Grant agreement No. 640979

ShaleXenvironmenT

Maximizing the EU shale gas potential by minimizing its environmental footprint

H2020-LCE-2014-1
Competitive low-carbon energy

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D12.9
Rock library

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WP 12 – Dissemination

Due date of deliverable	31/08/2018 (Month 36)
Actual submission date	31/08/2018 (Month 36)
Start date of project	1st September 2015
Duration	36 months
Lead beneficiary	NCSR'D
Last editor	S.Basu, A.P.Jones & J. Ahmed
Contributors	UCL, UOM, BG Broup
Dissemination level	Public (PU)

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History of the changes

Version	Date	Released by	Comments
1.1	31-08-18	S.Basu	Insert summary of changes made

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Key word list

Gas shale, mineralogy, thermal maturity, porosity, permeability, noble gases, carbon, nitrogen, (Palaeo)-redox/productivity, detrital elements, organic matter

Definitions and acronyms

Acronyms	Definitions
OM	Organic matter
TOC	Total organic carbon
T_{max}	Temperature corresponding to 'S2' peak during Rock-Eval Pyrolysis indicating the hydrocarbon generating potential of the sample.
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
XRD	X-ray diffraction
SEM	Scanning electron microscope

Symbol	*Element*
C	Carbon
N	Nitrogen
He, Ne, Ar, Kr, Xe	Helium, Neon, Argon, Krypton, Xenon (Noble gases) *Systematic behaviour from light (helium) to heavy (xenon) noble gases during physical processes such as diffusion, adsorption and solubility.*
Al, Ti, Zr	Aluminum, Titanium, Zirconium (detrital elements) *Immobile during diagenesis and unaffected by biological processes.*
P, Ba	Phosphorous, Barium (Productivity tracers) *Enrichment due to formation of biogenic apatite and barite.*
Mo, V, Cr, Cu, Zn	Molybdenum, Vanadium, Chromium, Copper, Zinc *Reduced solubility under anoxic (oxygen deficient/free) conditions leading to their enrichment in sediments.*

Elemental ratio	
$^4He/^{40}Ar^*$	*Radiogenic helium (^4He) and Ar ($^{40}Ar^*$) are produced from the decay of uranium-thorium (U,Th) and potassium (K) respectively. Expected $^4He/^{40}Ar^*$ in a sample will depend on the measured U,Th and K content. Any deviation, indicates processes such as diffusional gas loss or secondary fluid infiltration.*
$^{20}Ne/^{36}Ar$	*^{20}Ne and ^{36}Ar have no known radiogenic/nucleogenic sources. Consequently, the $^{20}Ne/^{36}Ar$ in shales is characterized by the composition of air-saturated water (0.13-0.18) from circulating ground water and remnant pore water. Any deviation from this ratio indicates physical processes such as gas-liquid separation, diffusional gas migration etc.*
C/N	Carbon/Nitrogen *Can be used as tracer for the source of OM, but can be fractionated by diagenetic processes leading to preferential N loss.*

Isotopic ratio	
$\delta^{13}C$ (‰)	$[\{(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard}\}-1] \times 1000$ where, the established standard is the Pee Dee Belemnite. *In conjunction with C/N, can be used to trace the source of OM in shales (marine/lacustrine/continental).*
$\delta^{15}N$ (‰)	$[\{(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{standard}\}-1] \times 1000$ where, the established standard is the atmosphere. *Varies with thermal maturity or redox*

	depositional conditions of shales.
$^{40}Ar/^{36}Ar$	*Higher than atmospheric $^{40}Ar/^{36}Ar$ (~295.5) related to radiogenic $^{40}Ar^*$ from ^{40}K in clay minerals.*

1.   Introduction

Gas shales samples from three cores in East Texas US from the Haynesville-Bossier formation, have been made available to UCL and UOM by BG group for research purposes and are now stored in a corehouse in Wales. These samples are available for dissemination to the wider scientific community (contact: Prof: A.P.Jones & Prof. K. Taylor). This report is a brief summary of the available samples with related geological and geochemical information obtained by standard analytical techniques as well as recent developments pertaining to simultaneous carbon, nitrogen and noble gases' elemental and isotopic analyses of bulk rock samples. This report will aid researchers in appropriate selection of these samples for future studies based on existing characterisation. It will also provide a baseline for comparison with other potential European gas shales with respect to these well-characterised shales, already exploited successfully for natural gas. (12.9; rock library catalogue).

