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Feasibility of ASD AgriSpec analysis to indicate mineralogy of a potential shale gas reservoir from west Lancashire, UK

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Abstract

Mudrocks rich in organic matter present an attractive exploration target for unconventional gas and oil. The mid-Carboniferous Bowland Shale is considered the principal accumulation of gas-prone shales in the UK. One risk with exploitation of shales is that the rocks may exhibit ductile behaviour and not respond well to hydraulic stimulation programmes. The brittle behaviour of the rock is influenced by mineralogical composition. Approximately 15 m of core from the Bowland Shale, has been used to test the feasibility of using Near Infra-Red (NIR) Spectrometry to characterise the mineralogy of the shale, and compare to analysis using standard XRD techniques.

Keywords: NIR Spectroscopy;Shale Gas;Fracability;Bowland Shale.

1. Introduction

Up until 2008, interest in the petroleum potential of Britain's Carboniferous focussed on conventional oil reservoirs [1] and [2]. Since the advent of commercially viable gas production from shale source rocks in North America during the late 2000's, interest in the UK has concentrated on the Bowland Shale of the Pennine Basin, which underlies large parts of northern England [3]. The Mid-Carboniferous Bowland Shale (northern England) was identified as the principal geological target horizon for shale gas in the UK, hosting an estimated resource of 1300

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Tcf of gas [4] and [2]. It displays encouraging properties: typically 1-3% Total Organic Content; dominant kerogen type III (humic) and II (planktonic), reflecting a marginal marine environment of deposition, with significant input from adjacent emergent highlands [5]. Many basinal areas have, over geological time, had sufficient burial to become gas-mature, with significant thicknesses of shales with Ro values over 1.1% [4]. Where burial has been shallower, some areas of the Bowland Shale may be within the oil window and therefore represent a source of shale oil. Several phases of basin burial and inversion [4] and [6], have left many accumulations of the Bowland Shale in a present-day structural setting where it is at depths over 1000 m, and where in-situ pressures are considered high enough for commercial flow rates to be possible [7]. The Bowland Shale along with older shales of the Hodder Formation is notable as a potential shale reservoir as it's thickness exceeds 3500 m in several basins. This presents a particular challenge in devising exploration strategies that aim to identify the horizons of best potential productivity from these thick accumulations to maximise the resource.

Bedrock material to quantify the Bowland Shale is sparse; material derived from outcrop may be oxidised, and legacy core materials may not have been curated in optimal environments that maintain properties, such as rock strength and permeability, which are representative of present-day in-situ conditions. To date, exploration of the Bowland Shale has been restricted to desk studies, the acquisition of seismic reflection data and the drilling of four partially cored boreholes [8]. This has resulted in a paucity of fresh core material available for sampling and analysis. Currently, the best resolution stratigraphic framework for mid-Carboniferous shales in the Pennine Basin remains biostratigraphy using ammonoid fauna that rapidly evolved during the time that the Bowland Shale was deposited [9]. This relies on the preservation and subsequent identification of conches, which may be scattered throughout a particular interval, and difficult to identify where fragmented. As the identification of ammonoids usually necessitates breaking of core to expose lamiae on which they are preserved, the size of core material available for further testing can be limited.

There is an obvious need to preserve core material wherever possible as it represents a rare dataset that is expensive to acquire. The development of non-destructive core analysis is an obvious way to achieve this; in contrast to techniques such as XRD, analysis of core by infrared techniques provides such an opportunity to quantify the mineral content of shale intervals without destroying valuable core or outcrop material. The development of non-destructive analytical techniques allows for the preservation of core, maximising the scientific potential that can be realised from the available material, and reducing the need for additional drilling to acquire further samples,

Previous studies using Near Infrared (NIR) techniques have focused on the quantification of organic content of oil shale [10], there have also been comparisons of Fourier Transform Infrared (FTIR) with X-ray Diffraction (XRD) in the study of clay mineralogy of shale gas reservoirs [11], but few studies exist using NIR on gas prone shales. The physical properties of the shale (dark colour, density and particle size) make shale and mud rock mineralogical identifications challenging with NIR spectrometry [12]. Spectra are generally quite flat and absorption features are subdued and so automated techniques are not always successful. The manual interpretation of the spectra, which is required to gain an understanding of the mineralogy of the shale, is vital with this type of sample material and key minerals can be detected using NIR spectrometry.

