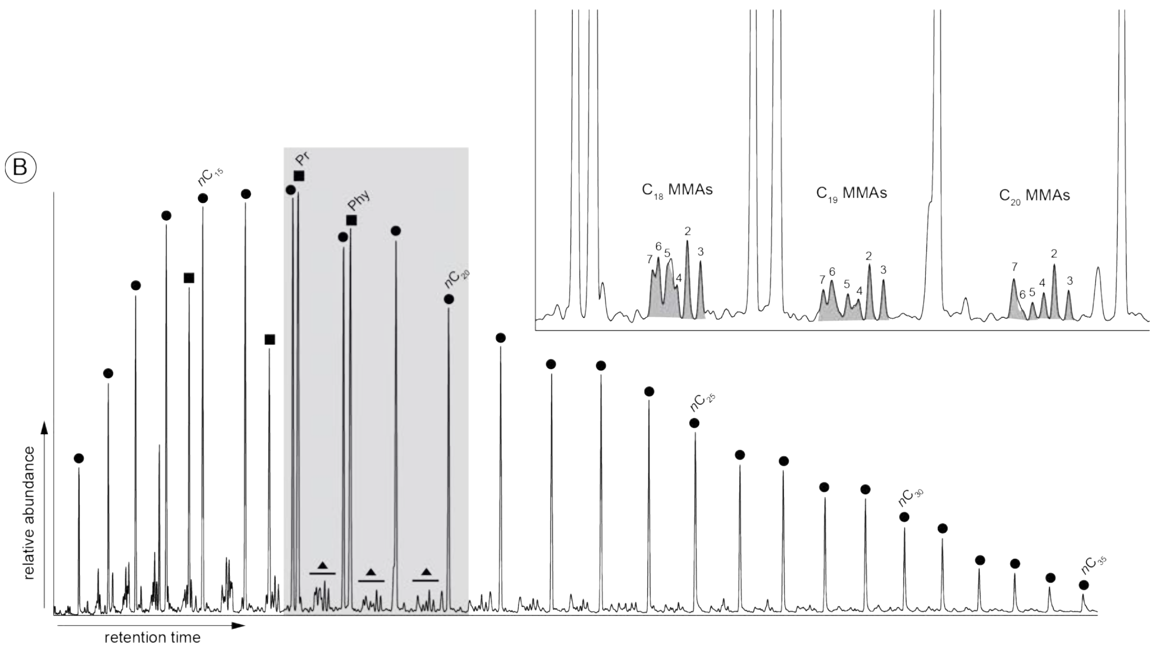


Position of Kupferschiefer samples in the OI-HI diagram in combination with $\delta^{13}C_{org}$ data confirm that the sedimentary OM was originated in marine organisms (algae, bacteria). Enhanced contributions of land plants occurred at marginal settings (blue triangles).

Paleo-ecosystems: upper Permian Kupferschiefer

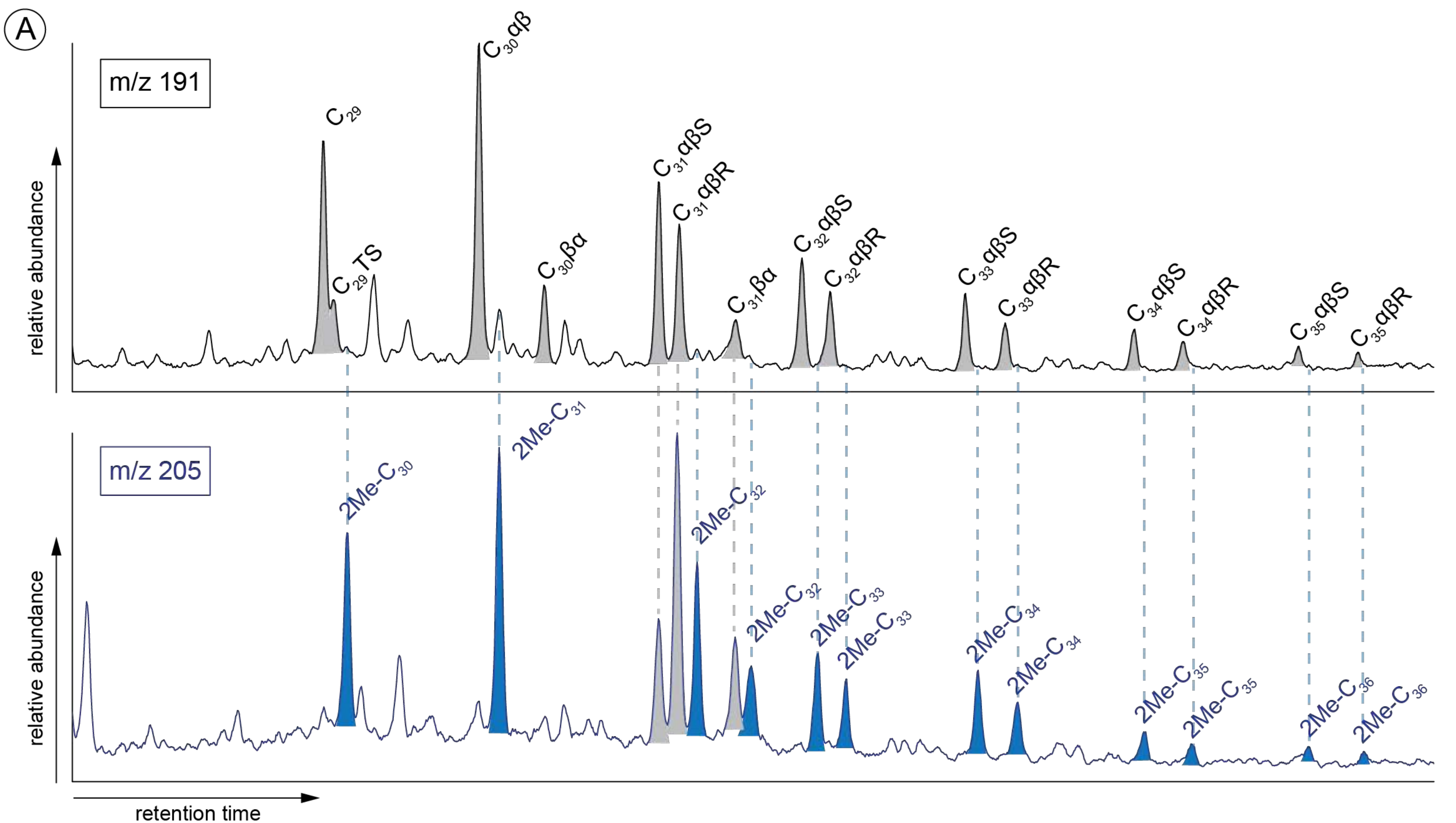


A: m/z 85 mass fragmentogram for a sample from the Ilfeld mine, representing a distal basinal setting. The dominance of short-chain n-alkanes indicate preferentially marine OM sources.



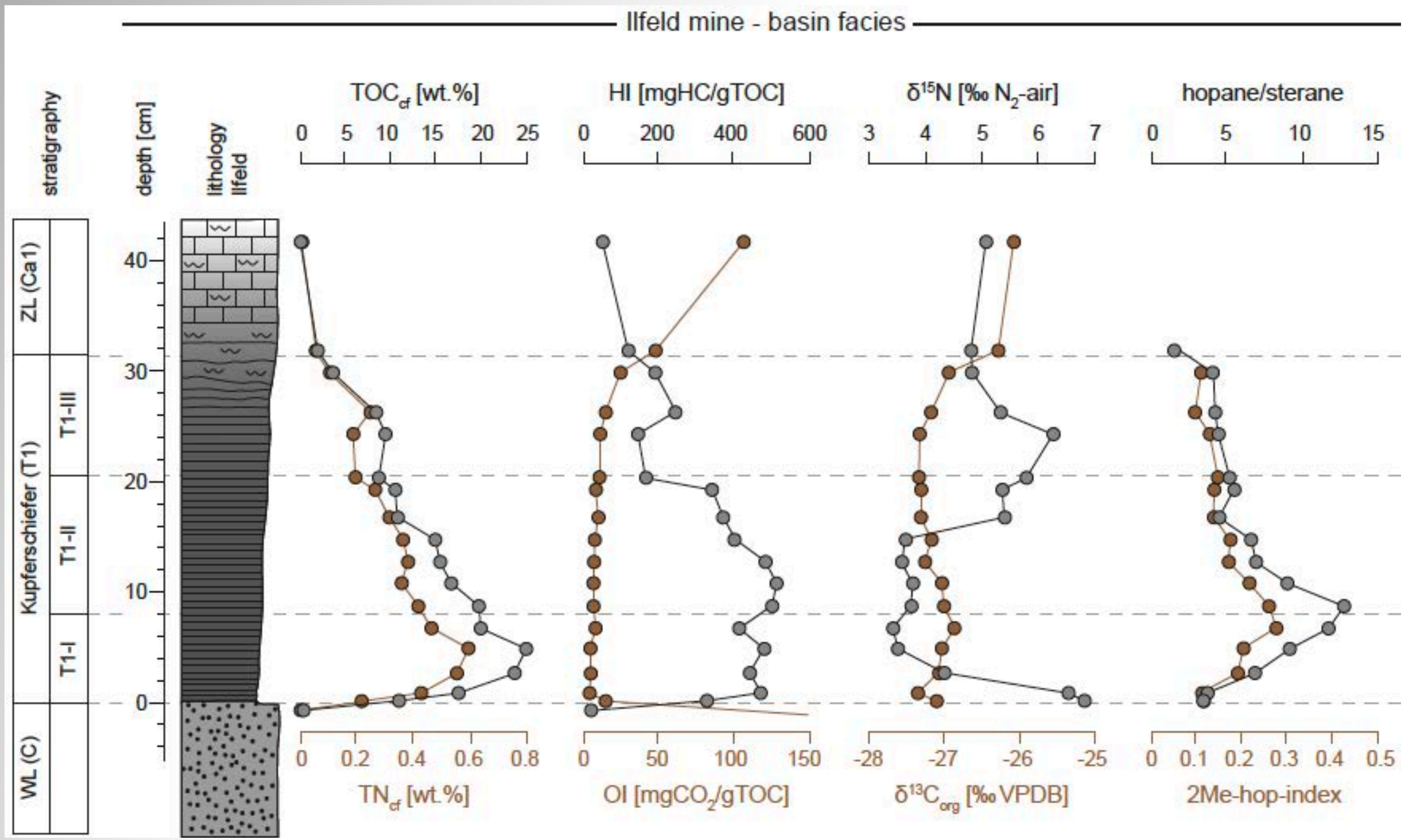
B: m/z 85 mass fragmentogram for a sample from the Gera lagoon, a setting in proximity to the paleocostline. Higher abundances of long-chain n-alkanes indicate land plant contributions.

Paleo-ecosystems: upper Permian Kupferschiefer



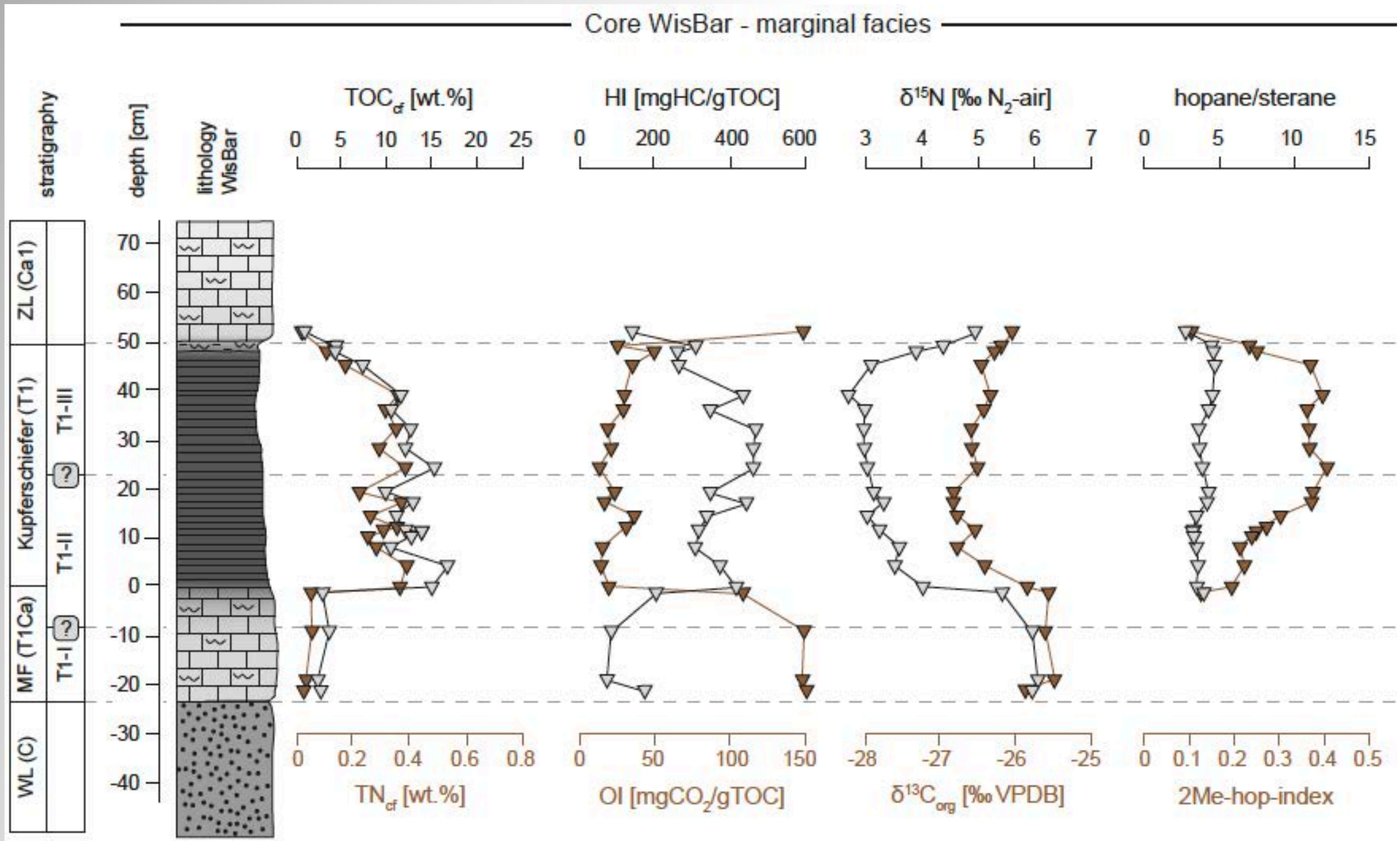
The m/z 191 and 205 mass fragmentograms showing the distribution of regular hopanes and 2α-methylhopanes. The later are known to be biosynthesized by heterocystous cyanobacteria (Summons et al., 1999).

Paleo-ecosystems: upper Permian Kupferschiefer



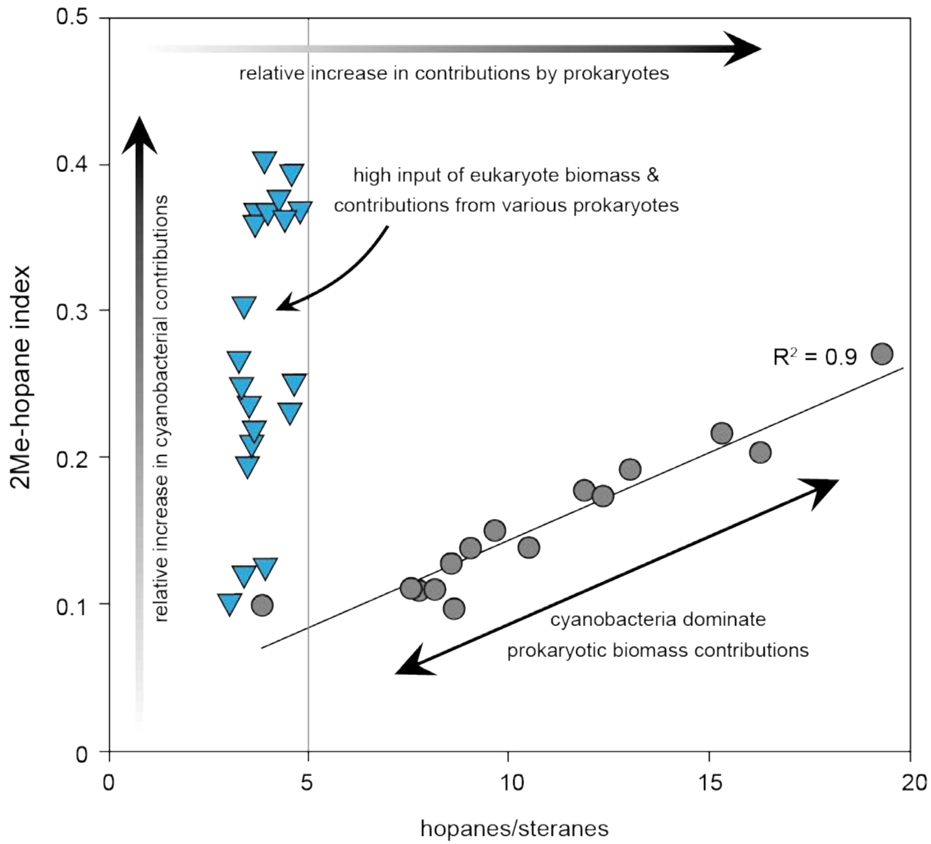
Geochemical trends for a Kupferschiefer profile from the Ilfeld Mine, representing a basinal setting.