Findings reported here build on collaboration with industry (BG Group) in terms of sample provision, research sponsorship as well as scientific input and have implications towards improving our understanding of rock-fluid interactions and fluid transport in shales. The results are being used to improve our understanding of European shales by better characterisation, using new methodology developed that were successfully tried on these American shales. The goal of this deliverable is to leave a legacy for the ShaleXenvironmenT project, by allowing future researchers to access rock samples and continue the investigations pioneered by this consortium.

This 'rock library catalogue' aims to disseminate results from our study of American shales to a wider scientific community. In addition, this documentation of the gas shales stored in the Wales storehouse, aims to leave a legacy on shale rocks for future researchers beyond the termination of this project.

1.1   General context

The Bossier-Haynesville shales from the East Texas Basin was deposited during the Jurassic period (156 – 145.5 million years ago). Their deposition is related to the opening of the Gulf of Mexico province following the breakup of Pangea and the separation of North and South America during the Triassic [1]. The formation is hydrocarbon bearing and can produce large amount of natural gas. It has been well studied for geology and geochemistry for standard gas shales' parameters using conventional techniques [*e.g.* 1,2]. Consequently, shales from this formation provide an opportunity for testing and advancement of existing techniques as well as developing new ones, in the backdrop of existing data. This enabled building up of the database for gas shales in general, and the Bossier-Haynesville shales in particular. Further, new analytical technique and protocol developed using these well characterized shales is being applied to other potential European shales (e.*g.* Bowland shale, UK; Ten Boer-Red Beds, Netherland; Westphalian shale, Germany) for characterisation and better understanding of sources and fluid loss/retention.

The shale samples available are from three wells, namely Hewitt Land (HL: 3453 – 3598 m), Jarvis East (JE: 3542 – 4037 m) and Brazell (BL: 3589 – 3657 m). The cores are available as whole/slabbed/wax-wrapped at different depths. They are generally well preserved, but sometimes affected due to their friable nature. Samples from Bowland shale has been collected from several outcrops and three boreholes, catalogued using ammonoid indices (see attached catalogue).

1.2   Deliverable objectives

The primary objective of this deliverable is to establish a legacy for the ShaleXenvironmenT project, by establishing a library of shale rock samples available to future researchers. UCL had the objective of taking ownership of rock samples from the BG Group (shale gas samples from North American formations) and to augment it with samples from Europe (predominantly UK).

Develop and improve technology and standardize protocol for better characterisation of potential gas shales [3].

Provide a database of gas shales from three cores preserved in Wales warehouse for future research.

Identify best storage practices of shale cores and sample retrieval techniques to obtain unaffected samples for analyses.

2.   Methodological approach

Gas shales have been studied for preliminary characterisation in terms of mineralogy, OM, porosity and permeability by standard techniques. The mineralogy of the shales have been constrained using XRD and petrographic studies. Rock Eval pyrolysis has been used to characterize the OM in terms of kerogen type and thermal maturity. Gas-filled porosity was determined on the samples as received while dry helium porosity was measured on crushed material. Permeability was determined by dry press decay on crushed material. Major, minor and trace elemental analyses by ICPAES and ICPMS have been used to constrain palaeo-depositional conditions.

A new technique has been developed to analyze carbon, nitrogen and noble gases simultaneously in bulk shales by combusting 5 to 10 mg of sample from 200 to 1400°C, incrementally at steps of 100°C each (Basu et al., 2018). Different components were decoupled and released at different temperature steps, aiding in characterizing source(s) of OM and also constraining processes of fluid losses.

