

IRON AND NICKEL PORPHYRINS IN MESSEL OIL SHALE

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Porphyrins present in sedimentary organic matter molecular are fossils of tetrapyrroles from photosynthetic organisms. In the past, the study, at the molecular level (HPLC, UV-Vis, MS, and NMR); of nickel porphyrins from the Messel oil shale (Eocene, Germany) lead to the structure determination of twenty of them (Ocampo Torres, 1985; Ocampo *et al.*, 1984, 1985, 1987, 1992; Bauder *et al.*, 1990; Huseby and Ocampo, 1997). Ten porphyrins were specifically correlated with biological precursors: algal chlorophyll *c* (4), sulphur photosynthetic bacteria bacteriochlorophylls *d* (3), and heme-like precursors (3). This allowed the use of porphyrins in the paleoenvironmental reconstruction of the Messel lake water column. Iron porphyrins have been already reported in geological samples (Bonnett *et al.*, 1990, Czechowski *et al.*, 1994, 1995). Here we report, for the first time, the presence of iron porphyrins in the Messel shale. The analyzed sample contains free bases, iron and nickel porphyrins. In this work only metal complexes were analyzed. Iron porphyrins were studied by UV-Vis, MS and NMR and nickel porphyrins by (HPLC, UV-Vis, MS and LC-MS). We will discuss the presence of iron and nickel porphyrins and compare the composition of different (alkyl, monoacid and diacid) porphyrin fractions isolated from this sample in terms of structure and biological precursor. Differences in composition toward earlier described samples will be also discussed and may be due to depositional and/or environment changes.

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