1.2 Objectives

The Bowland Shale is highly anisotropic in terms of variables including: composition; engineering behaviour and resource potential. Gross and local variations in mineralogy may contribute to the development of a chemo-stratigraphy based on the existing biostratigraphical framework. A quick and repeatable method is required to quantify gross and local variations in mineralogy of the shale. The mineralogy of the shale will influence the way in which the shale may respond to hydraulic stimulation. The brittle behaviour of the rock is strongly influenced by mineralogical composition and clay minerals in particular can influence the 'fracability' of the shale [11], essentially the ease with which a rock allows fractures to propagate and stay open. Clay minerals are easily detected using NIR spectrometry as they display distinctive absorption features in the Short Wave Infrared (SWIR) region of the electromagnetic spectrum. NIR spectrometry can be used to rapidly and non-destructively determine the clay mineralogy of the shale.

The objectives of this study were:

1. to determine the mineralogical composition of the shale, in particular clay mineralogy.
2. to compare the results with XRD and visual core logging observations.

R-processing can be used to quantify the minerals detected as the next stage of this research.

1.3 Grange Hill #1 core material

The Grange Hill #1 exploration well was drilled in 2011 near Blackpool (BGS reference number SD33NE/39, National grid Reference: [339181, 438941]), in the central part of the Bowland Basin. The cored interval selected for analysis was from core runs 16 - 22, from 10205 ft to 10255 ft (3111 – 3126 m). This proved a hemi-pelagic accumulation of mudrocks; stratigraphy is provided by [13]; and is interpreted as being from the lower part of the Bowland Shale unit, at a level equivalent to the Pendleside Sandstone of the Bowland Fells [14]. The core material comprises whole and longitudinally slabbed core that is approximately 2.5” (63.5mm) in diameter. Both slabbed sections and natural breaks across laminae provide smooth, flat surfaces that provide sampling sites suitable to accept the ASD Agrispec probe.

2. Methodology

The instrument used was the ASD Agrispec (Figure 1). The sensor measures reflected radiation in the wavelength range from 450nm to 2500nm, from the visible to the near infrared region of the electromagnetic spectrum (Figure 2). The technique is non-destructive and rapid and the instrument is portable so measurements could be acquired in the field if required.

Figure 1: ASD Agrispec assembled for use in the BGS core store

The light source within the spectrometer illuminates the sample causing vibrations within the molecular bonds of minerals present [15]. Certain wavelengths of light are absorbed due to these vibrations and it is the presence of these absorption features which indicate the type of bonds present allowing mineral identifications can be made. These absorptions are seen as minima in the spectra. The molecular bonds activated in the Short Wave Infrared (SWIR) are major constituents of clays, sulphates, carbonates and many other minerals. The wavelength position of the absorption features within the spectra will ultimately determine what minerals are present. For example most clay minerals have absorption features around 1400nm and 1900nm, carbonates have diagnostic features closer to 2300nm (Figure 2). These absorption features are due to the different chemical bonds present within the structures of the different minerals.

