



Application of Analytical Techniques to Petroleum Systems Problems

February 28th – 1st March 2017

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Application of Analytical Techniques to Petroleum Systems Problems

February 28th – 1st March 2017
Geological Society of London, Petroleum Group
Burlington House, London,

Welcome to Application of Analytical Techniques to Petroleum Systems Problems conference, which has been organised by the Petroleum Group of the Geological Society. In this booklet you will find the programme and abstracts for all of the talks and poster presentations over the two days of the conference. Information on the conference can also be found on the Petroleum Group Conference App.

The organising committee would like to thank the conference sponsors for their support of this event. The Petroleum Group and the Geological Society would not be able to continue to organise events of this scale without continued industry sponsorship.

Maximising existing production from known petroleum systems and identifying new plays despite economic constraints requires continued industry innovation. Various analytical techniques can provide insight into rock properties and improve understanding of how multiphase geochemical systems form and develop through geological and production timescales. Petroleum systems comprise a broad range of components and processes, from source, reservoir and seal development through to the generation, migration and accumulation of hydrocarbons. This conference therefore covers a wide range of topics. The conference theme of *imaging* will look at X-ray CT, SEM and automated mineralogy techniques and how they can be used to better understand the physical properties of rocks. The theme of *isotopes* will consider the use of 'traditional' radiogenic and stable isotopes in age dating of rocks and fluid generation, and more recent advances in the use of clumped isotopes and how this technique can be applied to geological systems. The *geochemistry at varying scales* theme examines chemostratigraphic, experimental, spectroscopic, organic and fluid analytical techniques from the wellsite, the outcrop and the laboratory. The *case studies and applications* theme evaluates how a range of techniques can be applied to solve complex petroleum systems problems.

Our thanks go to the Geological Society staff for their help and organisation, particularly Sarah Woodcock and Laura Griffiths for all of their hard work. The committee would like to take this opportunity to thank all contributors for their abstracts, presentations and posters, particularly the keynotes for committing to the conference early on in its development. Finally a very big thank you to all conference attendees; we hope that you will find the conference interesting, have an opportunity to exchange ideas and learn something new.

Convenors:

Patrick Dowey (University of Manchester)
Mark Osborne (BP)
Kevin Taylor (University of Manchester)
Herbert Volk (BP)
Christopher Veale (BP)

Reference:

Abstracts of '*Application of Analytical Techniques to Petroleum Systems Problems*', Petroleum Group of the Geological Society of London, Burlington House, London, UK, 28 February-1 March 2017

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PROGRAMME

CONFERENCE PROGRAMME

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10.00	Registration
10.25	Welcome
Session One: Imaging	
10.30	Keynote: Joanne Fredrich (BP) Image-Based Modeling & Simulation: Applications in Reservoir Characterization and Performance Prediction
11.00	Jenny Omma (Rocktype Ltd) Introducing Big Data Petrography: QEMSCAN based rock characterisation
11.20	J. Buckman (Heriot Watt University) Workflow model for the digitization of shale rocks
11.40	Break
12.00	Eddy Hill (Carl Zeiss X –ray Microscopy) Solving petroleum problems using the frontiers of imaging technology: Multiscale, correlative and in situ techniques
12.20	Andrew Fogden (FEI) 3D micro-CT imaging of the pore-scale distribution of oil, brine and air in place in reservoir shales and in sandstones after low salinity flooding, and relations to local mineralogy
12.40	Mark Osborne (BP) Understanding variations in reservoir porosity in the Eagle Ford shale using scanning electron microscopy- Implications for basin modelling
13.00	Lunch
Session Two: Isotopes	
14.00	Keynote: Cédric M. John (Imperial College London) Applications of clumped isotopes to the petroleum industry: a critical review
14.30	Richard H Worden (University of Liverpool) Compound specific sulfur isotopic analysis of organosulfur compounds to help reveal genetic links between the Lower Paleozoic oil fields from the Tarim Basin, NW China
14.50	Andrew C. Aplin (Durham University) Unravelling quartz, calcite and dolomite cementation histories in sandstones with in situ microanalysis of oxygen isotopes
15.10	Luca Mascheroni (Geolog Srl) Real time carbon isotopes analysis
15.30	Break

16.00	Junjie Liu (Durham University) Constraining the timing of oil generation and oil-source fingerprinting via the rhenium-osmium isotope system: Implications from the Duvernay Petroleum System, Western Canada Sedimentary Basin
16.20	P. C. Smalley Constraining Carbonate Cementation in Clastic Reservoirs Using Clumped Isotopes: A case study from the Bruce Field, UK North Sea
16.40	R. Honlet (KU Leuven) A novel approach to geobarometry by combining fluid inclusion (Th) and clumped isotope ($\Delta 47$) paleothermometry in hydrothermal dolomite (Cantabrian Zone, Northern Spain).
17.00	Claire M. Veillard (Imperial College London) Combining two novel methods for reservoir characterization: what can clumped isotope geochemistry and micro-CT imaging reveal about early dolomitization?
17.20	Finish
17.20	Wine Reception

Day Two	
08.30	Registration
	Session Three: Applications/Case Studies
09.00	Keynote: Brian Horsfield (Potsdam) Using pyrolysis techniques and high resolution mass spectrometry (FT-ICR MS) to evaluate the impact of fluid retention on bulk petroleum properties in shale
09.30	Nicolas Ville (BP) Implementation of advanced analytical technics at the wellsite: learnings from surface data acquisition, benefits and pitfalls
09.50	Scott Brindle (CGG) Application of automated mineralogical and textural data to rock physics models: A novel approach for generating wireline-equivalent elastic and mechanical properties from core and drill cuttings.
10.10	Gavin Hunt (Spectra-Map Ltd) The application of imaging IR spectroscopy for mineralogical analysis of core and cuttings
10.30	Break
11.00	Keynote: Pim van Bergen (Shell) Production Geochemistry – Fluids don't lie and the devil is in the detail
11.30	D. Misch (Montanuniversitaet Leoben) Source rock assessment from basin- to nano-scale: A case study from the Ukrainian Dniepr-Donets Basin
11.50	Claudio Delle Piane (CSIRO) A multi-disciplinary approach to the evaluation of thermal alteration of mineral and organic components of the Marcellus Shale. Analytical results and implications for transport properties.

12.10	Richard Kempton (CSIRO) Using fluid inclusions to trace petroleum systems – a integrated case study of oil and gas migration in the Bight Basin to constrain source, composition and timing.
12.30	Lunch
	Session Four: Geochemistry at Varying scales
13.30	Keynote: Clifford Walters (ExxonMobil) Organic geochemistry at millimeter to Ångstrom resolution
14.00	Herbert Volk (BP) Using petroleum inclusions to trace petroleum systems – a review
14.20	Stuart Jones (Durham University) Chlorite, chlorite everywhere but not an understanding on why it controls porosity? An HPHT experimental study of sandstone reservoir quality.
14.40	Patrick Whitelaw (BGS) Convergence of shale gas reserve estimates from a high pressure water pyrolysis procedure and gas adsorption measurements
15.00	Break
15.30	M. Barbarano (Chemostrat) Raman Heavy Mineral Analysis for understanding sediment provenance and reservoir heterogeneities in fluvial successions and optimising hydrocarbons production.
15.50	Andrea Schito (Università degli Studi Roma Tre) Raman spectroscopy: a new tool for the analysis of thermal evolution of amorphous organic matter rich kerogen in diagenesis
16.10	Mohinudeen Faiz (Origin Energy) Gas isotope fractionation in source rocks and implications for petroleum exploration
16.30	Will Meredith (University of Nottingham) Origin of solid bitumen in the Elgin/Franklin complex of the Central Graben
16.50	Finish

Poster Programme Day 1

<p>Lin Ma (University of Manchester) Multi-scale 3D quantification of an organic-rich mudstone, the Carboniferous Bowland Shale</p>
<p>John Ford (CGG) Reservoir quality assessment using QEMSCAN®: Quantification of authigenic kaolinite and its relationship with pore networks.</p>
<p>Joyce Schmatz (MaP - Microstructure and Pores GmbH) Multiscale visualization of fluid-fluid-mineral interfaces and pore connectivity using Cryo-BIB-SEM and Liquid Metal Injection: A case study on re-saturated North Alpine Foreland Basin sandstone.</p>
<p>Arjen Mascini (Thermo Fisher Scientific) Multiscale characterization of North Sea chalk samples using micro X-ray computed tomography and focused-ion beam scanning electron microscopy.</p>
<p>Richard H Worden (University of Liverpool) Improved Imaging and Analysis of Chlorite in Reservoirs and Modern Day Analogues: New Insights for Reservoir Quality</p>
<p>Duncan Pirrie (Helford Geoscience LLP) Automated mineral analysis; lithological, petrographic and diagenetic evaluation of well cuttings</p>
<p>Alex Finlay (Chemostrat) Oil generation West of Shetlands: Insights from Re-Os geochronology</p>
<p>David Selby (Durham University) Constraining the timing of oil and gas generation: Insights from Re-Os geochronology and Apatite Fission Track analysis in the Neoproterozoic-Palaeozoic reservoirs, South China Block</p>
<p>Zeyang Liu (Durham University) Investigation into the Controls of Rhenium-Osmium Fractionation in Organic-Rich Sedimentary Rocks: Implications for Re-Os Geochronology</p>
<p>Maria Gusarevich (Imperial College) Thermal history of Resolution Guyot using paired clumped isotopes and radiogenic isotopes in Cretaceous carbonates</p>
<p>Ruth Davey (Imperial College) Shale Gas: Deciphering the Isotopic Code</p>
<p>Chen Jin (Heriot-Watt University) Registering Scanning Electron Microscopy (SEM) and X-Ray Tomography (XRT) images for pore-grain characterization of cross-laminated siliciclastic rock samples</p>

Poster Programme Day 2

<p>Julien Bourdet (CSIRO) Gas, salinity and temperature evolution of formation water in gas-rich basins</p>
<p>D. K. Muirhead (University of Aberdeen) Making oil from Magma</p>
<p>Glenn T. Morrall (University of Liverpool) A Multidisciplinary Re-assessment of Calcite Cement in Brent Reservoirs, Heather Field, Northern North Sea</p>
<p>Michael J. Flowerdew (CASP) Dates through the ages: mineral fertility and bias in sedimentary provenance studies and some examples of how these may be identified and reduced.</p>
<p>Adrian Neal (Badley Ashton and Associates Ltd) Detailed characterisation of deepwater reservoir heterogeneity using automated core mapping tools.</p>
<p>T. Morgan (Chemostrat) Zircon geochronology, improving the understanding of the provenance of the Upper Carboniferous/Lower Permian sandstones in the SNS</p>
<p>Nipada Santha (Durham University) CFM study of brine effect on adhesion of silica face kaolinite</p>
<p>D. Gross (Montanuniversitaet Leoben) Maturity and facies effects on the abundance of acidic compounds in Upper Visean black shales from the Dniepr-Donets Basin (Ukraine): Source rock characterization via electrospray ionization fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR-MS)</p>
<p>Marianne Nuzzo (Integrated Geochemical Interpretation Ltd) Hydrocarbon and noble gas geochemical survey in a mud volcano province: Insights into oil-water-gas interactions and gas hydrate occurrences in the subsurface</p>
<p>Markus Doerner (University of Bergen) OG analytical methods in the Petroleum industry - Enhanced data density and method flexibility by multiple detector GC coupling</p>
<p>Reem Aboushoug Using old analytic techniques to generate new ideas: Satal Formation, Sirt Basin, Libya</p>

Oral Presentation Abstracts (Presentation order)

Tuesday 28th February

Session One

Imaging

Keynote: Image-Based Modeling & Simulation: Applications in Reservoir Characterization and Performance Prediction

Joanne Fredrich

BP Upstream Technology, Sunbury, UK

The premise of 'Digital Rocks' is to apply state of the art high-resolution 3D imaging technologies to derive digital descriptions of reservoir rocks which can be applied in Direct Numerical Simulations. These simulations can be interpreted to derive macroscopic static and dynamic rock properties, as well as improve understanding of pore-scale transport and displacement processes.

Whilst a vast number of scientific research papers have been published in this area over the last two decades, the technical advances themselves have been somewhat slow to find direct application in the practical world of the oil and gas industry.

This presentation will briefly describe the underlying technology and challenges associated with developing 'Digital Rocks' through to a proven capability sanctioned for use in the operating assets of a large multinational energy company. Case studies are used to illustrate practical applications of digital rocks technology. Key areas where improved understanding is required for further advancement are also described.

NOTES:

Introducing Big Data Petrography: QEMSCAN based rock characterisation

Jenny Omma¹, Henrik Omma¹, Jo Alexander^{1,2}

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²Alexander Geoscience Ltd, 61 Durban Road, London, SE27 9RW, UK

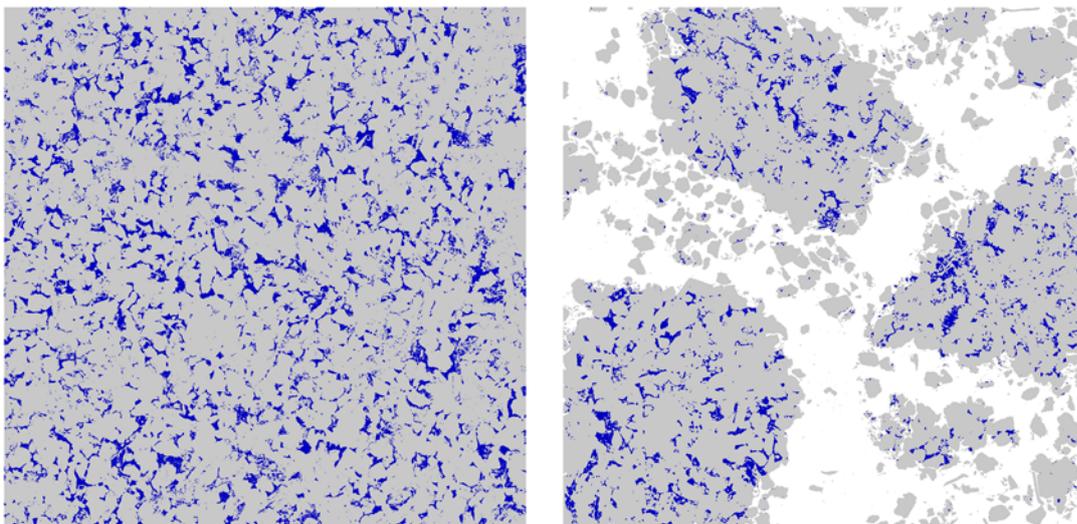
At Rocktype we wish to increase the value that rock characterisation data can bring to subsurface workflows, at the workstation and at wellsite. We are pioneering the field of Big Data Petrography – elucidating controls on rock properties through algorithm-led analysis of rich, digital datasets.

We aim to consolidate today's piecemeal combination of manually gathered rock property datasets (e.g. XRD, XRF, CCA, MICP, TOC, optical, petrography, SEM imaging) with a single, integrated, fully digital and Big dataset, better suited to the study of complex geological systems. We feel that SEM-based automated petrography is the key technology for this step change. FEI's (now Thermo Fisher Scientific) QEMSCAN® provides mineralogy, porosity, elemental chemistry, rock properties and rock texture from a single, ultrafast analysis and we are working to improve the capability of this and related technologies.

Important to the idea of Big Data petrography is that a near-continuous dataset is created for the interval of interest, enabling upscaling of properties and reducing sampling bias. This requires algorithm-led analysis of ditch cuttings. Cuttings represent a hugely underutilised resource that Big Data petrographic analysis can transform into high quality, value generating data.

In this talk, workflows for overcoming traditional challenges to working with cuttings are presented. Formation properties are isolated from drilling mud contaminants by 'digital washing' of the images and data. Individual cuttings in a sample are lithotyped based on mineralogical-textural characteristics and recombined to provide a near-continuous log of formation specific petrophysical values. Whole rock formation porosity, mineralogy and other properties can be estimated by careful sample preparation and analysis to exclude incorrect data resulting from bit damage to form cuttings (Fig. 1).

(a)



Subareas of original rock (left) 13.8% porosity, synthetic cuttings (right) 8% with cracks removed, 12.5% with cracks retained. Both images 5 mm across. **Grains Pores**

(b)

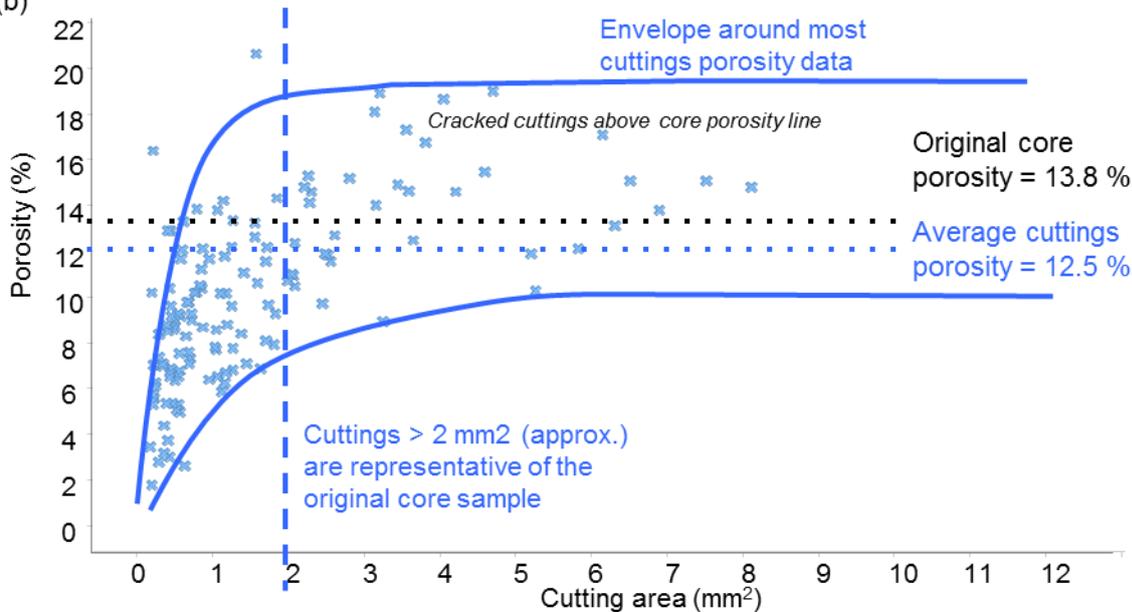


Fig.1. (a) Synthetic cuttings were created by crushing core material and the QEMSCAN results compared. (b) Cuttings porosity (when cracks are filtered out) greatly underestimates true formation porosity as (i) rocks fracture preferentially through larger pore networks and (ii) we don't measure pores on the outside edge of cuttings (the extreme being a single grain with 0% porosity). Smaller cuttings underestimate porosity more and should be size corrected or filtered out of the dataset. Minimum cutting size is grain size dependent. Cracks, formed by the action of the bit, provide an overestimation of formation porosity and must also be automatically filtered out of the dataset.

NOTES:

Workflow model for the digitization of shale rocks

¹Buckman, J., ²Mahoney, C., ¹Bankole, S., ¹Nazari-Moghaddam, R., ¹Couples, G., ¹Lewis, H., ³Wagner, T., ²März, C., ⁴Blanco, V., ¹Stow, D., ¹Jamiolahmady, M., & ⁵Ruffell, A.

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Shale rocks are known to be highly heterogeneous in a range of properties including: porosity / permeability, fissility, colour, particle type (composition), particle size and orientation, as well as degree of compaction and diagenetic history. Therefore it is important in any study of such material, that the maximum information be extracted in as efficient a manner as possible. One way to do this is by the collection of big-data sets, through high-resolution analysis of polished thin-sections by low-vacuum scanning electron microscopy (SEM). A workflow model for the digitization of shale rocks is presented herein, based on common practice developed at the Institute of Petroleum Engineering, Heriot-Watt University, using methods developed for a number of research groups working on such materials in relationship to organic and inorganic geochemistry, rock mechanics, gas permeability, and microfabric assessment for environmental analysis.

The collection of big-data and digitization of shale rock is approached using three SEM methods, which can be applied to whole slides or selected areas of interest. These are i) automated collection of image tiles, and stitching to form high-resolution large-scale montages (fig.1), ii) automated energy dispersive x-ray (EDX) mapping of large areas (fig.2), and iii) analysis of selected particles, in terms of morphology, composition and relative location (fig.3). This workflow is an alternative to other automated data collection systems, such as typified by quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN).

