Calibration of redox thresholds in black shale: Insight from a stratified Mississippian basin with warm saline bottom waters

Sen Li, Paul B. Wignall, Yijun Xiong, Simon W. Poulton

School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

ABSTRACT

Depositional models for black shale formation rely on detailed understanding of redox conditions and how they relate to basin development. Here we calibrate multiple redox proxies (Fe speciation, U and Mo systematics, pyrite framboid distributions) in the Bowland Shale, a major hydrocarbon unit in the Mississippian of northern England, and develop a depositional model for black shale deposition in basins adjacent to extensive carbonate platforms. The transition from deep ramp carbonates to basinal mudrocks initially occurred under oxic conditions, before anoxic conditions began to expand from basin center locations. By the end of Bowland Shale deposition, ~10 million years later, black shale deposition extended from the basin into shallow-water settings, the former being sites of platform-edge carbonates. By this stage, euxinic conditions were widespread throughout the Bowland Shale. The prolonged persistence of euxinia during younger Bowland Shale deposition, and the sharp transition to fully oxygenated facies at the basin margin, suggests there was a well-developed water column pycnocline. Black shale development in silled basins is traditionally interpreted to form beneath a halocline with a positive water balance caused by freshwater run-off (estuarine circulation). This model is not considered appropriate in this case. Bowland Shale deposition was terminated by the onset of turbidite deposition supplied by a major deltaic system, but for most of its history the basin was surrounded by carbonate platforms that are unlikely to have experienced brackish conditions. The encroachment of the clastic system saw the rapid improvement of basinal oxygenation in the uppermost Bowland Shale, and even minor turbidite sandstones within the black shales coincided with a weakening in the intensity of euxinia, suggesting that sediment-laden fresher waters flushed out and oxygenated the basin. We therefore suggest a warm saline bottom water model for black shale deposition, with basinal waters generated on the adjacent carbonate platforms due to evaporation. Such a scenario is likely more broadly applicable to basinal black shales developed adjacent to shallow-water carbonate successions.

INTRODUCTION

Controls on the extent and nature of oxygen-depleted (anoxic) deposition in marine depositional environments constitute a key debate in paleoenvironmental research (Demaison and Moore, 1980; Arthur and Sageman, 1994; Wignall, 1994). Oxygen levels reflect a balance between supply and demand, with two end-member scenarios that can both lead to anoxic, organic-rich sediment deposition. Firstly, elevated productivity can lead to "organic overload", where intense oxygen consumption by decaying, planktonic organic matter lowers the redox level in the water column. Such conditions can produce an intense mid-water oxygen-minimum zone either at the basin margin, where upwelling of nutrient-rich waters fosters high productivity, or adjacent to coastal areas where abundant terrigenous nutrient supply achieves the same effect (e.g. Jenkyns, 2010). Secondly, restricted vertical advection due to the presence of a strong density interface (pycnocline) within the water column, and/or restricted lateral advection due to a silled basin configuration, can hinder oxygen supply and lead to organic-rich sedimentation in settings where primary production is not unusually high (Demaison and Moore, 1980; Tyson and Pearson, 1991; Wignall, 1994; Algeo et al., 2008).

Typically, stratification is controlled by salinity, in which freshwater surface runoff isolates more saline, deeper waters, or by temperature whereby warmer surface waters overlie colder and denser deep waters (Tyson and Pearson, 1991; Wignall, 1994; Algeo et al., 2008). Surface water evaporation can also generate warm but dense saline waters that sink into deeper waters. Such warm saline bottom waters (WSBWs) are seen in the present-day Mediterranean, which is well-oxygenated at depth (Demaison and Moore, 1980), but oceanic anoxia in the Cretaceous and the Silurian has been attributed to WSBW stratification (e.g. Brass et al., 1982; Munnecke et al., 2003). Distinguishing between these scenarios (high productivity or restricted circulation) is a difficult undertaking in the geological record because productivity indicators are often ambivalent and water column stratification is difficult to diagnose. Here we examine the spatio-temporal redox record in a basin where a prolonged history of anoxic, organic-rich deposition produced one of the major black shale units of British stratigraphy, the Bowland Shale, and evaluate possible depositional models for this economically important source rock.

REGIONAL SETTING

Mississippian deposition in central northern England occurred in a series of interlinked, tectonically-active basins surrounded by shallow-water carbonate platforms at low southerly paleolatitudes (Fig. 1A). The Bowland Basin, now exposed in northern England, was one of the largest of these basins and was bordered to the north by an extensive carbonate platform developed on the Askrigg Block, with the Craven Fault belt marking the sharp transition between shallow-water carbonates and finer-grained basinal strata (Fig. 1B; Kirby, 2000). Carbonate shelf seas also fringed the basin to the south and east.

The initial phase of Bowland Basin infill consisted of fine-grained carbonate deposition interbedded with carbonate debris flow and sedimentary slide/slump deposits (the Pendleside Limestone Formation; Gawthorpe, 1986, 1987). The latter were especially common during two periods of tectonic activity that occurred in the late Tournaisian and the late Visean. Using the regional stage names, the latter phase of tectonism occurred during the Asbian to early Brigantian. This transformed the Bowland Basin (and others in the region) from one with extensive carbonate ramps to a basin with fault-bounded, steep margins, surrounded by carbonate platforms developed on both horsts and tilt blocks. (Gawthorpe, 1986; 1987; Ebdon et al., 1990; Fraser and Gawthorpe, 1990; Kirby, 2000; Manifold et al., 2021).

The increased subsidence rate during late Visean tectonism coincides with a diachronous transition from carbonate-dominated to dark gray shale-dominated deposition of the Lower Bowland Shale Formation in basinal areas (Fig. 2; Kirby, 2000). Several local, allochthonous limestones occur within the early Brigantian portion of this Formation, whilst thin sandstones make an appearance in the late Brigantian (Fig. 2). The latter are harbingers of a much-increased clastic influx into the Bowland Basin that would ultimately see shale deposition replaced by a thick succession of turbidite sandstones in the early Serpukhovian/late Pendleian stage (Waters et al., 2009; Kane, 2010). Prior to this, the transition from active rifting to more passive thermal subsidence around the Brigantian/Pendleian boundary caused the margins of the basin to subside following minor inversion, and dark gray shales of the Upper Bowland Shale Formation onlapped onto the southern margins of the Askrigg Block – an area that was previously the site of shallow-water carbonate deposition (Waters et al., 2017).

The geological history of the Bowland Basin is closely comparable to that seen in contiguous basins developed along strike. For example, in the Dublin Basin, 250 km to the west, the dark gray shales of the Donore Shale onlapped adjacent carbonate platforms during the Brigantian (Pickard et al., 1994; Kirby, 2000). The combined Lower and Upper Bowland

Shale formations range from several hundred meters to more than a kilometer in thickness, making them one of the thickest black shale successions in the onshore stratigraphy of the British Isles (de Jonge-Anderson and Underhill, 2020) and they have great economic importance as a potential source of shale gas and known hydrocarbon prospects. Unsurprisingly, the Bowland Shale has been the subject of numerous studies mainly focused on organic matter types (e.g. Gross et al., 2015; Fauchille et al., 2017; Hennissen et al., 2017; Newport et al., 2018; de Jonge-Anderson and Underhill, 2020). However, the controls on redox conditions and organic enrichment during the ~10 million year history of Bowland Shale deposition have been surprisingly little investigated. Emmings et al. (2020) reported that Upper Bowland Shale deposition in the NW region of the basin occurred beneath ferruginous anoxic and occasionally euxinic waters and suggested sea-level fluctuations were an important control. In order to evaluate the long history of redox development prior to and during deposition of the Lower and Upper Bowland Shale formations, we present a study of multiple redox proxies from numerous sections around the Bowland Basin and its margin, and develop a model for the development of this economically-important source rock.

METHODS AND APPROACH

Sample collection and field area

Fieldwork investigations (sedimentary logging and sample collection) were undertaken at 13 locations, mostly comprising stream and river outcrops: Dobson Brook (DB), Leagram Brook (LB), Smelthwaite Farm (SM), School Share (SS), Cow Close (CC), Moor Close Gill (MC), Dinckley Hall (DH), River Hodder (RH), Light Clough (LC), Swardean Clough (SC), Clough Head Beck (CH), Tory Log Clough (TLC), and Fell Lane (FL) (Fig. 3 and Supplemental Material[1]). These locations record deposition in settings ranging from basin center to basin margin. The two most extensive basinal sections were sampled at TLC and DH, and their combined record ranges from the mid Pendleside Limestone (Asbian Stage) to the Upper Bowland Shale (Pendleian Stage). A further seven, shorter sections, were also examined, thereby allowing the temporal and spatial variation of redox changes within the basin to be fully determined. Finally, additional study of four sites (SS, CC, MC and FL) from the Craven Fault Belt system on the northern margin of the Bowland Basin, allowed the redox conditions of the Bowland Shale Formation to be examined at a level where it onlaps platform carbonates on the southern margin of the Askrigg Block (Fig. 3). The study sections contain the Hodderense Limestone, Pendleside Limestone, and the Lower and Upper Bowland Shale formations, spanning the interval from

[1]Supplemental Material. Full list of outcrops information and geochemical data

the late Holkerian to early Pendleian (Fig. 2). High resolution correlation of sections is possible because of the associated goniatite fauna reported (see Supplemental Material). This long-established scheme utilises multiple lineages of goniatites (e.g. *Eumorphoceras*) and a short-hand, letter-number scheme (e.g. E_{1c} is the youngest zone of the Bowland Shale and has the zonal goniatite *Cravenoceras malhamense* and *Eumorphoceras* spp. present) to designate biozones (Waters and Condon, 2012).

Fresh samples were collected to avoid oxidation and to obtain detailed petrological and geochemical information, and in all cases, samples with visible evidence of later stage diagenetic or post-depositional overprints (e.g. veins, nodules, concretions, secondary euhedral pyritization) were avoided. An agate mortar was used to crush samples into homogeneous powder (<60 μm) for geochemical analyses. Selected samples were polished before carbon-coating to perform pyrite morphology analyses on a TESCAN VEGA3 Scanning Electron Microscope (SEM) using the backscatter mode.

Major elements

Total organic carbon (TOC) analyses were determined on a LECO Carbon-Sulfur Analyzer. Samples were de-carbonated prior to analysis using 10% HCl. Replicate analyses of certified reference material (Soil LCRM with carbon content of 10.8 ± 0.26 wt%) gave a relative standard deviation (RSD) of <1.5%, and accuracy was ensured by analyses within 1% of reported values. In terms of other major and trace elements, samples were ashed at 550°C for 8 h, followed by quantitative digestion using concentrated HNO_3, HF and $HClO_4$. H_3BO_3 was added to prevent the formation of Al hexafluorate complexes. Finally, the residues were re-dissolved with near-boiling HNO_3 and diluted with ultrapure 18MΩ H_2O prior to analysis by ICP-OES (major elements) and ICP-MS (trace elements). Accuracy and precision, estimated from the repeat analyses of United State Geological Survey standard SGR-1b (Green River Shale), were better than 5%. Enrichment factors (EF) were used to assess the behaviour of Mo and U in siliciclastic intervals, where $\text{element}_{EF} = (\text{element/Al})_{sample}/(\text{element/Al})_{AUC}$, and AUC represents average upper crust concentrations (McLennan, 2001).

Fe phase partitioning

Sequential Fe extractions were performed according to the technique of Poulton and Canfield (2005). The procedure targets different operationally-defined Fe pools that are considered highly reactive (Fe_{HR}) towards dissolved sulfide in anoxic conditions under near-surface conditions (Raiswell and Canfield, 1998; Poulton and Canfield, 2005). Firstly, 1 M sodium acetate (pH 4.5) was used to extract carbonate-associated iron (Fe_{carb}) at 50°C for 48 h. Subsequently, Fe (oxyhydr)oxide minerals (Fe_{ox}) were extracted by sodium dithionite (2 h at room temperature), followed by magnetite (Fe_{mag}) extraction via a 0.2 M ammonium oxalate/0.17 M oxalic acid solution (6 h at room temperature). All Fe concentrations were measured on a Thermo Scientific iCE-3000 series flame Atomic Absorption Spectrometer (AAS). Pyrite (Fe_{py}) and acid volatile sulfide (AVS) were measured on a separate sub-sample via a two-step chromous chloride distillation (Canfield et al., 1986). Liberated hydrogen sulfide was trapped as Ag_2S and its concentration was quantified gravimetrically. Replicate extractions of an international reference material (WHIT; Alcott et al., 2020) gave a RSD of <5% for each Fe pool, with analyses within 5% of reported values. No AVS was detected and therefore, Fe_{HR} in this study is defined as the sum of Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py} (Poulton et al., 2004; Poulton and Canfield, 2011). All geochemical data is tabulated in the Supplemental Material.

