Linking Redox Processes and Black Shale Resource Potential

Joe Emmings[1*, 2], Simon Poulton[3], Sarah Davies[2], Chris Vane[1], Mel Leng[1], Mike Stephenson[1], Simon Chenery[1], Gawen Jenkin[2], Vicky Moss-Hayes[1]

[1]British Geological Survey [2]University of Leicester [3]University of Leeds

*Email: josmin65@bgs.ac.uk

Introduction

- Organic-rich mudstones ("black shales") are conventional hydrocarbon source rocks and candidate targets for unconventional hydrocarbon exploration in the UK.

- Black shales can also host ore-grade enrichments in redox-sensitive trace metals such as Mo, U, V, Ni and Cu. V, for example, is used in redox-flow batteries for large-scale electricity storage.

- Here we show ancient redox processes exterted a key control on the distribution of organic and metal 'resources' through a UK Mississippian black shale succession.

Geological Setting

- The Mississippian (~330 Ma) Bowland Shale Formation is the primary target for unconventional hydrocarbon exploration in the UK[1,2] and in equivalents across Europe, including the Epen Formation[3] (Netherlands) and Upper Alum Shale Formation[4] (Germany).

- The upper unit of the Bowland Shale, termed the Upper Bowland Shale, is a highly complex, interbedded carbonate and siliciclastic succession[5] that developed in response to high magnitude glacio-eustatic sea level fluctuations and delta progradation. This complexity means the resource potential of this succession is poorly constrained. In order to improve understanding of this unit, we integrate sedimentology, organic and inorganic geochemistry from three time-equivalent Upper Bowland Shale sections (A-C) in the UK Craven Basin [Figs. 1-2].

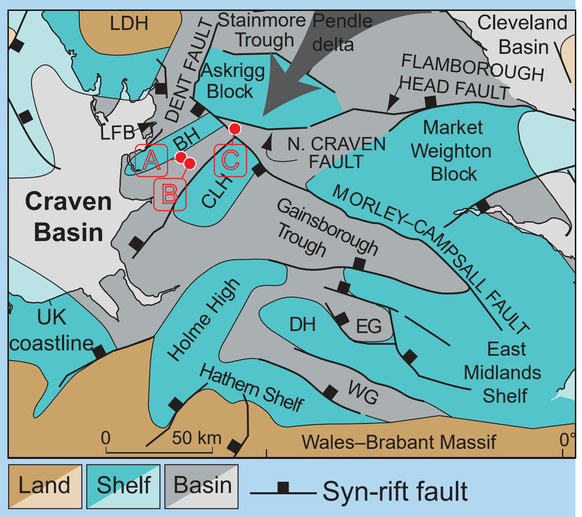


Fig. 1 (right) Palaeogeography modified from [ref. 6]. Study sites are located in the Craven Basin (Lancs., UK), a post-rift 'block-and-basin' setting[6], as part of the palaeo-equatorial Mississippian Rheic-Tethys epicontinental seaway.

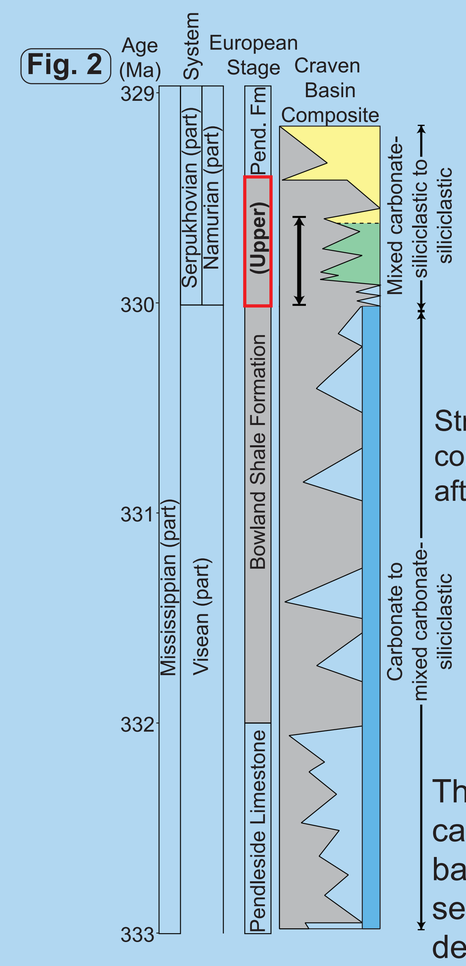


Fig. 2 Stratigraphic column and composite (left) from [ref. 5] after [ref. 7]