High-resolution large-scale images can be automatically collected and constructed, from backscattered electrons (BSE), secondary electrons (SE / GSE) or light photons (CL) imaging. Images are commonly formed from a series of 4,000-10,000 plus tiles per montage. Tiled images are typically recorded with a horizontal field of view (HFOV) of 518 μm , with higher resolution scans having 30 - 60 μm HFOV. Whole slide imaging can take between 30 minutes and 12 hours, depending on factors such as tile size, pixel resolution and scan time; the highest resolution images of whole slides may take between 2 to 3 days. Fully automated EDX mapping is also performed with the collection of individual tiles. Whole slides generally take longer than imaging alone, being dependent on the number of frame scans per tile, and are usually performed at lower tile resolutions. EDX maps typically contain hundreds rather than thousands of tiles per montage, with each tile typically 1 - 2 mm in width, and constructed with between 20 to 30 frame scans per tile. Particle analysis software can be set up for environmentally pertinent components such as pyrite and iron-oxides (as well as others such as TiO_2 and zircon). After thresholding of a representative BSE image, information that can be automatically gathered includes data on size, shape, composition and distribution of particles. For practical reasons, the maximum number of particles that can be analyzed (under the current regime) is restricted to in the region of 160,000 particles (or between 1-2 GB of data). In addition, data sets that are too big, become hard to manipulate due to restrictions in programs such as "Excel" in manipulating more than 32,000 cells at a time. Best practice involves analyzing thin transects across the slides (Fig.3), with runs of 2 - 4 hours commonly generating data sets with 4,000 or so particles. For all three methods, the resolution used and the size of the areas covered are all constrained by time, with it not being practical to run samples continuously in low-vacuum (or high-vacuum) for much in excess of 75 -100 hours. The other main constraint is that this workflow can easily generate several giga-bytes (commonly 2 - 4GB) of data per scan, which quickly becomes difficult to manipulate and transfer. Given the typical size of files, a centralized storage facility for all data is therefore highly recommended.

High-resolution BSE maps, in conjunction with corresponding elemental maps, can be thresholded through image analysis, and used to work out percentage coverage and relative distribution of phases present; for example to identify silicification of shale. High-resolution charge contrast image (CCI) maps, have also been used to differentiate carbonate produced through diagenesis, from that of original calcareous shells of foraminifera. In both

cases, this workflow has prevented the overestimation of detrital or pelagic biological components versus authigenic. Collected images are also used for a range of purposes, including porosity calculation, textural analysis (e.g. grain orientation), and as the basis for three-dimensional flow modeling. Such high-resolution coverage, at a variety of scales, over large areas (cm²) improves models used for up scaling, and is particularly important within heterogeneous mudrocks. The three forms of collected data, used in conjunction, can be useful for interpretation of Eh / pH conditions (through distribution of iron oxides and pyrite), as well as understanding overprinting / modification from diagenesis and weathering processes, helping to bring geochemical analysis of mudrocks to the micron-scale.

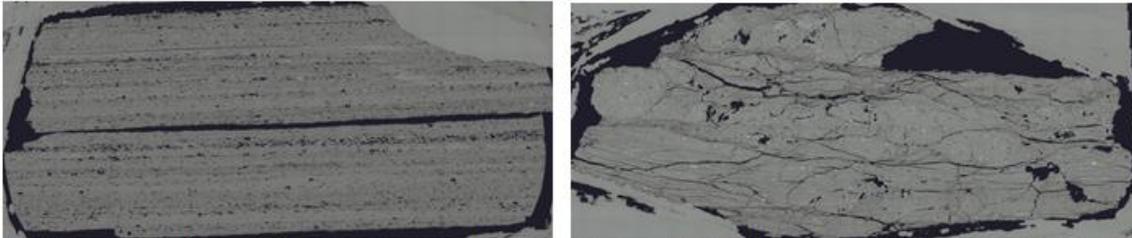


Fig.1: Typical stitched BSE images of whole shale slides, simple silicified laminated (left) and burrowed (right). HFOV each in the order of 35 mm.

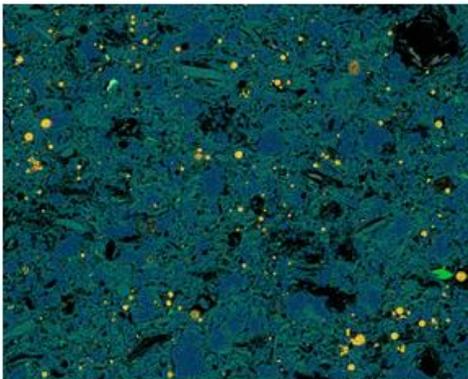


Fig.2: EDX layer map for Fe, S, Ti, Si and Al. Darker blue = silt (quartz), greenish blue = clay and mica, orange = pyrite, bright green = Ti oxide. HFOV approximately 1 mm.

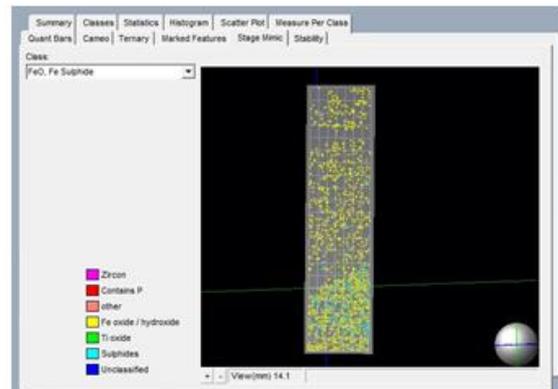


Fig.3: Stage mimic, showing distribution of Fe oxide and pyrite, with preferential occurrence of pyrite within the lower part. Slice scanned across total width of slide, approximately 10 mm.

NOTES:

Solving petroleum problems using the frontiers of imaging technology: Multiscale, correlative and *in situ* techniques

Matthew Andrew¹ & Sreenivas Bhattiprolu¹ Eddy Hill¹

¹Carl Zeiss X-ray Microscopy, 4380 Hopyard Rd., Pleasanton, California, USA

Pore scale imaging has developed over the last 20 years from a primarily academic technique used to visualize pore structures for fundamental research into an increasingly crucial industrial tool. High resolution imaging is today used for the characterization of a range of geological and petrophysical properties, including porosity & pore connectivity, absolute and relative permeability, mineralogy, geomechanical response, geological facies type and diagenetic history, and while much progress has been made, many challenges remain. Principal among these are the challenge of process and scale. First, pore scale problems involve complex multiphysical processes which direct imaging and modelling cannot always simply address. Their investigation may require multiple imaging techniques and modalities, and may even require direct experimental *in situ* investigation to acquire fundamental petrophysical properties inaccessible to any other technique. Secondly, the resolutions required to resolve fundamental pore structures frequently come at the expense of a field of view representative of true subsurface heterogeneity. This issue is particularly problematic when dealing with unconventional resources, or heterogeneous carbonate systems, where pore structures may extend down to the sub-nm scale yet sampled frequently display heterogeneity on the inch length-scale, or even higher.

In this presentation we will focus on 3 examples of how correlative, multiscale and *in situ* techniques can be used to solve these problems of scale and process. First we will show how 2D quantitative mineral mapping (acquired using SEM-EDS techniques) can be coupled to high resolution 3D X-ray microscopy to extend mineralogical information into 3D. This requires the multi-modality data to be integrated and spatially co-registered in a single multi-scale methodologically agnostic correlative environment, enabling direct correlation between analytical chemical information and 3D structural information (fig.1).

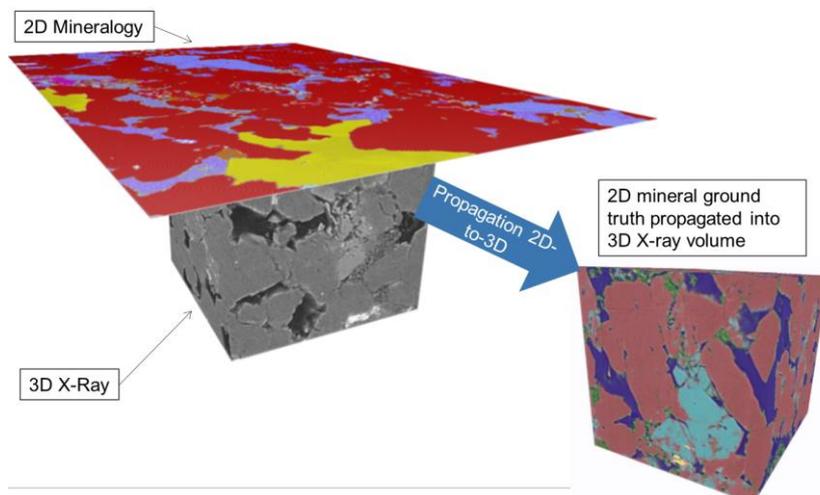
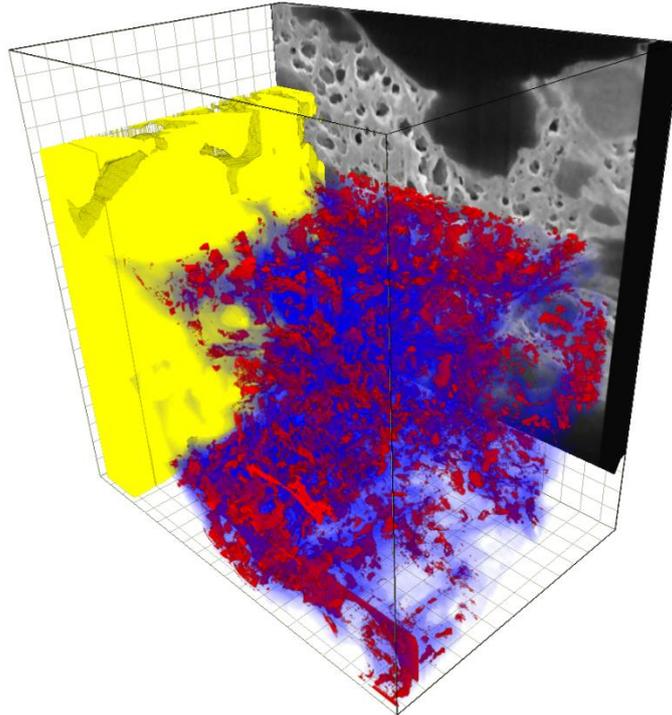


Fig. 1: 3D mineralogy by correlating 2D chemical information with 3D structural information.

Secondly, we will show how this multi-modal correlative framework can be used to characterize the porosity of a heterogeneous economic North American shale sample. This requires the integration of light, X-ray, electron (including quantitative mineral mapping) and helium ion microscopy, including the first results utilizing coupled Focused Ion Beam serial sectioning and sub-nm capabilities of Helium Ion Microscopy (FIB-HIM). This was used to analyze the connectivity of organic hosted nano-porosity, showing no percolating flow pathway, despite a moderately high porosity (around 10% of the organic region). This may well be due to the dramatic difference in pore shape between the secondary organic hosted porosity (typically convex in shape) and the primary intra-granular porosity familiar from conventional systems (typically concave in shape).

Fig.2: Connectivity of organic hosted porosity (red), segmented from the first 3D FIB-HIM dataset.



Finally we will show how the problems of scale and process can be addressed together by coupling multi-scale X-ray microscopy can be coupled with *in situ* flow experiments, used to characterize the wettability distribution across an 8" section of a 4" whole core of a heterogeneous carbonate. First the sample was rapidly imaged across its entire length using a high throughput industrial CT

scanner. This was then classified in 3D into different petrophysical units / lithologies, which were then used to target imaging efforts at higher and higher resolutions, both using industrial X-ray CT and X-ray microscopy. These lithological classifications were used to target micro-plug sampling from each lithology, maintaining the relationship between the sampled micro-plugs and macroscopic heterogeneity. These micro-plugs were then examined using *in situ* X-ray microscopy, where fluid distributions were mapped and wettability measured directly at the pore scale, showing that a high porosity oolitic packstone lithology was oil wet, whereas a low porosity bioclastic wackestone lithology was water wet.

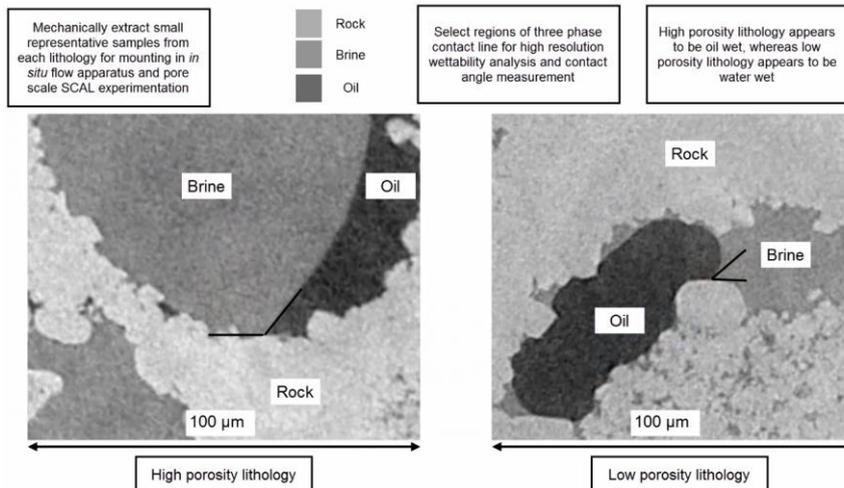


Fig.3: Wettability measurements for the high porosity lithology (left) and low porosity (right). Oil is the darkest phase, brine the intermediate phase and the rock is the lightest phase.

NOTES:

3D micro-CT imaging of the pore-scale distribution of oil, brine and air in place in reservoir shales and in sandstones after low salinity flooding, and relations to local mineralogy

Mehdi Shabaninejad¹, Qianhao Cheng¹, Alessio Arena², Silvano Sommacal² and **Andrew Fogden**²

¹*Department of Applied Mathematics, Australian National University,*

²*FEI Oil & Gas, Canberra, Australia*

Digital rock technology has advanced enormously over the past decade, and can now deliver integrated multi-scale, multi-modal images of rock samples for simulations of transport through the pore space. For complex systems or processes, these simulations need further guidance from 3D imaging of the actual pore-scale distributions of multi-phase fluids, either in preserved reservoir samples or after laboratory restoration and well-controlled flow experiments, e.g. for hydrocarbon recovery. This is especially the case for unconventional, in which little is known of the fine-scale distribution of oil, gas and water in preserved core plugs. Another important example is enhanced oil recovery (EOR) processes in conventionals, for which visualisation and quantification of the pore-scale displacement mechanisms are vital to optimisation of design of these relatively expensive recovery processes. In particular, EOR by low salinity waterflooding is widely regarded to be driven by in situ changes in interfacial interactions and wettability, but little direct evidence exists to demonstrate these pore-scale mechanisms in action.

This paper presents examples of studies based on micro-CT imaging and analysis of the pore-scale distribution of multi-phase fluids in reservoir shales and sandstones. For the case of shales, small plugs (sub-plugs) of 3-5 mm diameter were drilled from a set of calcareous mudstones. Micro-CT scanning of the preserved state cannot provide information on the detailed distribution of oil, air and water in place in such samples, owing to their tightness and to the similarly low X-ray attenuation of these three fluids. Instead, an approach in which the attenuation of these three fluids is separately and selectively boosted must be applied. To this end, each shale sub-plug was micro-CT scanned in a sequence of four prepared states, namely after 1) highlighting of in-place oil, 2) highlighting of in-place oil plus air, 3) cleaning to define the fully empty reference state, and 4) saturation to highlight all connected pore space. These four tomograms were then spatially registered to be exactly overlain in 3D, from which their differences isolated the spatially-resolved signal from each of the three fluids. After this non-destructive procedure, each shale sub-plug was sectioned and ion-milled for high-resolution backscattered SEM (BSEM) imaging and for SEM-EDS mapping of the distribution of minerals. These 2D images and maps were then registered into the corresponding virtual slice through the sub-plug tomogram, so that the distribution of in-place fluids (at tomogram voxel resolution) could be directly compared to the fine-scale morphology and mineralogy of pores, organic matter, grains and clays. In particular, the studies showed that most of the in-place oil in these samples was strongly associated with calcite and organic matter, while the matrix clays were predominately water-filled and water-wet.

The second example addresses the micro-CT imaging of the pore-scale distribution of oil in reservoir sandstone sub-plugs in a sequence of laboratory-prepared states, namely after 1) restoration (drainage and aging to define the initial state at irreducible brine saturation), 2) spontaneous imbibition of conventional flood brine (seawater), and 3) spontaneous imbibition of low salinity brine. A similar workflow to that mentioned above was then applied, involving tomogram registration and differencing for segmentation of fluid distributions, followed by BSEM and SEM-EDS imaging of a polished section. In this way the changes in oil distribution within the same pore due to low salinity flooding could be 3D visualised and quantified, and oil release could be directly compared to the mineralogy of the locally contacting rock surface. In particular, most release occurred from grain surfaces, rather than directly from clays (see Figure 1 below).

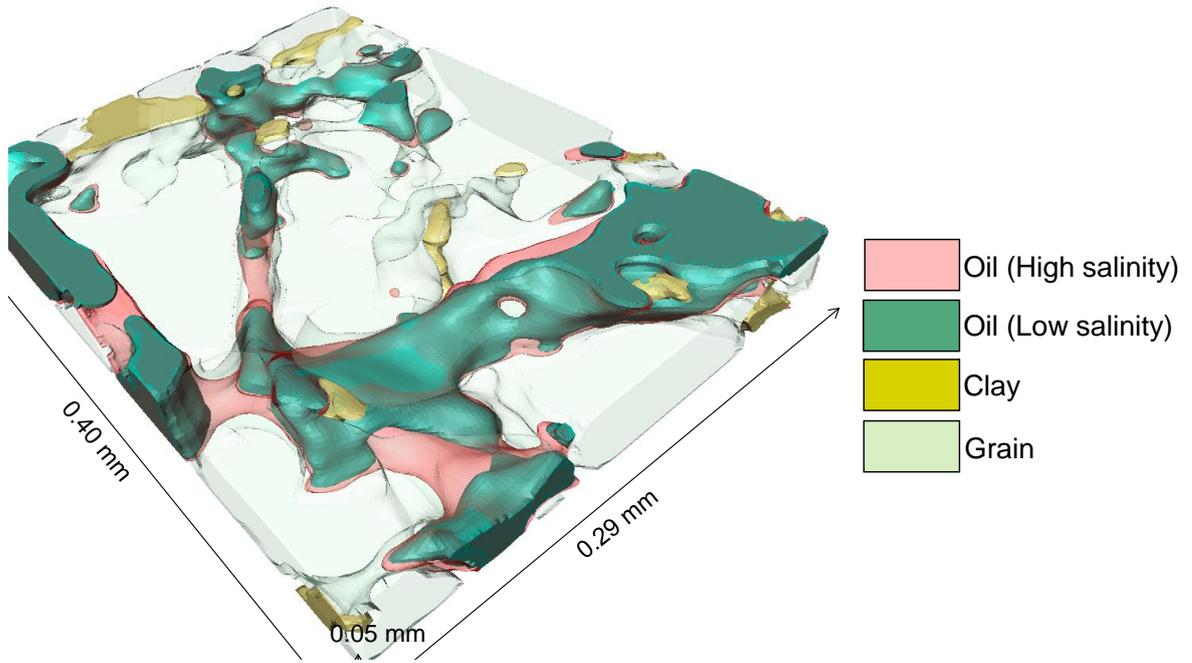


Fig. 1: Visualisation of a sub-region of the restored reservoir sandstone, showing the preferential release of oil from grains rather than from clays due to low salinity waterflooding.

NOTES:

Understanding variations in reservoir porosity in the Eagle Ford shale using scanning electron microscopy- Implications for basin modelling

Mark Osborne, Herbert Volk, Mark Hopkins
BP Upstream Technology, Sunbury, UK.

Productive shale reservoirs are low permeability source rocks, petroleum was generated within the source rock, and while much petroleum has been expelled a significant volume has still been retained within the source, either stored within the porosity or sorbed onto the organic matter. This retained petroleum is the resource we seek to extract from shale gas/oil reservoirs. These retained petroleum plays require the placement of long laterals and hydraulic fracturing before the petroleum will flow, because matrix permeabilities are very low.