3.   Summary of activities and research findings

Table 1: Average values of conventional parameters for gas shales with ranges in parenthesis.
Depth of analyses corresponds to HL – 3459-3582 m; JE – 3560-3724 m; BL – 3594-3656 m. N denotes the number of samples analyzed.

	HL (N=24)	**JE** (N=24)	**BL (**N=11)
Mineralogy (%)	Clay-46 (40-58)	*Clay-12 (3-21)	Clay-46 (40-58)
	Carbonate-14 (5-22)	*Carbonate-67 (22-93)	Carbonate-14 (5-22)
*Comment - The clay is mostly illitic while the carbonates are calcitic. Quartz, pyrite K-feldspar, plagioclase and apatite also present. *Corresponding depth of analyses of six samples: 3982-4012m.*			
Thermal maturity $(T_{max}$ - °C)	^{Y}438 (312-531)	318 (307-352)	N.A.
Comment - Immature OM in JE lacking hydrocarbon potential. ^{Y}Unreliable data as non-volatile OM content too low. N.A. Not analyzed.			
Porosity (% of bulk volume)	8.9 (3.4-10.4)	6.3 (4.2-7.9)	11.2 (4.2-14.4)
Comment - Not correlated with TOC suggesting that the pore spaces are not solely confined to OM.			
Permeability *(md)*	1.6 (0.7-3.2) [x 10^{-5}]	6.8 (0.004-69) [x 10^{-3}]	3.4 (0.5-24) [x 10^{-4}]
Not correlated with porosity. Possibly related to natural fractures present.			
TOC *(wt. %)*	1.7 (0.6-2.7)	1.3 (0.3-2.7)	$^{^}$1.5 (3592 m)
			$^{^}$3.4 (3630 m)
Comment - Increases with depth related to oxygen depletion. $^{^}$Corresponding depth of analyses indicated in parentheses.			

Table 2: Average values of trace elements for gas shales with ranges in parenthesis.
Depth of analyses corresponds to HL– 3465-3593 m; JE – 3542-3726 m; BL – 3592-3656 m.

	Element	**HL** (N=23)	**JE** (N=26)	**BL** (N=20)
Detrital influx *(%)*	Al	10(8-45)	10(3.5-32)	8.5(1.1-7.9)
	Ti	0.4(0.3-0.5)	0.4(0.2-0.5)	0.3(0.1-0.4)
	Zr(ppm)	197(135-902)	204(25-642)	158(21-523)
Comment - Detrital influx low for JE. Variation with depth for BL.				
Productivity indicators *(%)*	P	0.04(0.005-0.1)	0.3(0.005-1.9)	0.02(0.004-0.04)
	Ba	0.1(0.04-0.4)	0.4(0.04-3.1)	0.2(0.05-0.7)
Comment - Ba/Al and P/Al indicate high productivity particularly for JE.				
Redox indicators *(ppm)*	Mo	7 (1-69)	10 (2-31)	18 (3-51)
	V	144 (104-564)	145 (40-480)	194 (24-558)
	Cr	109 (76-451)	123 (41-406)	117 (15-418)
	Cu	21 (10-30)	28 (4-91)	23 (9-55)
	Ni	44 (28-91)	35 (15-52)	54 (23-91)
	Co	43 (11-142)	25 (10-70)	24 (4-54)
	Zn	332 (52-4423)	103 (21-195)	195 (31-546)
Comment - V/Cr, Cu/Zn and Ni/Co indicate deposition under oxic conditions.				

Table 3: Average values of C, N and noble gases for gas shales with ranges in parenthesis.
Depth of analyses corresponds to HL – 3459-3582 m; JE – 3560-3724 m; BL – 3594-3656 m.