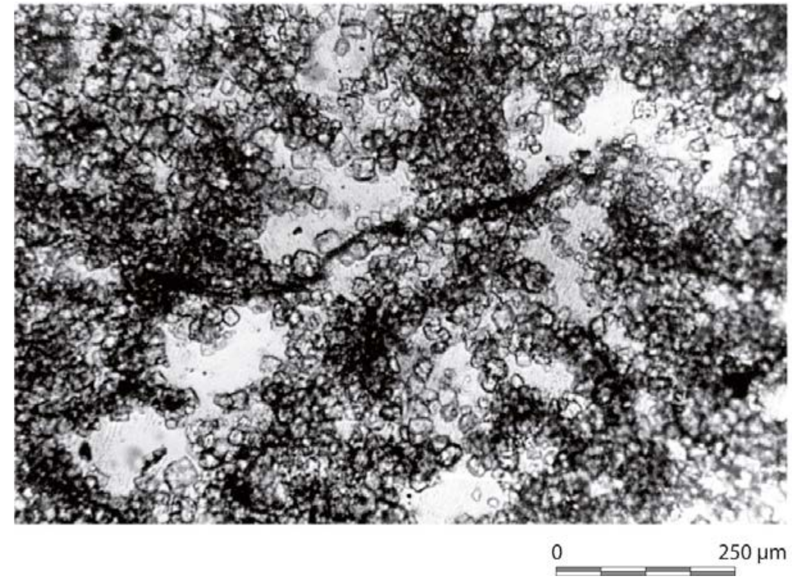
Paleo-ecosystems: upper Permian Kupferschiefer



Geochemical trends for a Kupferschiefer profile from the south-eastern Thuringian Basin, representing a marginal lagoon setting.

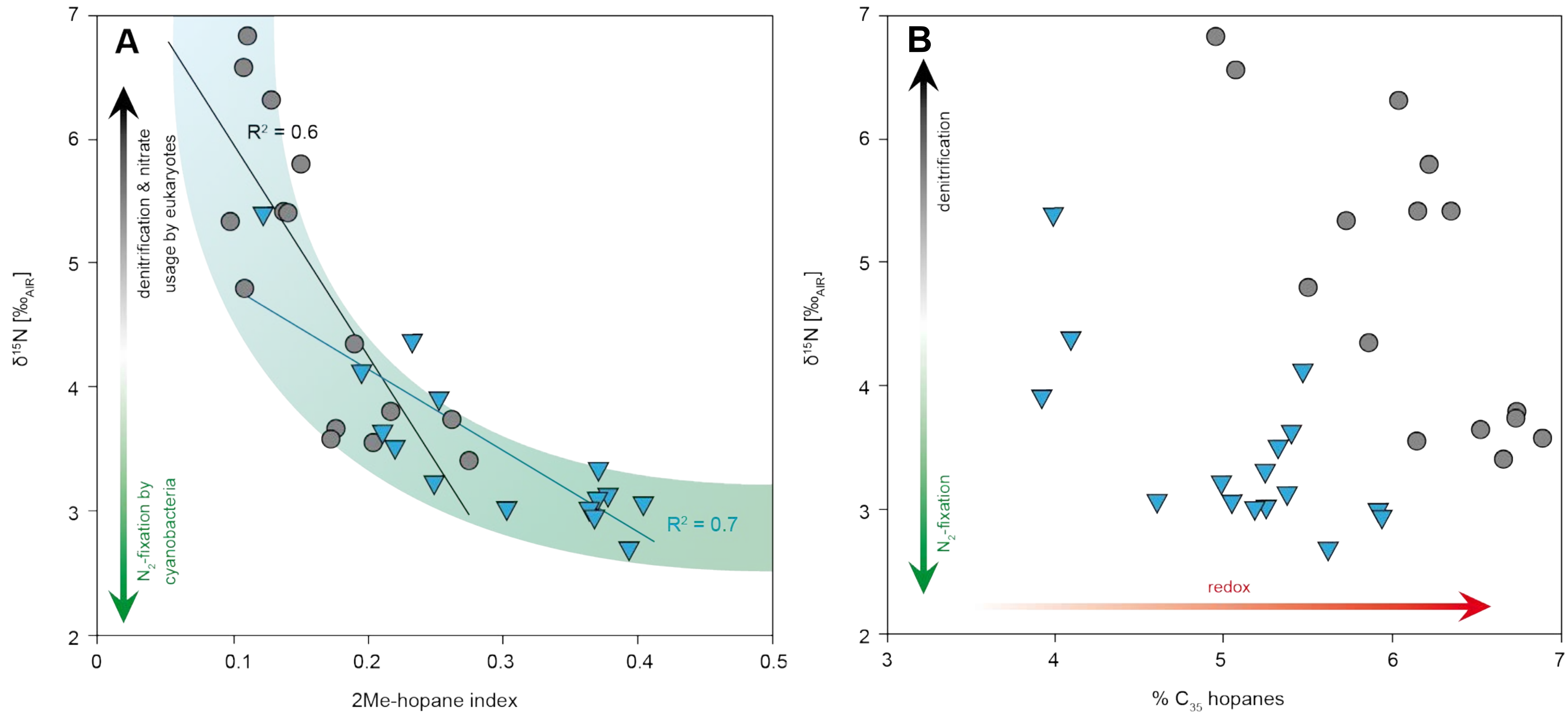
Paleo-ecosystems: upper Permian Kupferschiefer





At basinal settings, at least in the Thuringian Basin, cyanobacteria most likely dominated the primary producer assemblage. High methylhopane indices at marginal site attested to the presence of cyanobacteria. However, lower hopane/sterane ratios indicated higher contributions of biomass originated in eukaryotes.

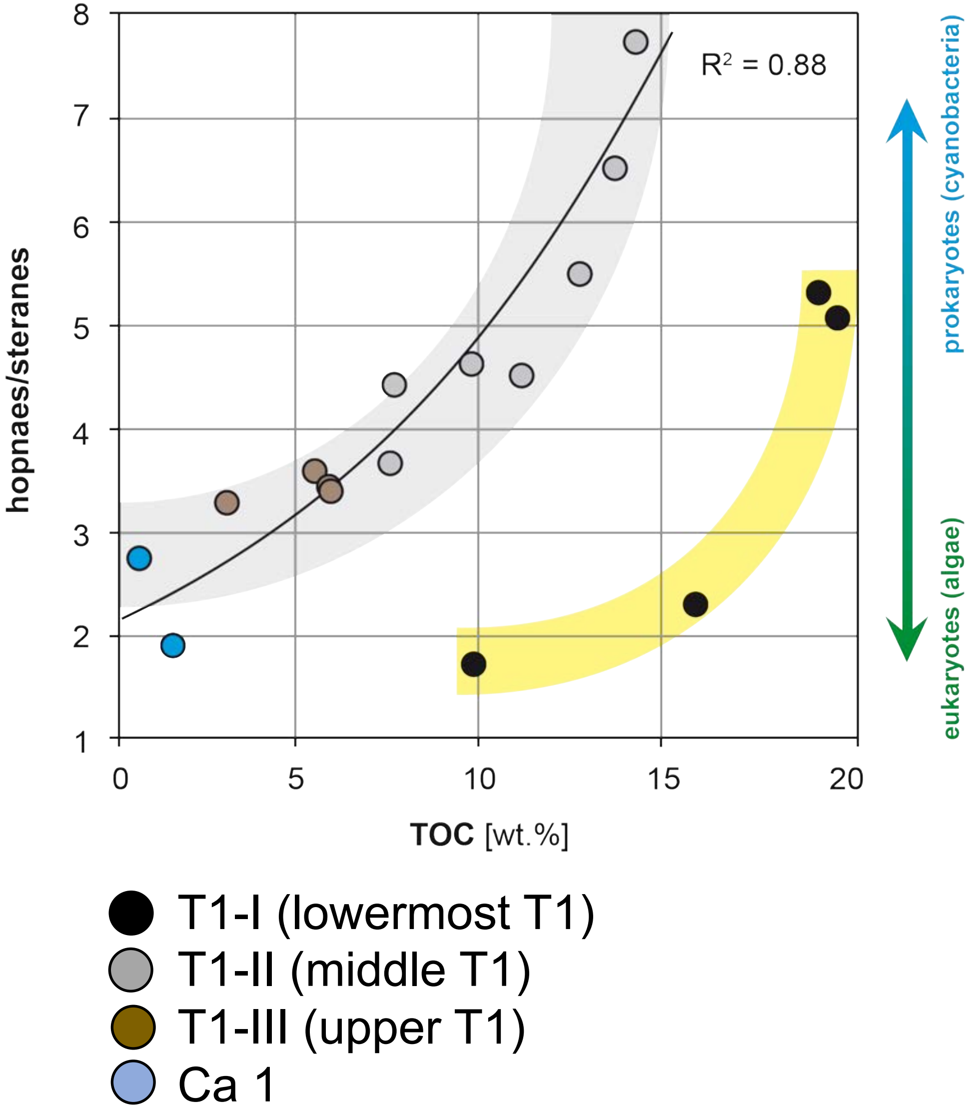
Paleo-ecosystems: upper Permian Kupferschiefer



A: Cross-plot of 2Me-hopane index with nitrogen isotope data, showing that the fixation of N_2 by cyanobacteria was an important process that significantly impacted on the nitrogen cycle in the Kupferschiefer Sea.

B: On the contrary, redox-related denitrification might have also impacted on nitrogen isotope values but was not the major factor controlling the nitrogen cycle.

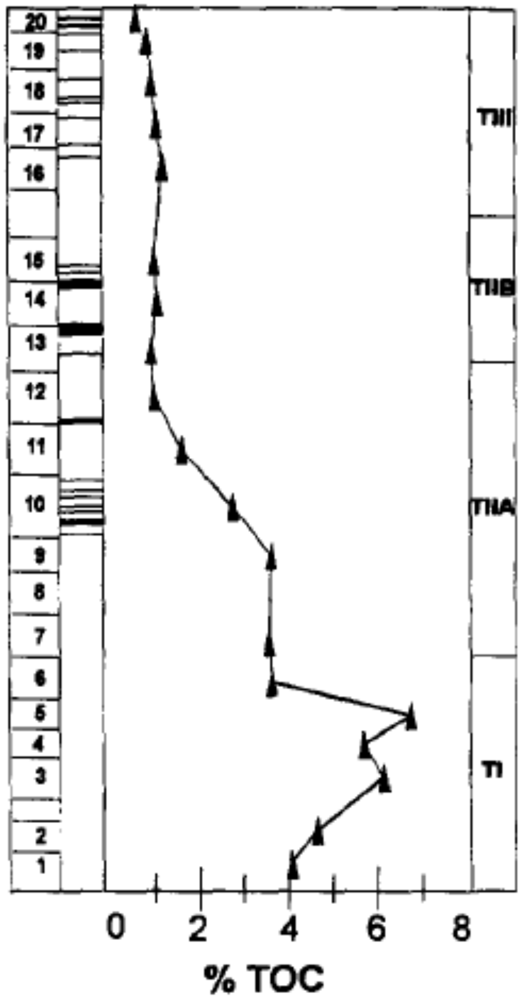
Paleo-ecosystems: upper Permian Kupferschiefer

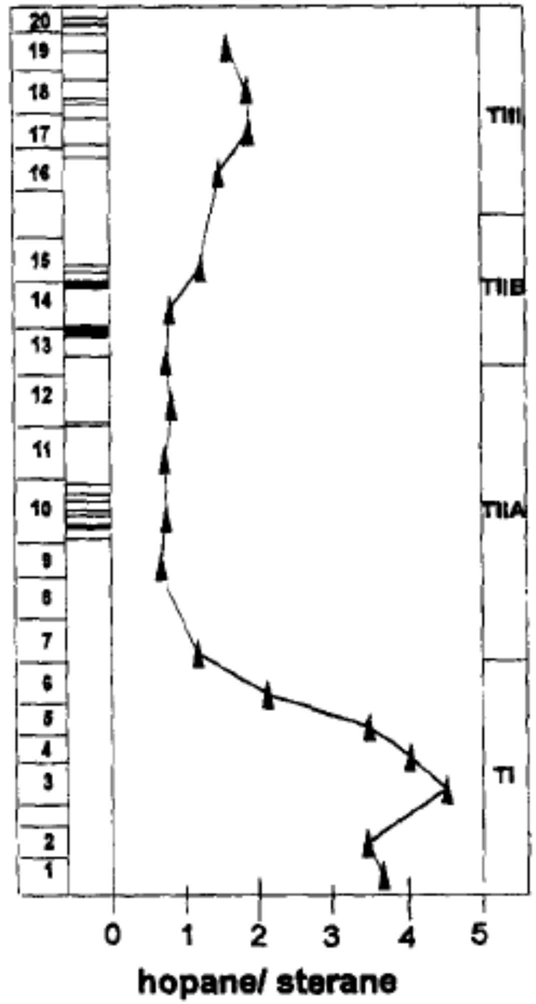


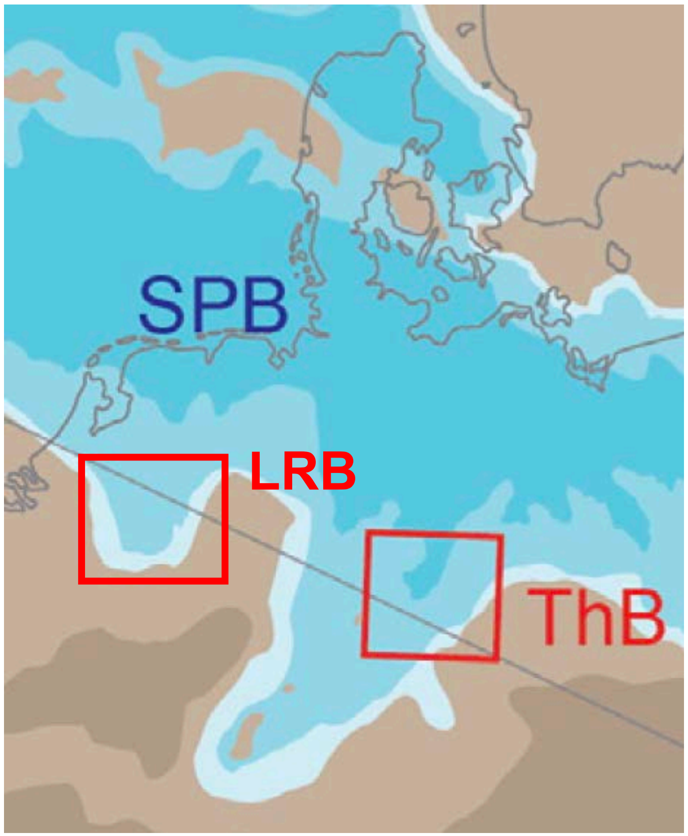
The strong correlation of hopane/sterane ratios with the TOC content indicate that bacteria significantly contributed to the sedimentary OM.

Black data points correspond to the basal Kupferschiefer that contained higher abundances of algae derived organic matter.

Higher abundances of algae might be related to the enhanced availability of bioavailable nitrogen that became successively limited during deposition of the upper Kupferschiefer Formation.