To evaluate potential shale plays reliably we require robust geological models which can simulate the generation and retention of petroleum, porosity and permeability in source rocks from first principles, and which can be implemented in basin modelling software. To be predictive, such basin models need to be calibrated against observations from real shale plays; a key control on the amount of retained petroleum is the porosity in the shale and the abundance of organic matter. Scanning electron microscopy of Ar-ion milled shale samples can potentially reveal systematic variations in the amount of porosity, pore types and distributions across a range of thermal maturities. These observed variations in porosity can be used to calibrate or 'sense check' basin modelling output and refine predictive models. For this reason BP has conducted scanning electron microscopy studies of shale plays including the Eagle Ford shale.

To develop a reliable imaging technique that worked for a range of shale samples of varying pore structure/composition and which gave consistent results was extremely challenging. The initial task was to produce excellent images to help characterise the pore types with the ultimate goal of using these quality images to produce quantitative data. Sample preparation is crucial so that the SEM can scan electrons over an extremely flat surface devoid of artefacts. We have largely overcome these challenges and have devised a set of instrument parameters and operating conditions that allow an expert operator to consistently obtain high quality images. Quantification of pore size was achieved using a modified version of BP's SEM based Pore Image Analysis (PIA), developed originally for conventional reservoir sandstones. This was applied to a series of 10 representative images taken at 10000X. Quantification of pore type was done by SEM image based point counting of 500 counts per sample (50 counts for each image). It was important to ensure that the fields of view selected were as representative of the rock as possible.

The results clearly show that the mean pore size decreases as thermal maturity increases and that organic matter (OM) hosted pores are absent in low thermal maturity samples (where $R_o < 0.7$) and become increasingly more abundant as thermal maturity increases. In moderate maturity samples there are OM-hosted pores that range in pore size from 5-500nm. In the high maturity samples small (<50nm) OM-Hosted pores predominate.

Our studies reveal that porosity evolution in organic rich shales is a complex process involving mechanical compaction, diagenesis, bitumen generation and development of secondary porosity within organic matter. The implications of these observations for basin modelling studies will be discussed.

NOTES:

Tuesday 28th February

Session Two

Isotopes

Keynote: Applications of clumped isotopes to the petroleum industry: a critical review

Cédric M. John

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The application of clumped isotope to paleothermometry in carbonates is now 10 years old, and many technical progresses have been made that make this a more mature and reliable analytical technique. The fundamental principle of clumped isotope is simple: given a stable isotopic composition for a carbonate mineral, it is possible to deduce the temperature of mineralisation thanks to the tendency of the heavy isotopes of oxygen and carbon to bond (“clump”) together within the mineral as a function of temperature. This principle means that clumped isotope offers a single-phase paleothermometer that does not suffer from some of the traditional limitations of other proxies: it can be applied without any need to estimate (or guess) the composition of the parent fluid, and it is applicable to any carbonate phases, even the cryptocrystalline phases lacking fluid inclusions. But what are the promises and known challenges of this technique, notably applied to oil and gas problems? For instance, at face value it appears that multiple calibrations have been published over the last few years, each with slightly different slopes, which can give non-expert the impression that major uncertainties still exist when using this approach. The reality is quite different, and major breakthroughs have been made recently that allow for greater inter-laboratory reproducibility and a more confident temperature estimate. As often, the published literature lags behind the new technical and methodological approaches. In this critical review of the field, I will attempt to provide a current overview of both the analytical approaches of clumped isotopes –highlighting best practices and pitfalls – as well as of published case studies focused on oil and gas applications. For instance, we will discuss the importance of applying an accurate ^{17}O correction, and I will present the common efforts of several laboratories (including ours) to obtain an inter-laboratory “universal” calibration from 0-250°C. We will also touch on improvements made in data reduction using dedicated software that improves inter-laboratory comparisons, and on new generations of mass spectrometers that improve the analytical resolution and open up the possibility to measure increasingly smaller samples. But it is the case studies that highlight the potential of the method to help petroleum geologists. Here, we will see that clumped isotopes have been successfully used to fingerprint the origin and formation history of diagenetic calcites and dolomites, to understand the mineralization of CO_2 as magnesite in ultramafic rocks, to improve our understanding of the thermal history of sedimentary basins and reservoirs, and to constrain fracture-related fluid-flow in the subsurface, to name a few examples. In conclusion, clumped isotope is now a mature technique that has proven its usefulness, but challenges remain and experience in acquiring data and interpreting it is key to a successful application of the technique to the oil and gas sector.

I gratefully acknowledge support from QCCSRC, funded by Qatar Petroleum, Shell, and the Qatar Science & Technology Park.

NOTES:

Compound specific sulfur isotopic analysis of organosulfur compounds to help reveal genetic links between the Lower Paleozoic oil fields from the Tarim Basin, NW China

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During thermochemical sulfate reduction (TSR), H₂S generated by reactions between hydrocarbons and aqueous sulfate back-reacts with remaining oil-phase compounds forming new organosulfur compounds (OSC) that have similar $\delta^{34}\text{S}$ values to the original sulfate.

Using compound specific sulfur isotope analysis (CSSIA) of alkylthiaadamantanes (TAs), alkyldibenzothiophenes (DBTs), alkylbenzothiophenes (BTs) and alkylthiolanes (TL), we have here attempted to differentiate OSCs due to primary generation and those due to TSR in oils from the Tarim Basin, China. These oils were generated from Cambrian source rocks and accumulated in Cambrian and Ordovician reservoirs.

Based on compound specific sulfur isotope and carbon isotope data, TAs concentrations and DBT/phenanthrene ratios, the oils fall into four groups, reflecting different extents of source rock signal, alteration by TSR, mixing events, and secondary generation of H₂S. Thermally stable TAs, produced following TSR, rapidly dominate kerogen-derived TAs at low to moderate degrees of TSR. Less thermally stable TLs and BTs were created as soon as TSR commenced, rapidly adopted TSR- $\delta^{34}\text{S}$ values, but they do not survive at high concentrations unless TSR is advanced and ongoing. The presence of TLs and BTs shows that TSR is still active. Secondary DBTs were produced in significant amounts sufficient to dominate kerogen-derived DBTs, only when TSR was at an advanced extent. The difference in sulfur isotopes between (i) TLs and DBTs and (ii) BTs and DBTs and (iii) TAs and DBTs, represents the extent of TSR while the presence of TAs at greater than 20 $\mu\text{g/g}$ represents the occurrence of TSR. The output of this study shows that compound specific sulfur isotopes of different organosulfur compounds, with different thermal stabilities and formation pathways, not only differentiate between oils of TSR and non-TSR origin, but can also reveal information about relative timing of secondary charge events and migration pathways.

NOTES:

Unravelling quartz, calcite and dolomite cementation histories in sandstones with *in situ* microanalysis of oxygen isotopes

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Oxygen isotopes preserve important information about the temperature at which minerals form and the nature of the fluids from which they precipitate. They have thus been used for decades in reservoir quality studies, specifically looking at the conditions under which key diagenetic minerals such as quartz and carbonates formed. In early studies of quartz, overgrowths were physically separated and a single analysis obtained for multiple overgrowths, with typical uncertainties of around 1-2‰. For diagenetic carbonates, microdrills have been used to obtain relatively small-scale samples but are still problematic for fine-grained, intergrown and replacive carbonate phases. Selective leaching was and is still used to separate bulk calcite and dolomite, but with variable success, especially for fine-grained phases.

Given the basic nature of the separation techniques, early isotope studies suffered from the problem of not knowing exactly what was being analysed. The analyses were accurate, but perhaps of the wrong material. A key breakthrough was thus the use of *in situ* Secondary Ion Mass Spectrometry (SIMS) to analyse single quartz overgrowths. However, the resolution of the early single collector SIMS instruments were around 20-30 μm, with an analytical precision of around ±2‰. For most overgrowths, therefore, only one, insufficiently precise analysis was possible.

A key problem with single or bulk analyses is that they reveal little or nothing about the growth histories of minerals – yet this is absolutely fundamental to our understanding of diagenetic process and thus to any predictive model of cementation and reservoir quality. Recent improvements in SIMS have allowed oxygen isotope analyses to be made at a resolution of 2-10 μm and with a precision of ±0.7‰ (2 μm; 2SD) to ±0.3‰ (10 μm; 2SD). Accurate analysis requires a suite of calibration standards (Śliwiński et al. 2016a, b). The sample size for a single, *in situ* 12 μm spot analysis is one million times smaller (ca. 2 ng vs. 2 mg) than in earlier, conventional studies of oxygen isotopes.

Here, we use case studies of quartz, calcite and dolomite cements to illustrate the kind of data that can be obtained with modern ion microprobes and how they help constrain diagenetic histories. All the analyses were made on the CAMECA IMS-1280 ion microprobe in the Wisconsin Secondary Ion Mass Spectrometer Laboratory.

Joe Harwood examined the growth history of single quartz overgrowths from sandstones from the Jurassic Ness Formation in the North Sea (Harwood et al. 2013) and the Palaeocene/Wilcox Formation in Texas. In both cases, ¹⁸O is systematically zoned by over 10‰ within single overgrowths. Whilst the determination of quartz growth histories is limited with 12 μm analyses, 2 μm diameter spots allowed around 25 analyses across single overgrowths. For the Ness, with a maximum burial temperature of 130 °C, results were consistent with quartz cementation models proposing that the bulk of quartz precipitates as a continuous process beginning at 60–70 °C. Results for the Wilcox were very similar, but with little evidence for quartz formation above ca. 140 °C (up to 185 °C), perhaps due to the formation of other minerals such as ankerite and grain-coating illite. In addition, isotopically distinct overgrowths on detrital quartz grains were also identified.

Calcite and dolomite cements are a major control on the quality of Devonian, middle Bakken siltstones/sandstones, the major tight oil formation of the Williston Basin. Petrographic data show that calcite cement is an early phase, and combined with mineralogical data suggests that much of the dolomite replaces calcite. Dolomitisation increased porosity slightly. BSEM and SEM-CL suggest several textural types of both calcite and dolomite and thus a potentially complex diagenetic history.

Conventional oxygen (and carbon) isotope analyses using selective leaching methods were used but of course only yielded a single data point; further, in this case, there was strong evidence that dolomite was partly dissolved along with calcite during the analytical procedure, so that these data had limited use. SIMS oxygen isotope analyses of

many individual calcite crystals gave a range of 4‰; for many individual dolomite crystals, there was a range of 6‰. There was no relationship between texture and isotopic composition so that in this case, petrography is a rather poor guide to diagenetic history.

Assuming that both calcite and dolomite precipitated from seawater, the temperature range over which calcite precipitated was ca. 10-30 °C, and 20-70 °C for dolomite. If $\delta^{18}\text{O}$ of the formation water increased to say +3‰ during burial, then dolomitisation continued to ca. 100 °C, compared to the maximum burial temperature of 130 °C. Emplaced into a burial history, these data suggest that dolomitisation occurred over > 100 million years: an ultra-slow process controlled by kinetics and perhaps the rate of supply of magnesium.

NOTES:

Real time carbon isotopes analysis.

Luca Mascheroni

Geolog Srl

In the last decades, the usefulness of isotopic analyses in petroleum exploration and development have been vastly proved. Interpretative models have been developed in order to describe several features of natural gas. Some models can result in the outline of the formation mechanisms, from the type of source rock, to its maturity at the time of the formation of the hydrocarbons mixture. Other ones are able to provide a description of the migration processes of the natural gas from the source rock to the reservoir, giving particular attention to leakage processes that occur through the cap rock. Early in the past, the introduction of online gas chromatography-combustion-isotope and ratio/mass spectroscopy has permitted the logging of mud gas isotopes in real time, directly at the rigsite. The scope of this paper is to highlight the reliability of isotopic data logging in real time at rigsite in order to take fast decision and avoiding waiting for laboratory analyses. Case histories will support a deep analysis of the various motivations.

Gas contained and released from the drilling mud is analysed in real time in the isotopic composition. This technique, combined with standard mud logging hydrocarbon analyses, has the scope to identify and characterize the gas coming from the reservoir. Traditional hydrocarbon analyses are not enough to fully understand the presence and the characteristics of the gas/oil bearing zones. The gas log itself is not sensitive to gas variations due to changes in drilling conditions neither it is able to discern events as suppressed gas readings resulting from overbalanced drilling. Mud gas isotopic analysis offers a method to overcome these difficulties, as the measurements of gas carbon isotope is essentially independent from concentration¹.

Mud gas isotopic logging is thus gaining increasing interest for the unique information it is able to provide. In challenging wells, where difficult drilling conditions (e.g. HPHT wells, H₂S rich formations, heavy OBM) inhibit the accuracy of downhole sampling techniques, real time isotope analysis has proved to be a powerful for reservoir characterization tool². In contrast with late coming laboratory geochemical analyses, the advanced mud log-derived data is obtained in near real time and can influence downhole data collection such as pressure points, fluid sample points, sidewall core or conventional core interval choice. In extended horizontal wells, where wireline data are limited, mud gas isotope analyses have been successfully used for prediction of pressure changes along the well after penetrating major faults. Through the combination of real time isotope analyses with mineralogy and TOC analyses, geochemical geo-steering in horizontal well drilling is an achievable target.

In order to get crucial information for field development decisions, carbon isotopic ratio logged at wellsite permits to take advantage of a huge dataset of isotopic data in real time. Gas samples collection and shipment for laboratory analyses could take days or weeks depending on the geographical location of the well, which could result in losing usefulness for taking in real time decisions. Moreover, the risk of missing interesting data to identify, for example, sampling spots (coring, pressure points) is thus reduced at minimum. A full characterization of the cap rock is also possible, allowing the study of migration/mixing phenomena.

Citing Ellis: "...serendipitous sampling of a boundary fault uncovered pure migrating thermogenic HC". With real time isotopic analysis no room for serendipity is left and it is possible to maximize the information coming from each well. Case histories will show the quality of real time isotopic analysis, providing a continuous characterization of the interested interval in line with laboratory analyses.

When gas reservoir compartmentalization is studied, a high data density allows the investigation of fluid heterogeneities, as a result of filling history or post accumulation hydrocarbon alteration. The ability to assess vertical and horizontal continuity of gas bearing reservoirs will be highlighted and described. Through the use of tools like the Bernard chart, different maturity grades of the analysed gas could help in understanding processes like faulting or differential charging. Moreover, a dataset obtained with frequent sampling through all the seal interval allows to follow the mixing phenomena and to gain information about the cap rock efficiency. Additional information about the origin of the gas present in the cap rock, whether it is autochthonous or migrated, could be also provided.

NOTES:

Constraining the timing of oil generation and oil-source fingerprinting via the rhenium-osmium isotope system: Implications from the Duvernay Petroleum System, Western Canada Sedimentary Basin

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Here we present a Re-Os study of the Duvernay Petroleum System of the Western Canada Sedimentary Basin to further demonstrate that the Re-Os isotope system has the ability to constrain the timing of oil generation and also be applied as an inorganic oil-source correlation tool.

The main stage of thermal maturation of the organic-rich Late Devonian Duvernay Formation is considered to have occurred during the Late Cretaceous / Early Eocene Laramide Orogeny with the generated oil having migrated into the interfingering Leduc reefs and the overlying Nisku carbonates. Previous studies and geochemical correlations have shown that the Duvernay Formation is the principal source of the Duvernay-Leduc/Nisku Petroleum System.

Despite the generally low Re (from less than 1 to 4 ng/g) and Os (10 to 40 pg/g) abundances in most of the asphaltene fractions (asphaltene being the main carrier of Re and Os in crude oil) of the analysed Duvernay oil samples, a Re-Os age of 66 ± 31 Ma ($n = 14$, MSWD = 6.7, initial $^{187}\text{Os}/^{188}\text{Os} = 0.77 \pm 0.20$) is defined by the asphaltene fractions. Although the defined date has a large uncertainty, the date, however, is broadly in agreement with the geological models proposing that oil generation occurred during the Laramide Orogeny (80~35 Ma) and distinctly different with the age of the Duvernay Formation source rock (~378 Ma). The uncertainty is not only caused by the uncertainties of Re-Os isotopic ratios due to the low elemental abundances, but also by the lack of identical initial $^{187}\text{Os}/^{188}\text{Os}$ (Os_i) values of crude oil at the timing of oil generation (0.77 ± 0.20).

The Duvernay source rock $^{187}\text{Os}/^{188}\text{Os}$ compositions at the timing of oil generation (Os_g) are between 0.46 and 1.48, with a weighted average of 0.83 ($n = 33$). These values are extremely similar to the initial $^{187}\text{Os}/^{188}\text{Os}$ (Os_i) values of the Duvernay-sourced oil (0.77 ± 0.20 , $n = 14$), which range between 0.55 and 1.06. Furthermore, the Os_g values of the Duvernay Formation are distinct from the $^{187}\text{Os}/^{188}\text{Os}$ compositions (Os_g) of other potential source rocks in the basin, indicating very limited contribution from these other sources to the Duvernay Petroleum System. The overall similarity of the Duvernay Formation Os_g values and the Os_i values of the Duvernay oil suggests that Os isotope compositions can be utilized as an additional parameter in oil-source correlation, which could be practical in highly biodegraded petroleum systems.

Further, a recent study suggests that basinal fluids could influence a crude oil's Re-Os systematics. However, this is not observed in this study. Despite the absence of direct Os data of basinal fluids in the Duvernay-Leduc/Nisku Petroleum System, the radiogenic Sr isotope composition of present day Leduc-Nisku brines and the diagenetic minerals suggests that the basinal fluids have interacted with the crystalline basement and/or Proterozoic/Lower Cambrian strata. The high initial $^{187}\text{Os}/^{188}\text{Os}$ values of the deep older strata, and the time span (>300 Ma) between their deposition and the timing of Duvernay oil generation result in a very radiogenic Os isotope composition of any basinal fluid. However, both the present day and initial $^{187}\text{Os}/^{188}\text{Os}$ values of the studied oils are not as radiogenic as that of the estimated Os isotope composition of any basinal brine in the Duvernay petroleum system. The very limited or no influence of basinal fluids on the Re-Os systematics of Duvernay oil, especially when considering the low elemental abundances, excludes the possibility of basin fluids as the significant contributor of Re and Os in oil.

In conclusion, this study of Duvernay Petroleum System confirms the ability of the Re-Os geochronometer to record the timing of oil generation and trace the source of an oil. We also consider basinal fluids to be only a very minor source of the Re and Os in Duvernay-generated oil.

NOTES:

Constraining Carbonate Cementation in Clastic Reservoirs Using Clumped Isotopes: A case study from the Bruce Field, UK North Sea

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Carbonate cementation is widespread in sandstone reservoirs and can be detrimental to porosity and reservoir connectivity. Determining the timing and extent of carbonate cement formation in the context of the burial history and hydrocarbon charging is therefore important for development scenarios. However, this is often hampered by the lack of constraints on the temperature and timing of formation of the carbonate phases. Here we apply carbonate clumped isotope palaeothermometry to calcite and dolomite cements from the Bruce Field reservoirs, UKCS, where carbonate cements had previously been identified as potentially forming barriers. We sampled calcite and dolomite phases from 4 wells across the field, to 1) constrain the timing of precipitation of carbonate cement phases, 2) reconstruct the variation of $\delta^{18}\text{O}_{\text{porewater}}$ during burial, and 3) to assess the use of the technique in identifying whether the carbonate cements are forming barriers. Our results suggest that both the calcite and dolomite phases formed early, prior to hydrocarbon charging, at low burial temperatures (40°C and 50°C respectively). They formed from fluids with $\delta^{18}\text{O}_{\text{porewater}}$ close to marine composition, despite having significantly different $\delta^{13}\text{C}_{\text{carbonate}}$ values (~-15‰ for dolomite, ~-5‰ for calcite). Thus, although the carbonate clumped isotope technique has the potential to help trace barrier formation in reservoirs, this approach relies on an assumption that the $\delta^{18}\text{O}_{\text{porewater}}$ diverged sufficiently between the different compartments of the reservoir. In the case of Bruce Field, the $\delta^{18}\text{O}_{\text{porewater}}$ in both compartments is similar. However, the new information that our clumped isotope data brings is the timing and $\delta^{18}\text{O}_{\text{porewater}}$ of cementation, and place them into the context of the burial history of the reservoir, in this case during shallow-burial. This information helps to understand the diagenetic behavior of the reservoir during burial and in relation to hydrocarbon charging.