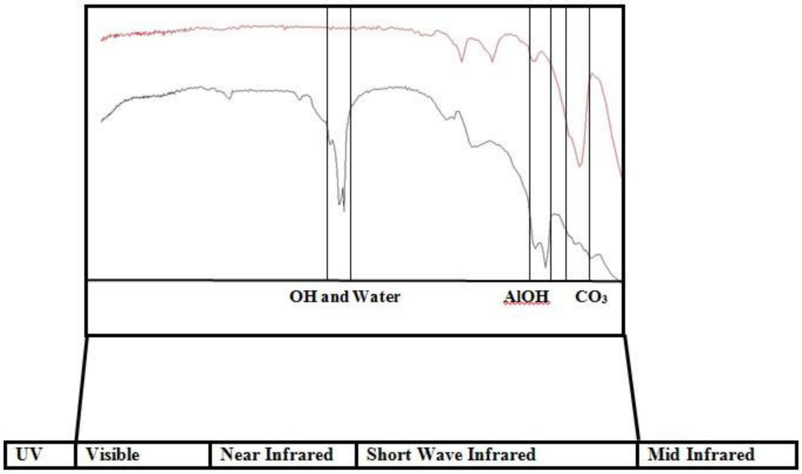

Figure 2: Visible to SWIR region of the electromagnetic spectrum with position of absorption bands for kaolinite and calcite (Adapted from Spectral Interpretation Field Manual, AusSpec International)

To gain knowledge of the spectral responses that can be acquired from shale, several cores have been measured using NIR Spectroscopy. So far Wray, Roosecote and Grange Hill have been measured. This is building up a picture of what minerals can be detected using this rapid, non-destructive technique. The main focus has been the Bowland Shale which makes up the Grange Hill core.

Measurements were taken every 2 to 3 cms with closer sampling acquired at smaller intervals where visible changes in mineralogy were present, in total 263 spectra were acquired over the length of the core. Following acquisition the spectra were converted to text files and imported into ENVI for spectral feature fitting and then manual interpretation. The manual interpretation was required due to the dark nature of the core as few mineral identifications were successful using the automatic feature fitting methods. Darker coloured samples produce lower reflectance and hence less prominent absorption features. Automatic feature fitting tools work best with deep absorption features as shallower features could be mistaken for noise within the spectrum. Visual interpretation is vital where darker samples are measured.

Clay minerals exhibit distinctive absorption features within the visible and SWIR region of the electromagnetic spectrum and these can be used to determine the type of clay present. Existing mineral libraries containing spectra of known minerals are used to compare the position and depth of absorption features which aids identification of minerals within the sample spectra.

Laboratory X-ray Diffraction (XRD) analysis was also produced for sample at regular depths along the length of the core. This was used for comparison purposes and it is planned use it to model confidences in the mineral identifications. Quantitative modelling will also be undertaken to better understand the quantities of the minerals present within the shale.

3. Results

The main focus of the mineral identification was to determine clay mineralogy. Certain clays can inhibit the transport of fluids (including hydrofracturing fluid, flow back water, oil and gas) through the shale and so it is important to know what type, and how much clay, is present with in the shale. Some clay mineral assemblages can also indicate the thermal maturity of the shale. Illite for example is a good indicator for the maturity of the shale as it forms at similar temperatures to hydrocarbons [16]. Table 1 shows the minerals identified through NIR spectroscopy compared to the XRD analysis results.