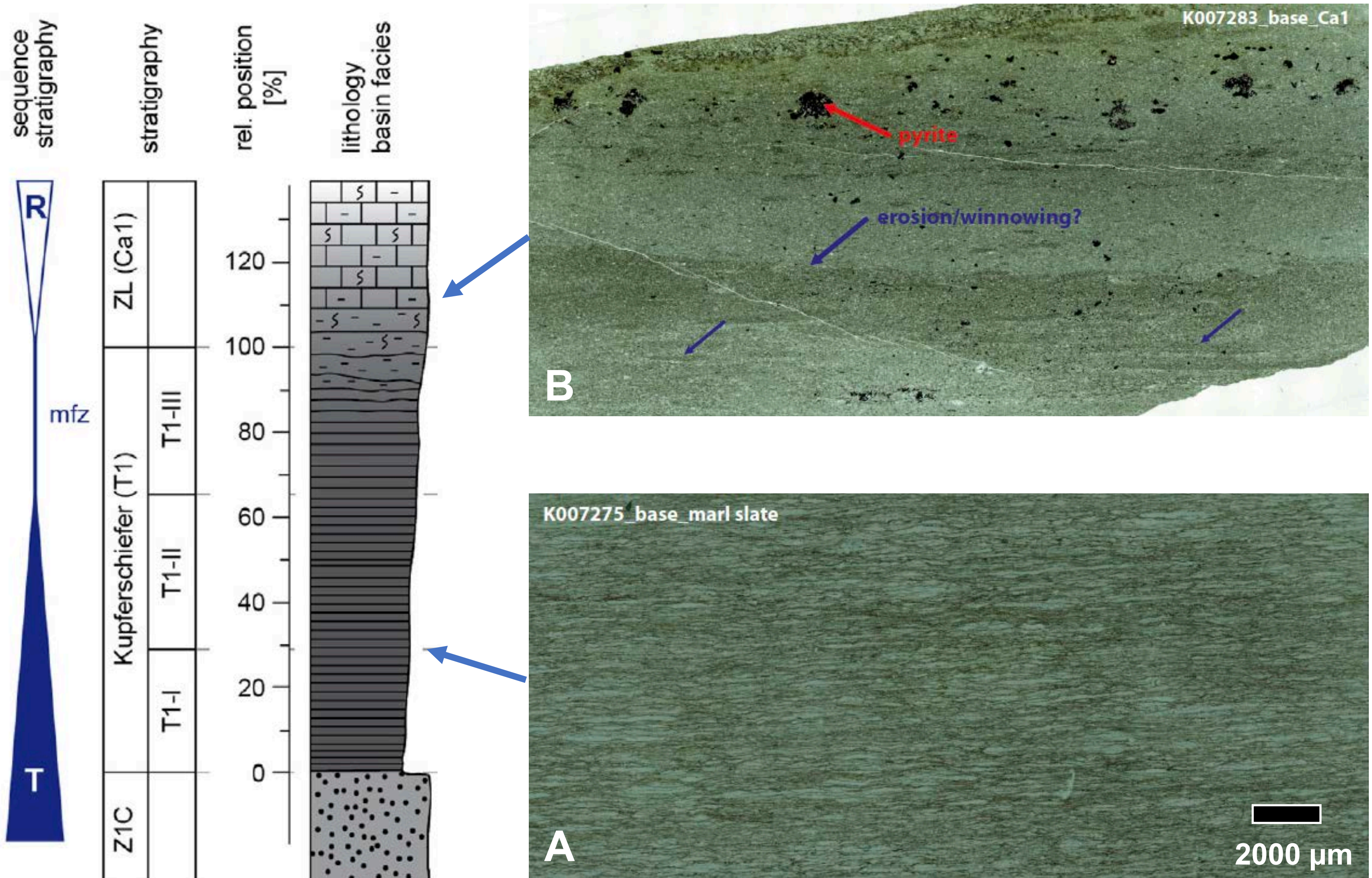




The importance of bacterial-derived biomass is also evident from the Lower Rhine Basin. As observed in the Thuringian Basin, high TOC-values were accompanied by high hopane/sterane ratios (Grice et al., 1997).

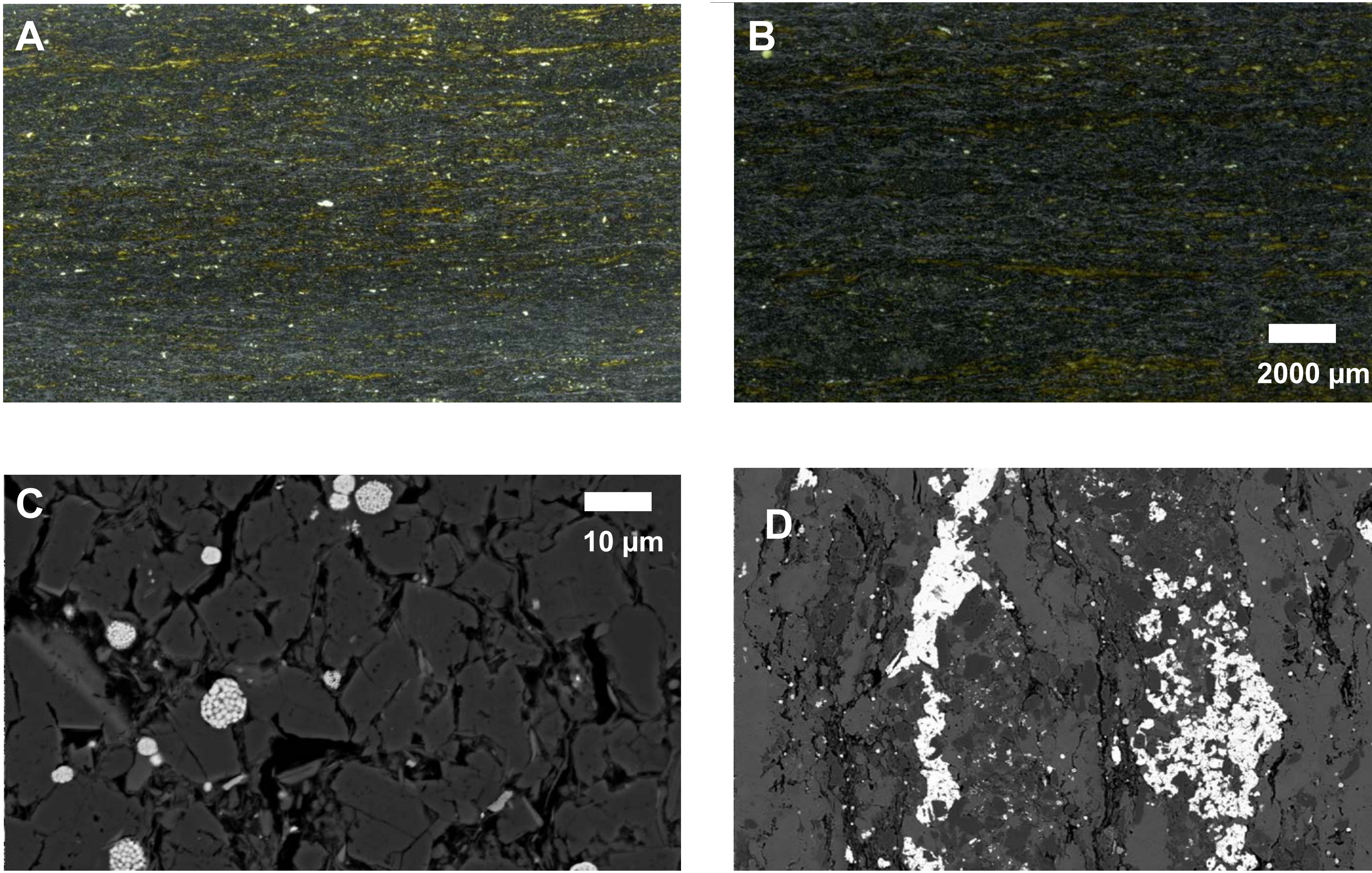
Oceanography and depositional conditions in the Kupferschiefer Sea

Paleo-ecosystems: upper Permian Kupferschiefer



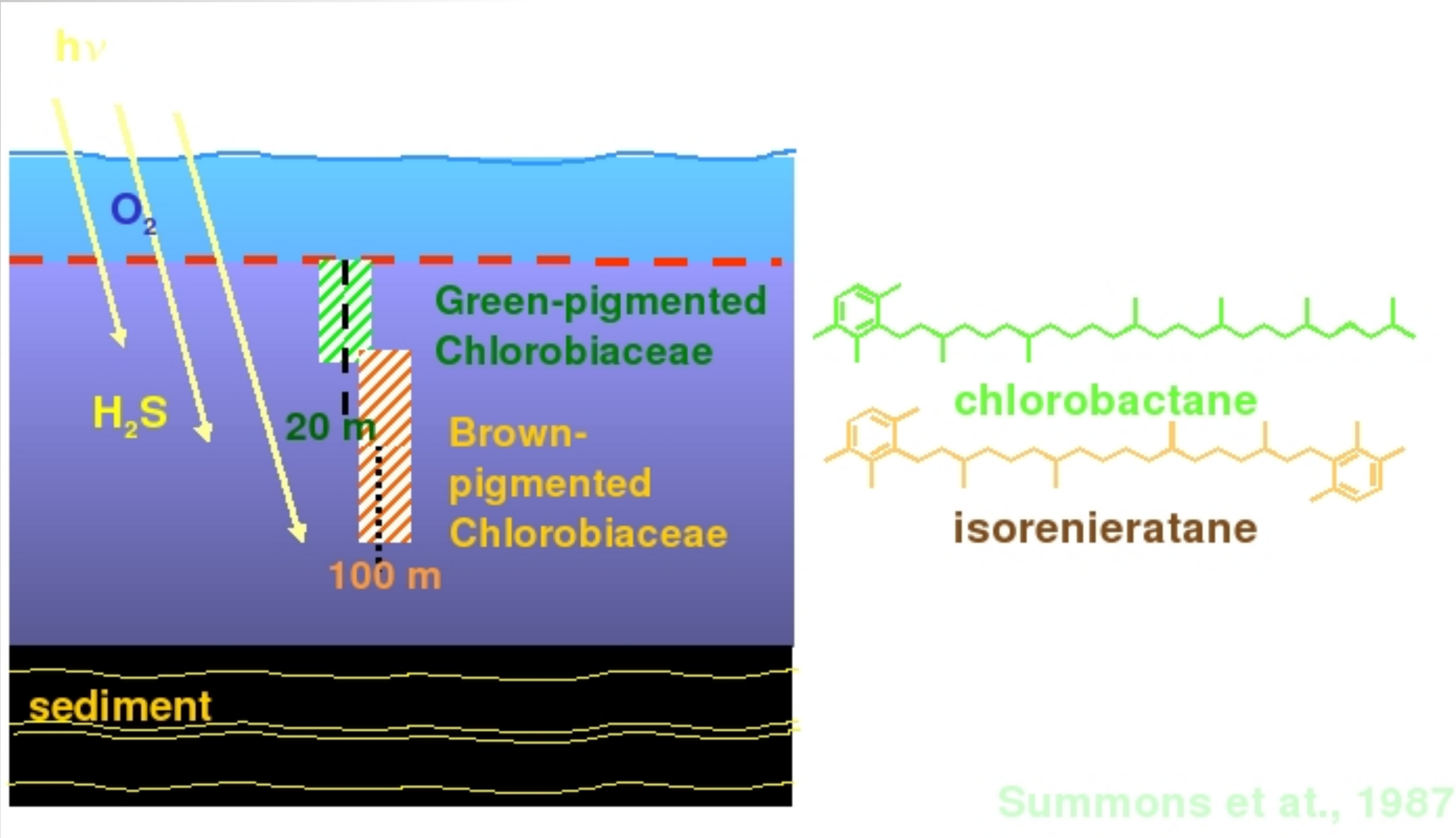
A: Lenticular lamination of the Kupferschiefer point to a low-energetic depositional environment and to the absence of benthic activity. **B:** During deposition of the Ca1 sediment reworking was related to the activity of benthic organisms and/or stronger bottom currents.

Paleo-ecosystems: upper Permian Kupferschiefer

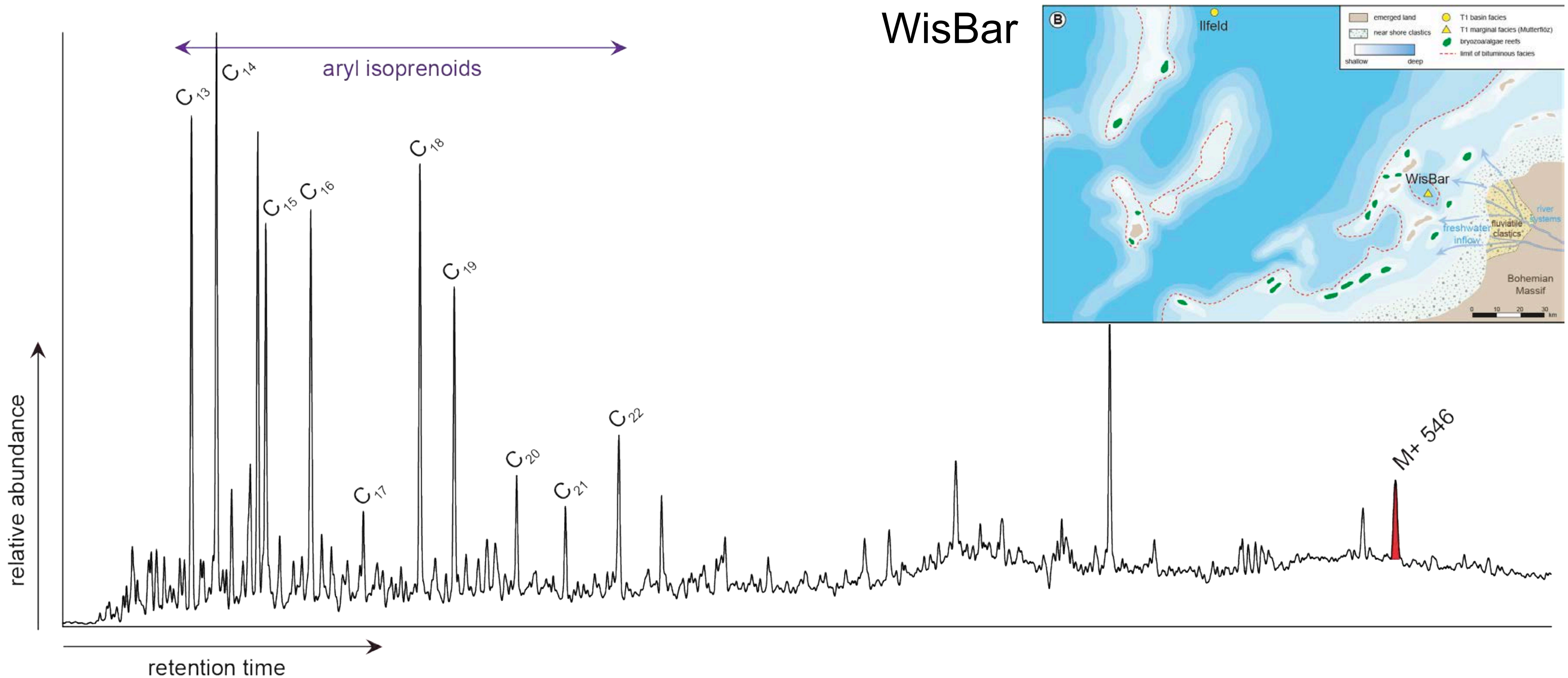


A, B: Organic matter and pyrite enriched in distinct layers (algae/bacteria mats). **C:** pyrite framboids (<10 µm) attested to euxinic bottom waters. **D:** Euhedral diagenetic pyrite.