NOTES:

A novel approach to geobarometry by combining fluid inclusion (T_h) and clumped isotope (Δ_{47}) paleothermometry in hydrothermal dolomite (Cantabrian Zone, Northern Spain)

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Hydrothermal dolomitization affected Carboniferous mud-dominated carbonate platforms in the Cantabrian Zone (Variscan foreland fold-and-thrust belt in NW Spain). The dolomitizing fluids circulated through thermal convection cells and created fracture-related dolomite geobodies with irregular geometries and a heterogeneous distribution of reservoir properties. The diagenetic framework and timing of the Late Carboniferous to Early Permian (300-270 Ma) dolomitization has been previously constrained (Gasparri et al., 2006a). Homogenization temperatures obtained from fluid inclusions range from 100 to 150°C (Gasparri et al., 2006b). Towards the end of the dolomitization event (about 270 Ma) a wide spectrum of ore deposits formed in fracture damage zones from fluids at temperatures up to 250°C.

This well-constrained diagenetic setting provides a natural case study for an evaluation of the clumped isotope (Δ_{47}) paleothermometer (Ghosh et al., 2006) on high temperature dolomite phases, affected by a successive thermal event. Do the dolomites presently record the initial temperature of dolomitization, or did the thermal anomaly associated to ore mineralization result in solid-state diffusion of the clumped isotope signal? Such alteration of the initial signal through solid-state diffusion has been reported for calcites in both experimental and natural case studies (Passey & Henkes, 2012; Henkes et al., 2014).

This study focuses on dolomite geobodies cropping out in the Bodón Unit, one of the major thrust units in the southern Cantabrian Zone. After a detailed field and petrographic study, 12 samples of dolomite cement were selected to apply both fluid inclusion and clumped isotope paleothermometry. Clumped isotopes yield temperatures between 110 and 160°C, well in line with the fluid inclusion homogenization temperatures.

Based on the fluid inclusion (T_h) and clumped isotope (Δ_{47}) temperatures, and fluid isochores, estimations of pressure correction allowed the calculation of presumed trapping pressures. They broadly correlate with indirect estimations based on fluid inclusion composition and possible paleo-barometric gradients (Gasparri et al., 2006b).

This case study indicates that high-temperature fluids, responsible for ore mineral formation within the partly dolomitized limestone hostrocks, did not influence the clumped isotope signatures of the original dolomite minerals. Solid-state diffusion did not occur in the studied dolomites, even in samples close to the mineralized areas. This is a promising conclusion towards application of clumped isotope paleothermometry in complex geodynamic settings experiencing several thermal events.

NOTES:

Combining two novel methods for reservoir characterization: what can clumped isotope geochemistry and micro-CT imaging reveal about early dolomitization?

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Dolomitization can improve or lower carbonate reservoir quality, and is therefore a critical process to understand in oil and gas reservoirs. It is, however, challenging to constrain the temperature and diagenetic fluid chemistry leading to dolomitization, in part owing to uncertainties surrounding common proxies used in diagenetic reconstructions. This leads to major uncertainties in the prediction of dolomitization-related reservoir heterogeneities. Here, we use two novel methods to understand the genesis and the spatial distribution of early dolomite within limestones. The clumped isotopes paleothermometer (Ghosh et al., 2006; Eiler, 2007) can be used to independently determine the temperature of dolomite precipitation or recrystallization. We apply this temperature measurement to dolostone samples of the two carbonate platforms of the Marion Plateau (NE Australia), an excellent analogue to dolomitized Miocene reservoirs producing hydrocarbons in South East Asian fields. Preliminary results indicate that the temperature of dolomite precipitation varies laterally and with depth. This illustrates the complex history of different dolomitization episodes in the two platforms, including potential recrystallization events. An intriguing result is that the temperatures measured with clumped isotopes are cooler than the 60-70-degree isotherm where most of the dolomitization occurs in reactive transport models (Whitaker, 2004), highlighting the fact that we still poorly understand the kinetics of dolomitization.

In addition, we investigated a range of samples with different degrees of dolomitization at the pore scale using a 3D XCT scanner. Initial results show that image segmentation techniques allow for a 3D qualitative and quantitative identification of the distribution of dolomite and calcite, and reconstruction of the pore network. This information shows where the dolomite nucleation sites are located and allows for quantification of the mineral specific surface areas. These properties are key inputs in reactive transport models. XCT images also reveals that 99% of the dolomite within a given volume is connected through large pores in the 3D imagery. Microporosity is below the resolution of the imagery, and this thus suggests that in the case of the Marion Plateau microporosity did not play an essential role in controlling the flow of the dolomitization fluid. The results of this study will help to better constrain dolomitization models and thus reduce uncertainties in the characterization of dolomitized reservoirs.

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Wednesday 1st March

Session Three

Applications/Case Studies

Keynote: Using pyrolysis techniques and high resolution mass spectrometry (FT-ICR MS) to evaluate the impact of fluid retention on bulk petroleum properties in shale

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In shale plays the liquid-gas cut-off must be known precisely, and production from the liquid-prone zone optimised; in-place does not necessarily correspond to produced GOR in shales because of fractionation during production. The first step in unravelling the fractionation phenomena is to determine the bulk composition of the petroleum that is generated in the source rock as a function of facies and maturity. This is because all subsequent processes simply act upon and modify the original signal.

We begin by examining bulk petroleum properties in the Eagle Ford Shale. The produced GOR exhibits regional trends that are broadly correlated with maturity, but with local aberrations linked to differences in predicted versus actual in-situ PVT properties. A database of over 140 field PVT reports has been compiled, covering the entire width of the formation within a narrow maturity range (condensate) and visualized as phase envelopes. With increasing maturity the organic matter in the Eagle Ford maturity series retains more and more oil as evidenced by an increasing oil saturation index up to a T_{max} of 455°C. High retention values can be seen over a broad range of maturity levels (440-475°C). Highest maturity samples show a decreased retention capacity. Oil quality ($S1/(S1+S2_{Whole\ Rock}-S2_{Extracted\ Rock})$) increases concomitantly with progressive maturation.

By analysis of the “instantaneous” fluids generated over narrow maturity ranges, using MSSV pyrolysis, we were able to generate PVT-SnapShots of unconventional petroleum fluids produced from the Eagle Ford. Our conceptual model comprised two reactive components: (A) a mixture of kerogen and bitumen that generated petroleum within the low permeability matrix and (B) bitumen alone which was the precursor of gas in zones of enhanced porosity within the matrix. The enhanced generation of gas from both kerogen and bitumen, and the significant retention of C7+ fluids were all crucial to matching the compositions and phase behavior reported in the field. The model predicted near identical compositions to the target well and its physical properties (saturation pressure, cricondenbar, cricondentherm, volume factors) which also fit very well into the general area around the chosen target well.

We then move on to present new insights into the evolution of petroleum properties, relating structures within kerogen to retained and expelled fluid chemistries as a function of maturity. Pyrolysis-gc and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) were used to investigate source rock extracts, oils and pyrolysates. While pyrolysis-gc lends itself well to analyzing structural units in kerogens and extracts using small compounds of low polarity (e.g. hydrocarbons), FT-ICR-MS is a perfect tool for rapidly characterizing polar NSO compounds in complex mixtures from pyrolysates, extracts and crude oil. NSO compounds are of high interest because they feature functional groups and thus strongly influence sorption, solubility and partitioning of petroleum compounds within unconventional shale system.

Differences in the evolution of the petroleum composition of unconventionally and conventionally reservoir oils are revealed by comparing the polar compound composition of (1) extracts of six Posidonia source rock samples with maturity levels between 0.43 and 1.45% Ro, (2) open-system pyrolysates of those six source rocks, and (3) four Posidonia sourced medium gravity conventional crude oils. The aromaticity and degree of condensation was found to increase much more pronouncedly with increasing maturity for retained NSOs than for oil NSOs. Pyrolysate NSOs hold “intermediate” compositions, pointing to a preferential expulsion of smaller compounds in the crudes and enhanced cyclisation and aromatization processes within retained fluids. The latter process was shown to occur at the cost of aliphatic precursors. A genetic link of the fluids as well as the likely timing of petroleum expulsion was revealed by comparing carbon number distributions in connection with alkyl-chain length distributions. The chemical differences documented here are manifested in the sorptive properties of fluids, and need to be taken into account in formulating production strategies.

NOTES:

Implementation of advanced analytical technics at the wellsite: learnings from surface data acquisition, benefits and pitfalls

Nicolas Ville

BP, Global Wells Organization

A new series of measurements has been brought to the well site thanks to technology improvements. Many of these technics allow to performing measurements directly from the rock cutting collected at the shakers or from the formation fluid content extracted from the drilling fluid once conveyed to the surface as it is done today for several hydrocarbon components.

It is therefore essential to understand what benefits using these technics could bring when deployed at the rig site, depending on the project considered, and also what pitfalls can be foreseen based on past experience with the surface data acquisition process.

Data acquisition for formation evaluation at the rig site is not new and many of the advantages and limitations are known. This contribution is about refreshing ideas around the pertinence of using these surface data along with sharing lessons learnt, and applying these to new measurement technics, such as continuous isotopes measurements, C1 to C8 quantitative measurement or Fourier Transform Infrared Spectroscopy to determine mineralogy composition and kerogen origin. It is also about highlighting how these new sources of information can be integrated and valued into a more global data acquisition strategy allowing comparison with downhole spectroscopy or fluid sampling analysis for instance.

Amongst other benefits of acquiring data from surface, the reduction of rig time dedicated to downhole formation evaluation data acquisition and the de-risking of the operation will be discussed. The surface conditions can create an advantage or an inconvenience that have to be factored in the availability and reliability of the data acquired. Besides, not all technics may be today compatible with the time scale of real time work. Indeed the preparation of the samples and their analysis remains a limiting factor in terms of the resolution that can be achieved depending on the rate of penetration during drilling. Also the diversity of the offer of advanced analytical technics is such that it can be difficult to build the best combination of measurements. Therefore expectations have to be carefully thought through for each project. Finally some aspects of data quality in relation to the process of projection versus depth of time data will be discussed in detail based on hydrocarbon analysis example to explore limitation of data resolution, possible misleading information and validity for decision making.

NOTES:

Application of QEMSCAN mineralogical and textural data to rock physics models: A novel approach for generating wireline-equivalent elastic and mechanical properties from core and drill cuttings

Scott Brindle, Richard Windmill, Peter Wellsbury
CGG Services U.K Ltd, Tyn Y Coed, Llandudno, Conwy, LL30 1SA.

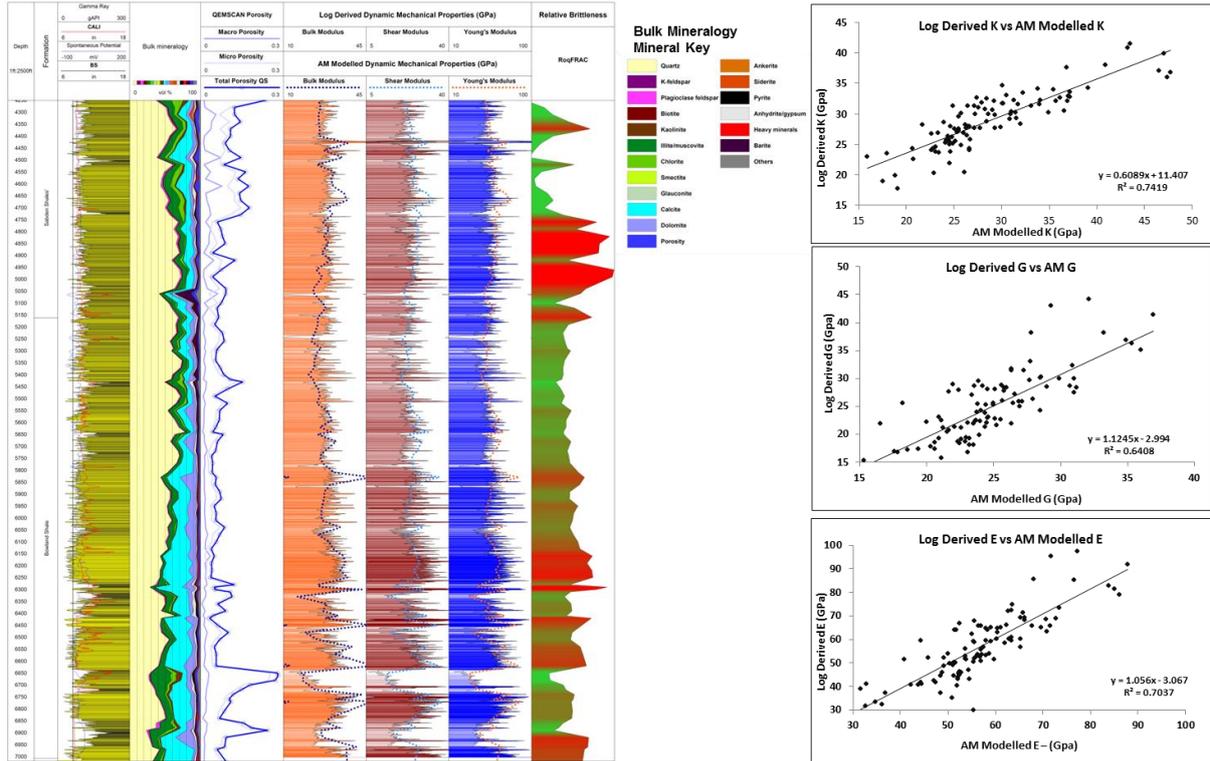
The quantification and distribution of mechanical and elastic properties through oil and gas reservoirs – particularly unconventional - is critical for accurately appraising hydrocarbon potential and for optimising stage placement for hydraulic stimulation.

Currently, oil and gas operators use wireline data logging tools to acquire petrophysical rock properties at the wellbore such as density, acoustic travel times and porosity. Based on those data, important mechanical and elastic properties of the rock such as bulk modulus, shear modulus, Young's modulus and Poisson's ratio can be derived at any point along the logged wellbore. However, wireline logging is expensive and can be risky especially in horizontal wellbores which are becoming more common in the development of hydrocarbon reservoirs.

Rock physics models have been developed to estimate the elastic and mechanical properties of the rock from these petrophysical interpretations of wireline logs. Typical input logs used are gamma ray, mineral volumes, neutron porosity and fluid saturations derived from resistivity. Typical output logs are bulk density, P-wave and S-wave velocities. Mechanical properties of the rock like Young's modulus and Poisson's ratio can be directly derived from those three elastic properties.

Here we present an innovative alternative approach to generate 'pseudo elastic and mechanical logs'. Mineralogical and pore fabric data were obtained from core and cuttings samples using QEMSCAN and high resolution SEM imaging and used as petrophysical inputs to rock physics models. This approach has the advantages of allowing rock properties to be determined without the need for wireline tools, which are expensive to run and also carry an additional risk for damage or loss when lowered into the well.

This approach can also be applied to older wells or production wells, which may or may not have had wireline analysis at the time of drilling, allowing rock properties to be determined purely from legacy geological material. The elastic data generated by the technique could also provide extra well controls for large scale seismic inversion studies. Furthermore analytical tools such as RoqScan exist which are portable enough to generate the data at wellsite in near real time to provide inputs for completion plans and stage placement for hydraulic fracturing. We present case studies from the major shale plays in the UK and the USA demonstrating successful attempts to reproduce wireline-equivalent elastic properties from detailed mineralogical and pore fabric data obtained through QEMSCAN analysis of drill cuttings.



Downwell plot from the Thistleton-1 well (NW England), showing mineralogy and porosity data on the left, with wireline-derived mechanical properties bulk, shear and Young's modulus (shaded logs) overlain by pseudo mechanical properties (dotted lines) modelled from QEMSCAN data. The crossplots on the right show a good correlation of pseudo elastic properties derived direct from QEMSCAN data with those derived from a traditional wireline-based approach

NOTES:

The application of imaging IR spectroscopy for mineralogical analysis of core and cuttings

Gavin Hunt

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The use of infrared spectroscopy for mineral identification dates back several decades, and is complementary to other mineral analytical techniques, such as XRD or point counting. However, a major drawback of these techniques, including the older point sampling IR spectrometers, is that they require sample preparation – an expense in both time and money. More importantly they cannot provide continuous quantitative mineralogical data to aid reservoir characterisation.

The most recent advance in IR spectroscopy is the use of real-time imaging reflectance spectrometers. These are non-contact and non-destructive, and acquire continuous mineral data in a detailed sub-mm pixel image format. The first of these introduced to the UK oil industry in 2008 is the portable SpecCam imaging spectrometer. It has been designed for detailed and automated mineral logging from cuttings and core and plugs over the mm to metre scale

The current SpecCam design can characterise many of the key molecular vibrations associated with amorphous and crystalline minerals that are important to understanding the performance of tight and unconventional reservoirs. The IR image data can be used to accurately discriminate and quantify different polytypes of the swelling and non-swelling clays, carbonates and sulphates. It also uniquely provides hydrocarbon information (presence or absence) and whether the oil is 'light', 'heavy' or an invasive OBM.

Figure 1 (right) shows a SpecCam False Colour Composite image (A) from a one metre section of clastic core from the North Sea. The IR data can be used to create image maps of any mineral identified, in this example showing the chlorite content (B), phengite content (C) and the Hydrocarbon type (D). The latter shows the 'heavy' bituminous foresets colour-coded blue and the liquid, 'lighter' oils in green, yellow or red pixels. Oil is absent in the chlorite-rich interval.

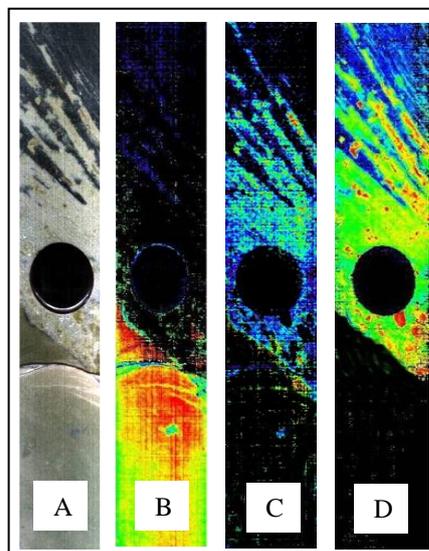
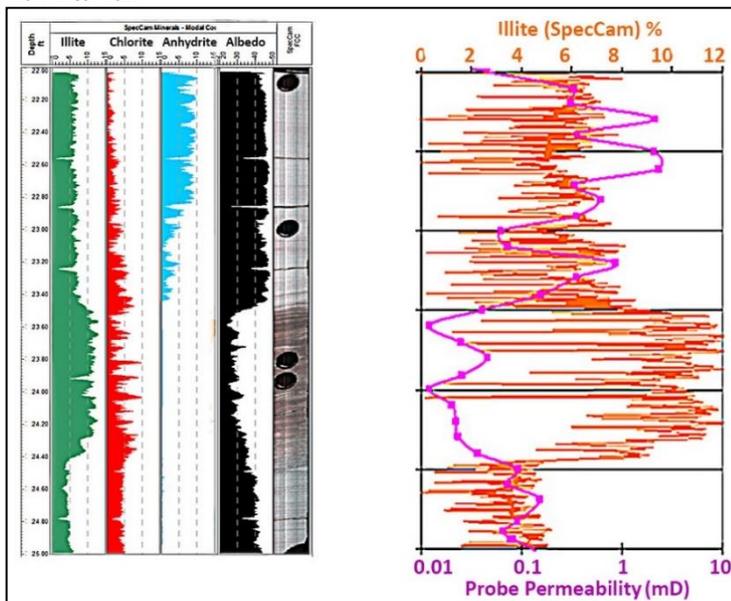


Fig.1.



The ability to image and map subtle compositional and crystallinity changes in a variety of important reservoir-influencing minerals can help identify unconformities and aid well to well correlations. In addition, the impact and interrelationship of clay (See Fig.2) and carbonate mineralogies (See Fig.3) on hydrocarbon distribution and permeabilities can be studied.

Fig.2.

Fig.2 (left) shows the effect an illite 'baffle' has on permeability in a clastic section from the Rotliegend. The continuous mineral profiles derived from SpecCam image data, show an inverse relationship between illite and permeability. Above the baffle illite is the dominant clay, and average permeability is 6 mD. Illite values are lower below the baffle, yet average permeability is low at around 0.1 mD, suggesting that the presence of chlorite is significant in reducing permeability in this part of the reservoir.