Framework for redox interpretation

We use three independent approaches to assess water column redox conditions: pyrite petrography, iron speciation and trace metal systematics. Pyrite framboid sizes have been widely utilized to diagnose redox conditions, and are particularly useful for identifying euxinic (anoxic, sulfidic) conditions (Wilkin et al., 1996; Wilkin and Barnes, 1997; Wignall and Newton, 1998; Wignall et al., 2010). In modern euxinic environments, framboids form in the water column and only achieve a small size with narrow distribution (Wilkin et al., 1996), whereas under anoxic-dysoxic conditions, framboids can grow larger and are accompanied by higher proportions of diagenetic pyrite (Wilkin and Arthur, 2001; Wignall et al., 2010; Li et al., 2022).

Iron speciation data potentially allow oxic water column conditions to be distinguished from ferruginous (anoxic, Fe(II)-containing) and euxinic conditions (Poulton and Canfield, 2011; Poulton, 2021). Oxic conditions are indicated when highly reactive Fe over total Fe (Fe_{HR}/Fe_T) ratios are <0.22, and anoxic conditions are suggested if this ratio is >0.38 (Raiswell and Canfield, 1998; Poulton and Canfield, 2011). Ratios of 0.22-0.38 are considered equivocal, and further consideration is required to evaluate such samples (see below). For samples diagnosed as anoxic, Fe_{py}/Fe_{HR} ratios are applied to distinguish euxinia (>0.8) from ferruginous conditions (<0.6). Ratios in the range 0.6-0.8 are considered to potentially reflect euxinic depositional conditions, but again, further consideration is required

(Poulton et al., 2004; Poulton and Canfield, 2011; Benkovitz et al., 2020; Poulton, 2021). We note recent challenges to the utilization of Fe speciation in reconstructing ocean redox conditions (Pasquier et al., 2022), and indeed, a number of considerations must be evaluated when applying the technique. For example, Fe speciation may not provide reliable results when applied to sediments with low Fe contents (<0.5 wt% Fe_T; Clarkson et al., 2014), sediments experiencing rapid deposition (e.g. turbidites; Canfield et al., 1996), and those in proximity to hydrothermal inputs (Raiswell et al., 2018) or directly adjacent to (sub)tropical mountainous regions, where highly weathered sediment may supply a high proportion of Fe_{HR} directly onto the continental margin (Wei et al., 2021), thus circumventing the preferential trapping of Fe_{HR} that usually occurs in inner shore environments (Poulton and Raiswell, 2002). These caveats have been well described in the literature, but were ignored in the analysis of Pasquier et al. (2022). In addition, the Fe speciation framework has been independently calibrated against ancient marine rocks that have by definition undergone diagenesis (e.g. Raiswell et al., 2021; Clarkson et al., 2014), in contrast to the modern sediments that were solely investigated by Pasquier et al. (2022). As also described in the literature, Fe speciation is best used in combination with other indications of water column redox chemistry (e.g. pyrite framboid and redox sensitive trace metal systematics) and within the context of the sedimentological conditions of the depositional environment (Poulton, 2021). This is done here, and is typically done in the literature, providing the most accurate assessment of the chemical conditions of deposition. Indeed, we also note that pyrite framboid sizes (see below) and pyrite-sulfur isotope systematics (Emmings et al., 2020) are entirely consistent with syngenetic or very early diagenetic pyrite formation, which is factored into the Fe speciation proxy.

We utilize the redox-dependent behaviour of Mo and U to provide further independent insight into redox conditions. Molybdenum accumulation in the sediment is highly dependent on redox conditions, where uptake of Mo via Fe-Mn (oxyhydr)oxide minerals is the major removal mechanism under oxic conditions (Bertine and Turekian, 1973). Under ferruginous conditions, Mo accumulation can be promoted by a particulate shuttle mechanism (e.g. Algeo and Tribovillard, 2009; Tribovillard et al., 2012) via uptake during the water column precipitation of Fe minerals such as Fe (oxyhydr)oxides or green rust (e.g. Zegeye et al., 2012). However, with the presence of H_2S in the water column, the molybdate anion is converted to particle-reactive thiomolybdate (Helz et al., 1996), leading to pronounced Mo accumulation in the sediment, once a dissolved sulfide threshold of ~11 μM is passed (Emerson and Huested, 1991; Helz et al., 1996; Erickson and Helz, 2000). By contrast, uranium reduction primarily occurs in anoxic sediments rather than in the water column, and U is therefore enriched beneath anoxic bottom waters, regardless of whether euxinic or ferruginous conditions dominate (Anderson et al., 1989; Klinkhammer and Palmer, 1991). Therefore, when combined with other indicators of the water column redox state (e.g. Fe speciation and pyrite framboid systematics), U/Mo ratios can be used to provide further support for either euxinic water column conditions (i.e. low U/Mo ratios) or anoxic non-sulfidic conditions (i.e. moderate to highly elevated U/Mo ratios).

RESULTS

TOC variability

Holkerian-Asbian

The carbonate-dominated units of the Hodderense Limestone and Pendleside Limestone generally have relatively low concentrations of TOC compared to the overlying Lower Bowland Shale. For example, the oldest strata in the RH section have TOC concentrations averaging 0.78 ± 0.28 wt% in 6 samples (Fig. 4). Similarly, at the TLC location, TOC concentrations average 0.66 ± 0.34 wt% in 26 samples of calcareous mudstone and micritic limestone from the Pendleside Limestone (Fig. 5). The onset of the Lower Bowland Shale is generally marked by an increase in TOC, although concentrations and trends are quite variable at this transition. At DB, TOC is 2.03 ± 1.04 wt% in the B_{2a} zone, but becomes slightly higher in the B_{2b} zone (3.20 ± 1.11 wt%; Fig. 6). A more pronounced increase is seen at the LB section, where low TOC values (0.57 ± 0.17 wt% in the lowermost 6 samples) in the B_{2a} zone are followed by a sharp increase to 3.41 ± 1.25 wt% in the upper B_{2a} zone and through the B_{2b} zone (Fig. 6). By contrast, at TLC, TOC values remain low (0.70 ± 0.38 wt%) until the P_{1a} Zone of the Lower Bowland Shale where it reaches a peak of 10.54 wt% (Fig. 5). The SM section, on the other hand, displays a pronounced increase in TOC concentrations to 9.45 wt% with the onset of Lower Bowland Shale in the late B_2 zone, succeeded by a gradual decline to 3.80 wt% at the end of the P_{1a} zone (Fig. 4). An overall increase is also found in the SC section, ranging from 1.71 to 3.27 wt% (Fig. 7). By contrast, low TOC concentrations (0.49 ± 0.26 wt% in 12 samples) are recorded in the P_{1a} zone of the Ravensholme Limestone in the CH section (Fig. 7).

Early Brigantian ($P_{1b\text{-}d}$ zones)

The shale-dominated units in the lower part of the Lower Bowland Shale display moderate to elevated TOC values. At the start of the DH section, shale samples in the P_{1b}

zone have relatively consistent TOC values, averaging 3.42 ± 0.45 wt% (10 samples) with a peak of 5.82 wt% (Fig. 8). Concentrations remain around 3 wt% (2.92± 0.17 wt%) in the P_{1c} zone (e.g. at the DH (Fig. 8) and TLC sections (Fig. 5). The SM section is condensed and has elevated but variable TOC concentrations (5.56 ± 1.84 wt% in 16 samples) through the P_{1b} - P_{1c} zones (Fig. 4). The FL section was deposited on the northern edge of the Lower Bowland Shale outcrop on the margins of the Bowland Basin (Fig. 9), and interestingly the TOC values in the early Brigantian are amongst the highest seen anywhere in the basin at that time (Fig. 9). In the zone of P_{1b}, TOC values average 5.23 ± 1.10 wt% (9 samples) in shales, while the interbedded micritic limestones average 2.38 ± 0.93 wt% (5 samples) (Fig. 9). The TOC values decline somewhat in the overlying P_{1c} shales at FL and are generally around 3 wt% (2.81 ± 0.91 wt%), a value typical for this level throughout the basin.

Late Brigantian (P_2 zones)

The DH section provides the most continuous section of the late Brigantian portion of the Lower Bowland Shale (Fig. 8). This exhibits a long-term trend of TOC enrichment (averaging 3.42 ± 0.93 wt% in 39 samples), reaching peak values in the late P_{2c} zone at 5.43 wt%, although there is a low point in the mid P_{2a} zone where the concentrations for a few samples drops below 2 wt% (Fig. 10). Shales from the P_{2c} zone are also seen in the expanded LC section, and they too show increasing TOC concentrations in the mid- to upper-part of the Lower Bowland Shale (rising from around 3.0 wt% to 5.27 wt%), before a gradual decline to 1.85 wt% in topmost meters of the P_{2c} strata (Fig. 10). P_{2c} shales at SS, on the margin of the Bowland Basin, have TOC values of 2.75 ± 0.21 wt% (Fig. 10).

Pendleian (E_1 zones)

TOC values in the Upper Bowland Shale have moderate to high values, albeit with considerable variation from sample-to-sample. At DH, E_{1a} shales have average TOC concentrations of 4.38 ± 1.04 wt%, which decline slightly to 4.02 ± 0.88 wt% (11 samples) in the E_{1b} zone (Fig. 8). TOC values are similar in the nearby LC section (Fig. 10). In contrast to the high, but variable, concentrations of TOC in the basinal sections, TOC levels from the northern margin of the Bowland Basin show more consistency (e.g. at SS, TOC = 2.82 ± 0.22 wt% in 12 samples, and at MC, TOC = 2.59 ± 0.34 wt% in 14 samples, Fig. 11), although values at CC peak at 4.92 wt% (Fig. 11).

Total Fe and Fe speciation

Holkerian-Asbian

The Hodderense Limestone Formation has an average Fe_T content of 1.18 ± 0.33 wt% (RH section; Fig. 4), whereas the calcareous mudstone samples of the Pendleside Limestone Formation show variable Fe_T, from 1.4 to 6.2 wt% in both the RH and TLC sections (Figs. 4 and 5). Thus, these samples contain sufficient Fe_T for reliable analyses of Fe speciation to be undertaken (Clarkson et al., 2014).

In the RH section, the Hodderense Limestone data show elevated values of Fe_{HR}/Fe_T above 0.38 (0.62 ± 0.32, 4 samples, Fig. 4). The overlying Pendleside Limestone has persistently low values (0.32 ± 0.16) falling in the equivocal oxic/anoxic zone for the RH section, with more scatter and a higher ratio (0.44 ± 0.19 in 30 samples) in the TLC section (fluctuating between the equivocal and anoxic regions; Figs. 4, 5). Fe_{py}/Fe_{HR} ratios generally show considerable scatter but all are below 0.6 (0.32 ± 0.16 in the Hodderense Limestone and 0.09 ± 0.12 in the Pendleside Limestone of the RH section; 0.33 ± 0.23 in the Pendleside Limestone of the TLC section).