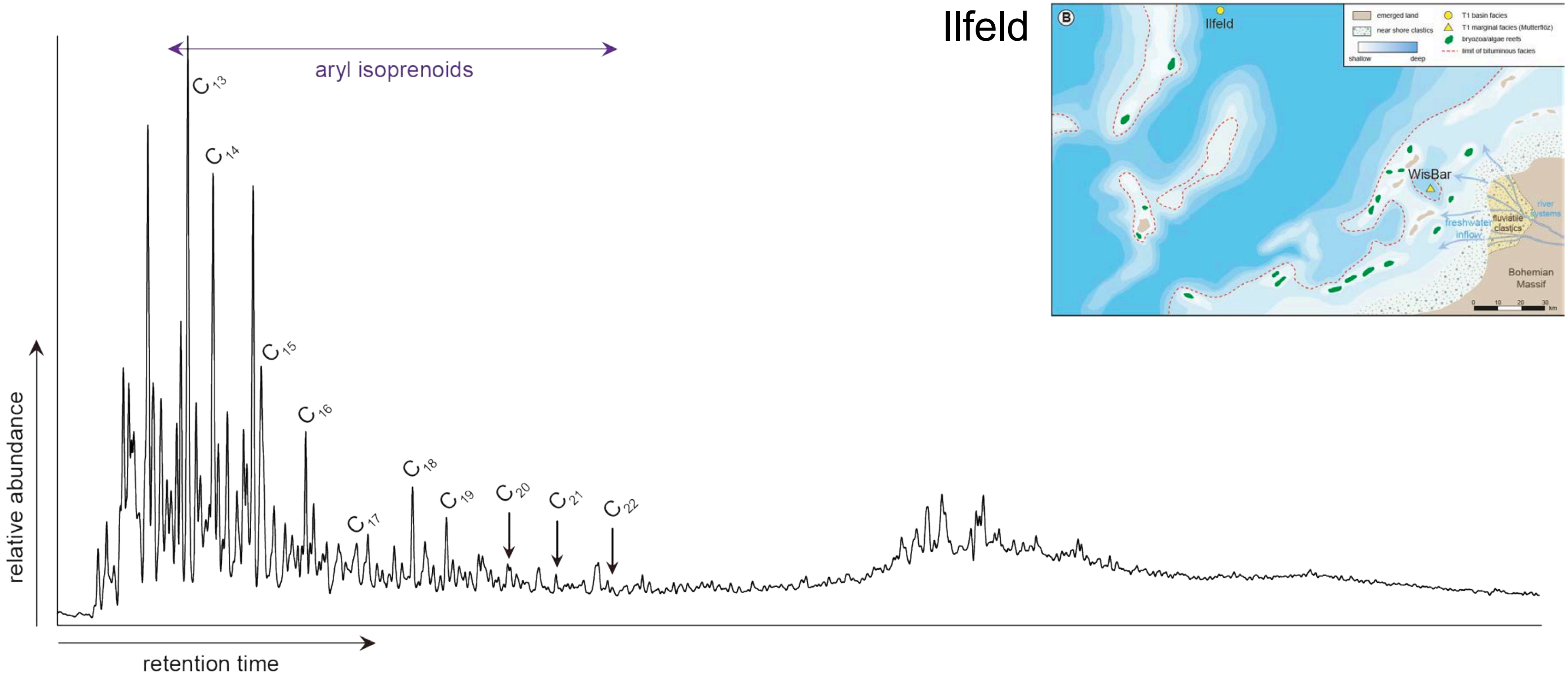
Molecular geochemical evidence for euxinia



Paleo-ecosystems: upper Permian Kupferschiefer



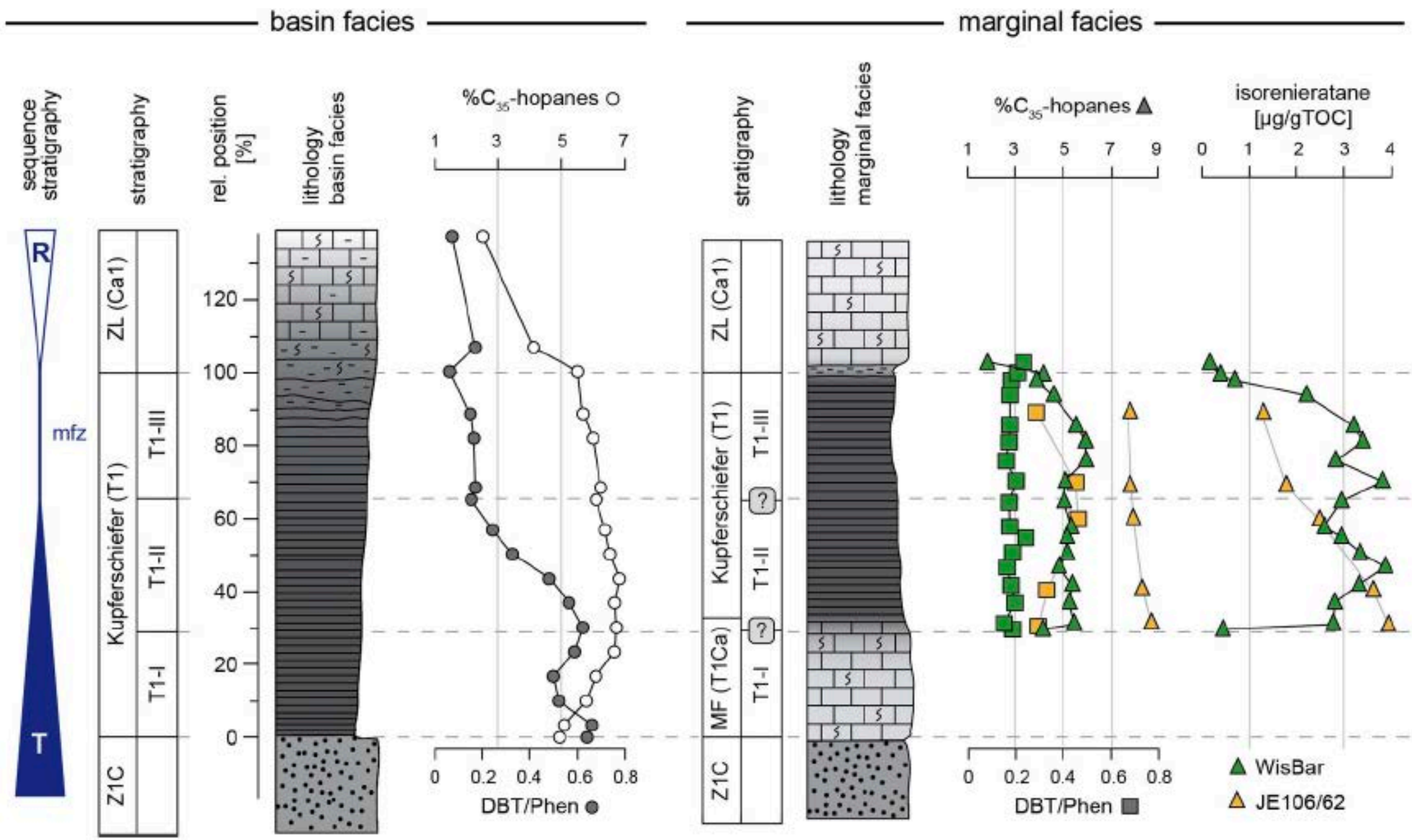
The m/z 133 mass fragmentogram for a Kupferschiefer sample from the Gera lagoon, a marginal euxinic lagoon environment. Euxinic conditions that extented into the photic zone (PZE) is indicated by the occurrence of isorenieratane, a diaromatic carotenoid biosynthesized by brown-pigmented green photoautothrophic sulfur bacteria (Chlorobiaceae). Long-chain aryl isoprenoids (C_{18-22}) occurred at high abundances.



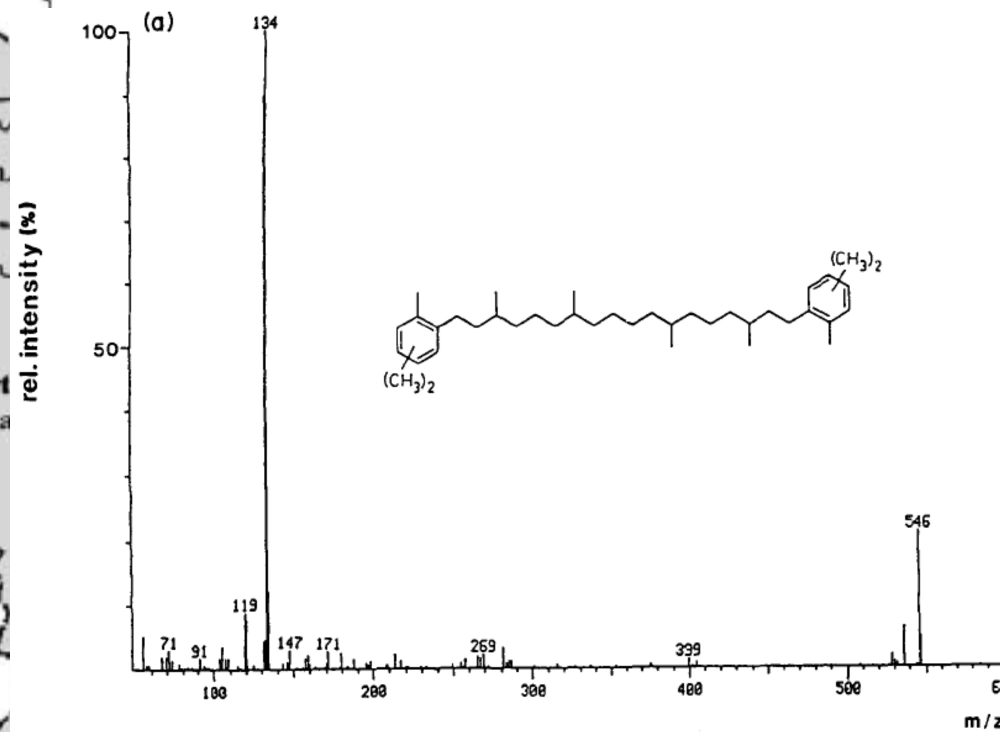
The m/z 133 massfragmentogram for a Kupferschiefer sample from the Ilfeld mine, representing a basinal depositional setting. Isorenieratane is not present in the sample and long-chain aryl isoprenoids occurred at only low abundances.

This might be explained by a higher thermal maturity, resulting in the degradation of this compounds. Alternatively, H_2S might have been limited to the aphotic zone.

Paleo-ecosystems: upper Permian Kupferschiefer

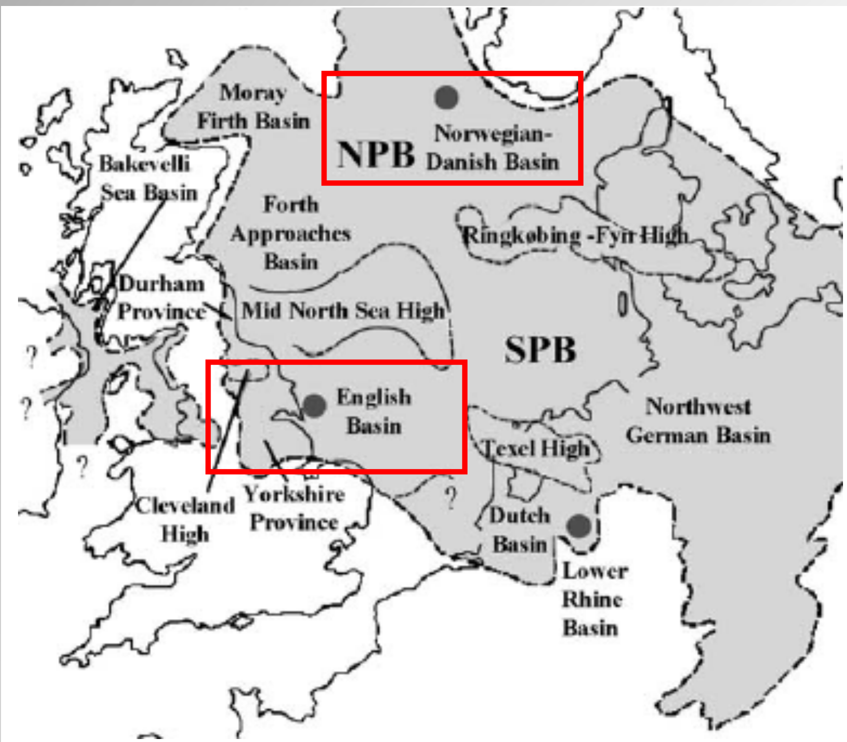


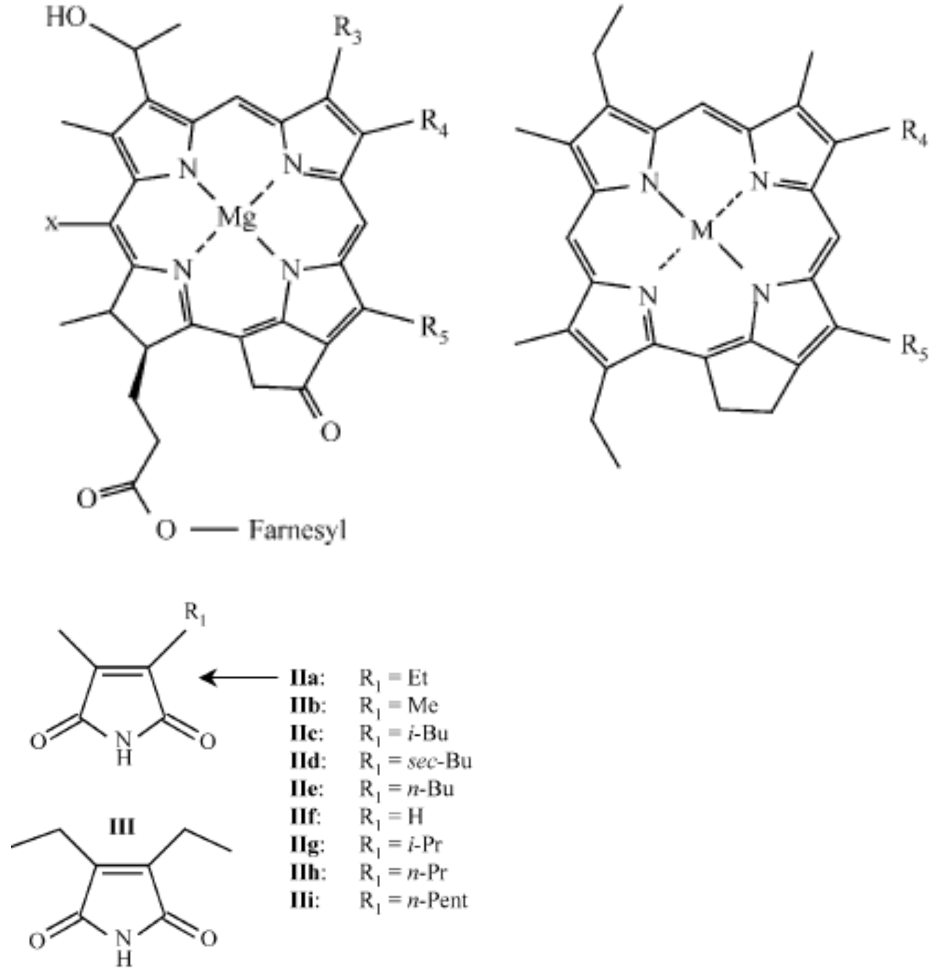
Molecular geochemical proxies attested to prolonged reducing conditions in basinal and marginal depositional settings. PZE was, however, only confirmed for marginal lagoon settings.



The presence of isorenieratane in Kupferschiefer samples from the Lower Rhine Basin attested to H_2S-rich water that have extended into the photic zone (Schwark & Püttmann, 1989). Similar to the Thuringian Basin, the lower Rhine Basin was a marginal basin and did not represent the central Kupferschiefer Sea.