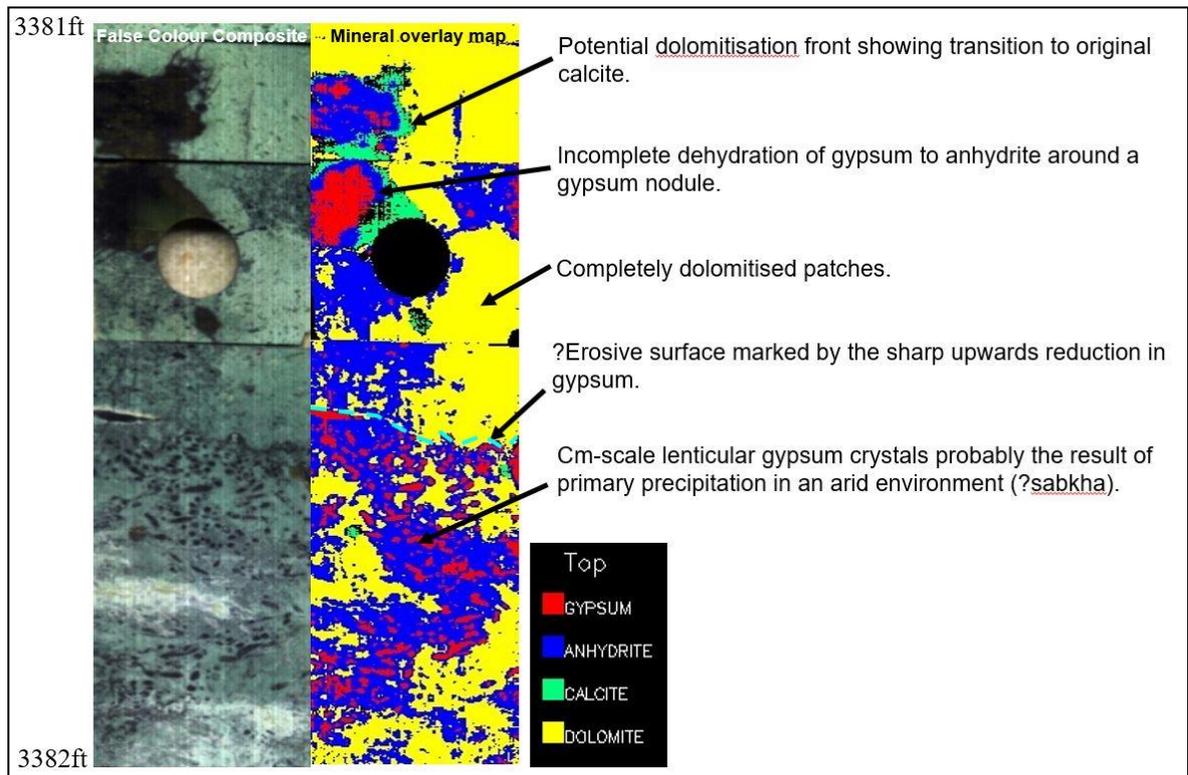


Fig.3.

Fig.3 (above) shows a SpecCam False Colour Composite and a mineral overlay map from a one foot section of carbonate core from Texas. The identification of the carbonate minerals calcite and dolomite, plus the discrimination of the sulphate minerals gypsum and anhydrite, show how the SpecCam image data can be beneficial in aiding and refining sedimentological understanding, as well as understanding the true poroperm characteristics of these complex rocks.

The SpecCam IR imaging technology addresses 3 major limitations of point sampling techniques – low productivity, inability to show detailed spatial distribution of minerals and low data density. These limitations have direct implications for the reliability and use of these data. Imaging IR spectrometers, such as the SpecCam, overcome these limitations and can provide a unique, spatially-detailed and continuous dataset, which provides a link between point sampling methods and continuous logs.

NOTES:

Keynote: Production Geochemistry – Fluids don't lie and the devil is in the detail

Pim van Bergen and Marc Gordon

Specialist Geology Team, Geochemistry, Shell UK Limited, Aberdeen

Production geochemistry is an integrated part of Shell business in the operating units. Detailed geochemical analyses of both the gas and liquid phases are routinely used to aid our understanding of Reservoir Connectivity, as part of Well, Reservoir and Facility management (WRFM) and to provide crucial base line data for Decommissioning.

The collection of geochemical data starts at the front end of the life cycle of a field including the use of isotubes. These are low volume atmospheric gas samples collected from the mud gas stream during drilling operations. Both the molecular and isotope composition of the gas is analysed to assess hydrocarbon source, maturity as well as within well connectivity. These are now routinely collected in all exploration and appraisal wells and in many production wells. Critical in this respect is the collection of isotubes in as much of the overburden as possible, as these data may become critical during late life production and end of field life. The importance of these data will be shown in a number of case studies from Central North Sea fields.

Standard reservoir characterisation also includes detailed geochemical fingerprinting to assess reservoir connectivity. Where possible both gas and liquid are evaluated as they often yield complementary data rather than similar data. Examples are shown where the geochemistry shows clear fluid discontinuities in fields as well as evidence of within field mixing.

Finally, Shell geochemical fingerprints of liquids using Multi-Dimensional Gas Chromatography (MDGC) are regularly used to allocate between different input streams (i.e. commingled production zones, wells or fields). An example of a multi-well single pipeline production allocation will be discussed revealing an improved understanding of pipeline residence time and a more accurate determination of the contributions of the different wells.

Source rock assessment from basin- to nano-scale: A case study from the Ukrainian Dniepr-Donets Basin

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The emerging exploration for unconventional resources in Central Europe coincided with a rapid development of new high-resolution imaging techniques, aiming for a better characterization of shale microstructures (e.g. Klaver et al., 2015a; Keller et al., 2013; Curtis et al., 2012). While such techniques are of great interest regarding the general understanding of storage and release of hydrocarbons from fine-grained rocks, their main limitation arises from the fact that the great advantage of enhanced resolution down to the nanometer-scale coincides with the decrease of representativeness due to extremely small sample sizes. Furthermore, pore space development is seldom related to changes in the geochemical properties of the organic matter within hydrocarbon-bearing rocks, focusing too much on the properties of individual samples. Therefore, the present study aims for a multi-scale characterization of the most prolific source rock in the Ukrainian Dniepr-Donets Basin (DDB), linking both facies and maturity changes, reflected by geochemical proxies, to the creation of nanopores in organic matter.

Primarily, oil-source rock correlation was performed to reveal the contribution of several potential source rock horizons to the charging of conventional hydrocarbon reservoirs in the northwestern (NW) and central DDB. It could be proven by combined isotopic and biomarker data as well as pyrolysis experiments, that Rudov Beds and adjacent organic-rich Upper Viséan intervals are likely the most important source for gas, but also oil, despite prevailing type III/II kerogen. Furthermore, study results revealed a correlation between $\delta^{13}\text{C}$ of the aliphatic fraction of crude oils and the $\delta^{13}\text{C}$ of methane in gas samples, arguing for a common (Upper Viséan) source. Following the general proof that Upper Viséan black shales in the NW DDB are partly prone to the generation of liquid hydrocarbons, a laterally well-resolved evaluation of their shale oil/gas potential was performed focusing on the key parameters (i) shale thickness, (ii) thermal maturity, (iii) mineralogy, as well as (iv) generation potential based on pyrolysis-gas chromatography and kinetic experiments. Considerable shale thickness (up to 100 m) and average TOC contents (>4 %) especially within the central part of the NW DDB suggest a potential for unconventional production, whereas a low maturity gradient and consequently low transformation ratios, as well as highly variable and often disadvantageous mineralogy with high clay mineral contents (especially kaolinite), diminish the economic value of this major target. Earlier hydrocarbon generation, e.g. due to presence of type IIS kerogen, might attenuate the negative impact of a low maturity gradient to depth, but cannot be assumed based on the performed kinetic experiments. Furthermore, strong facies variations between terrestrially dominated, gas-prone rocks in marginal areas and oil-prone rocks in more central locations were detected, causing variable hydrocarbon generation properties.

To link these facies variations with the microstructure of Rudov Beds, combined SEM and FIB/BIB-SEM investigations were performed to evaluate the total and organic matter (OM)-hosted porosity of Rudov samples from different locations throughout the basin. This procedure was chosen to achieve a representative characterization of (i) a wide maturity range (0.65 – 2.1 %Rr) and (ii) to resolve facies-induced differences in pore space generation within OM (gas-prone vs. oil-prone kerogen). Nanopores are not abundant in primary macerals (e.g. vitrinite) even in overmature rocks, whereas they develop within secondary OM (bitumen) formed mainly at gas window maturity. Frequently occurring sub-micrometer porosity, probably related to gas generation from bituminous OM, was detected within mudstones at a vitrinite reflectance >2.0 %Rr. However, such pores have also been detected in solid bitumen of oil-prone samples at oil window maturity (0.65-0.8 %Rr), arguing for the necessity to combine organic geochemical analysis with high resolution-imaging, for a better characterization of pore growth in organic matter. Quantification of the fraction of OM-hosted porosity (compared to total porosity) by pore segmentation from BIB-SEM high-resolution maps was performed for an oil-prone (early oil-mature) and a gas-prone (wet gas-mature) sample, to quantify the effects of kerogen composition on the porosity distribution (Fig. 1a,b). Despite lower maturity, the sample from the early oil window, comprising a higher amount of oil-prone kerogen, hosts more porosity in OM, compared to the wet gas-mature sample with predominantly gas-prone kerogen. Therefore,

differences in kerogen type, clearly visible from pyrolysis-gas chromatography and other organic-geochemical proxies, superimpose the effect of thermal maturation on the development of OM-porosity, although the main stage of pore generation is still strongly maturity-controlled, occurring between 1.3 and 2.0 %Rr. Nevertheless, although OM-hosted nanopores might contribute to some extent to gas storage and release from Rudov Beds, the main fraction of total pore volume is formed by intra-clay mineral porosity, mostly in the sub-micrometer range. Total porosity estimated from BIB-SEM maps is rather low for both investigated samples from the early oil and wet gas window (1.1 and 1.7 %, respectively). Apart from that, liquid metal injection (LMI) revealed comparably low connectivity of pores, arguing for predominance of pore throat sizes below the penetrable diameter of ~ 3 nm (Klaver et al., 2015b). In summary, the applied multi-scale, interdisciplinary approach revealed several limitations to the economic potential of this unconventional play, despite a considerable amount of oil/gas-in-place.

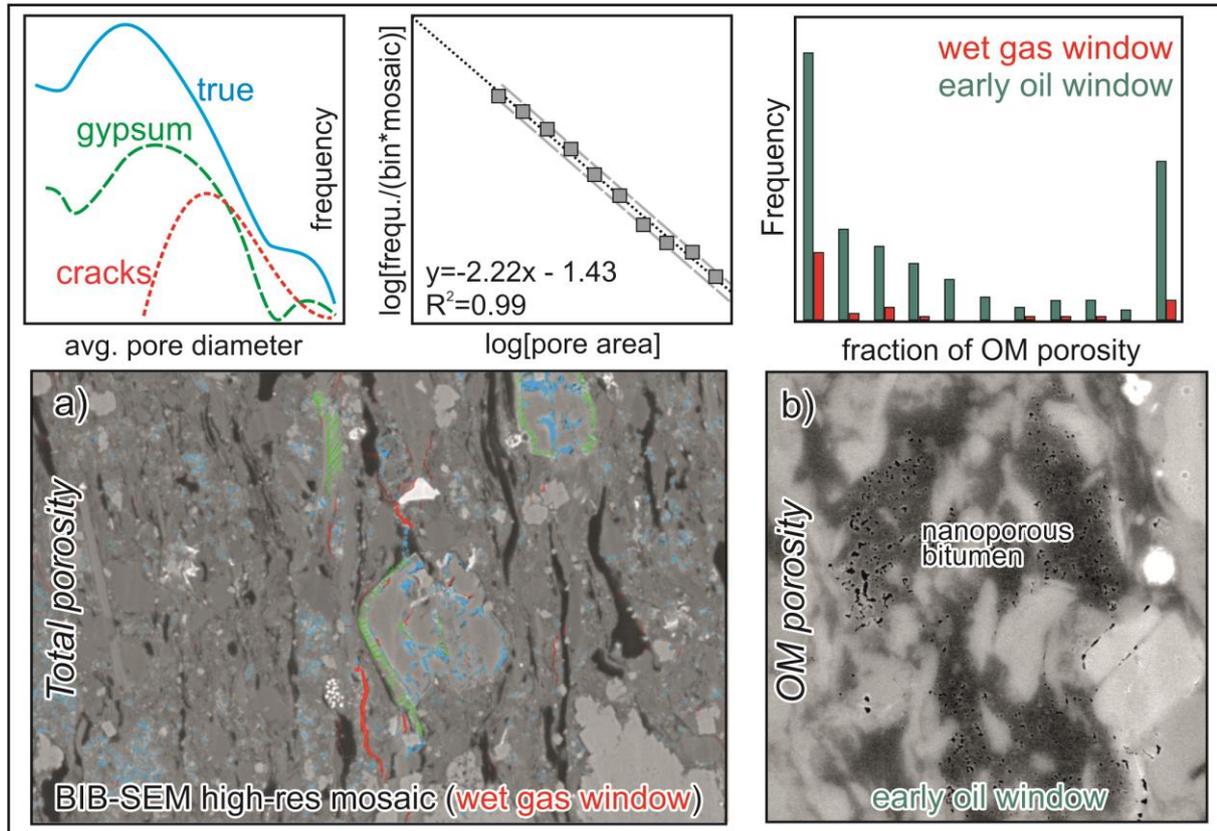


Fig. 1: (a) Segmentation of total porosity for a wet gas-mature sample from a high-res BIB-SEM mosaic. Artificial cracks and gypsum (core alteration) can be separated from true porosity by overlaying EDX and BSE/SEI maps and applying geometry factors. (b) High-res BSE image of an oil window-mature, oil-prone sample, hosting nanoporous bitumen. Isolated segmentation of OM-hosted porosity revealed a higher amount of porous OM in the oil-prone sample at lower maturity. This coincides with differences in extract composition and composition of hydrocarbons generated during pyrolysis.

Notes:

A multi-disciplinary approach to the evaluation of thermal alteration of mineral and organic components of the Marcellus Shale. Analytical results and implications for transport properties

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The Middle Devonian Marcellus formation in the Appalachian Basin has attracted great attention as an important gas-producing unit in North America and is considered to be one of the main sources of natural gas in the United States.

In this research, we studied samples from the high thermal maturity ($R_0 > 4\%$) part of the Marcellus shale-gas play. Of particular interest was an interval of high gamma-ray and anomalously low electrical resistivity. These samples offer the opportunity to study diagenetic effects on the mineral and organic components of the rock and their impact on petrophysical response in a context of deep burial at conditions close to incipient metamorphism.

High resolution electron microscopy images were collected from broad ion beam milled samples and from selected areas polished in situ with focussed ion milling. In particular, we concentrated on evaluating the porosity distribution between organic and mineral phases and on assessing the microstructural characteristics of detrital and diagenetic phases. Raman spectroscopy was used to quantify the degree of thermal alteration recorded in the organic material (OM). Finally, high resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) were used to i) visualize the nanometre-scale structure of the OM and ii) assess the extent of its thermally induced aromatization.

The results indicated a relatively rich organic content (3-7 wt. %) and mineralogical composition, assessed via X-ray diffraction, comprising quartz, illite, calcite, chlorite, albite, and pyrite. Illite was identified as the high temperature 2M1 polytype with crystallinity quantified by the Kubler index ranging between 0.34 and 0.43, placing the samples in the anchizone or prehnite-pumpellyite metamorphic facies and indicating burial temperature of at least 200°C.

Diagenetic phases identified via SEM analysis included framboidal pyrite, often associated with organic particles, blocky pyrite replacing shell fragments, micron scale quartz overgrowths and calcite, appearing as euhedral crystals dispersed in the clay matrix and as fibrous replacements of shell fragments.

The majority of the OM was highly porous bitumen and its position with respect to the quartz overgrowth indicates that it was emplaced following quartz precipitation (Figure 1a). Matrix porosity was also observed, especially within the clay aggregates and at the interface between rigid clast and clay minerals. Raman spectra collected from the detrital organic particles and migrated bitumen show the presence of a number of bands typical of thermally altered carbonaceous material (Figure 1b). Quantification of the full peak width at half maximum peak height for each of the bands allowed the use of a Raman geothermometer to assess the maximum temperature the sediment had been exposed to. This was evaluated to be 260-284°C, consistent with the analysis of illite crystallinity and legacy data on vitrinite reflectance ($R_0 \sim 4.5\%$).

HRTEM images show an abundance of short-range ordered domains with lattice spacing of ~ 0.335 nm within the OM (i.e. turbostratic structure) indicative of partial graphitization of the rock's organic component (Figure 1c). This is confirmed by the EELS spectra displaying features that can be ascribed to the π^* (285 eV) and σ^* (291 eV) peaks of carbon with features typical of partially graphitic material (Figure 1d).

In conclusion, the diagenetic history of the Marcellus shale encompassed an early stage of mechanical compaction at shallow burial followed by chemical alterations at greater depth represented by quartz overgrowths, clay mineral transformations, calcite and pyrite nucleation. Organic matter migration into skeletal pores and along grain boundaries likely occurred during petroleum expulsion (catagenesis) to form a connected network. As the sediment reached the gas window, OM cracked to methane (metagenesis) creating porosity. At peak pressure and temperature the residual, migrated organic material assumed a partially crystalline structure and transformed into a highly electrically conductive network.

The preservation of porosity suggests that this organic network can contribute not only to the electrical properties but also to the hydraulic properties of the Marcellus Shale.

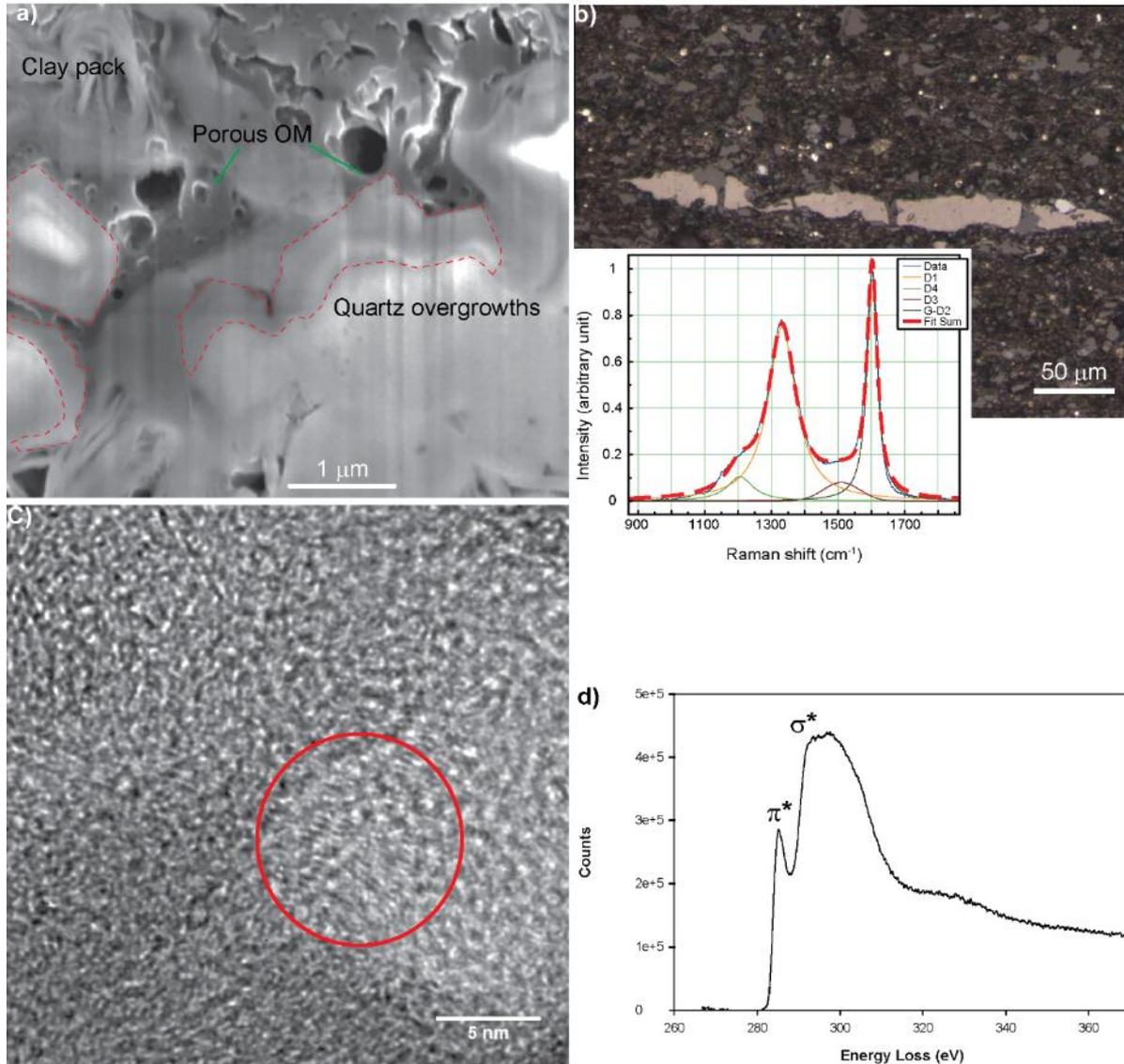


Fig.1: a) SEM image of a FIB cross-sectioned region showing quartz overgrowths and of porous organic matter (OM). b) Reflected light optical image of a bitumen particle and characteristic Raman signal for organic matter from the Marcellus shale. c) HRTEM image of organic particle with regions of nano-scaled ordered structures (e.g. within the red circle). d) EELS spectrum collected from the organics found in the Marcellus shale.