The transition to the Lower Bowland Shale in the late Asbian is marked by an overall increase in Fe_{HR}/Fe_T ratios, to values that commonly greatly exceed the threshold indicative of anoxic conditions. At the TLC section, the onset of organic-rich shale in the P_{1a} zone sees a rapid increase both in Fe_{HR}/Fe_T (reaching 1.0 in the anoxic zone) and in Fe_{py}/Fe_{HR} (reaching 0.8 in the euxinic zone; Fig. 5). Correspondingly, an elevated Fe_{HR}/Fe_T (0.87 ± 0.15 in 12 samples) in the anoxic zone is also evident in the LB section, and Fe_{py}/Fe_{HR} ratios fluctuate (0.61 ± 0.20 in 12 samples) between ferruginous and possibly euxinic (Fig. 6). By the end of the Asbian, all sections have high ratios, both in Fe_{HR}/Fe_T, which plot in the anoxic zone, and in Fe_{py}/Fe_{HR} ratios, which lie between 0.6- 0.8 throughout the Bowland Basin (Figs. 6, 7). The exception occurs at CH where the dark shales of the Bowland Shale are replaced in the P_{1a} zone by the calcareous shales and micritic limestones of the Ravensholme Limestone Member (Fig. 7). Here, the Fe_T content fluctuates between 1.32 and 3.45 wt% (2.42 ± 0.70 in 14 samples), giving suitable concentrations for Fe speciation analyses. The Fe_{HR}/Fe_T ratios straddle the equivocal and anoxic regions (0.52 ± 0.25 in 14 samples), while variable Fe_{py}/Fe_{HR} ratios are commonly below 0.8 (0.31 ± 0.24 in 14 samples) (Fig. 7).

Early Brigantian (P_1 zones)

Generally, early Brigantian strata (P_1 zones) has an Fe_T content of 2-4 wt%. In basinal settings, there are consistently high Fe_{HR}/Fe_T ratios (0.87 ± 0.10 for the SM section; 0.95 ± 0.05 for the DH section) that fall in the anoxic zone (Figs. 4, 5 and 8). The exception occurs in the early P_{1c} zone at TLC, where values decline to 0.32 (the equivocal zone), but bounce back rapidly (0.83 ± 0.20; Fig. 5). This trend is not seen in other sections. Fe_{py}/Fe_{HR} ratios dominantly fall in the possibly euxinic zone, while a few samples are below 0.6 (0.67 ± 0.14 for the SM section; 0.69 ± 0.15 for the DH section) (Fig. 5). A scattering of lower values below 0.6 (0.61 ± 0.18) is seen at the TLC section, at the same level where Fe_{HR}/Fe_T ratios plot in the equivocal zone (Fig. 5). At the FL section, on the northern basin margin, Lower Bowland Shale deposition began at the start of the Brigantian with shales onlapping onto the shallow-water limestones of the Pendleside Limestone Formation (Fig. 9). The shales here have elevated Fe_{HR}/Fe_T ratios (0.83 ± 0.15) falling in the anoxic zone and Fe_{py}/Fe_{HR} ratios (0.69 ± 0.14) that mainly plot in the possibly euxinic zone (Fig. 9).

Late Brigantian (P_2 zones)

With the exception of Fe_T concentrations, which show considerable variability, the Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} ratios of late Brigantian strata maintains the relative stability established in the early Brigantian, falling in the anoxic and possibly euxinic zones, respectively. The basin-center sections at DH and LC have high Fe_{HR}/Fe_T values (0.90 ± 0.12 in 40 samples at the DH section; 0.95 ± 0.05 in 25 samples from the LC section) plotting in the anoxic zone (Fig. 8, 10). The high proportion of reactive iron is due to the pyrite-rich nature of the sediment (e.g. at LC, Fe_{py}/Fe_{HR} is 0.74 ± 0.12 in 25 samples; at DH, Fe_{py}/Fe_{HR} is 0.69 ± 0.12 in 40 samples). At SS, on the basin margin, the P_2 black shales also display elevated ratios both in Fe_{HR}/Fe_T (0.72 ± 0.06 in 5 samples) and Fe_{py}/Fe_{HR} (0.73 ± 0.08 in 5 samples).

Pendleian (E_1 zones)

There is no major change in lithology at the transition to the Upper Bowland Shale Formation; dark gray and black shales persist. In biozone E_{1a}, Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} ratios exhibit persistently high values, plotting in the anoxic and possibly euxinic zones, respectively. At the DH section, Fe_{HR}/Fe_T is 0.96 ± 0.08 and Fe_{py}/Fe_{HR} is 0.69 ± 0.10 in 45 samples, and both ratios are 1.0 at the LC section (Fig. 10). However, values fall in the succeeding E_{1b} zone, as seen in the basinal DH section, where Fe_{HR}/Fe_T declines from peak ratios of 0.97 to approaching 0.38, and there is a corresponding fall in Fe_{py}/Fe_{HR} ratios from 0.86 to 0.21 (Fig. 8). This decline is associated with the appearance of thin beds of turbidite sandstone (Fig. 8). Ratios of Fe_{HR}/Fe_T in the equivocal zone also occur at this level in the early E_{1b} zone in basin margin locations: Fe_{HR}/Fe_T drops to 0.26 and 0.22 at the SS and CC sections, respectively. The decline is short-lived, however, and values increase in the late E_{1b} zone (e.g. 0.87 ± 0.04 for Fe_{HR}/Fe_T and 0.72 ± 0.03 for Fe_{py}/Fe_{HR} at the SS section; 0.83 ± 0.14 for Fe_{HR}/Fe_T and 0.75 ± 0.04 for Fe_{py}/Fe_{HR} at the MC section; Figs. 10, 11). These increased values are not seen at DH, probably because the younger part of the E_{1b} zone was not sampled there. The youngest levels of the Upper Bowland Shale (E_{1c} zone) were only sampled at MC, where Fe_{HR}/Fe_T ratios (0.71 and 0.50) plot in the anoxic zone, and Fe_{py}/Fe_{HR} ratios are 0.68 on average (Fig. 11).

Mo and U systematics

Holkerian-Asbian

The pink and light gray micrites of the Hodderense Limestone have low concentrations of Mo and U at RH (peak values of 2.88 and 2.93 ppm, respectively; see Supplemental Material), which result in low enrichment factors (Fig. 4). The succeeding Pendleside Limestone shows a slight decline to even lower Mo and U concentrations. For example, at RH in four samples Mo is 0.40 ± 0.27 ppm and U is 1.65 ± 0.06 ppm, and at TLC Mo is 0.32 ± 0.23 ppm in 24 samples and U is 1.82 ± 0.91 ppm in 27 samples (Fig. 5).

The transition to the Lower Bowland Shale, within the B_2- P_{1a} zones, is marked by the appearance of dark gray shales, although the boundary is gradational because thin beds of micritic limestones and calcarenites persist above the formational boundary in several sections (e.g. the TLC section). A gradational upwards increase in redox-sensitive trace metal concentrations is evident in most sections. At the expanded TLC section, the lowest shales in the B_2 zone do not show enrichment in Mo and U, but all values increase slightly in the latest Asbian P_{1a} zone (Fig. 5). In the shale-dominated SC section (Fig. 7), Mo and U concentrations are similarly low in the B_2 and earliest P_{1a} zone (Mo is 0.70 ± 0.31 ppm in 10 samples, U is 3.51 ± 1.01 ppm in 11 samples) whilst U/Mo values are consistently above 2. Concentrations increase substantially in the late P_{1a} zone to peak values not seen at any other section in the basin at this level (Mo reaches values of 58.0 ppm, U reaches 13.2 ppm, with correspondingly high EFs) whilst U/Mo drops below 2 (Fig. 7). In contrast to the shale-dominated record at SC, the P_{1a} zone at CH records the development of the Ravensholme Limestone, and the interbedded mudrocks show little trace metal enrichment: Mo values remain below 0.8 ppm, U concentrations are below 3 ppm and U/Mo is above 2 (Fig. 7). The B_{2a} - early P_{1a} trend at LB is different again, with little evidence of trace metal enrichment in the lowest part of the section, although U (but not Mo) increases in the mid-B_{2a} zone and remains at near-constant levels above this, whilst U/Mo ratios are variable but generally >2

(Fig. 6). At the condensed SM section, U and Mo are only modestly enriched in the B_2 zone, but values rise late in the P_{1a} zone (Fig. 4). Overall, trace metal trends in the lower part of the Lower Bowland Shales show upwards enrichment, but the timing of this increase varies considerably throughout the basin, as do the peak concentrations.

Brigantian (P_{1b} —P_2 zones)

The Brigantian portion of the Lower Bowland Shale generally has more elevated trace metal concentrations than the Asbian portion, although once again the limestone-dominated section at TLC shows the lowest values (Fig. 5). Modest trace metal enrichments occur in the early P_{1b} zone at TLC, before values decline to around 5 ppm and 9 ppm for Mo and U, respectively and U/Mo ratios are below 2. By contrast, the P_{1b} strata in the SM section has strong trace metal enrichments, with Mo values around 70 ppm and U values around 20 ppm (Fig. 4).

The DH section provides a shale-dominated section of the entire Brigantian part of the Lower Bowland Shale, and shows high trace metal enrichment values throughout (Fig. 8). Mo concentrations are typically around 40 ppm for much of the section, but concentrations decline substantially in the early P_{2a} zone to ~10 ppm, before increasing again in the mid P_{2a} zone where several values exceed 80 ppm (Fig. 8). The U concentrations at DH broadly follow those of Mo, with the lowest values in the early P_{2a} zone (the lowpoint is 2.46 ppm) and highest values of 23.1 ppm occur towards the top of the P_{2c} zone (Fig. 8). Generally U/Mo values are less than 2 throughout the Brigantian at DH, only in the early P_{2a} zone, do some values exceed this (Fig. 8). A thick development of the P_{2c} zone is seen at the LC section where it has elevated Mo_{EF} values and low U/Mo ratios comparable to the same level at DH (Fig. 10).

The early Brigantian saw onlap of the Bowland Shales onto carbonate facies at the basin margin, a transition recorded at FL where coarse calciturbidites dominate the section and black shales occur as thin interbeds (Fig. 9). The latter begin in the P_{1b} zone where there is a rapid rise in Mo concentrations from 4.92 ± 1.15 ppm (7 samples) to a peak of 38.4 ppm at the top of the zone, before values decline again to around 7.75 ppm in the P_{1c} zone (Fig. 9). Uranium concentrations are also generally higher in the P_{1b} zone (with a peak of 44.7 ppm at the top of the zone) relative to the P_{1c} zone (8.65 ± 3.52 ppm, 15 samples). The U/Mo ratios at SC rapidly decline in the P_{1b} zone to below 2 before increasing and fluctuating in the P_{1c} zone.

Pendleian (E_1 zones)

Within the basinal DH and LC sections, the transition to E zones initially sees little change in trace metal concentrations in the earliest E_{1a} zone, but in the younger part of the zone there is substantial enrichment, with Mo and U reaching 107.4 and 40.1 ppm, respectively (Fig. 8). This is followed by a temporary decline in trace metal concentrations in the overlaying E_{1b} zone of the DH section (Fig. 8), a trend also seen on the basin margin (see below). The U/Mo ratios in the Pendleian are consistently below 2 until the E_{1b} zone where the overall decline of trace metal enrichment sees a major increase of values peaking at 26.5 (Fig. 8).

The early Pendleian saw the transition to the early post-rift stage of basin development when black shale deposition extended for a few kilometres beyond the northern margin of the Bowland Basin, onto the Askrigg Block. Trace metal concentrations in the marginal locations are generally as high as those seen in the basin. Both the CC and SS sections occur at the northern limit of the Upper Bowland Shale outcrop and initially, in the early part of the E_{1b} zone, trace metals have low values at these locations before increasing dramatically in the later part of the zone (e.g. at CC, Mo is initially <10 ppm, before increasing to >50 ppm, although U trends are less clear and the U/Mo ratios vary; Fig. 11). The youngest levels of the Bowland Shale were only sampled at the basin margin locations of CC and MC. At the former, late E_{1b} to early E_{1c} zone shales show a prolonged decline in trace metal concentrations, culminating in Mo and U levels in the MC section of 2.35 and 6.08 ppm, respectively (Fig. 11).

Pyrite petrography

Framboids are generally present in most samples from the Pendleside Limestone, and consistently show mean diameters of 6-12 μm and maximum values greater than 30 μm (Figs. 4, 12). In a Wilkins diagram these populations plot in the dysoxic- oxic field, with some straying into the euxinic field (Fig. 12; cf. Wilkin et al., 1996). The latter framboid populations are from the B_1 (early Asbian) interval of the TLC section (Fig. 5).

Framboids become common within the mudrocks of the lower Lower Bowland Shales and generally have smaller mean diameters (between 6-8 μm) compared to those from the underlying Pendleside Limestone, although both intervals have similar standard deviations. As a result, in the Wilkins Plot, framboid populations mostly occur in the lower dysoxic fields, with only two samples in the euxinic field (Fig. 12). Framboids remain common in the younger part of the Lower Bowland Shale and populations generally have mean sizes around 6 μm, whilst maximum framboid sizes gradually decline from around 25 μm to 10 μm (Fig. 8). In the Wilkin Plot, these populations straddle the lower dysoxic to euxinic fields (Fig. 12).