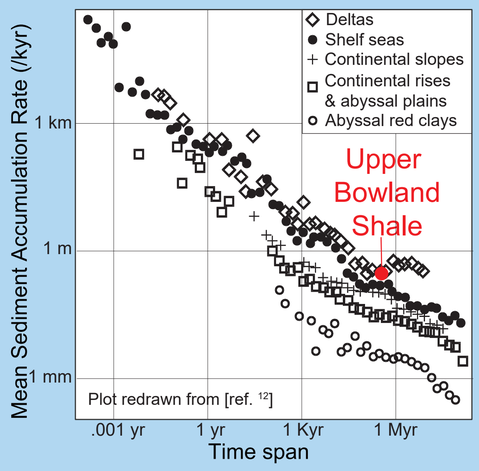


Fig. 3

The Bowland Shale includes discrete, macrofauna- bearing, carbonate-rich sedimentary packages termed 'marine bands'[8,9]. Marine bands are interpreted as 'condensed sections'; sediments starved of terrigenous material deposited during periods of maximum marine flooding[10] in response to far-field ice-sheet volume on Gondwana[11].

Results

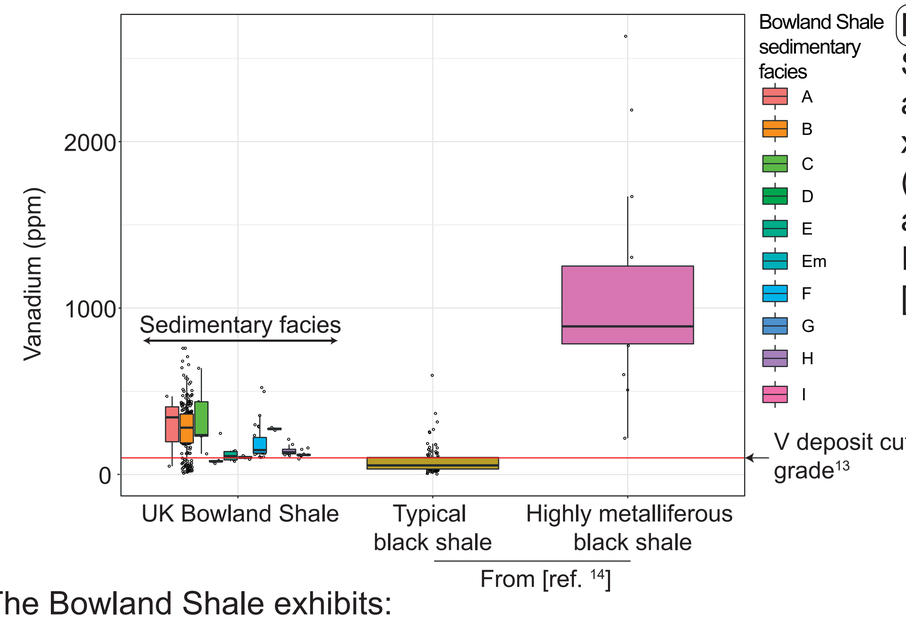


Fig. 4 Bowland Shale V data acquired using x-ray fluorescence (XRF) from [ref. 15] and laser ablation ICP-MS [unpublished].

The Bowland Shale exhibits:

- Moderate enrichment in many redox-sensitive trace metals (Mo, U, Ni, Cu) that is generally comparable to 'typical' black shales (using a global dataset from [ref. 14]).

- Facies-specific V enrichment is comparable to 'highly metalliferous black shales'[14], including the Talvivaara Formation (Finland) that is mined for metals including V.