NOTES:

Using fluid inclusions to trace petroleum systems – a integrated case study of oil and gas migration in the Bight Basin to constrain source, composition and timing

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Fluid inclusions offer a unique method to test for petroleum migration that would otherwise remain hidden in the rock. While a range of fluid-inclusion analytical techniques are available, the advantage comes from integrating these techniques to investigate petroleum systems. We present a case study from a frontier basin, the Bight Basin of southern Australia, to show the application of fluid inclusion studies in providing information on source, composition and timing. Because this information is derived from core and cuttings, the results can be used to calibrate petroleum systems models.

To detect hydrocarbons, a reconnaissance-scale fluid inclusion study of Jurassic to Cretaceous sandstones was undertaken using CSIRO's Grain with Oil Inclusion (GOI™) technique. While oil-bearing, and in some cases gas-rich, inclusions were detected at low abundance in all wells, their presence provides proof of oil generation and migration in both the deep-water Ceduna Sub-basin and the flanking margins. The presence of hydrocarbon inclusion indicates that petroleum systems were active which, in turn, implies the presence of effective source rocks. Geochemical fingerprinting of fluid inclusion (FI) oil by the Molecular Composition of oil Inclusions (MCI) and novel gas-isotope techniques were performed on minute quantities of oil and gas extracted from the fluid inclusions. The results show significant differences in the type of organic matter input for the extracted hydrocarbons, with algal and terrestrial co-sourcing significant in the central Ceduna Sub-basin and terrestrial-only input on the margins. The bulk $\delta^{13}\text{C}$ isotopic composition of methane and ethane from fluid inclusions in Gnarlyknots-1A suggests a thermogenic origin for hydrocarbon gases, most likely derived from terrestrial organic matter. This bulk geochemical information derived from these oil migration intervals, with low hydrocarbon inclusion abundances, represents an advance in the technique while still achieving robust datasets.

The timing of oil and gas migration was determined from a number of wells spanning the basin depocentre to margins. Phase reconstructions by Petroleum Inclusion Thermodynamic (PIT), along with modelling of coeval aqueous inclusions, provided *pressure-temperature (PT)* constraints for individual hydrocarbon assemblages that are then related to independently derived burial history curves. The Bight Basin results indicate oil charge in the basin depocentre occurred from the Late Cretaceous from by sediment loading of the Upper Cretaceous succession, and later oil, gas-condensate and gas charge from the Miocene in both the depocentre and flanking margins.

The application of these novel fluid inclusion techniques has improved the prospectivity of the Bight Basin that, prior to this, had limited proof for active petroleum systems. Similar fluid inclusion studies could also be applied at different scales to brown-fields exploration and development activities.

This study was undertaken as part of the Great Australian Bight Research Program, a collaboration between BP, CSIRO, the South Australian Research and Development Institute (SARDI), the University of Adelaide, and Flinders University. The Program aims to provide a whole-of-system understanding of the environmental, economic and social values of the region; providing an information source for all to use.

NOTES:

Wednesday 1st March

Session Four

Geochemistry at Varying Scales

Keynote: Organic geochemistry at millimeter to Ångstrom resolution

Clifford Walters

ExxonMobil

Geochemists are early adapters of the latest advances in analytical chemistry. Many of the emergent techniques provide molecular and isotopic measurements at high spatial resolution, allowing for real-time imaging of dynamic systems, and *in situ* analysis at scales ranging from millimeters to Ångstrom resolution. Several of these techniques will be highlighted.

Two-dimensional mass spectral imaging is possible at millimeter to ~20 µm resolution using spatially selective ionization methods such as desorptive electrospray ionization (DESI), laser desorption ionization (LDI), and direct analysis in real time (DART). Chemical maps of fossils can monitor selective diagenetic processes and identify matrix effects on the preservation of organic matter. Core analysis of *in situ* organic matter reveals heterogeneities in source and reservoir rocks. Chemical composition can be correlated to bulk physical properties, such as specific gravity and viscosity, and can evaluate reservoir facies performance.

Secondary ion mass spectrometers (SIMS) can provide molecular and isotopic information at <10 nm resolution. Here, the sample is bombarded with focused ion beams (e.g., O⁺, Cs⁺, or C₆₀⁺) and the ions that are sputtered off from the surface are detected with a mass spectrometer. Organic are best examined using ToF-SIMS, while elemental and isotopic measurements can be made on magnetic sector nano-SIMS instruments. The technique is readily applied to microbiological studies where organisms can be grown using labeled compounds and the spatial distribution of the metabolites within a cell can be imaged. For geochemical studies, stable isotopic measurements of carbon, oxygen, nitrogen, and sulfur can be made *in situ* at useful precisions (± 1-3‰) provided the matrix effects are known.

Production of gas and liquids from fine-grained rocks has outpaced our knowledge of fluid flow in sub-micron pore systems. X-ray µ-CT allows us to examine fluid flow in real-time. Gas shales appear to have several different avenues for flow: micro-cracks that allow for relatively rapid lateral flow and a slower, diffusive flow within a largely organic matrix. The significance of organic porosity was not fully appreciated until it was imaged by scanning electron and helium ion microscopy. The size distribution of pores can be further characterized by small angle neutron scattering (SANS), which also has shown that methane condenses within the nm-scale pores. The presence nm-domains of graphitic carbon in source rocks can be examined using Raman spectroscopy and imaged by TEM. The order and frequency of these graphitic-domains increase with maturity and at very high levels (>3 %R_o) influence the electrical conductivity of the bulk shale.

Imaging organic molecules is now possible using the advanced TEM and atomic force microscopy (AFM). While FTICR-MS is capable of revealing the molecular formulae and mass distribution of asphaltenes, there are disputes concerning their structure: "island" vs. "archipelago." AFM is able to image individual asphaltene molecules and is providing illuminating descriptions of their configuration.

NOTES:

Using petroleum inclusions to trace petroleum systems – a review

Herbert Volk

BP Upstream Technology, Sunbury, UK

A reconstruction of charge processes that have led to the accumulation of petroleum in the subsurface routinely makes use of observations on fluids as encountered in reservoirs at present time. Variations of petroleum properties such as GOR, viscosity or sulphur content can often be explained by variations in source rock facies and source rock maturity in charging source kitchens, and by the timing of petroleum trapping in relation to oil and gas generation and secondary migration along vertical or lateral fill-spill chains. In the reservoir, further changes to the fluid properties may occur, e.g. by in-reservoir cracking, biodegradation, or fluid instability induced by changes in pressure and temperature. Therefore, the present day composition of petroleum records the end-point of cumulative processes in the geological past.

Fluid inclusions are small encapsulations of paleo- fluids that offer a window into this geological past. They enabling us to better constrain charge histories by providing calibration points that can be projected back in time. In sediments of petroliferous basins, they often trap petroleum, which is readily detectable by fluorescence microscopy.

The distribution and optical properties of petroleum inclusions provides stratigraphic and petrographic context for subsequent geochemical analyses of petroleum inclusions, most of which are very time-consuming and can only be conducted in specialised, clean laboratories. Selecting the most suitable samples for subsequent geochemical analyses is therefore very important. Microthermometry, coupled with qualitative and quantitative UV microscopy are the most widely applied techniques.

Some geochemical techniques use mass spectrometry without prior chromatographic separation. Other geochemical techniques geared towards obtaining more detailed molecular information, e.g. on biomarkers, involve chromatographic separation prior mass spectrometry. Isotopic analyses of petroleum inclusions are also possible. The analyses involve crushing of bulk samples, cleaned to variable degrees. While not routine, they have been widely applied to constraint petroleum charge histories.

Often different fluid inclusion assemblages in the same mineral grains can be identified by optical means, but obtaining geochemical information on these different groups of inclusions in the same mineral is difficult. Indirect methods of inferring on their chemical compositions are UV and FTIR spectroscopy, where advances have been made by using synchrotron beams. Methods of directly accessing individual inclusions involve the use of lasers followed by thermal extraction – GC-MS, or mass spectrometric mapping of minerals by using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), a surface-sensitive analytical method that uses ion beams to ablate into minerals.

In this contribution I will review approaches of extracting geochemical information from petroleum inclusions, and how this can be used to constrain petroleum systems.

NOTES:

Chlorite, chlorite everywhere but not an understanding on why it controls porosity? An HPHT experimental study of sandstone reservoir quality

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Quartz cementation is one of the main porosity reduction mechanisms in siliciclastic sandstone reservoirs. Detrital grain coatings, in particular chlorite, illite, mixed layer smectite/chlorite clays and microquartz frequently inhibit quartz formation and thereby preserve reservoir quality to greater burial depths than is normally predicted. The extent and mode of detrital grain coatings is crucial for the preservation of porosity, with often higher coat coverage leading to less quartz cementation. Laboratory experiments have already clearly identified in the literature the role played by high temperatures (>100°C) in controlling authigenic clay coatings on detrital quartz grains. However, there has been little work undertaken to investigate how high pressure and high temperature (HPHT) influence the development of chlorite clay coatings and the amount of quartz cementation in sandstone reservoirs.

In this study, hydrothermal reactor experiments have been undertaken using an autoclave AE self-sealing reaction vessel rated to 250 MPa and operating temperatures up to 650°C. Experiments were performed to derive new information about how chlorite grain coats inhibit quartz cement and preserve porosity in deeply buried HPHT sandstone reservoirs. Equally the importance of high pore pressures has been investigated on the potential reduction of quartz cementation in sandstones. Samples used in experiments were from i) the Lower Jurassic Cook Formation of the Oseberg Field, Norway (30/6-7A) where the sands have known berthierine clay coatings (precursor to chlorite) and, ii) clean quartz sand with no clay coatings or detrital grain components. Experiments were carried out with a constant temperature (250°C) and different pore pressures from 7 – >60 MPa over the duration of 5 days for each experiment in solutions of 0.1M Na₂CO₃. A source of silica gel was used to maintain silica super-saturation during all experimental runs. Samples were inspected prior and after the experiments at differing pore pressures using SEM, BSEM, SEM-Cl, SEM-EDX and elemental mapping.

The experiments in this study confirm the widely held view that chlorite grain coats preserve porosity in deeply buried sandstones by inhibiting late quartz cement, but provide a new interpretation for the mechanisms by which this inhibition occurs and the role played by high pore fluid pressures. Of particular importance is berthierine clay can act as a precursor for chlorite but importantly may be accompanied by an increase in grain coat coverage and coat quartz grains with no precursor clay coatings. At high pore pressures (>40 MPa) chlorite-coat effectiveness as a nucleation barrier appears to decrease. The silica supersaturated pore solutions demonstrate precipitation through the coatings to open grain surfaces between chlorite platelets. Furthermore, at moderate to high pore pressures (>10MPa) there was a noticeable reduction in the amount of quartz cementation compared to normally pressured sandstones at the same temperature. Any quartz precipitated was microquartz, as grain coatings. This research demonstrates the important role played by pore fluid pressure in controlling quartz cementation in HPHT reservoir sandstones and highlights how microquartz cement nucleation beneath chlorite coats may occur. This research has important implications for not only assessing reservoir quality of deeply buried HPHT sandstones, but also for the understanding of precipitation of microquartz in HPHT sandstone reservoirs that may significantly affect microporosity, petrophysical properties and grain framework strength.

NOTES:

Convergence of shale gas reserve estimates from a high pressure water pyrolysis procedure and gas adsorption measurements

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Shale gas has transformed the US energy sector, accounting for over 50% of gas production in 2015. The UK has been looking to emulate this success, due to shale gas being one of the cleanest non-renewable sources of energy, and the desire for increased energy independence. However, the geological differences between the respective shales is one of the factors that has limited exploitation to date, along with accurate assessments of the UK's shales gas reserves. Shale gas is produced from shale rocks with high source rock thermal maturity (vitrinite reflectance (R_o) >1.4%) Jarvie (2012). Gas produced from the Barnett Shale in the USA is composed of 80-90% methane (Jarvie et al. 2005; 2007), sourced from kerogen Type II marine shales. Although research into shale gas has increased greatly during the past decade, the mechanisms of gas generation and retention in shale systems are still not that well understood. Regarding the assessment of shale gas resources using laboratory pyrolysis procedures, the gas estimate will depend upon the maturity range over which dry gas generation occurs and the pyrolysis procedure used.

A preliminary study estimated that the Upper and Lower Bowland Shale unit (North of England) contains an estimated gas in place (GIP) of 164-447 and 658-1834 tcf (trillion cubic feet) of gas respectively (Andrews, 2013). This is Upper and Lower Bowland Shale estimates are equivalent to about 55-149 years and 219-611 years respectively of gas supply based on the current UK consumption of 3 tcf per year. This estimate was based Rock Eval pyrolysis using the source rock potential, and assumed that shale gas was generated at VR of 1.1-1.9% R_o . A pyrolysis technique (termed water pressure sequential pyrolysis) that simulates petroleum generation and expulsion in geological basins has been developed and applied to shale rock from the Rempstone-1 well (Widmerpool Basin in the Upper Bowland Shale). This source rock is immature (0.58% R_o , HI of 410 mg HC/g TOC, Tmax of 436 °C, and TOC of 6.69%), and contains a mixture of Type II and III kerogens. The sequential high water pressure pyrolysis experiments conducted on rock chips (2-5 mm particle size) at a pressure range of 300 and 800 bar produced dry gas in later stages of source rock maturation, unlike many conventional laboratory pyrolysis experiments that do not produce dry gas.

Sequential experiments conducted in the absence of water (non-hydrous pyrolysis) for comparison produced higher gas yield compared to 800 bar water pressure, and the gas contained < 70% methane due to cracking of oil retained in the source rock thereby producing more gas with high proportion of C₂-C₅ hydrocarbons. In the water pressure sequential experiments, gas yields were highest for source rock with initial VR of 1.26% R_o (21 mg/g TOC), but the methane content was only 50%. Typical dry shale gas 80 and 90% methane was generated from source rocks with initial VR of 2.03% R_o (7.4 mg/g TOC of gas) and 2.25% R_o (4.7 mg/g TOC of gas) respectively.

The gas in place (GIP) estimates calculated (using gas yield obtained for 800 bar sequential pyrolysis) at different maturities between 1.26-2.34% R_o assumes that all the gas generated remains within the shale which of course may not be possible if there is insufficient porosity. The GIP was highest at lower maturity range (1.26-2.03% R_o), but was a factor of 2-3 lower at R_o >2.0% with gas containing 80-90% methane. To provide precise estimates, the wetness of gas and maturity range for dry gas generation needs to be defined. For example, over a maturity range of 2.25-2.34% R_o and a gas dryness of 90%, the GIP estimate was ca. 22 tcf, 12 times lower than 264 tcf reported by Andrews (2013) for the Upper Bowland Shale unit assuming the source rocks had an initial HI of 475 mg HC/g TOC.

To relate predictions of gas generated to amount that can be held within the shale, porosity has been characterised with nitrogen, CO₂ and high pressure methane adsorption isotherms conducted on shales both with and without moisture to provide information on the micropore structure of the shale. The meso/macropore structure was also

characterised by Mercury Intrusion Porosity (MIP). Increasing maturity gives rise to an increase in micro/mesopore volume, due to the removal of oil, but a similar effect was not seen in the meso/macropores. The similarity between the nitrogen and CO₂ adsorption isotherms indicates that diffusion is non-activated in the shale. MIP indicated that the increase in macro/mesoporosity is similar for sequential and non-sequential pyrolysis meaning that the greater quantity of oil remaining in the non-sequential experiments is largely in the micropores.

The high pressure methane adsorption isotherms are Type I for the initial shale and indicate that that moisture present reduces methane adsorption by a factor of 4. The mono-layer coverage from Langmuir plot was calculated for the wet and dry samples to be 1.2 and 4.5 (+/- 0.5) mg of methane per g. Assuming that matured shales have 2.5 times porosity of the initial shale, wet methane adsorption, dry adsorption would give mono-layer coverage of ca. 10-12 mg of methane per g of shale, compared to 3 mg wet. In reality, the actual methane adsorption could lie between these extremes but the overall range of 3-12 mg is virtually identical to the gas yield of 4-10 mg/g of hydrocarbon gas per g of shale obtained from the 800 bar water pressure experiments for gas with a dryness of 80-90% methane. However, the methane adsorption is significantly lower than 21 mg/g of hydrocarbon gas per g of shale with only 50% methane obtained at 800 bar. Clearly, more work is needed to understand adsorption mechanisms for methane but these results provide strong evidence that there is insufficient capacity within the rock to adsorb larger quantities of gas that would be generated assuming that shale gas is generated at lower and over a wider thermal maturity range (1.1-1.9% Ro) as suggested by Andrews (2013).

NOTES:

Raman Heavy Mineral Analysis for understanding sediment provenance and reservoir heterogeneities in fluvial successions and optimising hydrocarbons production

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Having a high-resolution geologic model of reservoir – including knowledge of heterogeneities – is the key to optimise hydrocarbon production in many depositional environments. Moreover, paleodrainage reconstructions – constrained by sediment provenance interpretation – can give extremely useful information. Mineralogical techniques are commonly applied to identify sediment provenance, and can be also used for establishing reservoir architecture and understanding reservoir behaviour during production. In this contribution, we apply heavy mineral (HM) analysis – via both Raman spectroscopy and optical identification – on an un-named fluvial succession, to provide constrains for provenance interpretation. By doing this, we demonstrate the applicability of Raman spectroscopy as an automated heavy mineral identification tool. Furthermore this cost effective and fast technique can provide further information about mineralogical composition (e.g., garnet end-members; Figure 1c) and also enables fine grained sediment to undergo HM analysis, which cannot be undertaken by standard optical methods.

The study area is subdivided in two regions, belonging to the same fluvial formation. In the northern one, samples represent point bar deposits and are subdivided in following lithofacies: sandstones with mudclasts (lower part of the point bar), medium to coarse grained sandstones (lower to central part of the point bar), and very fine to fine grained sandstones (central part of the point bar) and have undergone both Raman spectroscopy and optical HM analysis. In the southern area, only optical HM analysis has been undertaken. In the both areas, the most commonly observed HM are zircon, tourmaline, rutile, garnet, kyanite, and staurolite, along with smaller amounts of chloritoid and other minerals. In the southern area, coarse grains of kyanite are abundant (up to 28.5%) at the base of the succession and also staurolite is more abundant than in the further upwell interval (Figure 1a).