The Upper Bowland Shale contains abundant small framboids with little size variation. These populations plot consistently in the euxinic field of the Wilkin Plot (Fig. 12), with the exception of the youngest sample (P_{1b} zone), which has a greater size range typical of the dysoxic field (Figs. 8, 12). Thus, the overall history of the Bowland Basin from Pendleside Limestone to Upper Bowland Shale deposition, recorded by framboid populations, is one of gradually increasing oxygen restriction culminating in prolonged euxinia.

DISCUSSION

Redox proxy threshold calibrations

Defining redox thresholds is critical for redox proxy application, and various studies have investigated the cut-off values for individual proxies. Scott and Lyons (2012) summarized sediment Mo concentrations observed in different redox settings in the modern ocean, suggesting that values of <25 ppm, 25-100 ppm, and >100 ppm can potentially indicate non-euxinic, intermittently euxinic or restricted (which may be persistently euxinic), and persistently euxinic conditions with limited restriction, respectively. In our case, we note below that basinal restriction was likely fairly constant, and hence Mo concentrations can be considered to provide a reasonable first order approximation of the relative intensity of euxinia. Algeo and Tribovillard (2009), on the other hand, suggest using enrichments factors of trace metal and Mo-U covariation to distinguish dysoxic, anoxic and euxinic conditions. Furthermore, based on modern data, redox-sensitive metals expressed as ratios of elements over Al, can provide thresholds to differentiate various conditions (Bennett and Canfield, 2020). However, such values can be basin-specific and so, where possible, redox thresholds should be refined for each individual basin (Algeo and Li, 2020; Poulton, 2021). Here, we calibrate redox thresholds for the Bowland Basin based on the covarying patterns observed between the different redox proxies we have applied.

Cross plots of U_{EF} vs. Fe_{HR}/Fe_T have recently been used to assess water column redox conditions (He et al., 2022), since both parameters respond to the development of anoxia (i.e. higher U_{EF} values during anoxic deposition should correspond to elevated (>0.38) Fe_{HR}/Fe_T ratios), because both have similar redox potentials (Zheng et al., 2002). Here, we find a close degree of consistency between U_{EF} values and Fe_{HR}/Fe_T ratios (Fig. 13A). Thus, samples plotting in the oxic field based on Fe_{HR}/Fe_T ratios, generally have U_{EF} values <1, whereas samples in the possibly anoxic Fe_{HR}/Fe_T field have U_{EF} values that straddle a U_{EF} value of 1, suggesting fluctuating redox conditions. By contrast, almost all samples that have Fe_{HR}/Fe_T ratios consistent with anoxia (i.e. >0.38) also have elevated U_{EF} values (U_{EF} >2), supporting anoxic depositional conditions. These observations from two independent indicators of anoxia provide strong support for the robust nature of our redox interpretations, and underlines the utility of the Fe speciation proxy, when applied correctly (*contra* Pasquier et al., 2022). Consequently, for our samples, a U_{EF} threshold of >1-2, combined with Fe_{HR}/Fe_T ratios >0.38, provides a clear indication of anoxic depositional conditions (Fig. 12A).

Significant molybdenum accumulation occurs only when a critical sulfide threshold is met in the water column, and thus weakly euxinic conditions may be characterized by no, or limited, Mo enrichment, whereas significant enrichments are expected under highly euxinic conditions (Helz et al., 1996). Therefore, we determine Mo enrichment thresholds attributable to euxinia based on covariation between both Mo and U, and between Mo and framboid size distributions (Fig. 13B, D). In the Bowland Basin, U/Mo values are consistently <2 in samples with Fe_{py}/Fe_{HR} indicative of possibly euxinic and euxinic values (e.g. Fig. 8) indicating enrichment of Mo in a sulfidic water column. The U versus Mo relationship can also be examined in more detail in cross-plots of Mo_{EF} and U_{EF}. In detail, Mo_{EF} values remain low when U_{EF} values are <1.37, albeit with variation as each binned U_{EF} range increases (Fig. 13B). These fluctuations in Mo_{EF} may reflect fluctuations in the sulfide content of the water column under weakly euxinic conditions, thus limiting extensive Mo drawdown (Emerson and Huested, 1991; Helz et al., 1996; Wegwerth et al., 2018), or may potentially reflect fluctuations between euxinic and non-euxinic anoxia (Scott and Lyons, 2012). Thus, U_{EF} values in the range 1.37-3.0 co-occur with a mean Mo_{EF} value of 4.8, and this defines our lower limit for weakly euxinic conditions in the Bowland Basin.

It has been previously been suggested, based on modern euxinic settings, that Mo concentrations >100 ppm indicate stable, highly euxinic conditions where Mo supply is not limited (e.g. in unrestricted basins; Scott and Lyons, 2012), but such levels are seldom evident in the Bowland Basin data. However, Mo-determined redox thresholds are likely basin-specific. Our pyrite framboid data provide independent support for permanently euxinic conditions in some intervals (Fig. 12). Small populations of framboids, around 6 μm in diameter, form at the sulfidic chemocline in the water column of modern euxinic basins (Wilkin et al., 1996; Dubinin et al., 2022) and are preserved in the underlying sediments (e.g. Wignall et al., 2010). In the Bowland Basin, framboid populations with a relatively large (>6 μm) mean size occur in sediments with Mo_{EF} values of around 10 (Fig. 13d). For samples with average framboid sizes of 6 μm or less, associated Mo_{EF} values are >40 (Fig. 13D), and we consider such values to be diagnostic of Black Sea-like euxinic conditions, where there is a substantial volume of deep, highly sulfidic water (e.g. Wilkin et al., 1996).

We also consider a Mo_{EF}-Fe_{py}/Fe_{HR} cross-plot to further examine this refined threshold (Fig. 13C). Oxic samples have a range of Fe_{py}/Fe_{HR} ratios but very low Mo_{EF} values, reflecting pyrite formation during diagenesis. Nevertheless, most oxic samples plot below 0.6 (0.37 ± 0.24). Similarly, while anoxic ferruginous samples have low Mo_{EF} values, and Fe_{py}/Fe_{HR} ratios are higher than oxic samples on average (0.51 ± 0.28), most plot below the 0.8 threshold for robust identification of euxinia. By contrast, both weakly and highly euxinic samples have elevated Mo_{EF} values and higher Fe_{py}/Fe_{HR} ratios, with most samples falling in the possibly euxinic field. Some of these euxinic samples (as determined by Mo_{EF} enrichments) have relatively low Fe_{py}/Fe_{HR} ratios (<0.6), which could potentially be due to relatively low sulfide concentrations during diagenesis. In this scenario, enhanced sulfide generation in the euxinic water column may limit sulfate availability (and hence additional sulfide production) during diagenesis, thus preventing the additional sulfidation of Fe_{HR} phases, which is a general requirement for the production of high Fe_{py}/Fe_{HR} ratios (Xiong et al., 2019; Poulton, 2021). Overall, our approach highlights the value of combining independent redox proxies to assess paleoredox conditions, and confirms the general agreement and robust nature of the different proxies we have applied, as well as providing a more nuanced interpretation of the data.

Evolving redox trends during Bowland Basin development

Holkerian-Asbian (B_1-P_{1a} zone)

The oldest interval examined comprises the deep-water pelagic strata of the Holkerian-age Hodderense Limestone. Only sampled at the RH section, Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} ratios indicate ferruginous deposition, which is supported by the slight U enrichments and limited Mo accumulation (Figs. 4, 14). The Hodderense Limestone is thought to be the product of a major transgressive episode/basin deepening (Riley, 1990), and the anoxic conditions may have been widespread in Bowland Basin bottom waters at this time, but a detailed appraisal awaits a more widespread study.

The transition to carbonates and mudstones of the succeeding Pendleside Limestone Formation (Gawthorpe, 1986) is marked by a decline in Fe proxy and trace metal values, indicating improved oxygenation at this (early-mid Asbian) stage in the basin history (Figs. 4, 5 and 14). The oldest Pendleside Limestone Formation, seen at RH, has Fe_{HR}/Fe_T ratios falling in the equivocal oxic/anoxic zone which accords with the limited U_{EF} values (Fig. 4). The succeeding interval is recorded at TLC, where similarly, U and Mo exhibit limited enrichment (Fig. 5), but fluctuating Fe_{HR}/Fe_T ratios occur, with a few samples suggesting anoxia (Fig. 5). These signals are consistent with overall oxygenated conditions at this site, potentially with periodic development of weak dysoxia to anoxia. The medium-high Fe_{py}/Fe_{HR} ratios, combined with the presence of large-sized framboid populations, indicates formation in sulfidic pore waters (Fig. 14).

The onset of dark gray shale-dominated deposition defines the base of the Lower Bowland Shale Formation (Fig. 14) and initially there is only local evidence for anoxic depositional conditions. Thus, the TLC section records low organic C contents, with no apparent enrichment of trace metals or elevated Fe_{HR}/Fe_T ratios in the B_2 zone (Fig. 5). This level also lacks framboids and Fe_{py}/Fe_{HR} ratios are low (Fig. 5). By contrast, for the DB and LB sections in the NW of the basin (Fig. 7), the Fe speciation and trace metal proxies indicate ferruginous to borderline euxinic conditions, especially in the B_{2b} zone (Fig. 6).

Evidence for widespread anoxic conditions in the Bowland Basin does not occur until the end of the Asbian (P_{1a} zone), when TOC levels rapidly increase (locally reaching nearly 10 wt%; Fig. 5), as do trace metal enrichments and Fe speciation ratios, whilst pyrite framboid populations decrease dramatically in size. The P_{1a} level also marks a transition in the Fe pool to one almost entirely dominated by Fe(II) in form of Fe_{carb} and Fe_{py}, showing near-complete reduction of Fe_{HR} phases and the onset of stable ferruginous conditions (Figs. 4, 7). Elevated Mo_{EF} and Fe_{py}/Fe_{HR} ratios, combined with a rapid decline of U/Mo ratios and small pyrite framboid size distributions, all provide evidence to suggest that the basin had tipped into a weakly euxinic state by the end of the Asbian (Fig. 14).

The exception to these changes is seen in the CH section, where the dark gray Bowland Shales are replaced with allochthonous carbonates of the locally-developed Ravensholme Limestone Formation (Fig. 2). The interbedded shales show only slight U enrichments (close to our defined threshold), limited Mo enrichments, and highly variable Fe_{HR}/Fe_T ratios, likely indicating variable redox conditions between dysoxic-ferruginous (Figs. 7, 14). It is possible that the Ravensholme Limestone records a carbonate debris fan that was somewhat elevated above the more intensely anoxic condition of the deeper basin floor.

Early Brigantian (P_{1b} —P_{1d} zones)

During the early Brigantian organic-rich shales (TOC ranges from 4-10 wt%) accumulated over the entire Bowland Basin and most U/Mo values are below 2, Fe_{py}/Fe_{HR} ratios are, with few exceptions, within the 0.6-0.8 range, indicating conditions were likely ferruginous to weakly euxinic (Figs. 4, 5, 8 and 9). Framboid populations show considerable variation and support this redox interpretation, and plot in the euxinic to weakly dysoxic fields (Fig. 12). The expanded TLC section records particularly variable redox levels, ranging from ferruginous to highly euxinic, based on fluctuations in Fe speciation systematics, trace metal enrichments, U/Mo ratios and framboid size distributions (Fig. 5). The Lower Bowland Shale at this location is replaced by the Ravensholme Limestone, a mix of interbedded limestones and dark gray shales. Like the development of this unit at the CH section, the development of the Ravensholme Limestone at TLC records an overall weaker intensity of anoxia than the surrounding basinal shales (Fig. 14), which may relate to a slightly more elevated depositional site within the basin compared to the shale-dominated sections.