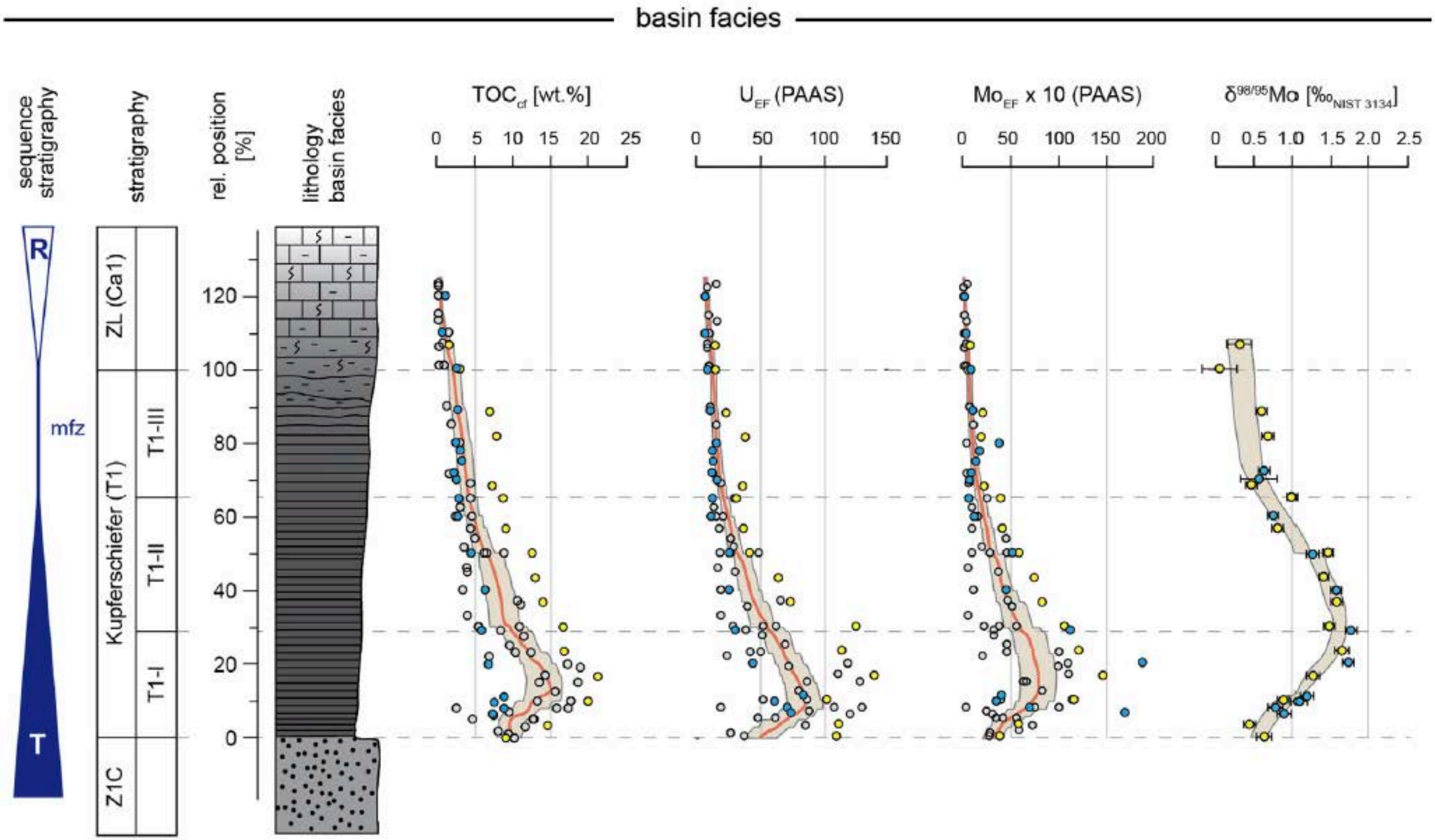
Paleo-ecosystems: upper Permian Kupferschiefer





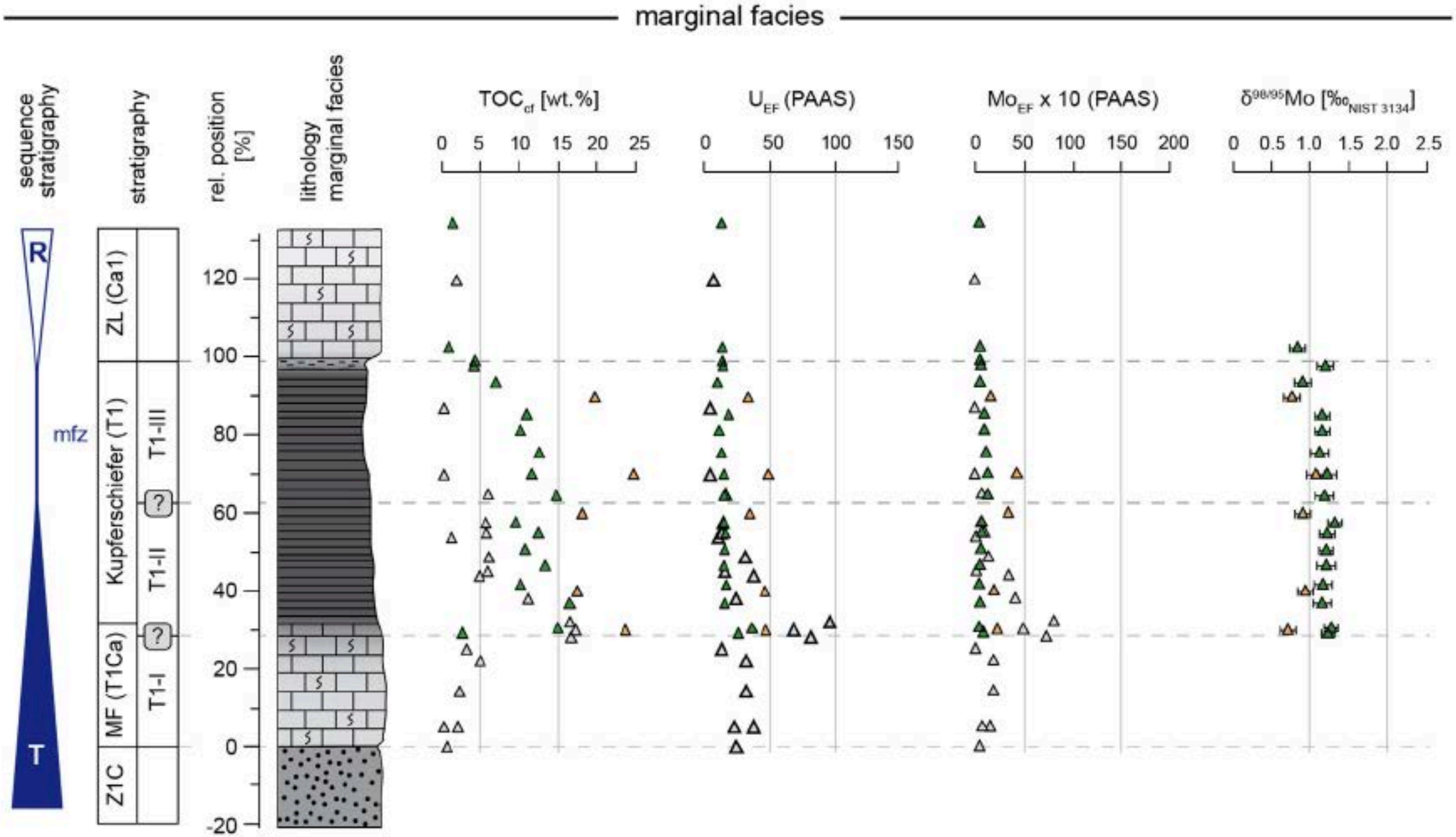
Me, i-Bu maleimide derives from bateriochlorophyll: c, d, e that is known to be synthesized by green sulfur bacteria. These compounds have been found in Kupferschiefer samples from the UK and Norwegian sector, indicating that photic zone euxinia occurred at these locations (Pancost et al., 2002).

Paleo-ecosystems: upper Permian Kupferschiefer



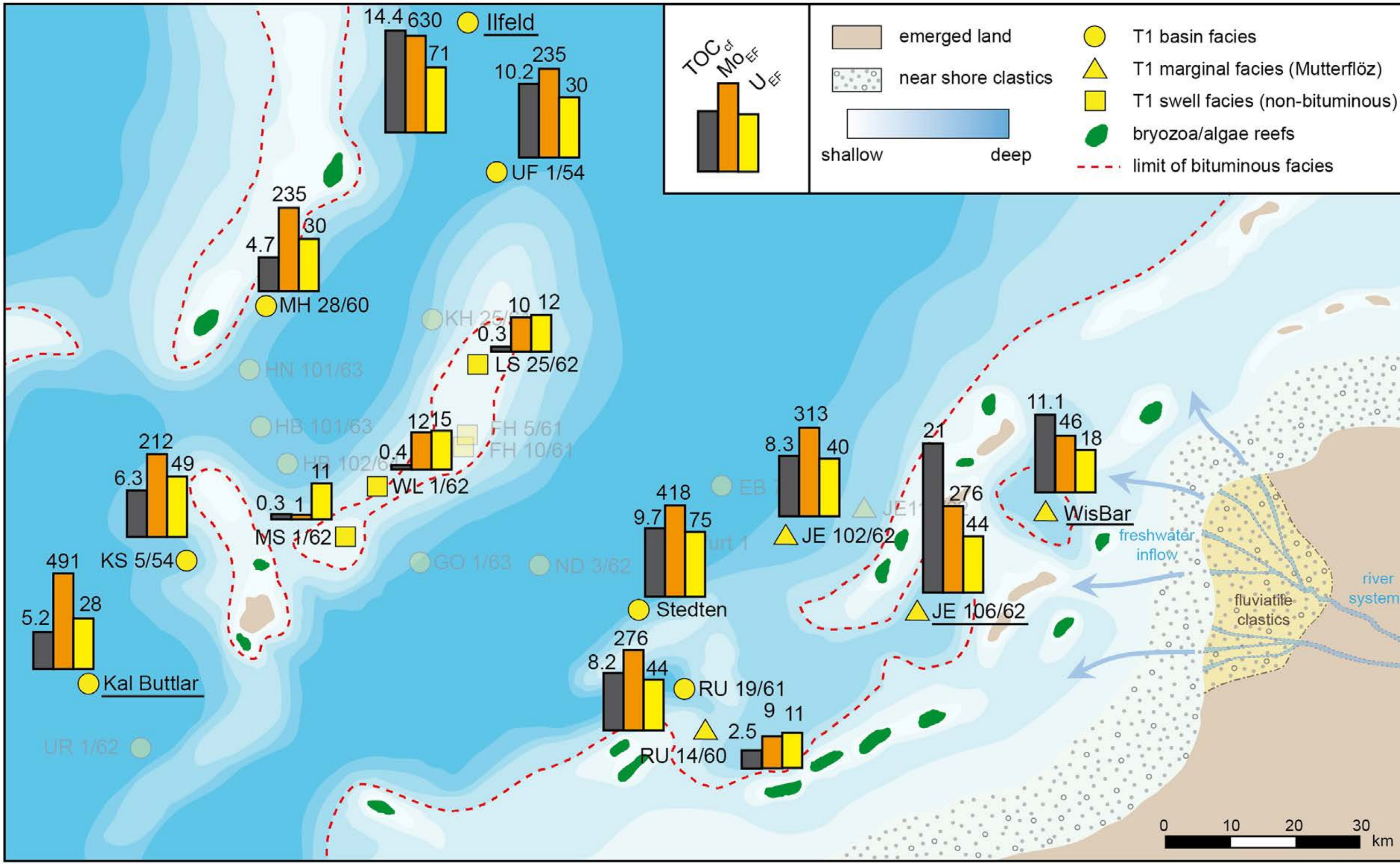
Sediment texture, high contents of sedimentary organic matter are indicative for preferentially reducing conditions in the bottom waters of the Kupferschiefer Sea. Oxygen-deficient conditions were also expressed by the accumulation of U and Mo as well as by molybdenum isotope signatures (Ruebsam et al., 2017).

Paleo-ecosystems: upper Permian Kupferschiefer



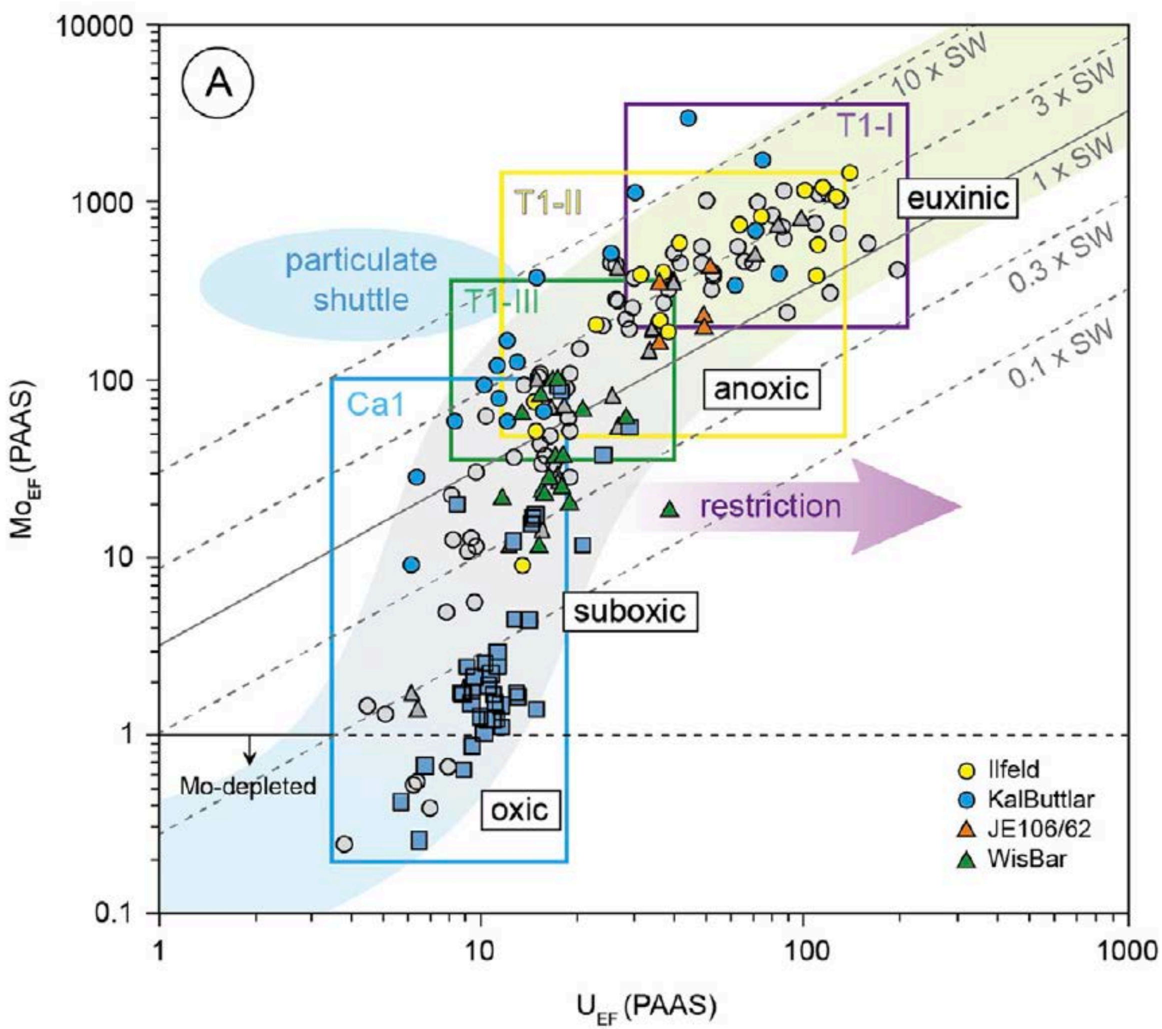
Preferentially reducing conditions were also indicated for marginal lagoon settings, but were not associated with the enrichment of redox-sensitive metals. Low sedimentary TE abundances are explained by a distinct local seawater chemistry (Ruebsam et al., 2017).

Paleo-ecosystems: upper Permian Kupferschiefer



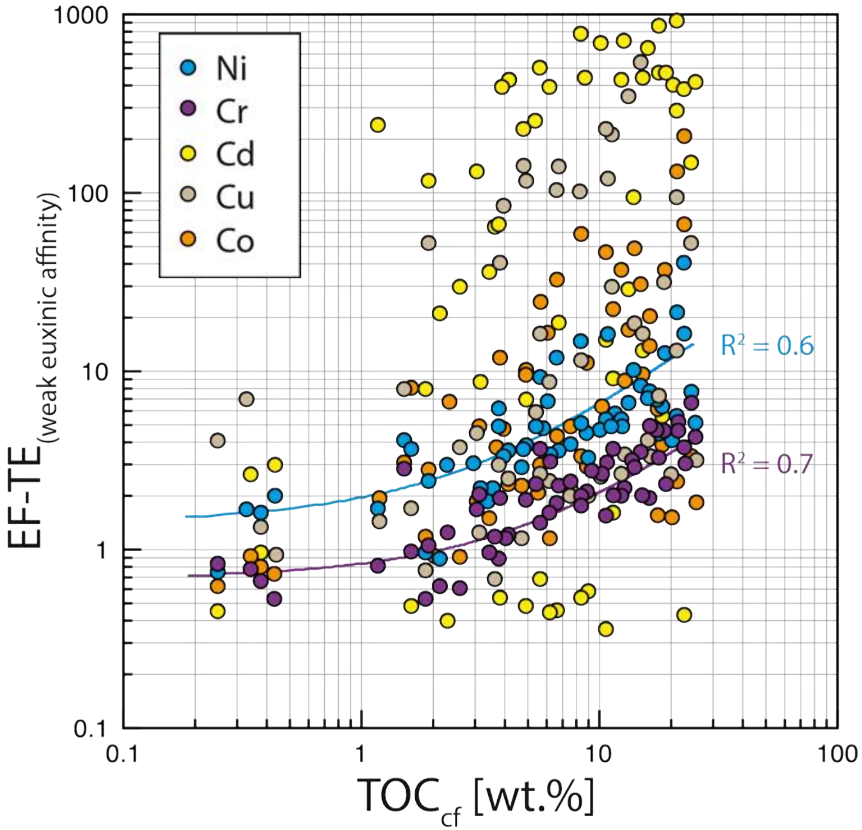
Map from the Thuringian Kupferschiefer Basin showing spatial variations in the enrichment of TOC (here TOC_{cf}), U and Mo (Ruebsam et al., 2017). Lagoon settings show high TOC, but low metal abundances.