BH		Depth			SSK	Mineral (wt%)									
						Silicates			Carbonates		Phyllosilicates/clay minerals			Sulphides	
	ASD sample number	ft	ft	m		quartz	plagio clase	K-feldspar	calcite	Fe-dolomite/ ankerite	'mica'	kaolinite	chlorite	pyrite	Minerals identified using NIR
Grange Hill 12 (SD33 NE/37)	gh007 and 008	10206'4"	10206.33	3110.89	59712	57.3	0.6		4.0	0.6	31.1	2.7	0.9	2.9	Very flat - possible muscovite
	gh017 and 018	10209'8"	10209.67	3111.91	59713	44.4			8.7	18.4	23.8	2.1		2.6	Very flat - possible kaolinite
	gh027 and 28	10212'4"	10212.33	3112.72	59714	50.6	0.7	<0.5	0.9	3.8	33.9	4.5	0.8	4.6	Calcite
	gh041	10215'4"	10215.33	3113.63	59715	41.7	1.5			2.3	38.8	6.9	1.3	7.4	Kaolinite and muscovite
	gh052	10217'10"	10217.83	3114.39	59716	41.7	<0.5			1.6	42.3	7.0	1.0	6.2	Kaolinite and muscovite
	gh070	10221'6"	10221.50	3115.51	59717	43.8	<0.5			1.3	36.9	7.0	1.8	8.7	Kaolinite and muscovite
	gh084 and 085	10223'10"	10223.83	3116.22	59718	49.7	0.8			5.2	31.3	5.4	1.6	6.0	Kaolinite and muscovite
	gh095	10226'8"	10226.67	3117.09	59719	39.4	0.6			1.0	39.7	6.7	1.6	11.0	Muscovite
	gh103 and 104	10229'7"	10229.58	3117.98	59720	38.7	<0.5			0.8	45.6	6.6	0.8	7.1	Muscovite
	gh113	10231'10"	10231.83	3118.66	59721	46.3	<0.5			1.6	41.1	5.1	1.1	4.5	Kaolinite and muscovite
	gh119 and 120	10234'	10234.00	3119.32	59722	46.3	0.7			0.6	35.6	7.2	1.5	8.1	Kaolinite and muscovite
	gh126	10236'8"	10236.67	3120.14	59723	48.7	<0.5			1.6	37.2	6.3	1.6	4.4	Kaolinite and muscovite
	gh131	10238'1"	10238.08	3120.57	59724	48.5	<0.5		1.6	1.0	37.0	6.1	1.5	4.1	Muscovite
	gh144 and 145	10241'6"	10241.50	3121.61	59725	46.0	<0.5			5.7	36.4	5.6	1.5	4.4	Kaolinite and muscovite
	gh153	10244'	10244.00	3122.37	59726	41.7	1.1			1.1	42.8	7.2	1.3	4.8	Muscovite
	gh158	10246'6"	10246.50	3123.13	59727	54.8	1.0		<0.5	3.9	28.1	5.6	1.2	5.0	Kaolinite and muscovite
	gh162	10249'5"	10249.42	3124.02	59728	48.2	0.9			2.1	34.6	6.3	1.5	6.4	kaolinite
	gh174	10253'	10253.00	3125.11	59729	38.9				1.0	47.5	4.8	0.9	6.9	Kaolinite and muscovite
	gh180	10254'10"	10254.83	3125.67	59730	51.6	0.8			2.0	32.4	6.7	1.6	4.9	Kaolinite and muscovite

Table 1: Table of minerals identified using XRD and NIR spectrometry

3.1 Minerals identified

3.1.1 Illite and Muscovite

Thermal maturity through illite detection can be quantified by measuring the depth of the absorption feature occurring around 2200nm, in comparison with the water absorption feature at 1900nm. With increasing thermal maturity the absorption feature at 2200nm deepens in relation to the 1900nm feature. Muscovite was detected rather than illite using NIR spectrometry, however, in the Grange Hill core. The absorption feature at around 2200nm was shifted to higher wavelengths, but more diagnostic was the water absorption feature at around 1915nm appearing much shallower than for illite spectra, where the water absorption feature is much more pronounced (Figure 3). This could also be explained by mineral mixing as many minerals will be present and this could also subdue the diagnostic absorption features of illite.

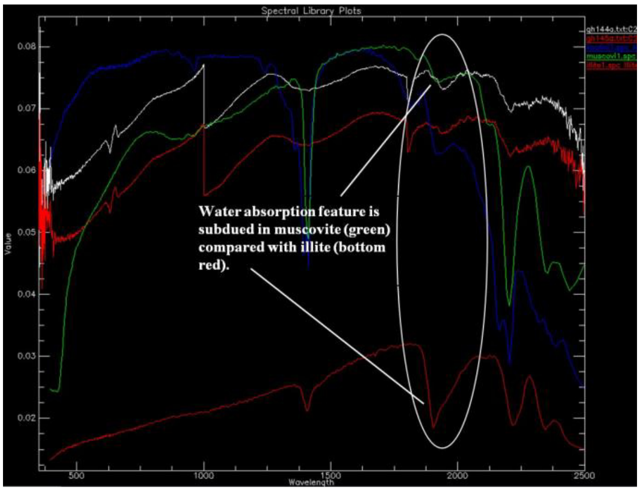

Figure 3: Water absorption feature is subdued in Muscovite compared to illite library spectra and in measured spectra from the Bowland Shale.

