

KEROGEN-BOUND ISORENIERATENE DERIVATIVES IN LOWER JURASSIC OIL SHALES (BÄCHENTAL, TYROL, AUSTRIA) - A CASE STUDY

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Aromatic carotenoids are prominent accessory pigments in anoxygenic phototrophs, and their fossil derivatives are important tools for tracking photic zone euxinia through Earth's history (e.g. Summons and Powell, 1986; Brocks et al., 2005). Despite widespread euxinic conditions in Proterozoic oceans (Canfield, 1998) and their overall high preservation potential in macromolecular networks (Hartgers et al., 1994), aromatic carotenoids are only rarely known from rocks of such age (cf. French et al., 2015). It is as yet unclear, whether this scarcity reflects a paleoecological signal or a preservational bias. We address this question by investigating the taphonomy of these carotenoids in Lower Jurassic oil shales of the Allgäu Formation (Bächental, Tyrol, Austria). These rocks are thermally immature (Neumeister et al., 2015; our results) and contain a variety of isorenieratene derivatives (Köster et al., 1995; Koopmans et al., 1996) in different sedimentary facies. To critically assess the preservational pathways of these compounds, the bitumens and corresponding kerogens were analyzed with catalytic hydropyrolysis (HyPy; Love et al., 1995) and gas chromatography-mass spectrometry (GC-MS).

All analyzed bitumens contained a considerable variety of isorenieratene derivatives, especially isorenieratane, related aromatized C₄₀ compounds, as well as a homologous series of 2,3,6-trimethyl aryl isoprenoids. Sulfur containing isorenieratene derivatives were only present in traces. HyPy of pyridine-swelled and rigorously extracted kerogens yielded almost the same 2,3,6-trimethyl aryl isoprenoids as observed in bitumens, but only traces of isorenieratane and cyclized derivatives. Experimental maturation of Bächental kerogens using closed-system pyrolysis in gold capsules confirmed the low amounts of aryl isoprenoids including isorenieratane in the bitumen generated. As a preceding loss of these molecules from kerogen by thermal expulsion is in disagreement with the overall low maturity, it is likely that the major portion of isorenieratene and its derivatives were never covalently bound into kerogen.

The Bächental basin was at least temporarily euxinic (Neumeister et al., 2015). Such environments are usually considered favorable for the incorporation of functionalized moieties into kerogen via organic sulfur cross-linkages (e.g. Sinninghe Damsté et al., 1989; Kohnen et al., 1991). However, all analyzed samples show high iron contents (Fe/S > 1) while containing abundant pyrite aggregates. This suggests that reduced sulfide was effectively scavenged by iron and was possibly not available for the formation of intermolecular linkages. Likewise, the exclusive presence of isorenieratane and further aromatization products in the bitumens indicates that rapid reduction of conjugated double bonds and/or cyclization occurred early during diagenesis. Both processes may have hampered a substantial incorporation of isorenieratene into the kerogen network and

represent an effective taphonomic filter that could have resulted in a scarce preservation of these biomarkers in Proterozoic deposits.

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