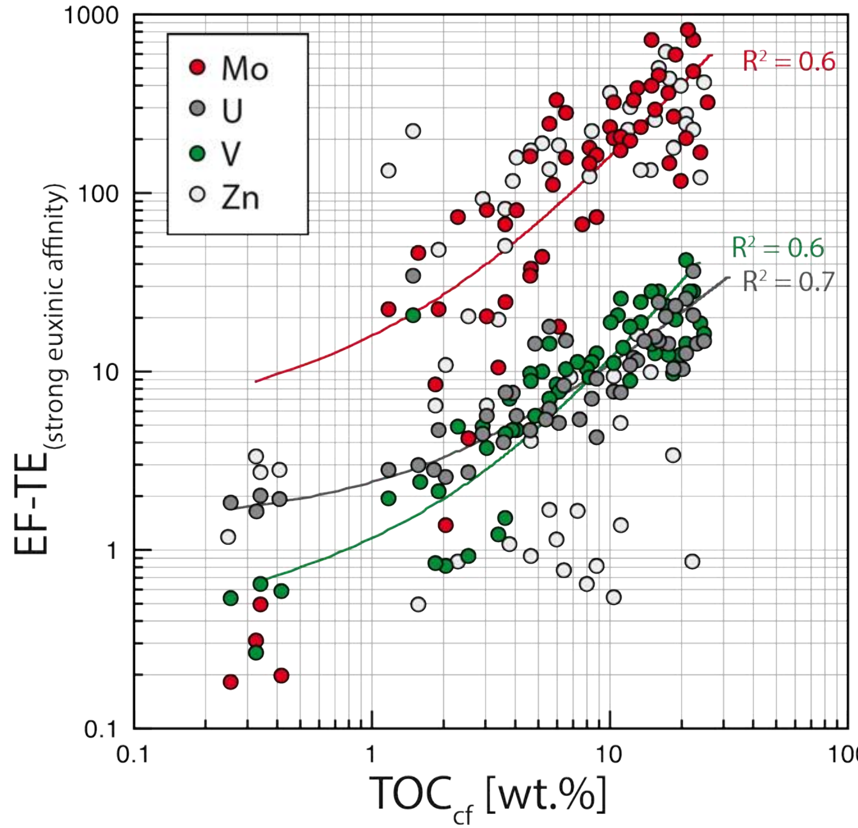
Paleo-ecosystems: upper Permian Kupferschiefer



U-Mo enrichment pattern allow distinguishing oxic, suboxic, anoxic and euxinic depositional conditions (Algeo & Tribovillard, 2009).

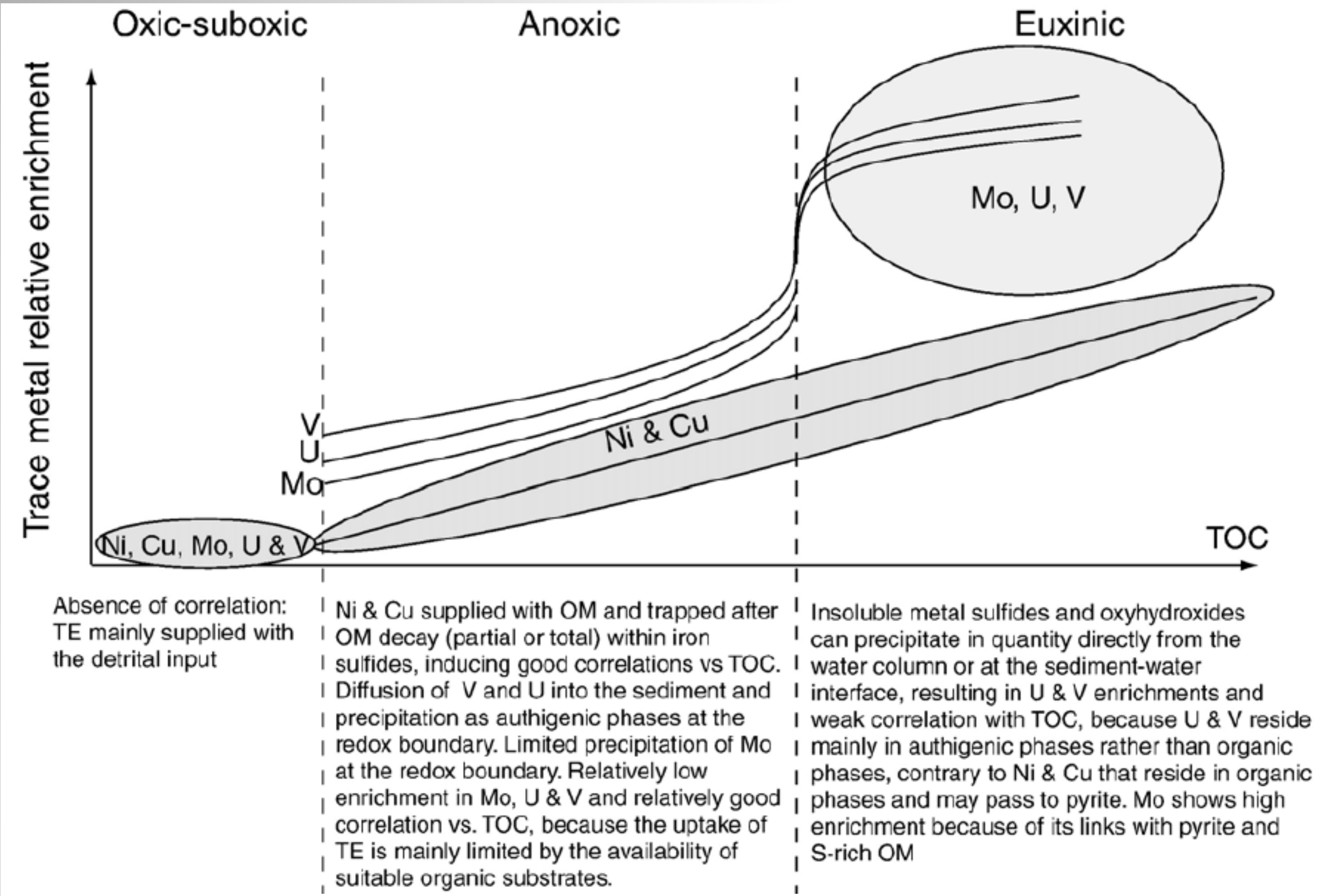
Paleo-ecosystems: upper Permian Kupferschiefer



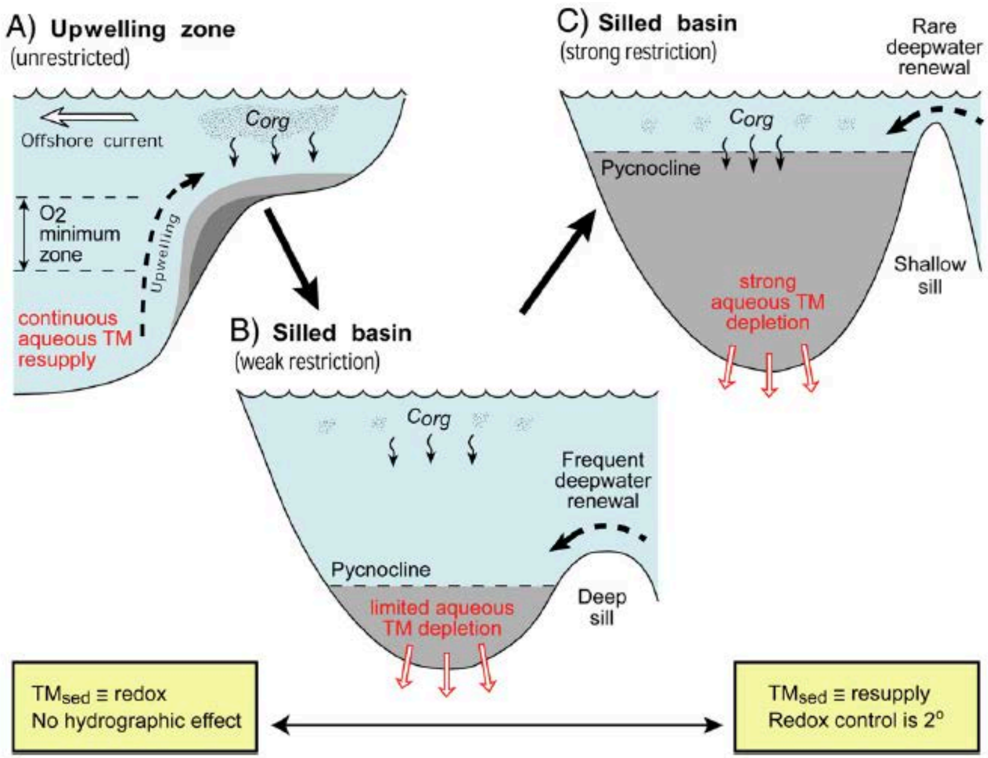


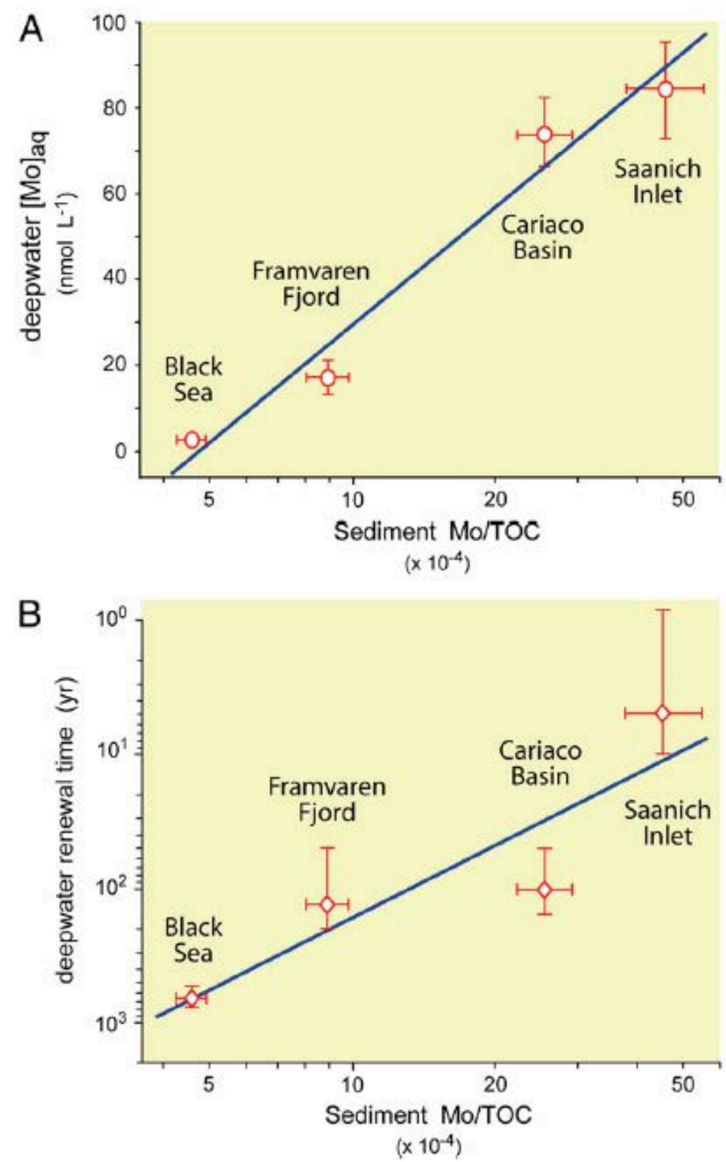
Concentrations of TOC_{cf} showed a strong covariations with trace elements with weak (Ni, Cr) and strong (Mo, V, U) euxinic affinity. The later pattern point to only low H_2S concentrations and thus only weakly euxinic conditions in the Thuringian Basin during Kupferschiefer deposition.

Paleo-ecosystems: upper Permian Kupferschiefer

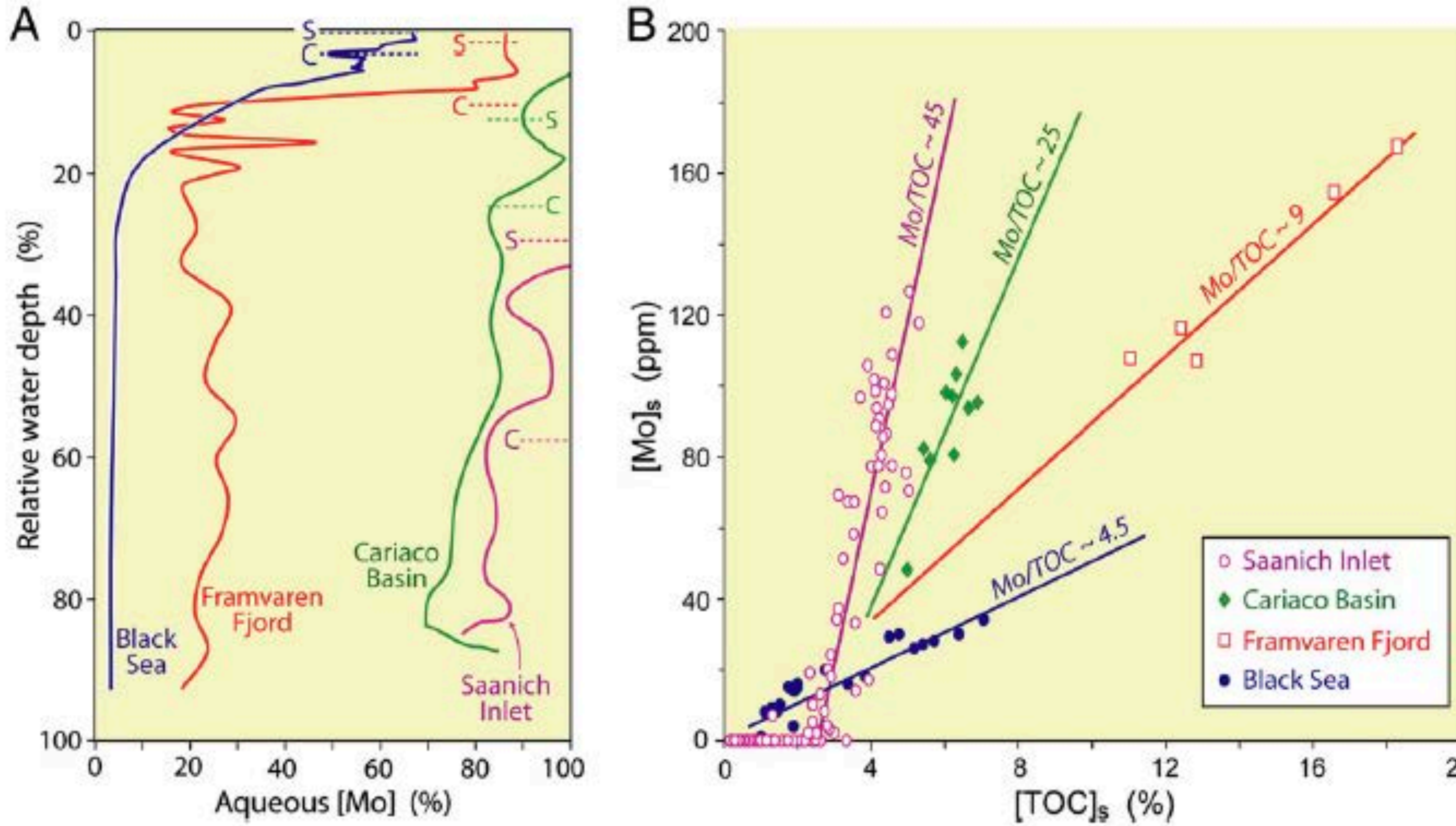


Mechanisms of redox-sensitive trace element enrichment (Tribovillard et al., 2006).