3.1.2 Kaolinite

Kaolinite displays two diagnostic double absorption features around 2204nm and 1416nm (Figure 4). The top two spectra present in figure one are reference spectra of kaolinite and kaosmectite from the USGS spectral library. The red coloured spectrum is a sample taken from around 10216'' depth down the Grange Hill Borehole.

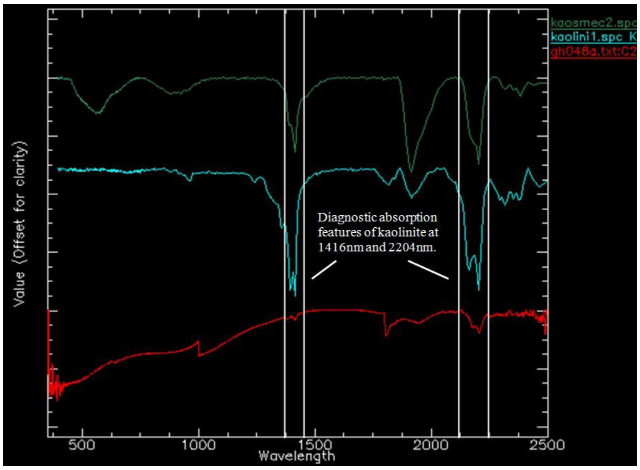

Figure 4: Diagnostic 'doublet' absorption features for kaolinite at 2204nm and 1416nm.

3.1.3 Carbonates: Calcite

Other minerals such as carbonates have also been detected at various depths along the Grange Hill core and two examples are given below. The presence of such minerals can indicate the transition from one deposition environment to another. The upper parts of the core show high amounts of calcite present. This mineral has distinctive absorption features at 2335nm with a shoulder at 2301nm (Figure 5). Calcite has been verified at this level in the core by both XRD and acid testing.

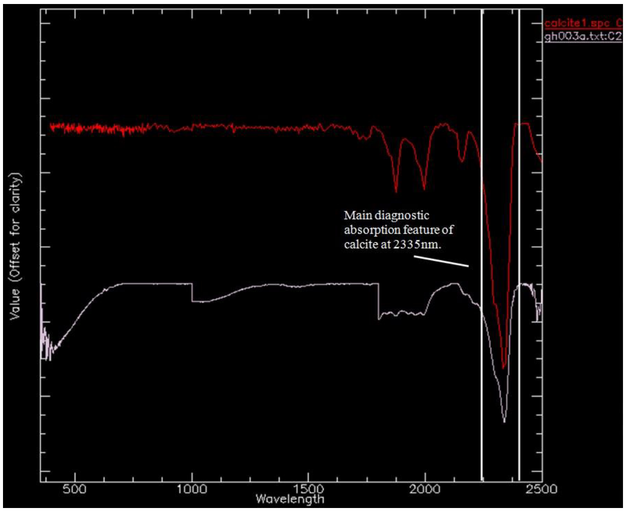

Figure 5: Calcite absorption feature at 2335nm show in both reference spectra (red) and measured sample (white).

3.1.4 Carbonates: Siderite

Siderite has also been identified within a discrete horizon within the core (Figure 6). The presence of siderite is indicated by the wide, shallow absorption feature at 1952nm. It is characterised by visual inspection as a pale brown colouration on the surface of the slabbed core in a diffuse band. Siderite is present in the lower part of the core only.