Active faulting in the early Brigantian saw the expansion of Lower Bowland Shale deposition to the north of the bounding South Craven Fault system (Fig. 3). Here, the FL section initially displays high Fe_{HR}/Fe_T ratios and U enrichments, suggesting ferruginous conditions early in the P_{1b} zone. This is quickly followed by a sharp increase in Fe_{py}/Fe_{HR} ratios and Mo_{EF} values, and a decline in U/Mo ratios later in the zone, indicating the onset of highly euxinic conditions in the late P_{1b} zone, before the development of weak euxinia in mid-P_{1c} times (Fig. 9). Through the rest of the FL section, Mo enrichments and Fe_{py}/Fe_{HR} ratios decline, indicating a shift back to ferruginous conditions. Thus, for a period during the late P_{1b} zone, the basin margin FL location was recording more intense euxinia than seen in the center of the Bowland Basin, whilst for the remaining early Brigantian, redox levels were comparable to those in the basin center (Fig. 14); a change that is discussed below.

Late Brigantian (P_2 zone)

The late Brigantian continued to see weakly euxinic conditions prevailing in the Bowland Basin (Fig. 14). An especially thick development of P_{2c} shales is seen at the LC section, which shows a low degree of variability in redox proxies at this level near the top of the Lower Bowland Shale Formation (Fig. 10). At the DH section, for the most part, Fe phase partitioning, trace metal enrichment levels and U/Mo values indicate euxinic conditions, with occasional development of ferruginous conditions. Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} ratios gradually decrease during the early P_{2a} zone, along with a decline in U and Mo (Fig. 8), whilst framboids increase in size and TOC falls to around 2 wt%. These trends independently suggest a transition from euxinic to ferruginous conditions, with sulfidic pore waters (Helz et al., 1996; Poulton and Canfield, 2011; Poulton, 2021). The first influx of terrigenous sand into the basin occurs at this time: the Pendleside Sandstone Member, a small turbiditic body, as seen at the top of TLC section (Figs. 2, 5). The role of turbidity currents and basin oxygenation is discussed below.

Pendleian (E_1 zones)

There was no change in depositional regime with the onset of Upper Bowland Shale deposition; organic-rich shale deposition continued to prevail throughout the basin beneath a euxinic water column (Fig. 14). Thus, E_{1a} zone black shales have pronounced U and Mo enrichments (U/Mo is <2), persistently high Fe proxy ratios, and very small framboid populations (Fig. 12). Black shale deposition continued its gradual onlap of the Craven Fault Belt marginal zone, and this region also saw euxinia developed (Fig. 14), whilst well-ventilated, shallow-water deposition occurred only a few kilometres to the north on the Askrigg Block (Arthurton et al., 1988).

Oxygenation levels improved in the early E_{1b} zone, both in the Basin and on its margin (Fig. 14). In the basinal DH section, Fe_{py}/Fe_{HR} values fall rapidly from >0.8 to 0.2 whilst Mo declines, U remains steady in concentration (therefore U/Mo increases), and framboids increase in size (Fig. 8). These trends suggest a transition from intensive euxinia to ferruginous conditions. This improved ventilation is also recorded in the SS and CC sections on the southern margin of Askrigg Block, where there is a major decline in Mo_{EF} values and Fe speciation ratios, as well as an increase in U/Mo ratios (Figs. 10, 11). Following the improved redox conditions in the early E_{1b} zone there was a rapid return of euxinia, indicated by increased Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} ratios and enrichment of trace metals (Figs. 10, 11). As with the transient improvement in oxygenation during the early P_{2a} zone, the short-lived improved ventilation in the early E_{1b} zone also coincides with the local appearance of thin turbidite sandstones (e.g. at DH; Fig. 8). These have a thicker development in the NW of the basin where they are called the Hind Sandstone (Kane, 2010).

The youngest levels of the Upper Bowland Shale (basal E_{1c} zone) were only sampled at the MC section, where declining trace metal enrichments and Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} ratios from the mid E_{1b} zone record a gradual transition from intensely euxinic to weakly euxinic conditions in the final stages of Upper Bowland Shale deposition (Figs. 11, 14). Emmings et al. (2020) studied drill core from the topmost levels of the Upper Bowland Shale (E_{1c} zone) from the northern edge of the outcrop belt (close to the FL section). Their data record a rapid improvement in oxygenation level to oxic conditions in the 20 m of mudstone occurring beneath the sharp transition to the coarse, turbiditic sandstones of the succeeding Pendle Grit Formation.

Controls on oxygenation in the Bowland Basin

Broadly speaking, oxygenation in marine settings is a balance between oxygen supply and oxygen consumption. The former is achieved by both vertical advection and lateral mixing, and is therefore dependent on water depth and the connectivity of the deeper waters (Algeo et al., 2008). The Bowland Basin evolved from a carbonate ramp setting to a fault-bounded graben surrounded by shallower areas of carbonate deposition (Gawthorpe, 1987; Fig. 1B). The transition occurred around the Asbian/Brigantian boundary and coincides closely with the onset of Bowland Shale deposition, suggesting that basin isolation was a major player in the development of oxygen restriction in the basin, although anoxic deposition initially occurred only locally within the basin (Fig. 14).

Oxygen consumption is controlled by the abundance of decaying organic matter, which is dependent on primary productivity, and thus the nutrient supply to surface waters. Modern zones of high productivity are either fed by upwelling of nutrient-rich, deep water or from nutrient-rich riverine influx. Upwelling is primarily a phenomenon of ocean-facing continental margins and is unlikely in the Bowland Basin, which lay a long distance from the nearest ocean (Fig. 1A); there was no feasible route for nutrient-laden, deep waters to reach the basin without passing through shallow-water areas en route (Fig. 1B). Terrestrial nutrient influx is a more viable alternative and high levels have been favored as a cause of organic enrichment in a previous Bowland Shale study (Emmings et al., 2020). However, for much of its depositional history, the Bowland Basin was surrounded by carbonate platforms and shelves (Fig. 1b). It is therefore unlikely that the basin received abundant terrestrial nutrients because carbonate productivity on adjacent platforms would have been affected. This places the onus on depositional models that invoke restricted oxygen supply. Potential factors controlling the redox conditions are discussed below.

Connectivity versus isolation

Values of Mo/TOC have been used to evaluate the connectivity and degree of bottom water replenishment in silled basins (Algeo and Lyons, 2006; Algeo et al., 2007). Cross-plots generally show a positive correlation, but the gradient is controlled by the availability of aqueous Mo. In euxinic environments, rapid Mo drawdown into the sediment can result in water column concentrations that become severely depleted. Thus, in strongly restricted euxinic basins with weak deep-water renewal (such as the modern Black Sea), the enrichment of Mo relative to TOC is reduced and the gradient of Mo/TOC is low (~4). By contrast, less restricted basins, such as the modern Saanich Inlet, have gradients up to ten times steeper (Algeo and Lyons, 2006).

During the depositional history of the Bowland Shale, regression lines for Mo-TOC covariation (Fig. 16) have slope (*m*) values of ~44 in the early Brigantian, ~38 in the late Brigantian, and 40 in the early Pendleian, which are all typical of weakly restricted, silled basins (as also found in Emmings et al., 2020). However, the thermal maturity of the Bowland Shale is sufficiently high to have experienced hydrocarbon maturation and decreased TOC values. Vitrinite reflectance values in the region average 1.1 (Andrews, 2013), indicating a maturity on the threshold of gas generation within the basin, whilst shales from the NW margin of the basin are oil mature (Emmings et al., 2020). Calculating the original TOC values requires a suite of organic geochemical data that is not available for our study sites, but Emmings et al. (2020) report hydrogen indices (HIs) of ~180 from the Upper Bowland Shale in the NW of the basin. Assuming original HIs of >400 for the type II/III kerogens, and using the approach of Hart and Hofmann (2022), suggests original TOC values that were ca. 30% higher. Thus, the original Mo/TOC gradients within the Bowland Basin would plot between modern Framvaren Fjord and Black Sea data, indicating deep water renewal times approaching 1000 years and poor Mo replenishment (Algeo and Lyons, 2006). Interestingly, the lowest Mo/TOC gradients are seen in the marginal sub-basin developments of the Bowland Shale, where "puddles" of black shale developed in the newly subsiding Craven Fault Belt, especially in the early stages of their history (Fig. 15B). For example, the late P_{1a} black shales at FL has a Mo/TOC *m* of only 3.8, which is amongst the lowest encountered at any point in the basin's history (Fig. 16). We suggest that such settings were initially rather isolated from the main deep-water mass of the adjacent Bowland Basin, perhaps because they were perched above the main volume of bottom waters, and so developed even stronger Mo-depletion beneath highly euxinic bottom waters (Fig. 15B).

The degree of isolation of the Bowland Basin has been suggested to be controlled by sea-level variations (Gross et al., 2015; Emmings et al., 2020). A major phase of glacioeustasy is thought to have begun around the Asbian/Brigantian and had a clear influence in shallow marine areas (Manifold et al., 2021). For example, to the north of the Bowland Basin, eustasy is considered to have been a major control on the development of heterolithic, shallow-water cycles (Yoredale cycles) of the Brigantian-early Pendleian interval (Wright and Vanstone, 2001). Contemporaneously, in the Bowland Basin, it has been argued that transgressive phases improved connectivity, allowing fully marine goniatite and bivalve faunas to invade (Gross et al., 2015; Emmings et al., 2020; Waters et al., 2020). However, such fossils are present throughout Bowland Shale deposition and no cyclicity is manifest in either the sedimentology or the redox proxies (e.g. Fig. 6). Therefore, it is unlikely that eustatic fluctuations influenced Bowland Shale deposition or basin connectivity. The Bowland Basin was probably sufficiently deep that eustatic oscillations, which may only have been only a few tens of meters (Tucker et al., 2009), had little impact on deposition.

Stratification: salinity versus temperature

Whilst most Bowland Shale deposition likely occurred beneath a water column several hundred meters deep, organic-rich deposition also extended to the fault-bounded margin where depths were shallower. The transition to a post-rift phase in the Pendleian saw the Craven Fault Belt region subside and euxinic shales onlap the margin of the adjacent platform (Fig. 15C). It is likely that black shale deposition at marginal locations was at shallow water depths because the shales pass laterally into well oxygenated platform facies of the Yoredale cycles, which contain a diverse and abundant benthic fauna, over a distance of ca. 1 km (Rayner, 1953). For example, at FL, large limestone boulders and calciturbidites are interbedded with euxinic shales (Fig. 9), indicating the close proximity of shallow, well ventilated conditions. This abrupt lateral transition is likely only possible in a strongly stratified water column where a sharp pycnocline separates a sulfidic lower water column from an oxygenated upper water column (Fig. 15B, C). The most intense and persistent euxinia coincides with Upper Bowland Shale deposition (Fig. 15C) when we infer that the thickness of sub-pycnocline waters were at their greatest. This may well have favoured their stability because re-oxygenating such a large volume of the lower water column would require major mixing.

Salinity stratification provides a highly effective mechanism to isolate the lower water column from surface waters, due to the strong density variations of water with different salinities. Models for black shale accumulation in silled basins frequently invoke an “estuarine circulation model” in which the basin has a positive water balance (like an estuary), with more water exported via low salinity surface waters than are replaced by influx of deeper, more saline waters (Tyson and Pearson, 1991; Algeo et al., 2008). This model is especially popular for the Jurassic black shales of western Europe (e.g. van de Schootbrugge et al., 2005; McArthur et al., 2008), and has also been invoked for the Bowland Shale (Gross et al., 2015; Emmings et al., 2020). However, the link between the intensity of oxygen depletion and run-off into the Bowland Basin is the opposite of that which would occur if a freshwater-fed halocline was isolating basin bottom waters. This is especially clear in the Upper Bowland Shale, where intervals of sandy turbidity flow, fed from deltas prograding from the north east (Waters et al., 2020), coincide with improvements in basinal oxygenation. For example, a substantial turbidite system (the Pendle Grits) succeeds the Bowland Shales, and the youngest (E_{1c} zone) shales immediately below the sand influx show a rapid improvement of oxygenation from euxinic to oxic conditions (Emmings et al., 2020, Fig 2B). More minor phases of turbidity influx are seen before this and these also coincide with improved ventilation. Thus, in the E_{1b} Zone a thin, turbidite sandbody is developed at a level where redox proxies indicate a short period of improved (ferruginous) conditions, interspersed within a euxinic interval (Fig. 14).