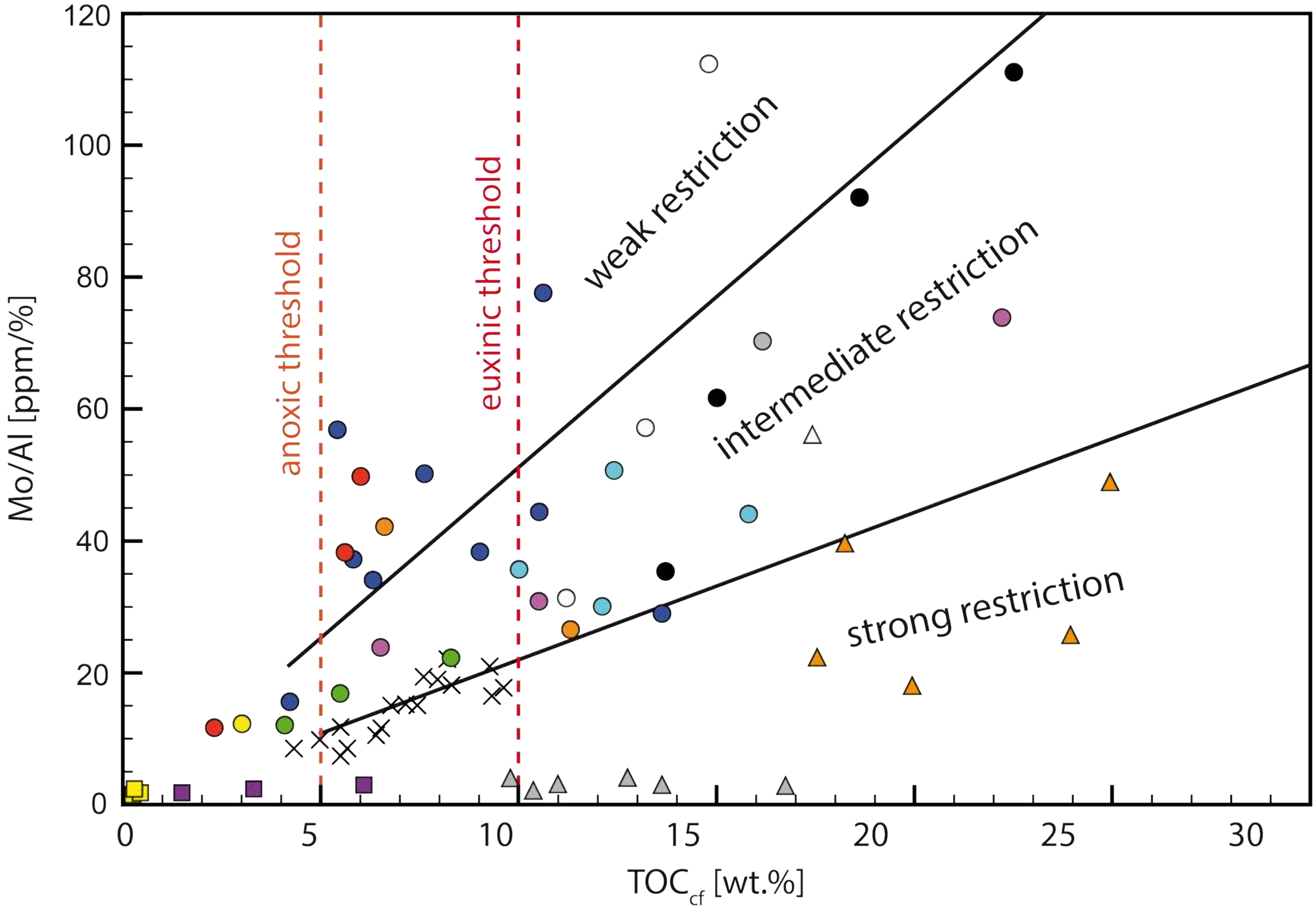




Models of influences on trace-metal (TM) accumulation in different settings. Also shown aqueous Mo concentration, deepwater renewal times and Mo/TOC ratios in recent anoxic/euxinic basins (Algeo & Rowe, 2012).

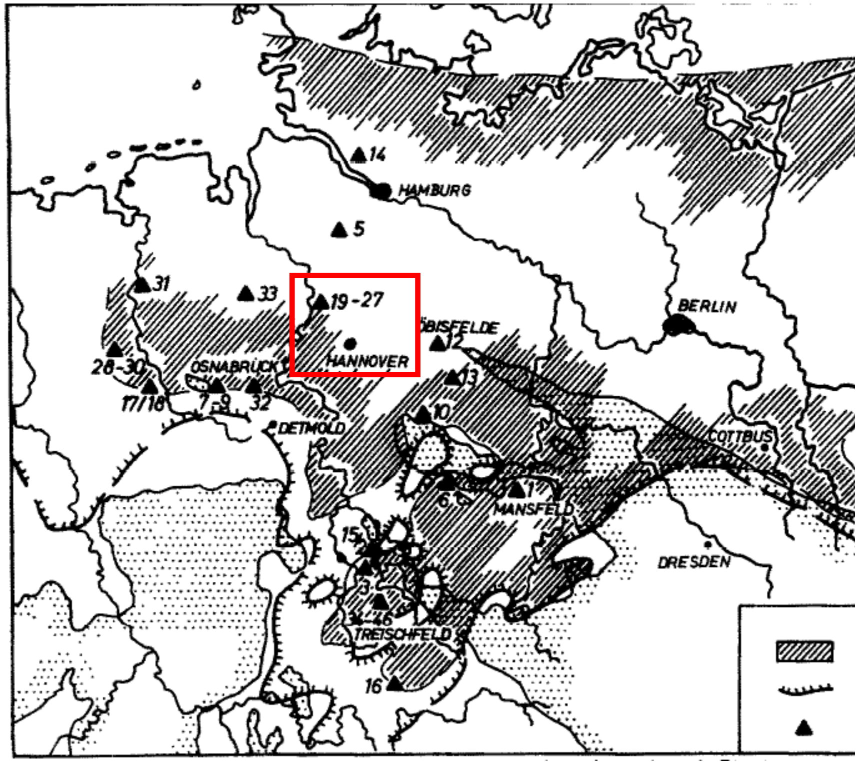


Vertical Mo-concentration profiles in recent anoxic/euxinic basins and associated MO-TOC covariations (Algeo & Rowe, 2012).



The covariation of TOC_{cf} with Mo/Al ratios documented in the Kupferschiefer from the Thuringian Basin and the Lower Rhine Basin. Long residence times in restricted euxinic settings will result in the near quantitative removal of aqueous Mo.

Paleo-ecosystems: upper Permian Kupferschiefer



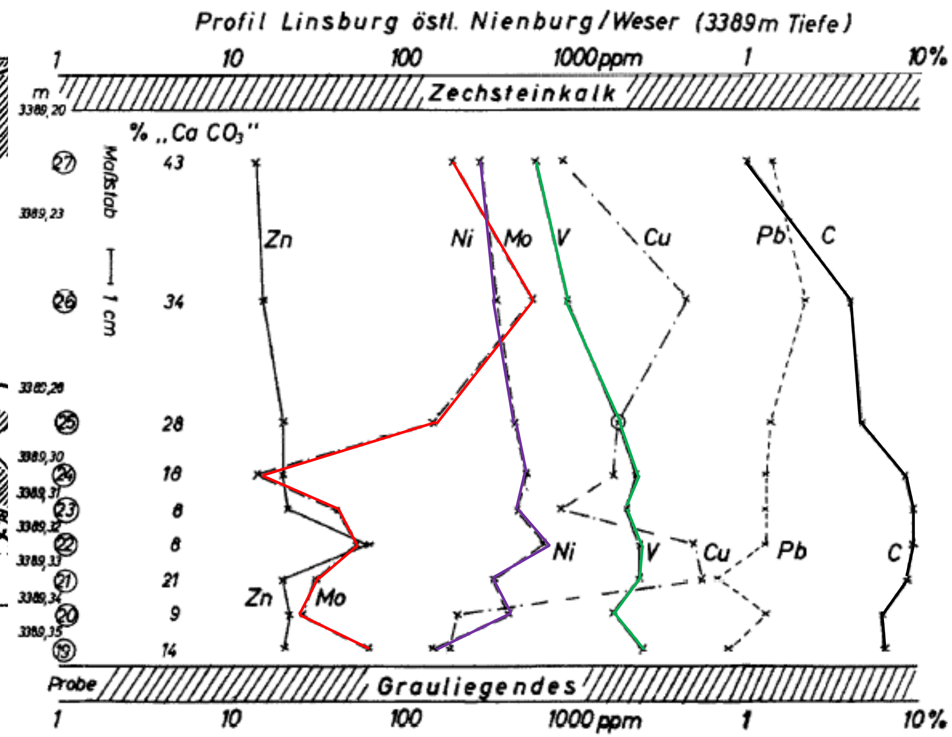


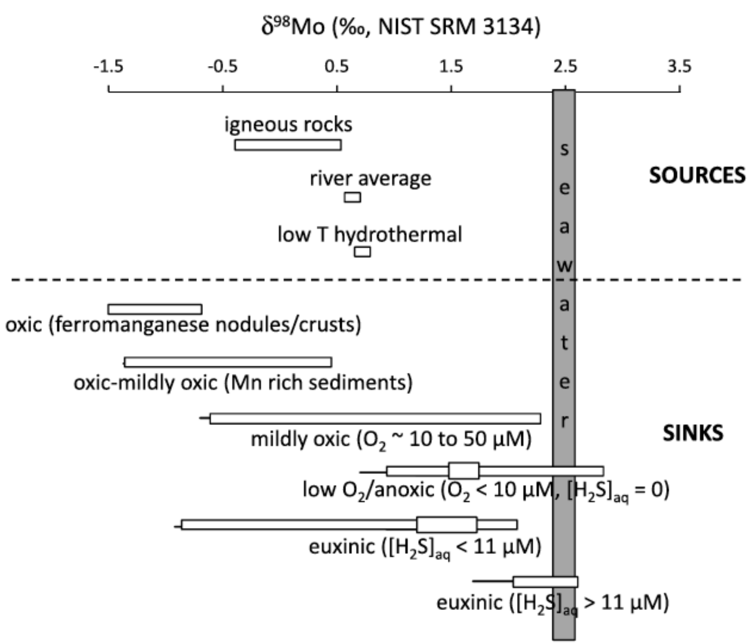
Abb. 11. Die Gehalte an Zn, Mo, Ni, V, Cu, Pb, C und Karbonaten im Profil Linsburg.

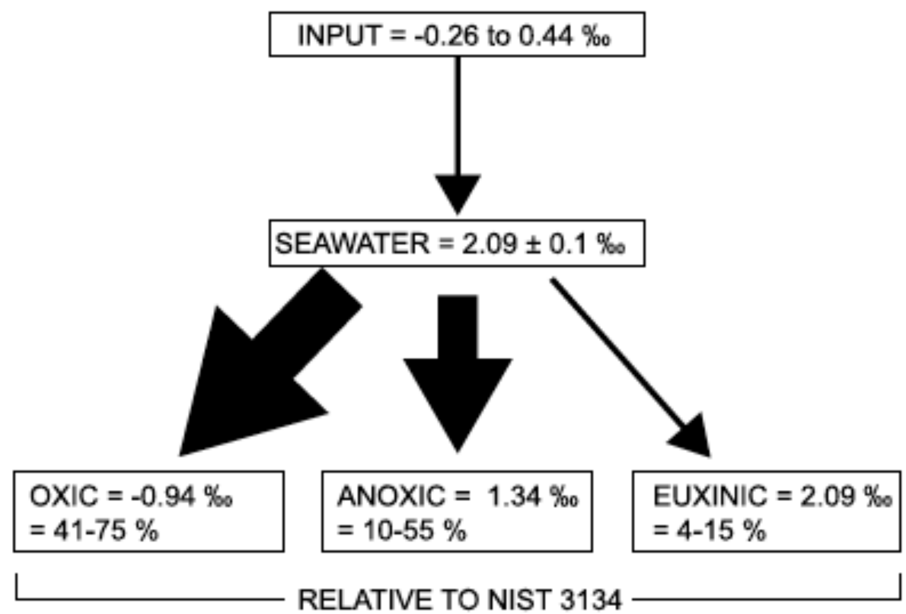
Data from the central Kupferschiefer Basin were published by Wedepohl (1964), but comprise only inorganic geochemical data.

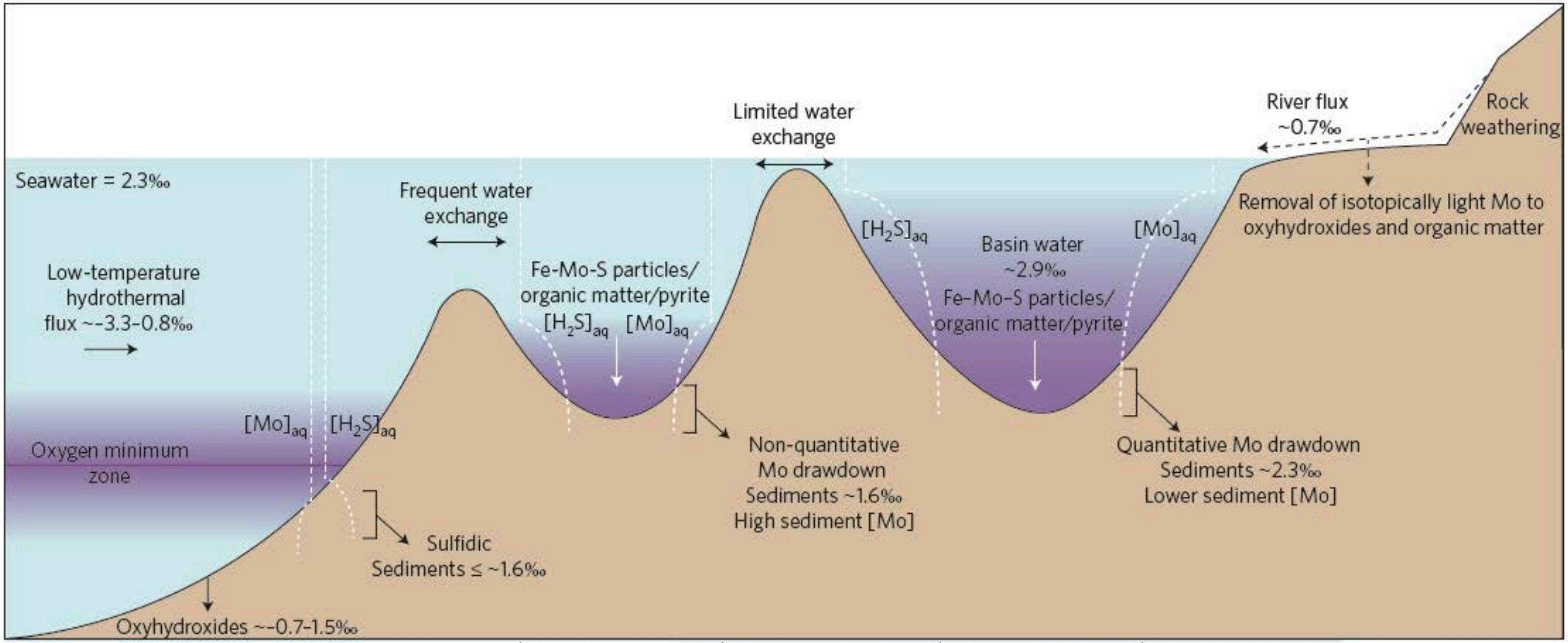
The profile Linsburg shows typical gradients for TOC, Ni, V (highest enrichments in the basal Kupferschiefer). Interestingly, the basal Kupferschiefer shows only low Mo abundances, which could point to an Mo-drawdown that occurred as the result of high H_2S concentration (e.g. Algeo & Rowe, 2012).