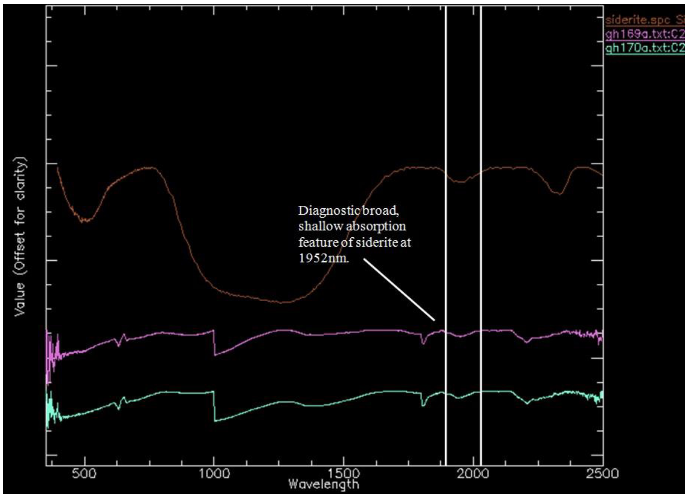

Figure 6: Siderite identified by the wide, shallow absorption feature at 1952nm.

4. Discussion

Variations in carbonate content in Carboniferous-aged shales from the Midland Valley, Scotland, have been identified [17]. In the Grange Hill core calcite is more dominant towards the upper part of the core. The presence of calcite is a strong indicator as to the prospectivity of the shale. Calcite is a brittle mineral and fractures filled with calcite could be reactivated and represent a target for hydraulic fracturing. Calcite also appears further down the core as calcite veins and fracture fills at various intervals. Shales rich in carbonate and quartz (biogenic or detrital) have been described as more prone to exhibit brittle behaviour [18]. Calcite is considered an important mineralogical component that may represent rock of a more brittle nature that could represent targets for hydraulic fracturing.

Kaolinite and muscovite are dominant in the middle section of the core, with occasional calcite veins. The distinction between the different clays is important when understanding how the shale will react under hydraulic fracturing and to also determine thermal maturity. Crystallinity of the clay minerals can point to the thermal maturity of the shale, this can be determined by shifts in the position of the doublets in kaolinite [15] and the depth of the diagnostic illite absorption feature [16].

A change then occurs near the bottom of the core from kaolinite to siderite as the dominant mineral. The presence of siderite is an important observation within the shale, it is an early diagenetic mineral and is an important environmental indicator that has been successfully identified using this technique. The presence of siderite may indicate an influx of more oxygenated waters into the basin at a depth below 10231'3''. If the flushing of the basin was particularly long-lived, it is possible that the benthic zone was oxygenated to such a point that organic matter would be oxidised, and this would have potentially significant impacts on the ability of the organic matter to generate hydrocarbons.

When comparing the XRD results with the spectral interpretation it is clear that there are some discrepancies. The XRD was acquired at regular intervals and so minerals like siderite and calcite have not been detected in the same amounts as using the NIR technique. Clay mineralogy is also different when comparing the two techniques. Illite is detected readily using the XRD but when observing the NIR spectra it is clear that kaolinite and muscovite are present, through the presence of double absorption features (kaolinite diagnostic feature) and a diminished water absorption feature (diagnostic of muscovite).

5. Conclusions

This research shows that ASD AgriSpec analysis can be an appropriate technique to quantify shale intervals, and has been successfully used to identify key aspects of the mineral composition of the Bowland Shale. This includes the identification of muscovite, carbonate minerals, kaolinite and smectite. The presence of these minerals is relevant to:

- palaeo-environmental reconstruction models
- identifying horizons of potentially more brittle behaviour

This technique relies on the availability of clean, dry sample material, which ideally has a surface area large enough and flat enough for the sensor probe to comfortably cover. XRD data is a useful additional dataset as it provides a dataset where confidences and ultimately quantities can be modelled, which is not yet possible using Agrispec analysis alone. Methods for quantifying quantities of the minerals identified, using statistical approaches, will be a further development of this technique.

The technique is rapid, non-destructive, time and cost efficient, and portable. The data being gathered are being used to better understand the complex mineralogy of the shale with greatly reduced laboratory testing.

6. Acknowledgements

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