Element		HL(N=7)	JE(N=7)	BL(N=5)
C	C (wt %)	2.7(2.1-3.5)	2.1(0.7-3.6)	3.4(1.9-6.0)
	$^{\Upsilon}\delta^{13}C_{organic}$ (‰)	-29(-34 to -25)	-26(-29 to -22)	-28(-38 to -20)
	$^{\Upsilon}(C/N)_{organic}$	38(15 to 295)	19(10 to 145)	16(8 to 85)
Comment - Continental source and/or fractionated marine OM. Evidences of methanogenesis.				
N	N (ppm)	1360(530-2755)	558(375-750)	950(600-1160)
	$\delta^{15}N_{bulk}$ (‰)	0.2(-2.0 to 5.3)	3.8(0.8 to 8.1)	1.2(-3.7 to 6.4)
Comment - N fractionated, bulk composition not related to thermal maturity or depositional conditions and should be used with caution for related interpretation.				
Noble gases	$^{40}Ar/^{36}Ar$	2700(1900-4170)	3000(950-6300)	890(450-1500)
	$^{20}Ne/^{36}Ar$	19(3-36)	20(3-54)	N.D.
	$^{4}He/^{40}Ar^{*}$	0.4(0.2-0.5)	2.1(0.1-13.3)	1.8(0.1-6.4)
Comment - Lower $^{4}He/^{40}Ar^{*}$with respect to expected values suggests gas loss by diffusion. Higher $^{20}Ne/^{36}Ar$ compared to expected, imply possible loss of a fluid phase with preferentially dissolved ^{36}Ar.				

$^{\Upsilon}$ Corresponds to the component released at 200 and 1000°C during incremental step combustion.
N.D. Not detected.

4.   Conclusions and future steps

Gas shales can be characterized using a combination of 'conventional' and 'unconventional' techniques. The conventional techniques already used as standard for gas shale evaluation, indicate palaeo-depositional conditions of the shales and their natural gas generating potential. The unconventional techniques focus on better source characterisation and identification of fluid/volatile movement leading to gas loss. The methodology can be applied to other gas shales for their evaluation.

In future, geochemical characterisation of wrapped cores including gas extraction and analyses from the central portion will focus on identification of any sample modification and gas loss of unwrapped cores post retrieval and during storage. There will also be a target to identify scope for development of a facility for long-term preservation of shale cores already available and, that expected to be retrieved during ongoing and future shale gas exploration.

This deliverable makes available a selection of shale rock samples on which future researchers can continue the work pioneered by the consortium ShaleXenvironmenT.
If interested in obtaining core shale samples, please contact: Prof. Adrian Jones (adrian.jones@ucl.ac.uk) and/or Prof. Kevin Taylor (kevin.taylor@manchester.ac.uk).

5. Publications resulting from the work described

S. Basu, J. Ahmed, A.P. Jones, A.B. Verchovsky (2018). Characterisation of carbón components and their isotopic composition in gas shales. *Energy Procedia* 146: 47-52.

S. Basu, A.P. Jones, A.B. Verchovsky, J. Mcquilken (2016). Noble gases in gas shales: Implications for gas retention and thermal maturity. *PETEX* 28.

S. Basu, A.P. Jones, A.B. Verchovsky (2016). Noble gases in gas shales: Implications for gas retention and circulating fluids. *Geophysical Research Abstracts* 18: 15169.

S. Basu, A.P. Jones, A.B. Verchovsky (2016). Understanding gas shales using inorganic, ternary geochemical systematics. *Geophysical Research Abstracts* 18: 15752.

6. Bibliographical references

1. P. Mainali (2011). Chemostratigraphy and the Paleoceanography of the Bossier-Haynesville Formation, East Texas Basin, TX and LA. *Geophysical Unpublished MS thesis* The University of Texas at Arlington: 90 pp.

2. K. Ratcliffe, J. Kharrazi, D. Spain (2013). Chemostratigraphy of the Haynesville Shale. *AAPG Memoir* 105: 137-154.

3. S. Basu, A.P. Jones, A.B. Verchovsky (2013). A New Strategy for Identifying Shales with High Gas Retention using Noble Gas, Nitrogen and Carbon. *Mineralogical Magazine* 77(5) 667.