Molybdenum isotopes as tracer for redox conditions:

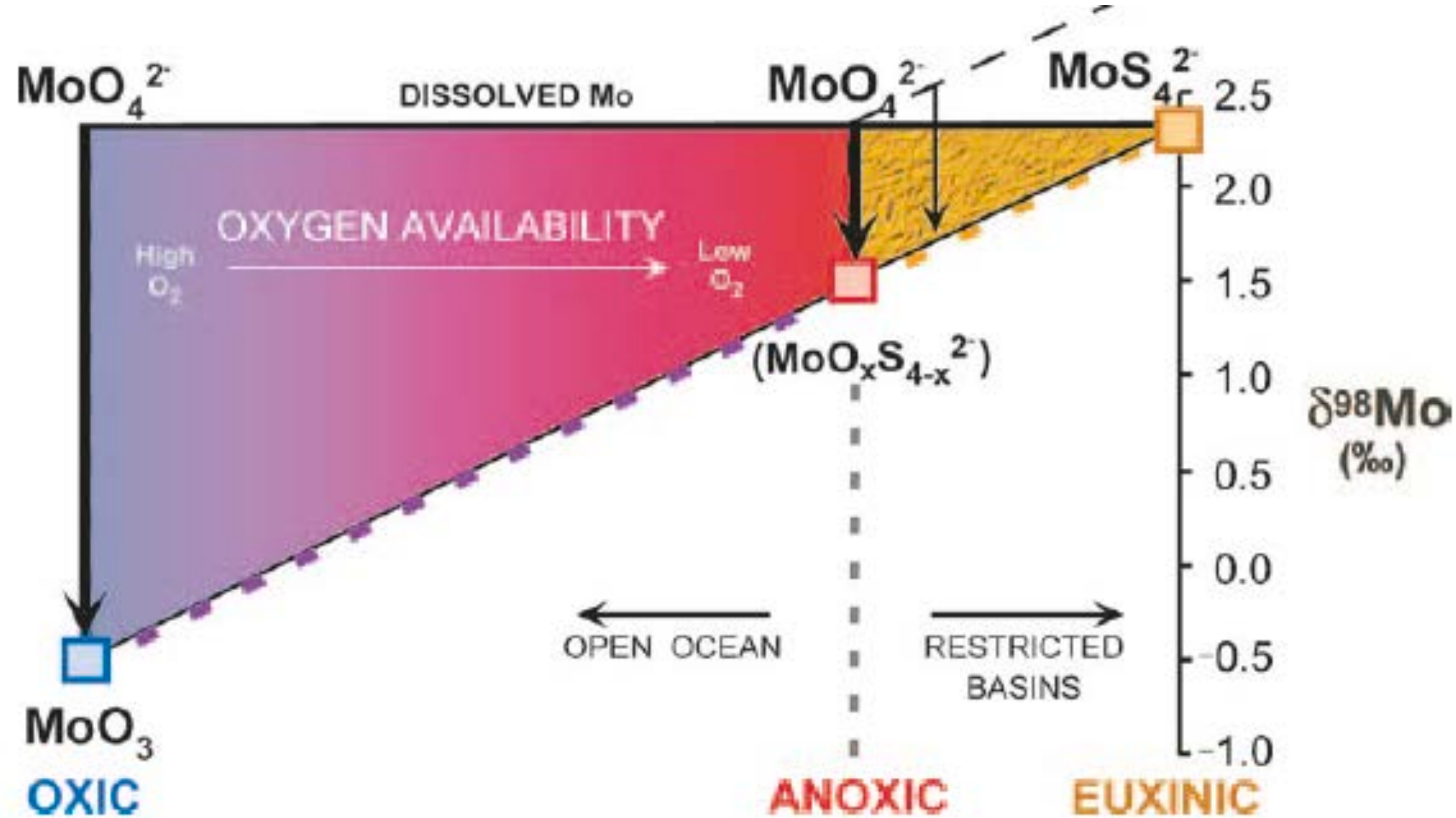
Mo is supplied to the oceans mainly by rivers, with an average isotopic composition of -0.26 to 0.44‰ (0.7‰). The isotopic composition of the sea water reflect the relative balance of oxic versus anoxic/euxinic sinks. Isotopic fractionation during Mo-burial is expressed in isotopic signature of the sedimentary Mo (e.g. Archer & Vance, 2008; Dickson et al., 2014; Goldberg et al., 2016; Dickson, 2017).



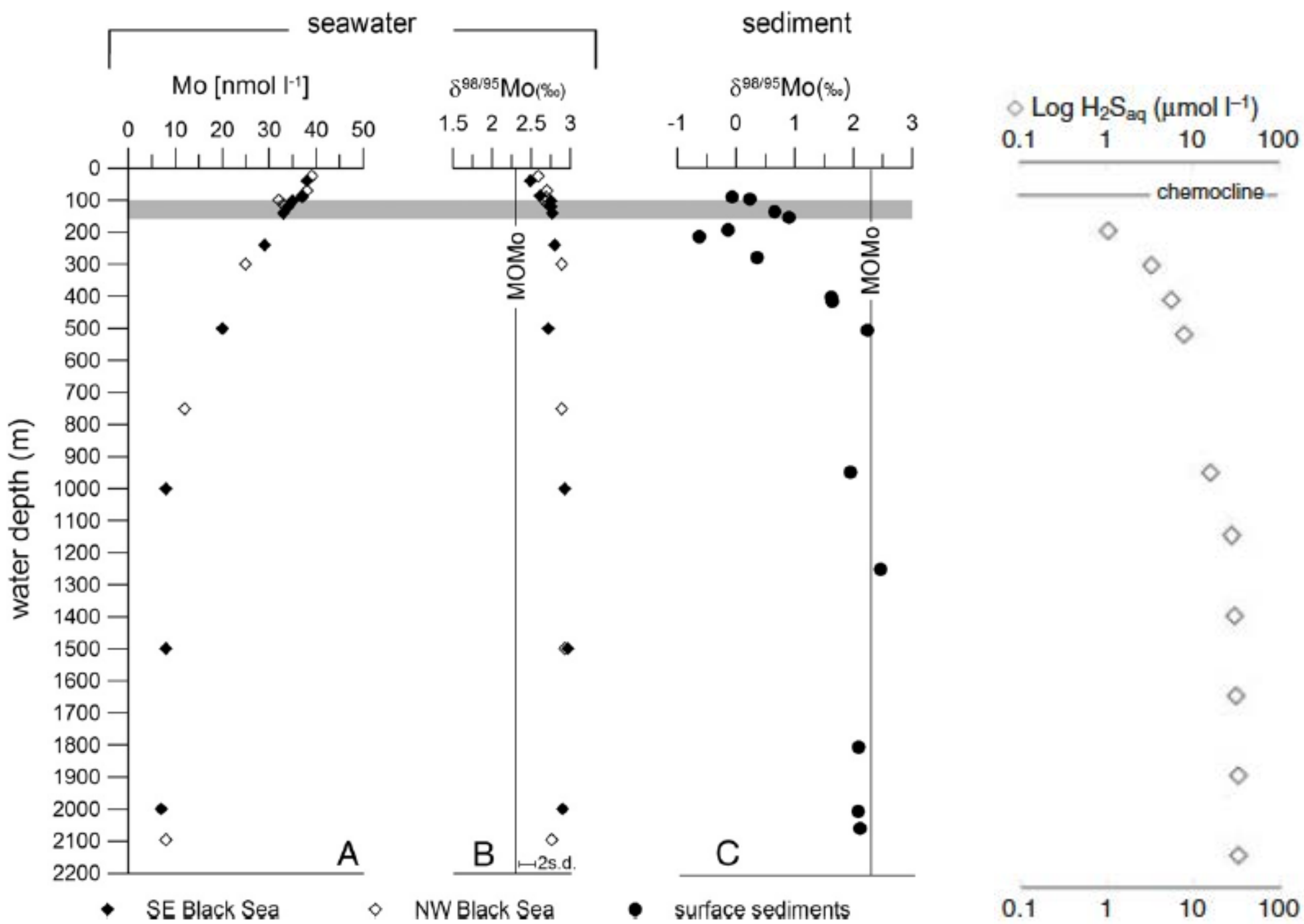




Molybdenum-isotope fluxes in the modern marine environment (Dickson, 2017). In combination with information on the redox state and and hydrology sedimentary Mo-isotopes can provide insight into local redox redox (H_2S concentration) as well as on the balance of global oxic versus anoxic/euxinic sinks.

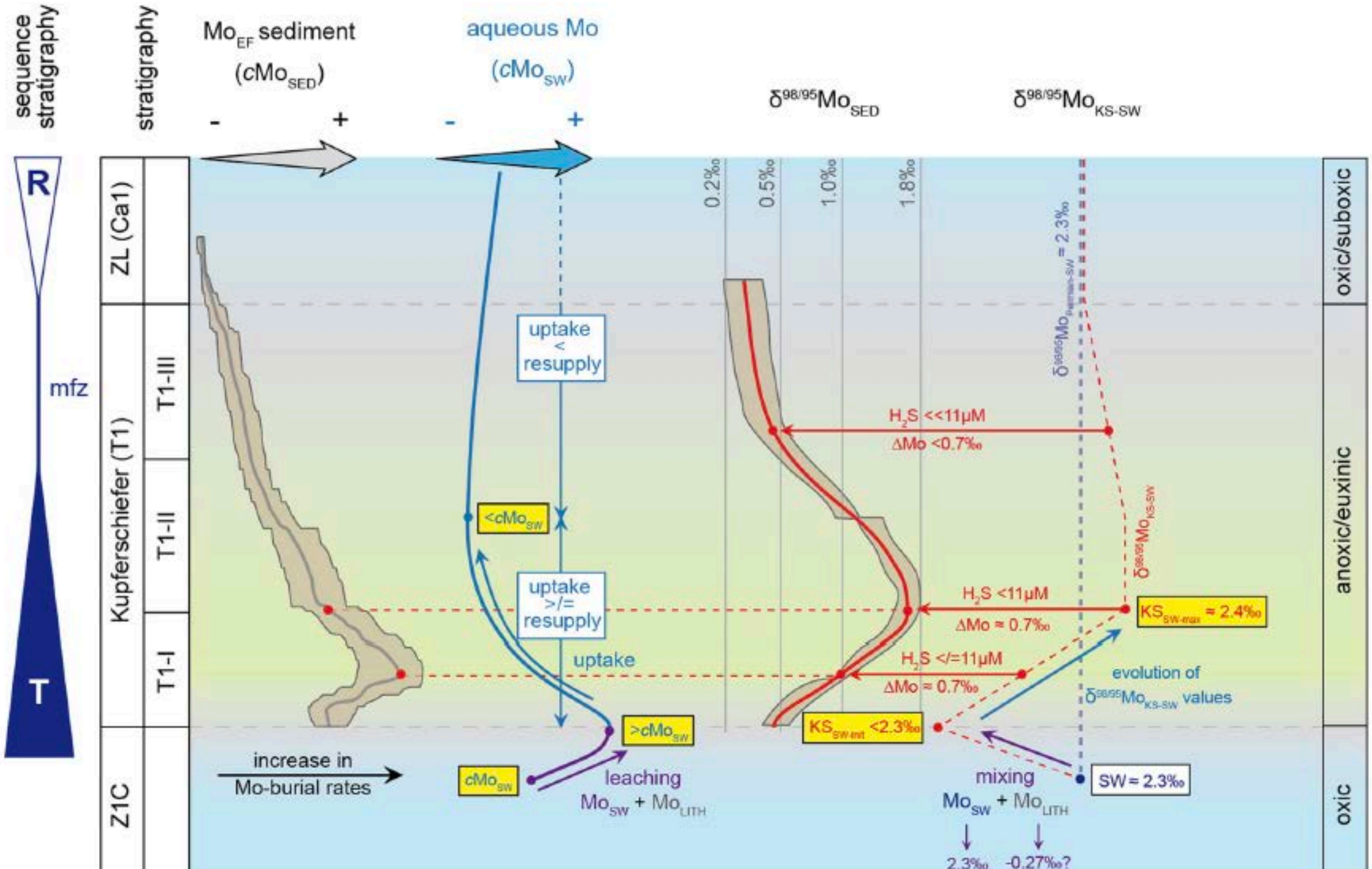


Mo-isotope system in marine sediments in dependency of the redox-state (O2 availability and H_2S concentration). Measured Mo isotope-values for restricted basin sediments suggest a change in the isotopic composition of aqueous Mo (dashed line at top) to heavier values as Mo is removed in the presence of dissolved sulfide (Poulson et al., 2006).



Mo-concentrations and its isotopic composition in the seawater and in sediments can be linked to the sulfidity and to deepwater renewal times (Neubert et al., 2008; Nägler et al., 2011).

Paleo-ecosystems: upper Permian Kupferschiefer



Mo-isotope systematics in the southern Kupferschiefer Sea. Highest Mo-isotope values of about 1.7‰ attested to only mildly euxinic conditions (H_2S <11µM).

Literature (some recommendations)

Kupferschiefer in general:

Paul, J., 1982. Zur Rand- und Schwellen-Fazies des Kupferschiefers. Z. Dtsch. Geol. Ges. 133, 571–605.

Paul, J., 2006. Der Kupferschiefer: lithologie, stratigraphie, fazies und metallogenese eines Schwarzschiefers. Z. Dtsch. Ges. Geowiss. 157, 57–76.

Paul, J., Huckriede, H., 2004. Riffe, Gips und Erze: Zechstein zwischen Saalfeld und Neustadt/Orla. Schriftenr. Dtsch. Geol. Ges. 35, 75–91.

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.

Strohmenger, C., Voigt, E., Zimdars, J., 1996. Sequence stratigraphy and cyclic development of Basal Zechstein carbonate-evaporite deposits with emphasis on Zechstein 2 off-platform carbonates (Upper Permian, Northeast Germany). Sediment. Geol. 102, 33–54.

Sweeney, M., Turner, P., Vaughan, D.J., 1987. The Marl Slate: a model for the precipitation of calcite, dolomite and sulfides in a newly-formed anoxic sea. Sedimentology 34, 31–48.

Vaughan, D.J., Sweeney, M., Friedrich, G., Diedel, R., Haranczyk, C., 1989. The Kupferschiefer: an overview with an appraisal of the different types of mineralization. Econ. Geol. 84, 1003–1027.

Wedepohl, K.H., 1971. “Kupferschiefer” as a prototype of syngenetic sediment ore deposit. Soc.Min. Geol. Spec. Issue 3, 268–273.

Application of geochemical proxies (biomarkers):

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, History (1132 pp.).

Pancost, D.R., Crawford, N., Maxwell, J.R., 2002. Molecular evidence for basin-scale photic zone euxinia in the Permian Zechstein Sea. Chem. Geol. 188, 217–227.

Schwark, L., Puttmann,W., 1990. Aromatic composition of the Permian Kupferschiefer in the Lower Rhine Basin, NW Germany. Org. Geochem. 16, 749–761.

Sinninghe Damsté, J.S., Schouten, S., 2006. Biological Markers for Anoxia in the Photic Zone of the Water Column. In: Volkman (Ed.), Marine Organic Matter. Springer Verlag, Heidelberg, pp. 127–163.

Summons, R.E., Powell, T.G., 1986. Chlorobiaceae in Palaeozoic seas revealed by biological markers, isotopes and geology. Nature 319, 763–765.

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Application of geochemical proxies (trace elements):

Algeo, T.J., Lyons, T.W., 2006. Mo-total organic carbon covariation in modern anoxic marine environments: implication for analysis of paleoredox and -hydrographic conditions. Paleoceanography 21, PA1016.

Algeo, T.J., Rowe, H., 2012. Paleoceanographic applications of trace-metal concentration data. Chem. Geol. 324–325, 6–18.

Algeo, T.J., Tribovillard, N., 2009. Environmental analysis of paleoceanographic systems based on molybdenum–uranium covariation. Chem. Geol. 268, 211–225.

Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. Chem. Geol. 232, 12–32.

Tribovillard, N., Algeo, T.J., Baudin, F., Riboulleau, A., 2012. Analysis of marine environmental conditions based on molybdenum–uranium covariation - applications to Mesozoic paleoceanography. Chem. Geol. 324–325, 46–58.

Application of geochemical proxies (molybdenum isotopes):

Archer, C., Vance, D., 2008. The isotopic signature of the global riverine molybdenum flux and anoxia in the ancient ocean. Nat. Geosci. 1, 597–600.

Barling, J., Anbar, A.D., 2004. Molybdenum isotope fractionation during adsorption by manganese oxides. Earth Planet. Sci. Lett. 217, 315–329.

Barling, J., Arnold, G.L., Anbar, A.D., 2001. Natural mass-dependent variations in the isotopic composition of molybdenum. Earth Planet. Sci. Lett. 193, 447–457.

Dickson, A.J., 2017. A molybdenum-isotope perspective on Phanerozoic deoxygenation events. Nature Geosciene, DOI: 10.1038/NGEO3028.

Dickson, A.J., Cohen, A.S., Coe, A.L., 2014. Continental margin molybdenum isotope signatures from the early Eocene. Earth Planet. Sci. Lett. 404, 389–395.

Nägler, T.F., Neubert, N., Böttcher,M.E., Dellwig, O., Schnetger, B., 2011. Molybdenum isotope fractionation in pelagic euxinia: evidence fromthemodern Black and Baltic Seas. Chem. Geol. 289, 1–11.

Neubert, N., Nägler, T.F., Böttcher, M.E., 2008. Sulfidity controlsmolybdenumisotope fractionation into euxinic sediments: evidence from the modern Black Sea. Geology 36, 775–778.

Poulson, R.L., Siebert, C., McManus, J., Berelson,W.M., 2006. Authigenic molybdenum isotope signatures in marine sediments. Geology 34, 617–620.

Siebert, C., McManus, J., Bice, A., Poulson, R., Berelson, W.M., 2006. Molybdenum isotope signatures in continental margin marine sediments. Earth Planet. Sci. Lett. 241, 723–733.

!!!Papers providing a nice overview and a good introduction (for a first reading) were highlighted red.