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Stream and slope weathering effects on organic-rich mudstone geochemistry and implications for hydrocarbon source rock assessment: A Bowland Shale case study

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A B S T R A C T

This study contributes to the exploration and quantification of the weathering of organic-rich mudstones under temperate climatic conditions. Bowland Shales, exposed by a stream and slope, were sampled in order to develop a model for the effects of weathering on the mudstone geochemistry, including major and trace element geochemistry, Rock-Eval pyrolysis and $\delta^{13}C_{org}$. Four weathering grades (I – IV) are defined using a visual classification scheme; visually fresh and unaltered (I), chemically altered (II, III) and 'paper shale' that typifies weathered mudstone on slopes (IV). Bedload abrasion in the stream exposes of visually fresh and geochemically unaltered mudstone. Natural fractures are conduits for oxidising meteoric waters that promote leaching at the millimetre scale and/or precipitation of iron oxide coatings along fracture surfaces. On the slope, bedding-parallel fractures formed (and may continue to form) in response to chemical and/or physical weathering processes. These fractures develop along planes of weakness, typically along laminae comprising detrital grains, and exhibit millimetre- and centimetre-scale leached layers and iron oxide coatings. Fracture surfaces are progressively exposed to physical weathering processes towards the outcrop surface, and results in disintegration of the altered material along fracture surfaces. Grade IV, 'paper shale' mudstone is chemically unaltered but represents a biased record driven by initial heterogeneity in the sedimentary fabric. Chemically weathered outcrop samples exhibit lower concentrations of both 'free' (S1) (up to 0.6 mgHC/g rock) and 'bound' (S2) (up to 3.2 mgHC/g rock) hydrocarbon, reduced total organic carbon content (up to 0.34 wt%), reduced hydrogen index (up to 58 mgHC/gTOC), increased oxygen index (up to 19 mgCO + CO_2/gTOC) and increased T_{max} (up to 11 °C) compared with unaltered samples. If analysis of chemically weathered samples is unavoidable, back-extrapolation of Rock-Eval parameters can assist in the estimation of pre-weathering organic compositions. Combining Cs/Cu with oxygen index is a proxy for identifying the weathering progression from fresh material (I) to 'paper shale' (IV). This study demonstrates that outcrop samples in temperate climates can provide information for assessing hydrocarbon potential of organic-rich mudstones.

1. Introduction

Organic-rich mudstones are prone to physical and chemical alteration at outcrop because they contain components that are out of chemical equilibrium with present day surface oxidising conditions (e.g., Goldich, 1938; White and Buss, 2013). In order to avoid any detrimental effects of modern weathering, geochemical studies of organic-rich mudstones preferentially focus on samples obtained from borehole core samples located sufficiently far from the surficial weathered zone. However, where borehole core material is not available or practical to acquire, analysis of samples is by necessity conducted on those collected from outcrop.

The Mississippian Craven Basin, UK, is an example of an emerging hydrocarbon province that includes many exposures that dissect the basin. These exposures include the organic-rich Bowland Shale that may represent a significant unconventional hydrocarbon resource (Andrews, 2013). However, uncertainties exist, such as variable burial history, composition of the organic matter (OM) and ultimately the

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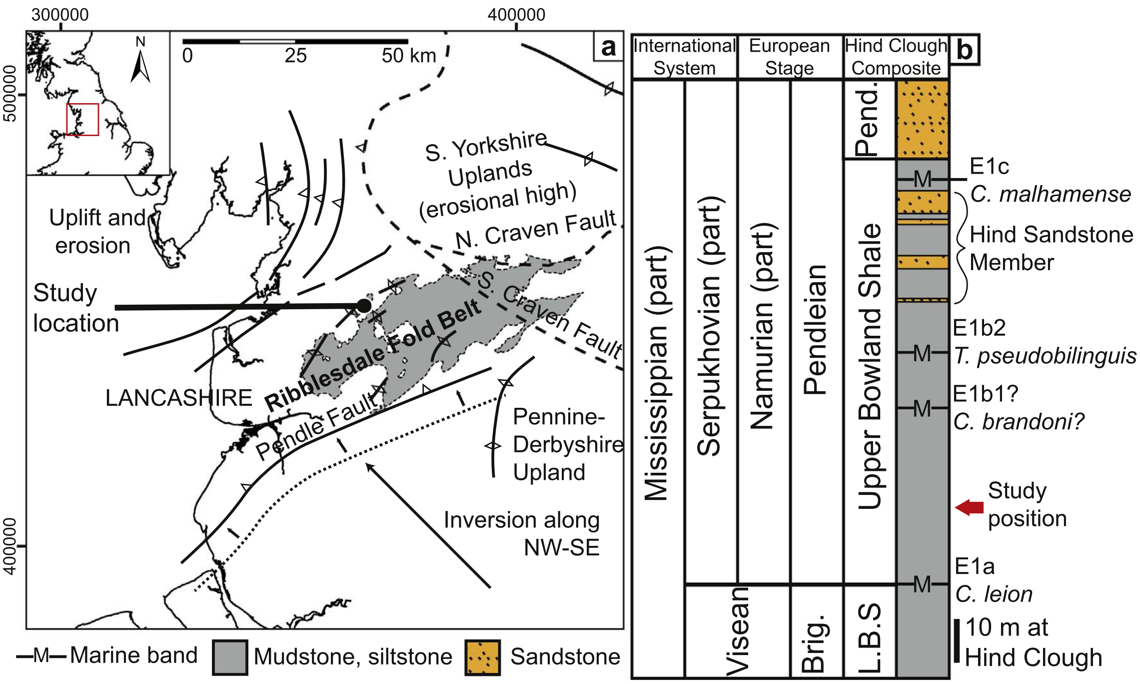

