

# De-risking unconventional hydrocarbon exploration through novel biogeochemical approaches: towards a systematic understanding of organic matter processes in the subsurface and their impact on the environment (Ref IAP2-18-170)

**Institute of Life and Earth Sciences, Lyell Centre, Heriot-Watt University**

**In partnership with Newcastle University, British Geological Survey**

## Supervisory Team

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## Key Words

**Shale gas; mobilisation of pollutants; dissolved organic carbon; microbial activity, environmental risks**

## Overview

Shale gas is a major new energy source but is yet to be commercially exploited in Europe. Depending on how this opportunity develops, the new source of gas could contribute to decarbonising of energy with the potential to support the transition to a localised hydrogen economy. Experience from commercial operations in North America, however, have shown that in-situ microbial activity and associated fluid-rock interactions can result in the unintentional mobilisation of harmful elements (e.g. heavy metals, hydrogen sulphide, and naturally occurring radioactive material, NORMs) in flowback water that will require additional processing to prevent impacts on near-surface/surface environment, and treatment. What is less known is if organic contaminants of environmental concern (e.g. PAHs) are associated are also mobilized, adding to environmental issues, and how these contaminants are possibly linked to the sources and preservation of organic matter in the shales.

All these challenges are of key for shale gas exploration in the UK and worldwide. The project will improve the understanding of the importance and impact of microbial action in the subsurface and how they may

affect the development of new subsurface technologies; this is key to the NERC large capital UKGEOS program, which provides a unique framework at the interface between science and industry.

Recent pioneering research at the Lyell Centre at Heriot-Watt University (HWU) has shown that by characterising the dissolved organic carbon (DOC) of water extracts using LC-OCD-OND (Fig. 1) from a variety of black shales and coals the geological ages, source and depositional environments (kerogen types), and thermal maturation levels can be determined, taking earlier work forward (Wilke et al., 2015; Zhu et al., 2015). Furthermore, shale environments subjected to hydraulic fracturing have been found to be able to host active microbial communities, despite the injection of biocides with the hydraulic fracturing fluids. This microbial community may be stimulated or suppressed by the introduction of oxygenated waters, organic compounds within the hydraulic fracturing fluids or by the release of natural DOC from the formation during hydraulic fracturing. The complex interactions between the fracturing fluids, formation minerals and microbes that maybe simulated during hydraulic fracturing have the potential to enhance the release of inorganic and organic contaminants of environmental concern (e.g. heavy metals, NORMs and

PAHs; He et al., 2017) as well as to enhance mineral precipitation (Jew et al., 2017), the production of H<sub>2</sub>S (Booker et al., 2017) and other undesirable substances. These changes can result in the reduction of pore space connectivity, the biocorrosion of infrastructure and the degradation of reservoir hydrocarbons. Ultimately, a thorough understanding of flowback and produced waters composition is critical to assessing their environmental risks and their effective treatment.

Our initial pioneering work has demonstrated that the quantity, composition, molecular size and structure of the DOC from rock-water experiments allow improved understanding of these subsurface processes, through separating and characterizing classes of DOM with different reactivities and properties. By pairing DOC characterization with inorganic analysis, surface imaging and microbial community analysis this project aims to determine the mechanisms by which DOC, metals and sulphur are released during hydraulic fracturing. Additionally, the selected student will explore whether the released DOC can stimulate microbial sulphur reduction and hydrogen sulphide production, which can lead to increased environmental risk, once transported to the surface.

With this scope this project sets a new theme of research, with a large potential to grow to more sophisticated experimental designs (high pressure and temperature experiments).



Figure 1: LC-OCD-OND (Liquid Chromatography/ Organic Carbon Detection/ Organic Nitrogen Detection) provides innovative solutions for characterisation of Natural and water-soluble organic matter (OM) and DOC (Dissolved Organic Carbon) and DON (Dissolved Organic Nitrogen) in natural and technical waters.

This project combines the expertise and capacities of three strategic partners, Heriot-Watt University (organic geochemistry/microbiology), Newcastle University (inorganic geochemistry/imaging) and BGS (strategic link to UKGEOS/industry, as well as geochemistry) offering a joined opportunity for integrated research between fundamental science that is directly relevant to the new UKGEOS program and its industrial partners in the UK. It is anticipated that the outcomes of this project will be applicable to the energy industry and inform the environmental debate.