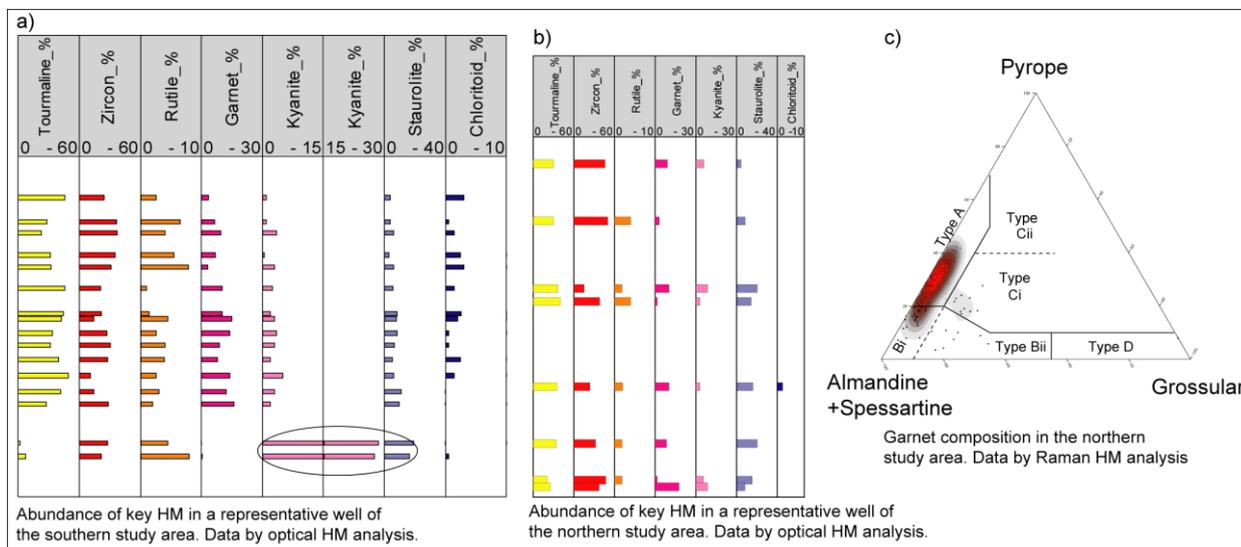


Fig. 1 – Mineralogical data from optical and Raman analysis

In the northern area results of Principal Component Analysis (PCA) of data obtained with the two analytical techniques give the same mineralogical associations and similar samples distribution (Figure 2b, 2c). In the both areas, the PCA shows different HM are enriched in different lithofacies. For example, zircon, rutile, and chloritoid are enriched in very fine and fine grained sandstones, whereas kyanite is enriched in medium and coarse grained sandstones (Figure 2). These observations can be explained as HM have a wide range of densities and thus are strongly affected by hydraulic sorting. Zircon and rutile, having similar density, are expected to be enriched in the same grain-size window and, in particular, in the finer grain-size ones, as they are ultradense. Furthermore, the

mineralogical habit can also influence the HM distribution in the sediment. Chloritoid having a platy habit is expected to be preferentially deposited in low energy settings. Different lithofacies are thus characterised by different HM assemblages, showing that HM analysis can help in refining the definition of depositional facies in the study fluvial succession.

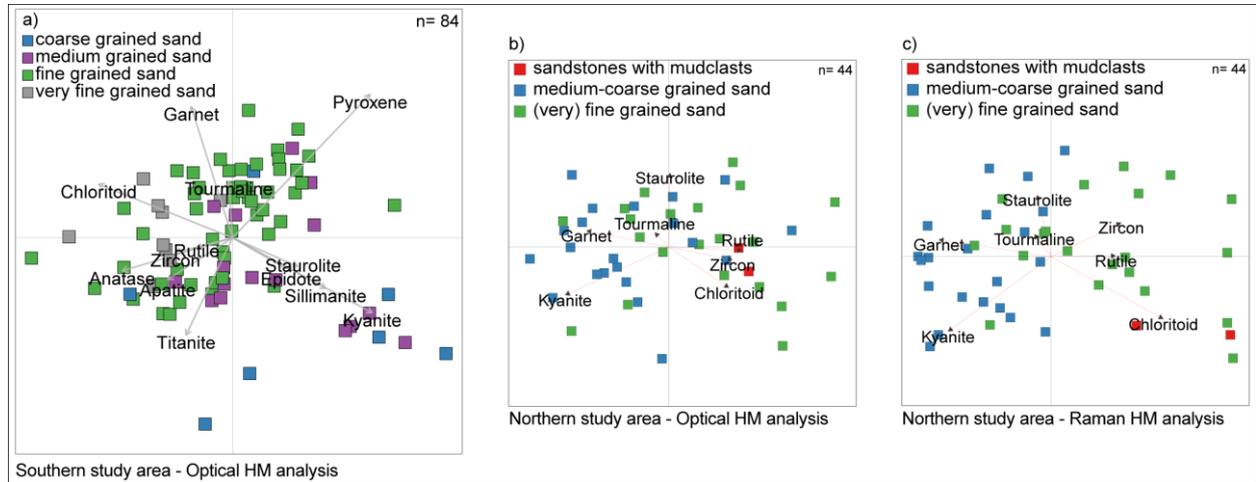


Fig.2 – Principal Component Analysis of mineralogical data

The observed mineralogical associations suggest the analysed fluvial succession has different source areas, comprising high-grade metamorphic units (providing kyanite and staurolite) and recycled sedimentary rocks (providing rounded ultrastable minerals). The abundance of kyanite and staurolite observed at the base of study wells in the southern area points to provenance from high-grade metamorphic units was more important in the lower formation and it was later diluted by sediment supply from other source areas, possibly suggesting a larger paleodrainage area for the upper formation. Moreover, Raman spectroscopy provides further information that are not available where only optical analysis are performed. It shows high percentages of Type A garnet (i.e., almandine, spessartine, pyrope-rich garnet) occur in the study formation (Figure 1c), suggesting provenance from granulite facies metasedimentary rocks.

NOTES:

Raman spectroscopy: a new tool for the analysis of thermal evolution of amorphous organic matter rich kerogen in diagenesis

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In the quantitative assessment of hydrocarbon generation from source rocks, a key topic is the correct calibration of numerical thermal models. Vitrinite reflectance has been always considered the most reliable thermal maturity indicator in sedimentary basins, even if many ambiguities can affect vitrinite reflectance reliability, in particular when dealing with amorphous organic matter rich kerogen. In this case, the main sources of errors derived from the paucity of vitrinite and from the vitrinite reflectance suppression phenomena that occur in the presence of high hydrogen content.

In this work we provided new thermal maturity indicators, derived from Raman spectroscopic analyses on the organic matter, that can be used as an alternative to vitrinite reflectance in thermal model calibration.

In detail, the maturity profile of a 5 km thick Oligocene-Miocene siliciclastic section, drilled in the Malembo Formation in the Lower Congo Basin (offshore Angola), was correlated against parameters obtained from Raman spectroscopy analyses performed on bulk kerogen.

Organic facies along the well are both vitrinite rich and amorphous organic matter rich and the maturity profile was calculated using a multimethod approach based on: 1) optical analyses (vitrinite and bitumen reflectance); 2) XRD for clay mineralogy characterisation and 3) FT-IR spectroscopy on the organic matter.

In this work we: 1. define how to turn the Raman apparatus suitable for kerogen investigation; 2. develop an six-band deconvolution scheme of Raman spectra on kerogen in the immature to mid-mature stage of hydrocarbon generation; 3. present a new Raman parameterization correlated against thermal maturity expressed as vitrinite reflectance equivalent suitable when organic facies are both vitrinite rich and amorphous organic matter rich; 4. discuss the main qualitative and quantitative approaches in the use of Raman spectroscopy to investigate carbonaceous matter at the solid state from diagenesis to metamorphism.

In particular, comparing our results with those obtained from previous works at low and high metamorphic grades, we were able to define and discriminate changes in Raman features moving from anthracite ranks to medium volatile bituminous coals ranks.

NOTES:

Gas isotope fractionation in source rocks and implications for petroleum exploration

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Geochemical analyses of Australian coal and organic-rich mudstones indicate that during desorption both molecular and stable isotope composition of gas change with time. The rate of change varies depending on gas composition and diffusivity as well as the source rock type. Therefore, a detailed understanding of the mechanism of isotope fractionation can improve our ability to accurately interpret the organic matter type and thermal maturity of source rocks that formed the hydrocarbons in reservoirs. Many of the published classification systems relating stable isotope composition of gas to source rock and thermal maturity do not consider the effects of such isotope fractionation.

The $\delta^{13}\text{C}$ of Australian Permian coals range between -22 and -26‰ (VPDB) and that of thermogenic methane generated from these coals range between about -25 to -40‰. The $\delta^{13}\text{C}$ value for a specific gas sample taken during desorption, however, varies with time due to molecular and isotopic fractionation effects. For example, in a set of deep Bowen Basin coal samples the difference in $\delta^{13}\text{C}$ for methane between early and late desorbed gas range between ~2‰ (-39.3‰ to -37.2‰) and ~29‰ (-39.9‰ to -10.8‰). For higher hydrocarbons this fractionation effect is lower, where for ethane it ranges between ~1‰ and 8‰ and for propane it is generally <3‰.

Similar isotope fractionation can be seen for gas desorbed from marine source rocks (Meso-Proterozoic Velkerri Formation mudstone) in the Beetaloo Basin. The $\delta^{13}\text{C}$ value for an immature isolated kerogen sample from the shallow Velkerri Formation is approximately -33‰. In the deeper parts of the basin the Velkerri Formation is fully gas mature and the desorbed methane shows $\delta^{13}\text{C}$ fractionation of about 28‰; early desorbed -40‰ and late desorbed residual gas -11.6‰. Ethane and propane show lower isotope fractionation where the difference between early and late desorbed gas is 1.6‰ and 0.9‰ respectively.

In both coal and organic-rich mudstones the molecular composition of the gas also fractionates, where early desorbed gas is relatively enriched in methane and later desorbed gas is increasingly enriched in heavier hydrocarbons. Light and scanning electron microscope analyses indicate a range of pore-size distribution in these rocks suggesting a "molecular sieve" type structure. Such a structure can lead to differential adsorption-diffusion properties for various hydrocarbon components and contribute to isotopic fractionation during expulsion.

Keywords: Isotopes, molecular fractionation, coal, source rocks, pore-size distribution.

NOTES:

Origin of solid bitumen in the Elgin/Franklin complex of the Central Graben

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The Upper Jurassic (e.g. Fulmar) sandstones are major oil and gas condensate reservoirs in the North Sea, although many of the reservoirs also contain small, but significant amounts of bitumen. These bitumens have been described as pyrobitumens generated by the cracking of an earlier oil charge (Isaksen, 2004), although analytical data to support this formation mechanism have not been published. Vandenbroucke et al. (1999) suggested that the Elgin/Franklin gas condensates were derived by the thermal cracking of an earlier oil charge, and produced a kinetic degradation model showing that the gas condensate composition could have been derived by the oil cracking process. Again the bitumen is assumed to be the thermal residue produced by the cracking process, although Vandenbroucke et al. (1999) did not present analytical data from either the bitumens generated in the laboratory during the oil cracking reactions, or from the bitumens in the Elgin/Franklin complex. The increase in temperature that occurs during the rapid Plio-Pleistocene subsidence in the Central Graben is thought to provide the thermal energy necessary for oil cracking.

Within the Fulmar reservoirs, the bitumens often impregnate the microporosity within the illite diagenetic cements (Wilkinson et al., 1997), and the bitumens therefore provide a key to understanding of the formation of the hydrocarbon charges and the timing of the diagenetic cements, which are very important to the economic success of the petroleum system. However, the analysis of the bitumens is very difficult using conventional petroleum geochemical techniques, due to the insolubility of the bitumens in most organic solvents. Bitumen insolubility can be overcome by using hydropyrolysis (HyPy) which has been used extensively to liberate covalently bound biomarkers from highly mature kerogens (Lockhart et al., 2008), heavily biodegraded oils (Sonibare et al., 2009) and mineral-bound asphaltenes to provide information on the charging of a North Sea reservoir (Russel et al., 2004).

Using both drill cuttings and core fragments, bitumen-stained samples were successively extracted using *n*-heptane, toluene and DCM/methanol. Asphaltenes were precipitated from the DCM/methanol extracts using *n*-heptane, with the HyPy of the asphaltenes releasing biomarkers bound within their macromolecular structure. Analysis was complicated by the use of oil-based drilling muds which perturb the biomarker distributions with both the solvent extractable free phase, and also the asphaltene bound phase due to the presence of fatty acid type additives which partitioned with the asphaltene during isolation. This necessitated the use of assessing the overall maturity of the aromatics released by HyPy, with both GC-MS and NMR indicate that the bitumens contain aromatics typical of mid-mature oils, as opposed to high maturity (with high concentrations of polyaromatic hydrocarbons) expected if the bitumens formed by thermal cracking of an oil. Indeed, the bitumen HyPy aromatics have the same maturities as mid-mature oils found in many of the North Sea reservoirs. Therefore, it may be necessary to invoke an alternative mechanism for the formation of these bitumens, which could include the biodegradation of an early oil charge, or pressure mediated combination reactions between the oil molecules, as recently observed during the high liquid water pressure pyrolysis of crude oils (Uguna et al., 2016; Xie et al., 2016).

Combination reactions are exothermic and will have occurred soon after overpressures had started to develop in the Fulmar reservoir, but well before the current model of formation during the Neogene produced by a combination of high temperatures and high pressures. If the bitumens were generated by such high pressure combination reactions, the bitumens must have been generated before the rapid Neogene-Quaternary burial which produced high temperatures unfavourable to exothermic combination reactions. This would imply that oil had been generated and trapped during the Cretaceous, which is much earlier than the Palaeogene onset of oil generation as predicted by current models (Cornford, 1994; Swarbrick et al., 2005). Bitumen generation in this model must have occurred soon after reservoirs became overpressured. Much earlier generation of the bitumens has implications for the timing of diagenesis and the reservoir porosity-permeability predictions.

Alternatively, the Elgin-Franklin bitumens could have been formed by biodegradation of an early oil charge during the period of uplift and erosion that generates the base Cretaceous unconformity. For this scenario to occur, then an even earlier oil charge would have to have occurred, i.e. Upper Jurassic oil generation, than predicted for the high pressure combination reaction model. Oil generation during the Upper Jurassic and biodegradation during the timing of the Lower Cretaceous unconformity implies that the diagenesis is much earlier than currently believed to be the case. Haszeldine et al (2003) considered that the onset of oil generation in deep grabens started at 120 Ma.

NOTES:

Poster Presentation Abstracts

Day 1

Multi-scale 3D quantification of an organic-rich mudstone, the Carboniferous Bowland Shale

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Multi-scale 3D X-ray computed tomography (XCT) and 3D electron microscopy (3D - EM) imaging techniques were used to produce 3D images with a resolution spanning three orders of magnitude from $\sim 7.7 \mu\text{m}$ to 7 nm for one typical Bowland Shale (Northern England), identified as the largest potential shale gas play in the UK. These images were used to quantitatively assess the size, geometry and connectivity of pores and organic matter. The data revealed four types of porosity: intra organic pores, organic interface pores, intra and inter mineral pores. Pore sizes are bimodal, with peaks at 0.2 μm and 0.04 μm corresponding to pores located at organic-mineral interfaces and within organic matter, respectively. These pore-size distributions were validated by nitrogen adsorption data. The multi-scale imaging of four pore types shows that there is no connected porosity at these scales with equivalent diameter of 20 nm or larger in this sample. However, organic matter and clay minerals are connected and so the meso porosity (~ 5 nm) within these phases provides possible diffusion transport pathways for gas. The mineral component percentages were quantified at all scales by XRD and TOC measurements.

This work confirms multi-scale 3D imaging as a powerful quantification and visualization method for shale reservoir characterisation allowing the representative volumes of pores, organic and mineral phases to be defined to model shale systems. The absence of connected porosity at scales greater than 10nm shows potential importance of the organic matter network in controlling hydrocarbon transport in these low permeability systems.

Reservoir quality assessment using automated mineralogical techniques: Quantification of authigenic kaolinite and its relationship with pore networks

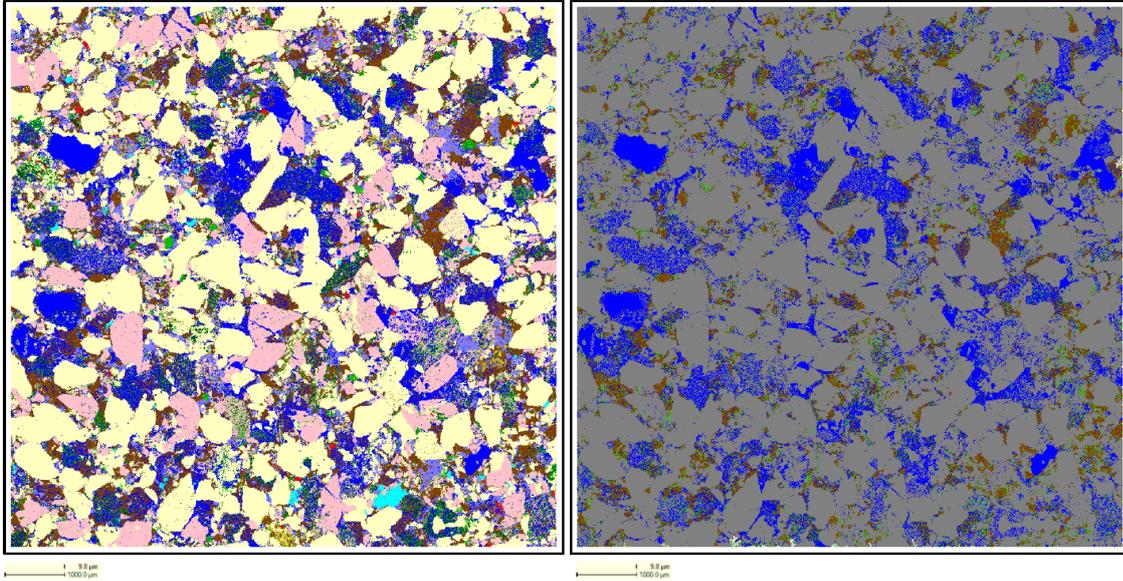
John Ford, Dean Rigby, Scott Brindle, Emma Cairns, Peter Wellsbury
CGG Services (UK) Ltd.

Methods/premise: Understanding and quantifying the roles of primary vs. secondary diagenetic controls on reservoir quality requires the differentiation of detrital from authigenic products. These phases must then be analysed in terms of their role in intergranular macropore alteration to truly understand their respective controls on reservoir quality. Elemental analysis of kaolinite volumes identified two forms; a 'pure', authigenic kaolinite comprising Al, Si and O only ('Authigenic Kaolinite') and a 'detrital' form containing additional variably low volumes of other elements ('Detrital Kaolinite'). By reviewing the proportion and associated bulk volumes of each kaolinite type in connection to porosity, a relationship can be observed that can help understand the relative macropore occlusion of detrital and authigenic clay types/species.

Results: Reservoir samples were analysed using a Quanta 650F FEG QEMSCAN. These samples comprised poorly sorted, variably coarse debris to hybrid-flow sand bodies. Initial qualitative analysis demonstrated key variations between both these kaolinite types in relation to the macropore system. 'Detrital' kaolinite formed small, irregularly shaped masses, commonly associated with later stage carbonate cements. 'Authigenic' kaolinite occurred as larger masses, commonly fully occluding macroporosities. Data were obtained using iDiscover to quantitatively assess these qualitative relationships.

At low bulk volumes (<1%) a linear relationship between 'detrital' and 'authigenic' kaolinite with porosity was observed. This linear relationship became skewed towards authigenic kaolinite between 1 – 2% bv. Above 3% bv this relationship became further skewed, with twice as much authigenic kaolinite in contact with porosity compared to detrital kaolinite volumes within the same sample. In combination with grain size, pore size distribution and CCA permeability data, these results can provide a threshold volume to identify when authigenic clay species outcompete detrital muds/clays to negatively affect macropore volumes.

Mineral maps of reservoir samples showing bulk sample composition (left) and distribution of kaolinite phases and their association with pore fabric (right)



Mineral Name

- Background
- Quartz
- K-Feldspar
- Plagioclase Feldspar
- Biotite
- Chlorite
- Illite
- Muscovite
- Glauconite
- Smectite
- Kaolinite
- Calcite
- Dolomite
- Ankerite
- Siderite
- Gypsum/Anhydrite
- Pyrite
- Heavy Minerals
- Pores
- Others/Contaminants

Mineral Name

- Background
- Kaolinite - Authigenic
- Kaolinite - Detrital
- Pores
- Others/Contaminants

Multiscale visualization of fluid-fluid-mineral interfaces and pore connectivity using Cryo-BIB-SEM and Liquid Metal Injection: A case study on re-saturated North Alpine Foreland Basin sandstone

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Pore geometries and associated mineral phases and fluids are important properties in reservoir rocks such as gas shales, (tight) sandstones and carbonates. Imaging of the pore space using Broad Ion Beam (BIB) milling and Scanning Electron Microscopy (SEM) allows accurate quantification of the pore space from centimeter to nanometer scale resolution on a relatively large area in these types of rocks, as shown over the past few years in numerous applied studies (Desbois et al., 2011; Klaver et al., 2015a). From the mm² size Argon-ion polished sample area we can obtain the mineral porosity by combining image data from SE, BSE and EDX detectors using dedicated image segmentation algorithms to automate the process of porosity analysis. Based on such pore segmentation pore statistics and physical properties of the materials, such as porosity and permeability, can be inferred. It was found that the visible pore sizes in fine-grained rocks follow a power-law behavior from the micrometer down to the nanometer range (Klaver et al., 2012; Hemes et al., 2013; Houben et al., 2013).