Fig. 1. (a) The Ribblesdale Fold Belt exposes part of the Craven Basin, including the Bowland Shale Formation at outcrop locality Hind Clough (Brandon et al., 1998). Main Westphalian structural elements are also provided (after Fraser and Gawthorpe, 2003). Outcrop extent data are based on DigiMapGB-625, published with permission of the British Geological Survey. British National Grid projection. (b) Craven Basin stratigraphy, Hind Clough (after Brandon et al., 1998; Menning et al., 2006; Waters et al., 2007). Brig. = Brigantian, Arns. = Arnbergian L.B.S = Lower Bowland Shale, Pen. = Pendleton Formation.

timing of hydrocarbon generation between basins. Analysis of outcrop samples can greatly improve the understanding of processes that operated within the Craven Basin to address these uncertainties, but only on the basis that fresh, unweathered samples are available. We delineate the effect of weathering in a temperate climate and assess the nature of weathered zones using a suite of short hand-held drill core samples of the Bowland Shale. We present a suite of Rock-Eval pyrolysis, carbon isotope compositions of OM ($\delta^{13}C_{org}$) and inorganic geochemical data typically used in the characterisation of hydrocarbon source rocks.

1.1. Controls on weathering of organic-rich mudstone

It is often assumed that relatively fresh outcrop samples may be acquired from the outcrop slope if ‘dug out’ from beneath the weathered surface zone (e.g., Littke et al., 1991; Tuttle et al., 2009). However, beyond visual inspection at the outcrop, it is difficult to rapidly assess whether samples are altered due to modern weathering and to estimate the thickness of the weathered zone. Weathering zones develop in response to specific physical and chemical conditions, driven by climate (for example tropical, humid, semi-arid or arctic climatic zones), including vegetation type (e.g., depth of the rhizosphere and water table; Leythaeuser, 1973), and the nature of the protolith.

The protolith may exhibit variable lithology, bulk density, inclination of beds, joints, and fractures, and exposure aspect, for example (e.g., Leythaeuser, 1973). The original concentration of redox sensitive components, such as OM and sulphides (e.g., ‘black’ and ‘grey’ shale), also results in differing rates of weathering through buffering and/or enhancement of weathering (e.g., by development of organic porosity; e.g., Petsch, 2014). The oxidation of these components is therefore a proxy for weathering (e.g., Wildman et al., 2004). Sulphides are considered to be a more useful proxy for weathering than OM because they are a faster electron donor during weathering (Petsch et al., 2000). Since the efficiency of weathering may be highly variable, the thickness of weathering zones varies from several centimetres (e.g., Fischer and Gaupp, 2005), decimetres (e.g., Clayton and Swetland, 1977) to metres (e.g., Tuttle et al., 2009).

Another consideration is whether exposures occur in weathered slopes or stream-cut sections. Away from coastal sections, stream-cut sections are preferred over slope sections. This is because perennial streams are thought to expose unweathered material at the outcrop surface, since the rate of physical erosion by bedrock abrasion is typically greater than the rate of chemical alteration (Small et al., 2015). Yet the assumption that fresh material can be acquired from streams has not been tested.

In this study, samples from two stratigraphically equivalent levels, a perennial stream and an adjacent weathered slope section are compared. We show that the perennial stream exposes fresh mudstone at the outcrop surface, because the rate of bedload abrasion is likely greater than the rate of chemical alteration. Natural fractures are a conduit for oxidising meteoric waters that promote leaching of mudstone adjacent to fractures, but these layers can typically be avoided during sampling or removed during laboratory sample preparation. Weathering on the slope generates bedding-parallel fractures that exploit heterogeneity in the initial sedimentary fabric. Along bedding-parallel fractures, millimetre- to centimetre-scale leached layers and iron oxide coatings are common. We demonstrate *in situ* material recovered from the surface of the weathered slope adjacent to the stream is not the most chemically altered, however, probably because physical weathering processes here dominate over chemical processes at the surface. The most chemically altered mudstone on weathered slopes is found several tens of centimetres into the outcrop, where the rate of chemical alteration is greater than the rate of physical weathering. Material sampled at the surface of the slope is chemically unaltered but potentially represents a biased record driven by the non-random development of fractures associated with initial sedimentary fabric heterogeneity (such as laminae).

2. Geological setting

The outcrop locality, Hind Clough (grid ref: 364430 453210, British National Grid projection), exposes a 124 m thick succession of