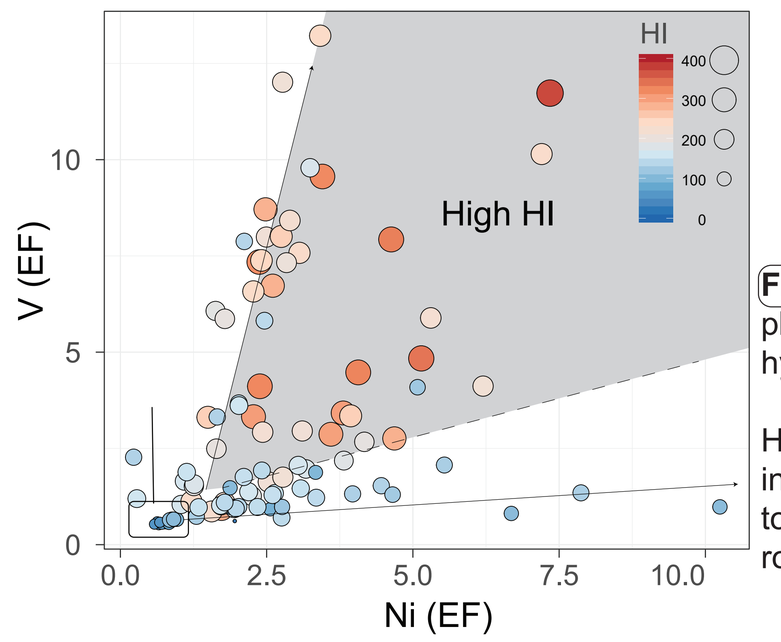


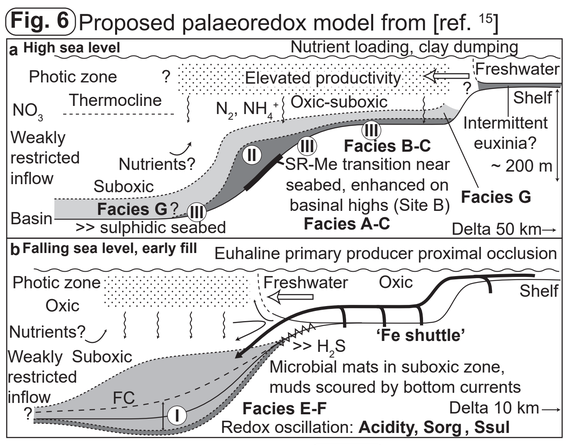
Fig. 5 V and Ni enrichment factors plotted with RockEval pyrolysis hydrogen index (HI).

HI is a measure for the H-content in organic matter (OM) and is used to assess hydrocarbon source rock potential.

Discussion & Conclusions

Bulk V and Ni bimodal 'competitive' enrichment (Fig. 5) is best explained by intermittent operation of 'redox oscillation'[16] in porewaters during deposition and early diagenesis.

Fig. 6 Proposed palaeoredox model from [ref. 15]



← Vanadiferous and H-rich OM = 'prospective' intervals?

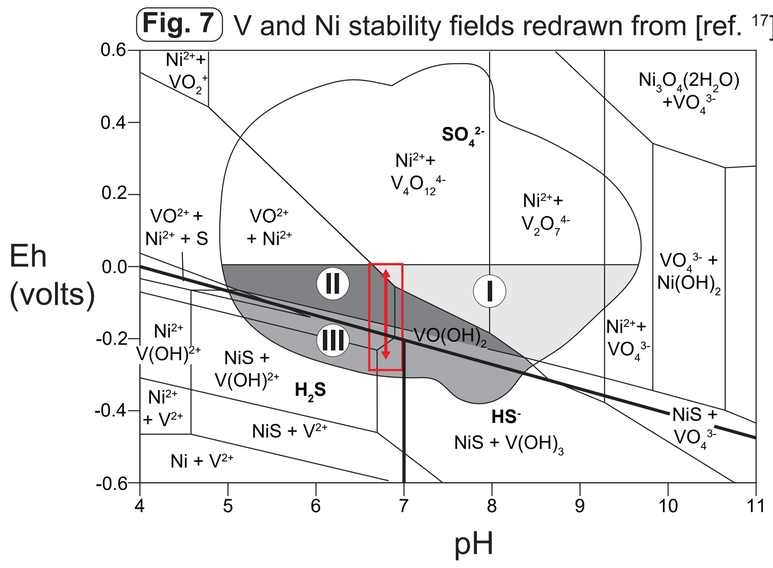
← V-poor and H-poor OM = not 'prospective'?

Redox oscillation describes the vertical fluctuation in Eh and pH conditions in shallow sediments. Organic-rich marine sediments subject to intense physical reworking and in receipt of a large supply of metal oxidants, such as in the modern Amazon fan, are prone to early diagenetic redox oscillation[16]. This process greatly enhances the rate of OM remineralisation in marine sediments by increasing the exposure time to oxidants yielding the highest free energy.

A high sediment accumulation rate (Fig. 3) combined with a relatively large supply of metal oxides and labile OM (Fig. 6) stimulated early diagenetic redox oscillation. Abundant reactive OM containing free-base porphyrins may explain the high V enrichments in the Bowland Shale compared to other 'typical' black shales.

Redox oscillation coupled to a high flux of OM to seabed exerted a key control on metal fixation, mineral authigenesis and preservation of OM, with implications for understanding the temporal and spatial distribution of resources through this black shale.

Fig. 7 V and Ni stability fields redrawn from [ref. 17]



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