Temperature-driven stratification can also isolate bottom waters in modern shelf seas, when warmer, lower density surface waters cap colder, deep water. The strength of such stratification is weaker than salinity-drive stratification, and thermoclines are often transient or seasonal (Tyson and Pearson, 1991; Tomašovỳch et al., 2017). The sharp, lateral transition between euxinic and oxic deposition on the Bowland Basin margin and long-term stability of euxinic deep waters argues for strong stratification. Therefore, thermocline development in the Bowland Basin is unlikely. Instead, the basin may have been salinity stratified, but with the bottom waters being both warm and saline. Warm saline bottom water development is frequently invoked for periods of oceanic anoxia whereby extensive low-latitude, shelf seas in warm, arid settings are subject to evaporation that elevates salinity (e.g. Railsback, 1990; Wenzel and Joachimski, 1996; Friedrich et al., 2008). This increases water density and over-compensates for the density decline caused by warming, resulting in waters that sink into deeper waters of adjacent oceans, which thus become stratified (e.g. Brass et al., 1982; Friedrich et al., 2008; MacLeod et al., 2011; Dummann et al., 2021). We propose that this model may also operate on a smaller, epicontinental-basin scale. The Bowland Basin lay in warm, tropical latitudes and was surrounded by extensive carbonate platforms (Fig. 1). Therefore, we envisage an anti-estuarine depositional model for the Bowland Basin, in which WSBW generated on adjacent carbonate shelves was the source of deep basin waters. Euxinic waters developed below the resultant strong pycnocline for several million years (Fig. 15). Such a scenario explains why delta progradation from the north coincided with improved oxygenation of the Bowland Basin: WSBW generation declined and dense, sediment-laden gravity currents flushed out and diluted the basinal waters, thereby improving ventilation.

An anti-estuarine basin model for black shale generation contrasts with the widely preferred estuarine, silled basin model proposed for many epicontinental black shales. However, our WSBW model may be widely applicable because many black shale occurrences occur in basins adjacent to broad carbonate shelves which are unlikely to have experienced estuarine circulation. For example, the Ravnefjeld Formation is a regionally important Permian source rock of East Greenland (Christiansen et al., 1993). The black shales were deposited in a series of narrow, laterally-linked syn-rift basins developed adjacent to carbonate platforms (Piasecki and Stemmerik, 1991), a situation closely comparable to the Bowland Shale. Organic biomarkers in the Ravnefjeld black shales indicate high salinities (Christiansen et al., 1993), and it is possible that their accumulation occurred beneath a halocline in which bottom waters were fed by highly saline surface waters. Furthermore, the Ravnefjeld shales show a remarkable persistence of organic richness along the length of their outcrop, despite considerable thickness variations (Christiansen et al., 1993), an attribute that is also similar to the Bowland Shales, especially in the Upper Bowland Shale Formation. This may be because WSBWs generate a strong, persistent halocline, with the result that sub-pycnocline conditions in the isolated bottom waters are remarkably uniform. Similarly, the Richardson Trough (Northern Yukon, Canada) was surrounded by the Great American Carbonate Bank during much of the Paleozoic, and records a prolonged history of anoxic deposition (Sperling et al. 2021). This is likely to be another example where the WSBW model is appropriate.

CONCLUSIONS

The Bowland Shales are an important regional hydrocarbon resource in UK stratigraphy; the general geochemistry, redox conditions and depositional environments from the best-exposed sections in the Bowland Basin have been studied here. Dark gray shale and minor calciturbidite and sandy turbidites accumulated in a rift basin surrounded by carbonate platforms and shelves during 10 million years of the late Mississippian. Independent proxies have been applied and calibrated to assess the evolving redox conditions during Bowland Shale deposition. The oxic/anoxic threshold is diagnosed by U_{EF} > 1-2 and Fe_{HR}/Fe_T > 0.38, whilst Mo_{EF} > 4.8 indicates weakly euxinic conditions and values > 40 denote highly euxinic environments. U/Mo ratios are also useful in distinguishing the transition to euxinic conditions where its value declines below 2. The redox boundaries are also corroborated by pyrite framboid size analysis: Mo_{EF} > 40 is consistently associated with mean framboid populations < 6 μm in diameter, whilst weakly euxinic Mo_{EF} values occur in samples with framboids > 6 µm (Fig. 13). These geochemical threshold values differ in detail from those encountered in other basins and reinforces the point made by Algeo and Li (2020) that, wherever possible, redox proxies should be calibrated separately for each basin.

Bowland Shale deposition began during a phase of rifting that saw ramp collapse and establishment of block-and-basin topography. Organic-rich shale deposition was initially localised and laterally variable, but by the late Asbian TOC-rich sediments (typically 4 wt% and reaching 10 wt%) were more extensive. The transition from syn- to post-rift conditions in the Brigantian saw continued expansion of black shale deposition onto the shoulders of the basin when highly euxinic waters were present throughout the basin (Fig. 15C). By this stage, black shale deposition had expanded into "perched sub-basins" on the basin margin which, at their initiation, were more intensely reducing than in the main basin, suggesting they had a strong degree of isolation (Fig. 15B). This is corroborated by low Mo/TOC gradients in the perched sub-basins compared with the main basin. Sediment-gravity flows introduced minor turbidite sandbodies into the basin in the later stage of Bowland Shale deposition. These coincide with improvements in basin oxygenation, suggesting the gravity currents flushed out and improved basin oxygenation. The re-oxygenation effect is minor for the thin turbidites, but the massive turbidite sand influx that terminated Bowland Shale deposition was preceded by a major improvement from euxinic to oxic deposition.

A warm saline bottom water model is developed for Bowland Shale deposition, in which basinal waters were generated by evaporation in the shallow waters of the adjacent carbonate platforms. The resultant halocline was strongly developed and accounts for the stability of sub-pycnocline conditions and the rapid lateral transition from euxinia into fully oxygenated shallow water facies at the basin margin. This anti-estuarine silled basin model contrasts with "typical" positive water balance circulation models proposed for many black shales. The inverse relationship between anoxia and clastic influx to the basin argues against the latter. Thus, the estuarine circulation model for black shale deposition is not a ubiquitous shibboleth. WSBW models may be common especially for black shales that formed in basins surrounded by extensive carbonate platforms.

ACKNOWLEDGEMENTS

Our gratitude goes to Professor Jeff Peakall, Dr. Kaixuan Ji, Yuxuan Wang, Yafang Song and Zhen Xu who provided valuable help during fieldwork. This work was funded by a University of Leeds research training grant (SL), and NERC grant NE/T008458/1 (SWP). We thank Erik Sperling and an anonymous reviewer for their constructive comments on our original manuscript.

FIGURE CAPTIONS

1. (A) Mississippian (340 Ma) global paleogeography (modified from Boucot et al., 2013), showing the northern England study area (black rectangle); (B) regional paleogeography of northern England during the Asbian (336- 332 Ma), showing the occurrence of isolated basins surrounded by carbonate platforms and shelves (modified from Cope et al., 1992).

2. Summary cross section through the Bowland Basin, Craven Fault Belt; ICS = International Commission on Stratirgraphy, Serpukhov. – Serpukhovian, Hol. = Holkerian; dashed lines show the formation boundaries (after Earp et al., 1961; Aitkenhead et al., 1992; Waters et al., 2017).

3. Study area in the Bowland Basin, Craven Fault Belt, and the southern Askrigg Block. Outcrop locations are Dobson Brook (DB), Leagram Brook (LB), Smelthwaite Farm (SM), School Share (SS), Cow Close (CC), Moor Close Gill (MC), Dinckley Hall (DH), River Hodder (RH), Light Clough (LC), Swarden Clough (SC), Clough Head Beck (CH), Tory Log Clough (TLC), and Fell Lane (FL).

4 Geochemical profile for TOC, Fe speciation, trace metal systematics and framboid analyses through the RH and SM sections. The dashed lines on Fe_{HR}/Fe_T plots represent the boundaries for distinguishing anoxic (>0.38) and oxic (<0.22) water column conditions. The dashed lines on Fe_{py}/Fe_{HR} plots indicate the boundaries for distinguishing euxinic (>0.8) and ferruginous (<0.6) water column conditions, and the open circles reflect oxic samples (determined via combined consideration of Fe speciation and trace metal systematics), while closed circles represent anoxic samples. In U and Mo plots, black circles and the diamonds present enrichment factors and concentration respectively. Diamonds are shown at zero if the concentration is below instrument detection limits. The gray bar and the dash lines indicate calibrated redox thresholds for U_{EF} and Mo_{EF} respectively (see text).

5. Geochemical profiles for TOC, Fe speciation, trace metal systematics and framboid analysis at the TLC section. See Fig. 4 caption for additional information.

6. Geochemical profiles for TOC, Fe speciation and trace metal systematics at the DB and LB sections. See Fig. 4 caption for additional information.

7. Geochemical profiles for TOC, Fe speciation and trace metal systematics at the CH and SC sections. PL: Pendleside Limestone Formation. See Fig. 4 caption for additional information.

8. Geochemical profiles for TOC, Fe speciation, trace metal systematics and framboid analyses at the DH section. See Fig. 4 caption for additional information.

9. Geochemical profiles for TOC, Fe speciation and trace metal systematics at the FL section. PL: Pendleside Limestone Formation. See Fig. 4 caption for additional information.

10. Geochemical profiles for TOC, Fe speciation and trace metal systematics at the LC and SS sections. LBS: Lower Bowland Shale Formation; UBS: Upper Bowland Shale Formation. See Fig. 4 caption for additional information.

11. Geochemical profiles for TOC, Fe speciation and trace metal systematics through the CC and MC sections. See Fig. 4 caption for additional information.

12. Wilkin Plot (mean framboid diameter against standard deviation) of framboid populations from the late Holkerian to early Pendleian of the Bowland Basin. Dashed line indicates the euxinic/oxic-dysoxic threshold, as determined in modern environments (Wilkin et al., 1996).

13. Redox threshold calibrations based on proxy covariation; open, light gray, dark gray and black circles illustrate oxic, ferruginous, weakly euxinic and highly euxinic samples. (A) U_{EF} and Fe_{HR}/Fe_T cross plot, upper part showing data points and lower part showing statistical analysis in which Fe_{HR}/Fe_T data are displayed as mean values (± 1 S.D), where U_{EF} is <1, 1-2, 2-3 and >3. (B) Mo_{EF} and U_{EF} cross plot and its corresponding statistical analysis showing there is no Mo accumulation with U_{EF} <1.37, but that Mo enrichment increases rapidly as U_{EF} increases above 3.0. (C) Mo_{EF} and Fe_{py}/Fe_{HR} cross plot showing scattered Fe_{py}/Fe_{HR} ratios for oxic and ferruginous samples, but with Fe_{py}/Fe_{HR} ratios dominantly falling in and above the possibly euxinic zone when Mo_{EF} is > 4.8. (D) framboid size distribution (points refer to mean value, and upper and lower limits represent the maximum and minimum framboid diameters) and Mo_{EF} cross plot showing a broad decline in framboid size as Mo_{EF} increases.

Large framboids (mean value > 6 μm) occur when Mo_{EF} is below 10, while framboid mean sizes < 6 μm commonly occur with Mo_{EF} > 10. With Mo_{EF} > 40, all framboid populations are < 6 μm in mean diameter. LOD: limit of detection.

14. Summary of the redox history of the Bowland Basin study sites showing a gradual increase in the extent and intensity of anoxia from the Asbian to the early Pendleian. The extent of Bowland Shale deposition also increases with onlap of the marginal Craven Fault Belt beginning in the Brigantian and extending onto the Askrigg Block in the late Brigantian-Pendleian.

15. Depositional model for the development of the Bowland Shale Formation from a carbonate ramp experiencing little oxygen restriction in the mid Asbian, to a fault-bounded syn-rift basin in the Brigantian with ferruginous-euxinic bottom waters, to a post-rift basin experiencing flank collapse and onlap of black shales onto the basin margin in the early Pendleian. Euxinic waters are envisaged to have been maintained beneath a salinity stratified water column in which warm saline bottom waters, generated on adjacent carbonate shelves, supplied the deep water.

16. Mo/TOC plots of euxinic samples from the Brigantian to early Pendleian in the Bowland Basin. The dash lines depict the gradients from three modern, euxinic basins (Algeo and Lyons, 2006).

