

# Trace Element Distribution in Palaeozoic Black Shales: "Kupferschiefer" (Germany) and Exshaw Formation (Canada)

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Sediments of the Lower Rhine Basin and Black Shales of the Canadian Exshaw Formation were investigated for their major and minor element composition in order to gain information on palaeo-seawater composition. A comparison of the minor element distribution patterns of Palaeozoic, Mesozoic and more recent black shales may provide new information on the environment of deposition. The Permian "Kupferschiefer" is a typical bituminous marl. Core Niederwald 1 in the Lower Rhine Basin comprises the underlying Carboniferous (S1), the "Kupferschiefer" (T1) and the overlying Zechstein limestone (Ca1). The "Kupferschiefer" has a total thickness of 2.19 m and can be divided into three subunits (T1I-III) (Paul, 1982) which were sampled at high resolution. Assuming a deposition time of 20,000 to 100,000 years for the "Kupferschiefer", an estimated resolution of 200 to 1000 years per sample was attained. In core Niederwald 1 the elements V, Mo, Ni, U, Ca, As, Re and Sb occur in high concentrations typical for black shales (syngenetic mineralisation). Furthermore Pb, Zn, Cu, and Ba and less distinct Ag, As, Cd, Co, Ni, Sb and Tl are enriched in discrete layers (epigenetic mineralisation). Generally secondary leaching-processes in the underlying Carboniferous are responsible for the epigenetic mineralisation (Vaughan et al., 1989). In Core Niederwald 1 the Re/Mo-ratio rises significantly in the upper part of the "Kupferschiefer" (T1 III) and the overlying Zechstein limestone (Ca1). This rise is likely caused by less intense reducing conditions during sedimentation (Crusius et al., 1996). The black shale of the Exshaw Formation (Famennian/Tournaisian) represents a marine, transgressive euxinic sediment (Richards and Higgins, 1988). Probably the laminated sediment has been deposited in an epi-continental upwelling area below storm-wave basis. Volcanic activity as a

possible source for different components has to be considered. The TOC-rich parts show strong enrichments in the minor elements Mo, Re, Cd, Tl, V, and U. The Re/Mo-ratio averages  $0.4 \cdot 10^{-3}$ , which is low with respect to seawater and confirms the existence of an euxinic depositional environment. A comparison of Palaeozoic black shales with Mediterranean sapropels, Cretaceous black shales and recent anoxic sediments shows comparable enrichments of certain minor elements (Mo, Re, Cd, Tl, V, U, As; see Fig. 1). On the other hand for some elements (Zn, Ni, Sb, Pb, Cu, Co, Ba, Mn) a stronger concentration variability is detectable. The availability of dissolved and suspended material and secondary processes seem to be very important. A more profound understanding of the geochemical behaviour of minor elements during early diagenesis is necessary for gaining information on palaeo-seawater composition.

This work is funded by the Deutsche Forschungsgemeinschaft.

Brumsack HJ, *North Atlantic Paleoceanography, Geol. Soc. Am. Spec. Publ.*, **21**, 447-462, (1986).

Crusius J, Calvert S, Pedersen T, Sage D, *Earth Planet. Sci. Lett.*, **145**, 68-78, (1996).

Paul J, *Z. dt. geol. Ges.*, **133**, 571-605, (1982).

Richards BC, Higgins AC, *Devonian of the world, Can. Soc. Petrol. Geol. Mem. 14*, **2**, 399-412, (1988).

Vaughan DJ, Sweeney M, Friedrich G, Diedel R, Haranczyk C, *Econ. Geol.*, **84**, 1003-1027, (1989).

Warning B, Brumsack HJ, *Palaeo. Palaeo. Palaeo.*, **158**, 293-309, (2000).

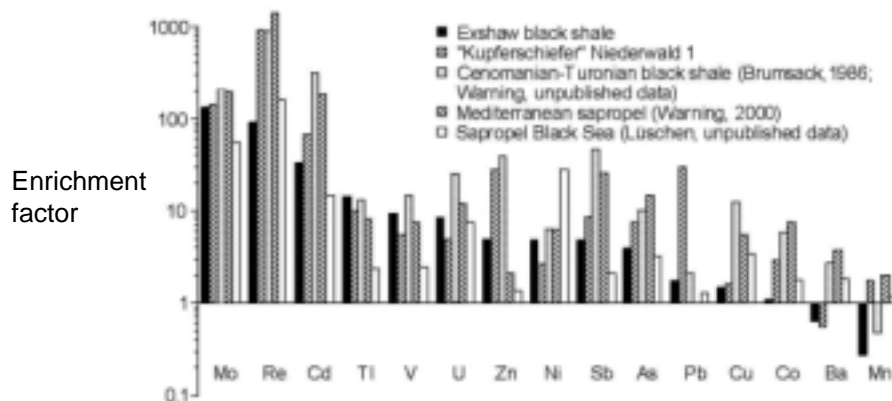


Figure 1: Enrichment factor versus Average Shale of minor elements in Exshaw Black Shale, "Kupferschiefer" and other selected anoxic sediments.