We propose a detailed study combining a wide range of disciplines (organic & inorganic geochemistry, sedimentology, microbiology). A simplified workflow will include:

1. Characterize shale (XPS, digestions, XRD).
2. After leaching, recharacterize the shale to determine what changes occurred in the mineralogy and pore space (XPS, digestions, XRD).
3. Characterizing the fluids post-leaching (LC-OCD-OND, GC/GC-MS, ICP-MS, IC, LC-MS).
4. Test whether and which microbes grow on the leachates (incubation experiments, qPCR).

Fundamental questions that will be addressed include:

- What compounds (organic and inorganic) are leached from these source rocks during hydraulic fracturing and at what rate?
- How does burial depth affect what is leached? How does the distribution and habitat of reactive minerals affect their leachability?
- Does the leached water have an effect on the subsequent formation they pass through?
- Do leachates stimulate unwanted microbial activity?
- What contaminants of environmental concern are potentially transported to the surface and how can they be mitigated?

The proposed research will inform the assessment of production cost, potential environmental/HSE risks associated with subsurface fracking, and inform the selection of treatment of flowback waters. The techniques and understanding developed will be relevant to all shale systems, with outcomes contributing to strategies to de-risk impacts associated with subsurface element mobilisation and the optimisation of subsurface resource in potential, developing and established shale targets across the world.

## Methodology

The project will involve broad and hands on training in organic and inorganic geochemistry, molecular microbiology, and imaging. New skills and experiences learned will include a selection of experimental extraction methods (incubation experiments), analysis of organic matter composition (Rock Eval Pyrolysis, LC-OCD-OND, GC and GCMS), quantification and spatial distribution of heavy metals and sulphur speciation (ICP-MS, ICP-OES, IC, LC-MS, XPS), and molecular microbiology (next generation sequencing and qPCR).

With direct context to the shale gas potential in the UK, the chemical composition of Carboniferous formation waters will be sourced by the BGS, using data from one of the UKGEOS sites (Cheshire/Glasgow) and/or a commercial operator. This will enable experiments on the Bowland Shale to

be calibrated using fluid chemistry representative of in-situ conditions.

Collaborative support and in-kind contributions will come from the BGS in the form of the identification and provision of appropriate samples of Bowland Shale; these will come from borehole core/cuttings from recently drilled exploration boreholes and be as far as practicable representative of the range of shale lithologies present in the Bowland Shale. BGS will further supply the geological context for these samples, allowing results of microbial, geochemical and image analysis to be understood in a geological context of sedimentation, burial history and current subsurface setting.

In addition to the work on the Bowland Shale, some small field work components may emerge throughout the project. They will however not be critical to overall success as shale samples for this project have already been secured through ongoing industry projects, including BGS (Bowland), Statoil (Eaglesford), and Shell (Jordanian Oil Shale, Tarfaya-Morocco). All samples are held within the Lyell Centre.

Utilising such a diverse selection of shale samples will allow comparisons to be made between resources in the US that are commercially exploited, and shales that are being explored (UK) and not currently considered for exploitation (Morocco).

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## Timeline

The general timeline of the project is shown below, however, we plan to build in flexibility to be able to respond quickly to any opportunities arising:

**Year 1:** Literature review, sample acquisition, laboratory training, optimization of analytical protocols, start with sample analysis.

**Years 2 and 3:** Conduction and completion of sample analysis with research visits to Newcastle and BGS Keyworth.

**Year 3.5:** Data integration, thesis completion, papers for international journals.

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## Training & Skills

As part of an IAPETUS2 studentship cohort, you will receive bespoke training, exclusive to the program.

Beyond the generic skills training at Heriot-Watt's Graduate School, you will gain specialist experience in organic and inorganic geochemistry, inorganic and

isotope geochemistry, and microbiology, providing a unique and broad skill set targeted at oil/gas and environmental careers, both in the commercial sector and in academia.

This project directly aligns and contributes to the UKGEOS mission, providing knowledge of interest to academia, industry and regulators. The research builds on existing Lyell Centre industry projects. The capacity building provided as part of this project will prepare the successful student with a unique set of skills that will assist in the management of resources and will inform policies with regard to environmental responsibility throughout the lifecycle of unconventional energy production.

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## Further Information

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