REFERENCES CITED

Aitkenhead, N., 1992, *Geology of the country around Garstang*: Memoir for 1: 50,000 Geological Sheet 67 (England and Wales): HM Stationery Office.

Alcott, L.J., Krause, A.J., Hammarlund, E.U., Bjerrum, C.J., Scholz, F., Xiong, Y., Hobson, A.J., Neve, L., Mills, B.J.W., März, C., Schnetger, B., Bekker, A., Poulton, S.W., 2020. Development of Iron Speciation Reference Materials for Palaeoredox Analysis: Geostandards and Geoanalytical Research, v. 44, p. 581–591, https://doi.org/10.1111/ggr.12342

Algeo, T.J., and Li, C., 2020, Redox classification and calibration of redox thresholds in sedimentary systems: Geochimica et Cosmochimica Acta, v. 287, p. 8–26, https://doi.org/10.1016/j.gca.2020.01.055.

Algeo, T.J., and Lyons, T.W., 2006, Mo-total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions: Paleoceanography, v. 21, p. 204–230, https://doi.org/10.1029/2004PA001112.

Algeo, T.J., Heckel, P.H., Maynard, J.B., Blakey, R.C., and Rowe, H., 2008, Modern and ancient epeiric seas and the super-estuarine circulation model of marine anoxia: Special Paper - Geological Association of Canada, p. 7–38.

Algeo, T.J., Lyons, T.W., Ronald, B., and Over, D.J., 2007, Hydrographic conditions of the Devono–Carboniferous North American Seaway inferred from sedimentary Mo–TOC relationships: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 256, p. 204–230, https://doi.org/10.1016/j.palaeo.2007.02.035.

Algeo, T.J., and Tribovillard, N., 2009, Environmental analysis of paleoceanographic systems based on molybdenum-uranium covariation: Chemical Geology, v. 268, p. 211–225, https://doi.org/10.1016/j.chemgeo.2009.09.001.

Anderson, R.F., Lehuray, A.P., Fleisher, M.Q., and Murray, J.W., 1989, Uranium deposition in Saanich Inlet sediments, Vancouver Island: Geochimica et Cosmochimica Acta, v. 53, p. 2205–2213, https://doi.org/10.1016/0016-7037(89)90344-X.

Andrews, I.J. 2013. The Carboniferous Bowland Shale gas study: geology and resource estimation: British Geological Survey for Department of Energy and Climate Change, London, UK. 56 pp open file report.

Arthur, M., and Sageman, B.B., 1994, Marine shales: depositional mechanisms and environments of ancient deposits: Annual Review of Earth and Planetary Sciences, v. 22, p. 499–551, https://doi.org/10.1146/annurev.earth.22.1.499.

Arthurton, R.S., Johnson, E.W., and Mundy, D.J.C., 1988, *Geology of the country around Settle*. Memoir for 1: 50,000 Geological Sheet 67 (England and Wales): HM Stationery Office.

Benkovitz, A., Matthews, A., Teutsch, N., Poulton, S.W., Bar-Matthews, M., and Almogi-Labin, A., 2020, Tracing water column euxinia in Eastern Mediterranean Sapropels S5 and S7: Chemical Geology, v. 545, p. 119627, https://doi.org/10.1016/j.chemgeo.2020.119627.

Bennett, W.W., and Canfield, D.E., 2020, Redox-sensitive trace metals as paleoredox proxies: A review and analysis of data from modern sediments: Earth-Science Reviews,

v. 204, p. 103175, https://doi.org/10.1016/j.earscirev.2020.103175.

Bertine, K.K., and Turekian, K.K., 1973, Molybdenum in marine deposits: Geochimica et Cosmochimica Acta, v. 37, p. 1415–1434, https://doi.org/10.1016/0016-7037(73)90080-X.

Boucot, A.J., Xu, C., Scotese, C.R., and Morley, R.J., 2013, *Phanerozoic paleoclimate: an atlas of lithologic indicators of climate*: SEPM (Society for Sedimentary Geology) Tulsa, v. 11.

Brass, G.W., Southam, J.R., and Peterson, W.H., 1982, Warm saline bottom water in the ancient ocean: Nature, v. 296, p. 620–623, https://doi.org/10.1038/296620a0.

Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., and Berner, R.A., 1986, The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales: Chemical Geology, v. 54, p. 149–155, https://doi.org/10.1016/0009-2541(86)90078-1.

Christiansen, F.G., Piasecki, S., Stemmerik, L., and Telnaes, N., 1993, Depositional environment and organic geochemistry of the Upper Permian Ravnefjeld Formation source rock in East Greenland: AAPG Bulletin, v. 9, p. 1519–1537, https://doi.org/ 10.1306/BDFF8EDE-1718-11D7-8645000102C1865D.

Clarkson, M.O., Poulton, S.W., Guilbaud, R., and Wood, R.A., 2014, Assessing the utility of Fe/Al and Fe-speciation to record water column redox conditions in carbonate-rich sediments: Chemical Geology, v. 382, p. 111–122, https://doi.org/10.1016/j.chemgeo.2014.05.031.

Cope, J.C.W., Guion, P.D., Sevastopulo, G.D., and Swan, A.R.H., 1992, Carboniferous: Geological Society, London, Memoirs, v. 13, p. 67–86.

de Jonge-Anderson, I., and Underhill, J.R., 2020, Structural constraints on Lower Carboniferous shale gas exploration in the Craven Basin, NW England: Petroleum Geoscience, v. 26, p. 303–324, https://doi.org/10.1144/PETGEO2019-125.

Demaison, G.J., and Moore, G.T., 1980, Anoxic environments and oil source bed genesis: AAPG Bulletin, v. 64, p. 1179–1209, https://doi.org/10.1306/2F91945E-16CE-11D7-8645000102C1865D.

Dubinin, A. V, Demidova, T.P., Dubinina, E.O., Rimskaya-korsakova, M.N., Semilova, L.S., Berezhnaya, E.D., Klyuvitkin, A.A., Kravchishina, M.D., and Belyaev, N.A., 2022, Sinking particles in the Black Sea waters : vertical fluxes of elements and pyrite to the bottom , isotopic composition of pyrite sulfur, and hydrogen sulfide production: Chemical Geology, v. 606, p. 120996, https://doi.org/10.1016/j.chemgeo.2022.120996.

Dummann, W. et al., 2021, Driving mechanisms of organic carbon burial in the Early Cretaceous South Atlantic Cape Basin (DSDP Site 361): Climate of the Past, v. 17, p. 469–490, https://doi.org/10.5194/cp-17-469-2021.

Earp, J.R., Poole, E.G., and Whiteman, A.J., 1961, *Geology of the country around Clitheroe and Nelson*: Memoir for 1: 50,000 Geological Sheet 68 (England and Wales): HM Stationery Office

Ebdon, C.C., Fraser, A.J., Higgins, A.C., Mitchener, B.C., and Strank, A.R.E., 1990, The Dinantian stratigraphy of the East Midlands: a seismostratigraphic approach: Journal of the Geological Society, v. 147, p. 519–536, https://doi.org/10.1144/gsjgs.147.3.0519.

Emerson, S.R., and Huested, S.S., 1991, Ocean anoxia and the concentrations of molybdenum and vanadium in seawater: Marine Chemistry, v. 34, p. 177–196, https://doi.org/10.1016/0304-4203(91)90002-E.

Emmings, J.F., Poulton, S.W., Vane, C.H., Davies, S.J., Jenkin, G.R.T., Stephenson, M.H., Leng, M.J., Lamb, A.L., and Moss-Hayes, V., 2020, A Mississippian black shale record of redox oscillation in the Craven Basin, UK: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 538, p. 109423, https://doi.org/10.1016/j.palaeo.2019.109423.

Erickson, B.E., and Helz, G.R., 2000, Molybdenum(VI) speciation in sulfidic waters: Geochimica et Cosmochimica Acta, v. 64, p. 1149–1158, https://doi.org/10.1016/s0016-7037(99)00423-8.

Fauchille, A.L., Ma, L., Rutter, E., Chandler, M., Lee, P.D., and Taylor, K.G., 2017, An enhanced understanding of the Basinal Bowland shale in Lancashire (UK), through microtextural and mineralogical observations: Marine and Petroleum Geology, v. 86, p. 1374–1390, https://doi.org/10.1016/j.marpetgeo.2017.07.030.

Fraser, A.J., and Gawthorpe, R.L., 1990, Tectono-stratigraphic development and hydrocarbon habitat of the Carboniferous in northern England: Geological Society Special Publication, v. 55, p. 49–86, https://doi.org/10.1144/GSL.SP.1990.055.01.03.

Friedrich, O., Erbacher, J., Moriya, K., Wilson, P.A., and Kuhnert, H., 2008, Warm saline intermediate waters in the Cretaceous tropical Atlantic ocean: Nature Geoscience, v. 1, p. 453–457, https://doi.org/10.1038/ngeo217.

Gawthorpe, R.L., 1986, Sedimentation during carbonate ramp-to-slope evolution in a tectonically active area: Bowland Basin (Dinantian), northern England: Sedimentology, v. 33, p. 185–206, https://doi.org/10.1002/9781444304473.ch31.

Gawthorpe, R.L., 1987, Burial dolomitization and porosity development in a mixed carbonate-clastic sequence: an example from the Bowland Basin, northern England:

Sedimentology, v. 34, p. 533–558, https://doi.org/10.1111/j.1365-3091.1987.tb00785.x.

Gross, D., Sachsenhofer, R.F., Bechtel, A., Pytlak, L., Rupprecht, B., and Wegerer, E., 2015, Organic geochemistry of Mississippian shales (Bowland Shale Formation) in central Britain: Implications for depositional environment, source rock and gas shale potential: Marine and Petroleum Geology, v. 59, p. 1–21, https://doi.org/10.1016/j.marpetgeo.2014.07.022.

Hart, B.S., and Hofmann, M.H., 2022, Revisiting paleoenvironmental analyses and interpretations of organic-rich deposits: The importance of TOC corrections: Organic Geochemistry, v. 170, p. 104434, https://doi:10.1016/j.orggeochem.2022.104434.

He, T.C., Wignall, P.B., Newton, R.J., Atkinson, J.W., Keeling, J.F.J., Xiong, Y., and Poulton, S.W., 2022, Extensive marine anoxia in the European epicontinental sea during the end-Triassic mass extinction: Global and Planetary Change, v. 210, p. 103771, https://doi.org/10.1016/j.gloplacha.2022.103771.

Helz, G.R., Miller, C. V., Charnock, J.M., Mosselmans, J.F.W., Pattrick, R.A.D., Garner, C.D., and Vaughan, D.J., 1996, Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence: Geochimica et Cosmochimica Acta, v. 60, p. 3631–3642, https://doi.org/10.1016/0016-7037(96)00195-0.

Hennissen, J.A.I., Hough, E., Vane, C.H., Leng, M.J., Kemp, S.J., and Stephenson, M.H., 2017, The prospectivity of a potential shale gas play: An example from the southern Pennine Basin (central England, UK): Marine and Petroleum Geology, v. 86, p. 1047–1066, https://doi.org/10.1016/j.marpetgeo.2017.06.033.

Jenkyns, H.C., 2010, Geochemistry of oceanic anoxic events: Geochemistry, Geophysics, Geosystems, v. 11, p. 1–30, https://doi.org/10.1029/2009GC002788.

Kane, I.A., 2010, Development and flow structures of sand injectites: The Hind Sandstone Member injectite complex, Carboniferous, UK: Marine and Petroleum Geology, v. 27, p. 1200–1215, https://doi.org/10.1016/j.marpetgeo.2010.02.009.

Kirby, G.A., 2000, *The structure and evolution of the Craven Basin and adjacent areas: subsurface memoir*: HM Stationery Office.

Klinkhammer, G.P., and Palmer, M.R., 1991, Uranium in the oceans: Where it goes and why: Geochimica et Cosmochimica Acta, v. 55, p. 1799–1806, https://doi.org/10.1016/0016-7037(91)90024-Y.

Li, S., Wignall, P.B., Poulton, S.W., Hedhli, M., and Grasby, S.E., 2022, Carbonate shutdown, phosphogenesis and the variable style of marine anoxia in the late Famennian (Late Devonian) in western Laurentia: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 589, p. 110835, https://doi.org/10.1016/j.palaeo.2022.110835.

