

## **Integrated Sedimentology, Palynology and Geochemistry of the UK Mississippian Bowland Shale Formation: An End-Member Source Rock?**

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The Mississippian Bowland Shale Formation is a target for unconventional hydrocarbon exploration in the UK<sup>1</sup> and in equivalents across Europe, including the Geverik Member (Epen Formation<sup>2</sup>) and Upper Alum Shale Formation<sup>3</sup>. Despite this interest, the sedimentological and biogeochemical processes that operated in epicontinental seaways, such as the Mississippian Rheic-Tethys, are poorly understood. This is especially true for the organic-rich Bowland Shale, beyond a few regional (e.g., <sup>4</sup>) and basin-specific studies (e.g., <sup>5-9</sup>) and some modern analogues<sup>10</sup>. Extrapolation between UK basins is challenging, because basins were compartmentalised; an expression of the underlying 'block, highs and basin' rift structures<sup>11</sup>.

Sedimentological, palynological and geochemical data are compared from three time-equivalent sites in the Craven Basin (UK)<sup>12</sup>, a basin with ongoing unconventional hydrocarbon exploration<sup>13</sup>. The Bowland Shale at these sites is a highly heterogeneous ~120 m thick succession comprising carbonate-rich, siliceous, and siliciclastic, argillaceous mudstones. These facies developed in response to a combination of fourth-order sea level cyclicity<sup>14-16</sup>, fault activity at the basin margins<sup>17</sup> and linkage with the Pendle delta system<sup>18</sup>. Fe-speciation, redox-sensitive trace element,  $\delta^{34}\text{S}_{\text{py}}$  and *n*-alkane (including Pr, Ph) biomarker data are utilised as palaeoredox proxies<sup>19-22</sup>, and demonstrate redox conditions during deposition were also highly variable.

Sea level highstand facies, termed 'marine bands', were deposited under an influx of 'open marine' waters that promoted carbonate export into deeper waters and restricted detrital sediments to the proximal shelf and slope. Thus (hemi-)pelagic deposition dominated over the supply of mud clasts during periods of high basin accommodation. Radiolarian tests are preserved within early cemented phosphate concretions in these facies. Elsewhere, radiolarian tests are absent but early diagenetic quartz cements are abundant, including infill of shelter porosity. This suggests that early diagenetic, biogenic (radiolarian) silica was an important source for early diagenetic authigenic silica and potentially clay mineral phases.

High rates of primary production in the water column triggered development of persistently anoxic and highly sulphidic (euxinic) conditions in bottom waters. Persistently sulphidic conditions promoted preservation of organic matter (OM) and therefore 'marine band' packages typically exhibit relatively high total organic carbon (TOC) content, high hydrogen index (HI) and a dominance of amorphous OM, suggestive of a bulk Type II OM composition. These conditions also likely promoted relatively early diagenetic transition into the zone of methanogenesis, which promoted preservation of primary carbonate and precipitation of carbonate cements, such as spherulitic limestone textures.

Falling sea level is linked to the initial deposition of lens-rich muds, followed by an interbedded succession of turbidites, debrites, hybrid event beds, and tempestites, indicating sediment transport in bedload, turbulent and hybrid flows. These facies typically exhibit relatively moderate to high TOC, but also significantly reduced HI and typically lacking primary (skeletal) carbonate, with potential implications for understanding the geotechnical properties (e.g., brittleness<sup>23</sup>) of these packages. These key differences (compared to 'marine bands') are attributed to an increased supply of 'reactive' Fe ( $Fe_{HR}$ ) linked to mobilisation of shelfal  $Fe_{HR}$  and shuttling into the basin.

Increased supply of  $Fe_{HR}$  promoted development of intermittently ferruginous conditions, due to the buffering of sulphide, in bottom waters and early diagenetic porewaters. Switching between ferruginous and euxinic conditions in porewaters, termed 'redox oscillation'<sup>24,25</sup>, is recognised by a distinctive redox-sensitive trace element enrichment pattern and diagenetic mineral suite. Importantly, redox oscillation

likely generated considerable acidity that promoted dissolution of primary carbonate. These conditions also promoted formation of organic sulfur and therefore a bulk 'Type II-S' OM composition. Continued progradation of the Pendle delta promoted ventilation of bottom waters, ultimately under fresh water conditions, and the preservation of dominantly Type III OM.

Mud export from the Pendle delta system to the Craven Basin was fast, despite the intrabasinal complexity, likely an order of magnitude higher than contemporaneous successions deposited in the UK and North America. Taking 100 m of uncompacted pelagic/hemipelagic sediment (assuming 55% compaction) and assuming this was deposited over ~333 ka (i.e., spanning three 'marine bands'<sup>16</sup>) yields an estimated 30 cm/kyr mean sediment accumulation rate (mSAR<sup>26</sup>). This compares with 1.4 cm/kyr for the contemporaneous Barnett Shale<sup>27</sup>, and 0.2-0.9 cm/kyr for North American Late Pennsylvanian Midcontinent Seaway cyclothems<sup>28,29</sup>. Mississippian epicontinental basins remotely linked to delta systems were capable of rapidly accumulating both sediment and OM under sulphidic conditions, and therefore were settings prone to early diagenetic redox oscillation processes. Thus the Bowland Shale Formation represents an end-member siliciclastic-type source rock, unlike organic-rich muds deposited in carbonate sedimentary systems typically characterised by relatively slow mSARs and relatively stable early diagenetic redoxclines.

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