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Candidate Sulphide-oxidising Microbial Mats in a Mississippian Black Shale

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Microbial mats are markers for compressed redox gradients at seabed, biostabilisers of sediment and are important mediators in cycling of S and C. Yet ancient examples are rare. We report candidate sulphide-oxidising microbial mats in the Mississippian Bowland Shale Formation, an organic-rich mudstone, from the Craven Basin (Lancashire, UK). This basin was remotely linked to a relatively large, tropical delta system and formed part of an epicontinental seaway that extended from western Europe to the Lublin Basin, Poland. Comparing sedimentological, palynological and geochemical data from three basin positions reveals the Bowland Shale to be highly heterogeneous, both in terms of sediment delivery mechanism and type of OM preserved. Sea level fluctuated as a far-field response to southern hemisphere glaciation, and yields a relatively high resolution temporal framework that suggests muds were deposited fast, with a mean sediment accumulation rate of $\sim$29 cm/kyr (i.e., deltaic-type). This considers 100 m of uncompacted sediment was deposited over $\sim$350 ka.

Palaeoredox proxies (Fe-speciation, trace elements, $\delta^{34}S_{py}$) demonstrate deposition under long-lived ferruginous anoxic to euxinic conditions in basinal positions. During a relatively late stage of basin infill, bottom waters were progressively ventilated. This is linked to delta progradation, basin desalination and reduced primary productivity. Mudstones spanning the transition from anoxic to oxic bottom waters ('Facies G') comprise clay-rich lenses (interpreted as partially consolidated rip-up clasts) and diffuse organic-rich laminae. Organic-rich laminae are also observed as rip-up clasts in down-dip hybrid event beds. Presence of early diagenetic pyrite nodules and rare pyritised micro-burrows in Facies G suggests highly sulphidic conditions persisted near or at seabed. Low oxygen index (Rock-Eval pyrolysis), high organic S content (Fe-speciation) and relatively abundant alkyl-benzenes and thiophenes (flash pyrolysates) suggests presence of S cross-links and heteratomic (S-containing) aromatic compounds. The palynological fraction extracted from Facies G is dominated by large (diameters of several 100s μm), 'granular', amorphous particles of OM.

Thus sedimentological, geochemical and palynological observations indicate that the transition from anoxic to oxic bottom waters was colonised by benthic microbial mats, primarily as sulphide-oxidisers. Proximity to a large tropical delta system likely precludes Fe-limitation as a driver for sulphidic conditions. Instead the persistence of sulphidic conditions at seabed coupled with oxygenated bottom waters is interpreted to indicate enhanced early diagenetic H_2S production. This was possibly driven by an inherently labile composition to marine OM that fueled sulphate reducers present in underlying muds, and explains why sulphide-oxidising mats were able to colonise this ancient prodeltaic setting.