MacLeod, K.G., Isaza Londoño, C., Martin, E.E., Jiménez Berrocoso, Á., and Basak, C., 2011, Changes in North Atlantic circulation at the end of the Cretaceous greenhouse interval: Nature Geoscience, v. 4, p. 779–782, https://doi.org/10.1038/ngeo1284.

Manifold, L., Strother, P. Del, Gold, D.P., Burgess, P., and Hollis, C., 2021, Unravelling evidence for global climate change in Mississippian carbonate strata from the Derbyshire and North Wales platforms, UK: Journal of the Geological Society, v. 178, https://doi.org/10.1144/jgs2020-106.

McArthur, J.M., Algeo, T.J., Van De Schootbrugge, B., Li, Q., and Howarth, R.J., 2008, Basinal restriction, black shales, Re-Os dating, and the Early Toarcian (Jurassic) oceanic anoxic event: Paleoceanography, v. 23, p. 1–22, https://doi.org/10.1029/2008PA001607.

McLennan, S.M., 2001, Relationships between the trace element composition of sedimentary rocks and upper continental crust: Geochemistry, Geophysics, Geosystems, v. 2, https://doi.org/10.1029/2000GC000109.

Munnecke, A., Samtleben, C., and Bickert, T., 2003, The Ireviken Event in the lower Silurian of Gotland, Sweden – relation to similar Palaeozoic and Proterozoic events: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 195, p. 99–124, https://doi.org/10.1016/S0031-0182(03)00304-3.

Newport, S.M., Jerrett, R.M., Taylor, K.G., Hough, E., and Worden, R.H., 2018, Sedimentology and microfacies of a mud-rich slope succession: In the Carboniferous Bowland Basin, NW England (UK): Journal of the Geological Society, v. 175, p. 247–262, https://doi.org/10.1144/jgs2017-036.

Pasquier, V., Fike, D.A., Révillon, S., and Halevy, I., 2022, A global reassessment of the controls on iron speciation in modern sediments and sedimentary rocks: A dominant role for diagenesis: Geochimica et Cosmochimica Acta, v. 335, p. 211–230, https://doi.org/10.1016/j.gca.2022.08.037.

Piasecki, S., and Stemmerik, L., 1991, Late Permian anoxia in central East Greenland: Geological Society Special Publication, v. 58, p. 275–290, https://doi.org/10.1144/GSL.SP.1991.058.01.18.

Pickard, N.A.H., Rees, J.G., Strogen, P., Somerville, I.D., and Jones, G.L.I., 1994, Controls on the evolution and demise of Lower Carboniferous carbonate platforms, northern margin of the Dublin Basin, Ireland: Geological Journal, v. 29, p. 93–117, https://doi.org/10.1002/gj.3350290202.

Poulton, S.W., 2021, *The Iron Speciation Paleoredox Proxy*: Elements in Geochemical Tracers in Earth System Science. Cambridge University Press. https://doi.org/10.1017/9781108847148.

Poulton, S.W., and Canfield, D.E., 2005, Development of a sequential extraction procedure for iron: Implications for iron partitioning in continentally derived particulates: Chemical Geology, v. 214, p. 209–221, https://doi.org/10.1016/j.chemgeo.2004.09.003.

Poulton, S.W., and Canfield, D.E., 2011, Ferruginous conditions: a dominant feature of the ocean through Earth's history: Elements, v. 7, p. 107–112, https://doi.org/10.2113/gselements.7.2.107.

Poulton, S.W., Fralick, P.W., and Canfield, D.E., 2004, The transition to a sulphidic ocean ~1.84 billion years ago: Nature, v. 431, p. 173–177, https://doi.org/10.1038/nature02912.

Railsback, L.B., 1990, Influence of changing deep ocean circulation on the Phanerozoic oxygen isotopic record: Geochimica et Cosmochimica Acta, v. 54, p. 1501–1509, https://doi.org/10.1016/0016-7037(90)90175-K.

Raiswell, R., and Canfield, D.E., 1998, Sources of iron for pyrite formation in marine sediments: American Journal of Science, v. 298, p. 219–245, https://doi.org/10.2475/ajs.298.3.219.

Raiswell, R., Hardisty, D.S., Lyons, T.W., Canfield, D.E., Owens, J.D., Planavsky, N.J., Poulton, S.W., and Reinhard, C.T., 2018, The iron paleoredox proxies: A guide to the pitfalls, problems and proper practice: American Journal of Science, v. 318, p. 491–526, https://doi.org/10.2475/05.2018.03.

Rayner, D.H., 1953, The Lower Carboniferous rocks in the north of England: A review: Proceedings of the Yorkshire Geological Society, v. 28, p. 231–235, https://doi.org/10.1144/pygs.28.4.231.

Riley, N.J., 1990, Stratigraphy of the Worston Shale Group (Dinantian), Craven Basin, north-west England: Proceedings of the Yorkshire Geological Society, v. 48, p. 163–187, https://doi.org/10.1144/pygs.48.2.163.

Scott, C., and Lyons, T.W., 2012, Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: Refining the paleoproxies: Chemical Geology, v. 324–325, p. 19–27, https://doi.org/10.1016/j.chemgeo.2012.05.012.

Sperling, E.A., Melchin, M.J., Fraser, T., Stockey, R.G., Farrell, U.C., Bhajan, L., Brunoir, T.N.,Cole, D.B., Gill, B.C., Lenz, A., Loydell, D.K., Malinowski, J., Miller, A.J., Plaza-Torres, S., Bock, B., Rooney, A.D., Tecklenberg, S.A., Vogel, J.M., Planavsky, N.J., and Strauss, J.V., 2021, A long-term record of early to mid-Paleozoic marine redox change: Science Advances, v.7, eabf4382, https://doi.org/10.1126/sciadv.abf4382

Tomašovỳch, A., Gallmetzer, I., Haselmair, A., Kaufman, D.S., Vidović, J., and Zuschin, M., 2017, Stratigraphic unmixing reveals repeated hypoxia events over the past 500 yr in the northern Adriatic Sea: Geology, v. 45, p. 363–366, https://doi.org/10.1130/G38676.1.

Tribovillard, N., Algeo, T.J., Baudin, F., and Riboulleau, A., 2012, Analysis of marine environmental conditions based on molybdenum-uranium covariation – Applications to Mesozoic paleoceanography: Chemical Geology, v. 324–325, p. 46–58, https://doi.org/10.1016/j.chemgeo.2011.09.009.

Tucker, M.E., Gallagher, J., and Leng, M.J., 2009, Are beds in shelf carbonates millennial-scale cycles? An example from the mid-Carboniferous of northern England: Sedimentary Geology, v. 214, p. 19–34, https://doi.org/10.1016/j.sedgeo.2008.03.011.

Tyson, R. V., and Pearson, T.H., 1991, Modern and ancient continental shelf anoxia: Modern and ancient continental shelf anoxia, p. 1–24, https://doi.org/10.2307/3515153.

van de Schootbrugge, B., McArthur, J.M., Bailey, T.R., Rosenthal, Y., Wright, J.D., and Miller, K.G., 2005, Toarcian oceanic anoxic event: An assessment of global causes using belemnite C isotope records: Paleoceanography, v. 20, p. 1–10, https://doi.org/10.1029/2004PA001102.

Waters, C.N., and Condon, D.J. 2012. Nature and timing of Late Mississippian to Mid-Pennsylvanian glacio-eustatic sea-level changes of the Pennine Basin, UK: Journal of the Geological Society, v. 169, p.37-51, https://doi.org/10.1144/0016-76492011-047

Waters, C.N., Haslam, R.B., Cózar, P., Somerville, I.D., Millward, D., and Woods, M., 2017, Mississippian reef development in the Cracoe Limestone Formation of the southern Askrigg Block, North Yorkshire, UK: Proceedings of the Yorkshire Geological Society, v. 61, p. 179–196, https://doi.org/10.1144/pygs2016-374.

Waters, C.N., Vane, C.H., Kemp, S.J., Haslam, R.B., Hough, E., and Moss-Hayes, V.L., 2020, Lithological and chemostratigraphic discrimination of facies within the Bowland Shale Formation within the Craven and Edale basins, UK: Petroleum Geoscience, v. 26, p. 325–345, https://doi.org/10.1144/PETGEO2018-039.

Waters, C.N., Waters, R.A., Barclay, W.J., and Davies, J.R., 2009, A lithostratigraphical framework for the Carboniferous successions of northern Great Britain (onshore).

Wegwerth, A. et al., 2018, Redox evolution during Eemian and Holocene sapropel formation in the Black Sea: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 489, p. 249–260, https://doi.org/10.1016/j.palaeo.2017.10.014.

Wei, G., Chen, T., Poulton, S.W., Lin, Y., He, T., Shi, X., Chen, J., Li, H., Qiao, S., Liu, J., Li, D., Ling, H.F., 2021. A chemical weathering control on the delivery of particulate iron to the continental shelf: Geochimica et Cosmochimica Acta, v. 308, p. 204-216, https://doi.org/10.1016/j.gca.2021.05.058

Wenzel, B., and Joachimski, M.M., 1996, Carbon and oxygen isotopic composition of Silurian brachiopods (Gotland/Sweden): palaeoceanographic implications: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 122, p. 143–166, https://doi.org/10.1016/0031-0182(95)00094-1.

Wignall, P.B., 1994, Black shales: Oxford University Press, Oxford.

Wignall, P.B., and Newton, R., 1998, Pyrite framboid diameter as a measure of oxygen deficiency in ancient mudrocks: American Journal of Science, v. 298, p. 537–552, https://doi.org/10.2475/ajs.298.7.537.

Wignall, P.B., Bond, D.P.G., Kuwahara, K., Kakuwa, Y., Newton, R.J., and Poulton, S.W., 2010, An 80 million year oceanic redox history from Permian to Jurassic pelagic sediments of the Mino-Tamba terrane, SW Japan, and the origin of four mass extinctions: Global and Planetary Change, v. 71, p. 109–123, https://doi.org/10.1016/j.gloplacha.2010.01.022.

Wilkin, R.T., and Arthur, M.A., 2001, Variations in pyrite texture, sulfur isotope composition, and iron systematics in the black sea: Evidence for late Pleistocene to Holocene excursions of the O_2-H_2S redox transition: Geochimica et Cosmochimica Acta, v. 65, p. 1399–1416, https://doi.org/10.1016/S0016-7037(01)00552-X.

Wilkin, R.T., and Barnes, H.L., 1997, Formation processes of framboidal pyrite: Geochimica et Cosmochimica Acta, v. 61, p. 323–339, https://doi.org/10.1016/S0016-7037(96)00320-1.

Wilkin, R.T., Barnes, H.L., and Brantley, S.L., 1996, The size distribution of framboidal pyrite in modern sediments: Geochimica et Cosmochimica Acta, v. 60, p. 3897–3912, https://doi.org/10.1016/0016-7037(96)00209-8.

Wright, V.P., and Vanstone, S.D., 2001, Onset of Late Palaeozoic glacio-eustasy and the evolving climates of low latitude areas: a synthesis of current understanding: Journal of the Geological Society, v. 158, p. 579–582, https://doi.org/10.1080/00167616608728616.

Xiong, Y., Guilbaud, R., Peacock, C.L., Cox, R.P., Canfield, D.E., Krom, M.D., and Poulton, S.W., 2019, Phosphorus cycling in Lake Cadagno, Switzerland: A low sulfate euxinic ocean analogue: Geochimica et Cosmochimica Acta, v. 251, p. 116–135, https://doi.org/10.1016/j.gca.2019.02.011.

Zegeye, A., Bonneville, S., Benning, L.G., Sturm, A., Fowle, D.A., Jones, C.A., Canfield, D.E., Ruby, C., MacLean, L.C., Nomosatryo, S., Crowe, S.A., Poulton, S.W., 2012. Green rust formation controls nutrient availability in a ferruginous water column: Geology, v. 40, p. 599–602, https://doi.org/10.1130/G32959.1

Zheng, Y., Anderson, R.F., van Geen, A., and Fleisher, M.Q., 2002, Remobilization of authigenic uranium in marine sediments by bioturbation: Geochimica et Cosmochimica Acta, v. 66, p. 1759–1772, https://doi.org/10.1016/S0016-037(01)00886-9.