Combining BIB-SEM with Liquid Metal Injection (LMI) enables to visualize the preferred transport pathways and to determine the controlling pore throat diameter and finally to infer the permeability. The LMI experiments followed by BIB-SEM illustrated the significant effect of fractures on transport pathways and the low connectivity of the clay-rich matrix in mudstones and cemented sandstones (e.g., Klaver et al., 2015b).

BIB-SEM under cryogenic conditions allows direct study of the oil-water-mineral system in hydrocarbon-bearing reservoirs, at resolutions of 10 nm. We quenched a range of mudstones (Desbois et al., 2013; Desbois et al., 2014), and also sandstone and carbonate reservoir samples, equilibrated with oil and brine (Schmatz et al., 2015, Schmatz et al., 2016), to liquid nitrogen temperature and subsequently sectioned them using BIB-cutting under cryogenic conditions. The flat cross-sections with dimensions of 4 mm² allow Cryo-SEM imaging of oil-brine-mineral interfaces, with high-resolution EDX-mapping for phase identification.

In this contribution we apply the imaging methods described above to investigate different reservoir units of the North Alpine Foreland Basin (Molasse Basin). In particular, Eocene and Turonian horizons were re-saturated with the formation fluids, in order to improve our understanding of the effect of mineralogy and fluid chemistry on the in-situ configuration of fluid-fluid-solid interfaces in reservoir sandstone. Due to their complex cementation pattern, which is partly controlled by the present pore fluid (oil/water), both reservoir sections offer a good opportunity to investigate the interdependencies between pore cementation and wettability, as well as recovery potential of hydrocarbons from tight reservoirs. The samples were previously investigated and well characterized with respect to both, mineralogy and fluid chemistry, using a comprehensive combination of standard analytical methods, such as optical microscopy, X-ray diffractometry, cathodoluminescence, SEM, WDX and molecular and isotopic composition of the formation oil (e.g., Gross et al., 2015a; Gross et al., 2015b).

Dry BIB-polished samples were studied in SEM to characterize the 2D pore network and the degree and nature of cementation. The results were used as a reference for the subsequent analysis of re-saturated samples. We use the LMI-BIB-SEM method to resolve the pore connectivity in the Turonian sample. The oven-dry sample was immersed in the molten LM in a pressure cell above 80° C. Then the pressure was increased up to 125 MPa in steps of about 30 MPa each 20 minutes. Following the Washburn equation with a surface tension of 0.4-4.9 N/m and a wetting angle of 130-140°, pores of 10 nm in equivalent diameter should get filled. The SEM images of the LM injected sample showed the alloy throughout the sample and filling up virtually all the pore space (Figure 1a). This indicates good pore connectivity, which was required for the imbibition sample preparation before applying the Cryo-BIB-SEM method. For re-saturation, the samples were first saturated with oil by capillary imbibition. In the second step brine was injected using an exsiccator at low vacuum pressure. We used Cryo-BIB-SEM to study the cryogenic-stabilized

samples in the SEM. First results show the local distribution of oil and water with respect to the different mineral surfaces and the pore morphology in the Eocene sample. Most part of the sample was saturated with the fluids; however, a few larger pores remained empty indicating that the cement prevented full percolation of the fluids in the pore space at given experimental conditions. Due to the saturation protocol the majority of the mineral surfaces behaved oil-wet. However, rough quartz surfaces as well as siderite surfaces were mixed-wet, showing contact-menisci of oil and brine visible in the larger pores (Figure 1b).

Future work will be a systematic study of the surface-dependent (mineralogy and surface roughness) fluid-fluid-solid contact angles in re-saturated Molasse samples with varying boundary conditions, such as pressure and temperature.

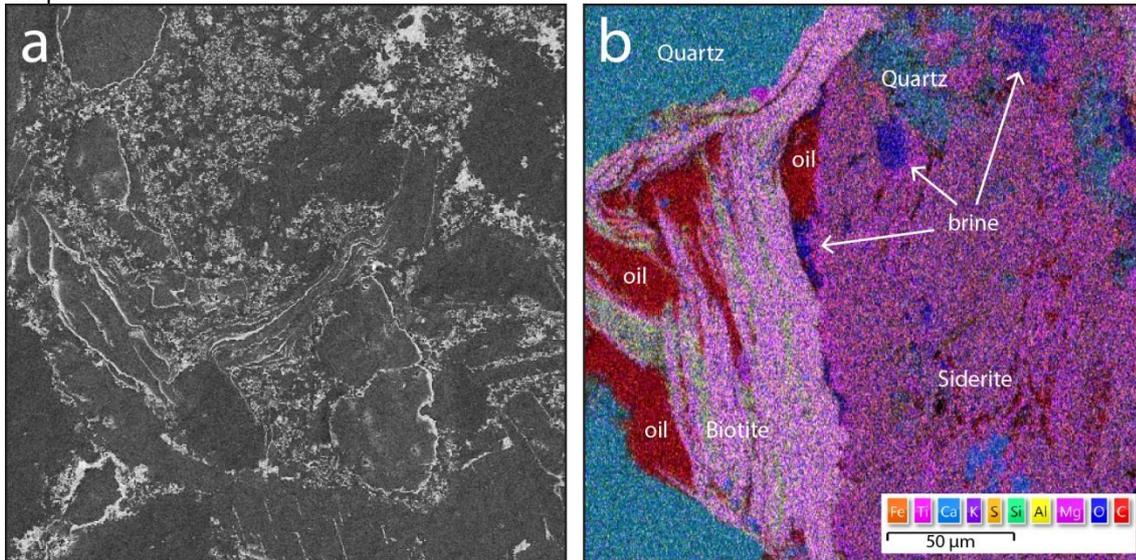


Fig.1 – (a) SEM micrograph showing alloy-filled pore space in Turonian reservoir sandstone. (b) EDX mapping of re-saturated Eocene reservoir sandstone showing the in-situ distribution of oil (red, Carbon is indicative for oil) and brine (blue, Oxygen is indicative for brine).

Multiscale characterization of North Sea chalk samples using micro X-ray computed-tomography and focused-ion beam scanning electron microscopy

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Chalk reservoirs are important producers in the North Sea. They comprise high porosity, low permeability rocks that are notoriously difficult to work with in core laboratories.

Chalk samples are very fine grained rocks that display heterogeneities at different scales. Because these heterogeneities might not be obvious to the naked eye, a deep understanding of the rock on a micro- and nanometre scale is required. In this paper we detail the multiscale imaging study of a 38mm diameter core plug of a chalk reservoir from the Norwegian sector of the North Sea using micro X-ray computed-tomography (mCT), back-scattered scanning electron microscopy (BSEM) with automated, quantified mineralogy analysis using energy dispersive X-ray spectroscopy (EDS) and focused-ion beam scanning electron microscopy (FIB-SEM).

Firstly, the core plug was imaged using helical mCT to investigate the heterogeneity and select a representative location of a sub-plug. A 4mm diameter sub-plug was cored out of the core plug for high resolution mCT imaging. Even at a resolution of 1.8 μ m per voxel, very little pore-space is fully resolved due to the very fine grained nature of the rock. The sub-plug was subsequently saturated with an X-ray attenuating brine and imaged again. By registering both images and subtracting one from the other, the porosity of the sample was characterized in 3D, even though the porosity was mostly below the resolution of the image. The 3D map of porosity was then used to investigate the heterogeneity of porosity in the sample.

The sub-plug was then cut, embedded with epoxy resin and imaged using BSEM to characterize the pores at the nm-scale followed by SEM-EDS analysis to obtain a high resolution mineral map. The BSEM image mosaic and quantified mineral map were then registered into geometric alignment with the 3D porosity map to see the connection between porosity, pore type, and mineralogy.

To characterize even the smallest pores in 3D, a 30x30x10 μ m region was selected for FIB-SEM imaging at 14.6nm voxel size. This volume was then segmented into the different mineral phases and porosity. This volume can then be used to calculate properties such as permeability and a primary drainage capillary pressure curve.

The porosity was calculated at around 30% and permeability was calculated to be in the order of microdarcies. The calculated values show a good match with previously obtained laboratory data.

FIB-SEM imaging works very well for chalk because the pores can be saturated with epoxy to minimize pore-back artefacts making segmentation straightforward. The FIB-SEM image is not large enough to be a representative volume for multi-phase flow simulations. Then the rock needs to be reconstructed in 3D using process based modeling.

Improved Imaging and Analysis of Chlorite in Reservoirs and Modern Day Analogues: New Insights for Reservoir Quality

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Chlorite is known to be a key mineral that controls reservoir quality in many siliciclastic rocks. Chlorite coats on sand grains in deeply buried reservoirs prevents quartz cement growth and leads to anomalously good reservoir quality. In contrast, an excess of chlorite, for example in clay-rich siltstone and sandstone, leads to blocked pore throats and very low permeability. However, determining what compositional type is present, how it occurs spatially, and quantifying the many and varied habits of chlorite that are of commercial importance, remains a challenge. With the advent of SEM-based automated mineralogical techniques, entire thin sections of rock can be scanned easily, leading to many tens of samples being examined. The resulting quantitative mineralogy and rock fabric data can be processed and compared off-line with other well or outcrop information.

In this paper we present examples of chlorite from different geological settings using automated and instant phase identification and mapping via a dedicated SEM. By illustrating the reliability of identification under automated analysis, and the ability to capture realistic textures in a fully digital format, we have been able to clearly visualize the various forms of chlorite. We have related chlorite formation to other grains and pore networks, both spatially and temporally, by knowing the sample's geological context.

This new approach has led to the creation of a digital chlorite library, where we have co-registered optical and SEM-based images, and augmented the mineral identification with complimentary techniques such as XRD and XRF. This new resource will be of interest and use to all those interested in the identification and formation of chlorite and the effects that diagenetic growth may have had on sandstone reservoir quality. The same approach will be adopted for other minerals relevant to petroleum reservoirs including smectite and carbonates.

Automated mineral analysis; lithological, petrographic and diagenetic evaluation of well cuttings

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Automated scanning electron microscopy (SEM) with linked energy dispersive spectrometers (EDS), based on the QEMSCAN platform, is a mature, proven technology for the analysis of geological materials. The initial application area of the instrumentation was in the analysis of mining feeds and waste streams and, as such, the technology is optimised for the characterisation of particulate geological materials. Hence, the method has also been widely applied in the petroleum geosciences and, in particular, in the analysis of drill cuttings.

For cuttings analysis, the electron beam is systematically and rapidly stepped across the particle and, at each point, the resultant ED spectrum is deconvoluted and assigned to a mineralogical grouping based on the chemical signature. Measurement provides mineralogical images of each particle together with quantitative modal mineralogy, mineral size, grain density, porosity and textural data. Each particle can be classified, based on these attributes, into a lithological grouping (or lithotype). Therefore, for a measured sample interval, mineralogical and lithological data can be reported for the whole sample, for specific lithologies, or even on a cutting-by-cutting basis.

The data acquired from cuttings can be widely used for inter-well correlation, in the calibration and validation of petrophysical models, and in stratigraphic or provenance studies. In addition, the textural data are invaluable in sedimentological, diagenetic and reservoir quality studies, especially over non-cored intervals. Through a selection of case studies we will outline the application of the technology in these key areas.

Direct cuttings measurement is equally applicable to the analysis of conventional carbonate and clastic reservoir targets as it is to the analysis of seal lithologies and source rocks, including unconventional reservoirs. In a low oil-price world, archived drill cuttings represent a huge resource for re-evaluation of existing fields and enhanced geological modelling.

Oil generation West of Shetlands: Insights from Re-Os geochronology

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Major aids in the successful understanding of petroleum systems are knowing the timing and source of oil generation, leading to increased success in exploration (both near field and basin wide) and production. Traditional petroleum geoscience utilises estimated burial histories, thermal inputs and pressure calculations to produce basin histories and so model when potential source units may generate oil. However, within basin models the variables are often only estimated with low confidence and common processes such as biodegradation preferentially removes light hydrocarbons from petroleum compromising traditional oil to source fingerprinting techniques. Furthermore, oil source rock identification uses organic chemical analysis of light oil fractions, such as GCMS and biomarker analysis, yet common effects such as biodegradation can hinder this.

This paper seeks to demonstrate the uses of Rhenium-Osmium (Re-Os) geochronology and elemental geochemistry to further the understanding of petroleum systems. Re-Os geochronology is distinct from other isotope chronometers in that it can be used to date organic material and so provide information on both the generation age of oil and depositional age of a source rock. In addition, the osmium isotopic composition of the oil combined with other elemental analysis can be used to link an oil to its source.

This paper will present a case study from the Faroe-Shetland Basin to demonstrate these uses through answering several key questions:

- Was oil generated in the cretaceous stored in motel then expelled into Palaeocene reservoirs?
- Is the source Jurassic or Cretaceous?
- Has volcanism destroyed the source rock and is there evidence for oil sub basalt?

Constraining the timing of oil and gas generation: Insights from Re-Os geochronology and Apatite Fission Track analysis in the Neoproterozoic-Palaeozoic reservoirs, South China Block

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The accurate timing of oil and gas generation within a petroleum system is significant to understand the entire evolution of a petroleum system and can directly aid in enhancing the success rate of petroleum exploration. However, the temporal and spatial understanding of hydrocarbon evolution, especially in complex tectonic settings, is a significant challenge for both academia and industry.

The South China block is a key oil and gas exploration target with significant gas reserves found since 1950 (e.g., Ziyang-Weiyuan, Puguang and Anyue gas fields). Bitumen, an important by-product of petroleum evolution, is also widely distributed in the reservoirs and in outcrop. However, the complex tectonism has hampered the understanding of the petroleum evolution. In order to quantitatively evaluate the oil and gas evolution, and its relationship with the tectonism, we apply traditional geochemical (vitrinite reflectance and fluorescence analysis), bitumen rhenium-osmium (Re-Os) isotope and Apatite Fission Track (AFT) analysis on two typical Neoproterozoic-Early Palaeozoic reservoirs (Majiang-Wanshan and Micang Shan reservoirs) in the South China Block.

Bitumen from the Kaili area of the Majiang reservoir are of low maturity ($BRo < 1.0$, yellow fluorescent and soluble in chloroform). However, all the other bitumen from South China Block is pyrobitumen ($BRo > 3.0$, $T_{max} \sim 540$ °C, no fluorescence and insoluble in the chloroform), which generated together with dry gas (CH_4) through thermal cracking.

In the Majiang-Wanshan reservoir, a Late Silurian-Early Devonian Re-Os date (429 ± 140 Ma) is yielded by low maturity bitumen. Although possessing a large uncertainty caused by low Re (1.5–4.3 ppb) and Os (76.4–206.4 ppt) abundance and the limited spread of $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ values, the nominal date broadly coincides with the initial oil generation time which is proposed by basin burial models, oil-bearing fluid inclusions (~ 100 °C) and bitumen Rb-Sr geochronology (405 ± 20 Ma). In contrast, the pyrobitumen possess higher Re (2.5–15.2 ppb) and Os (40.0–498.1 ppt) abundances and greater variability in the $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ compositions (87–497 and 1.52–1.97, respectively). The Re-Os data yield a Model 3 Re-Os date (69 ± 24 Ma, $Osi = 1.45 \pm 0.09$, $MSWD = 9.6$) which agrees with the timing of the high reservoir temperature (> 150 °C) and burial depth (> 5000 m) during Jurassic to Cretaceous based on basin models. The AFT analysis show a decrease in age from NW to SE in this area with the youngest tectonic uplift event (~ 70 Ma) present near the Majiang-Wanshan reservoir, which helps constrain the cessation time of gas generation.

Pyrobitumen in the Micang Shan Uplift, North Sichuan basin, also possess high Re (106.2–191.4 ppb) and Os (3030.4–5669.5 ppt) abundance and large variability in the $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ compositions (166.8 - 340.2 and 2.82–3.74). The Re-Os isotope data collectively yield a date of ~ 185 Ma. This Middle Jurassic date coincides with the basin modelling and gas inclusion data (> 180 °C), indicating timing related to gas generation. The AFT analysis show a sequence of complex tectonic uplift from ~ 150 to 80 Ma with ~ 3200 m of strata exhumed, which explains the absence of any gas reservoirs and wide distribution of bitumen in the Neoproterozoic-Cambrian strata at the surface at present.

In summary, the agreement of the Re-Os isotope analysis with AFT data and abundant geological evidence indicate the great potential of Re-Os isotope analysis to quantitatively constrain hydrocarbon evolution, with low maturity bitumen Re-Os dating yielding the timing of oil generation, and pyrobitumen Re-Os dating constraining the timing related to dry gas (CH_4) generation. As bitumen and pyrobitumen occurs in basins worldwide (eg: Alberta Basin (Canada), Dahoney basin (Nigeria) and Basque-Cantabrian Basin (Spain)), Re-Os geochronology (coupled with AFT thermal history) show great value to understand both the temporal and spatial evolution of hydrocarbon systems worldwide.

Investigation into the Controls of Rhenium-Osmium Fractionation in Organic-Rich Sedimentary Rocks: Implications for Re-Os Geochronology

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Here we present preliminary organic petrography coupled with new and existing rhenium-osmium (Re-Os) data to yield insights into our understanding of Re-Os fractionation within organic-rich sedimentary rocks, which will aid in knowing which intervals to target to have the best potential to both accurate and precise Re-Os geochronology.

The rhenium-osmium (Re-Os) isotope systematics of an organic-rich sedimentary rock can yield the depositional age of the rock. The use of new analytical (Selby and Creaser, 2003) and mass spectrometry techniques (Creaser et al., 1991; Völkening et al., 1991) and the most accurate ^{187}Re decay constant ($1.666 \times 10^{-11} \text{ year}^{-1}$; Smoliar et al., 1996), previous studies have shown that the Re-Os organic-rich geochronometer can yield precise (in some cases < 1 % uncertainty) depositional ages (e.g., Cohen et al., 1999; Georgiev et al., 2011; Kendall et al., 2009; Selby and Creaser, 2005; Xu et al. 2009; Cumming et al. 2012; Rooney et al., 2014). This is even possible for sedimentary units that possess very low total organic carbon ~0.1 wt% (e.g., Sperling et al., 2014).

The Re-Os geochronometer utilizes the isochron approach to accurately and precisely date organic-rich sedimentary rocks. This requires the Re-Os systematics of the sample to be free of any post-depositional disturbance, to possess identical initial $^{187}\text{Os}/^{188}\text{Os}$ compositions, and large range in $^{187}\text{Re}/^{188}\text{Os}$ values. The mechanisms that control Re-Os fractionation (i.e., the spread in $^{187}\text{Re}/^{188}\text{Os}$ ratios) are not understood. In some cases, stratigraphic sections display limited variation in the $^{187}\text{Re}/^{188}\text{Os}$ ratios, which hampers the determination of precise Re-Os dates. For example, sections of the Aptian/Albian, Cenomanian/Turonian, and Frasnian/Famennian stage boundaries yield accurate, but imprecise dates, which is largely due to the limited spread in the $^{187}\text{Re}/^{188}\text{Os}$ values (Turgeon et al., 2007; Selby et al., 2009; Harris et al., 2013).

Here we investigate the boundary interval which is recorded in the Devonian West Valley NX-1 core, drilled in Cattaraugus County, western New York, USA. This interval has been shown to possess a limited range in $^{187}\text{Re}/^{188}\text{Os}$ ratios (~ 20), with other intervals above (~6.4 m) and below (~2.9 and 8.2 m) the Frasnian/Famennian boundary exhibit a significant range in $^{187}\text{Re}/^{188}\text{Os}$ values (~200-300) (Turgeon et al., 2007). The Re-Os data for the latter yield precise dates (367.7 ± 2.5 , 374.2 ± 4.0 and 357 ± 23 Ma) for the strata, in contrast, the former yields highly imprecise date (476 ± 140 Ma).

Bitumen reflectance (BR_o) suggests that the NX-1 core below, above and across the Frasnian/Famennian boundary interval records a thermal maturity ($\text{BR}_o = \sim 0.6$) at the entrance to the oil window. Organic petrology (point counting of the macerals inertinite, *Tasmanites* and solid bitumen) of 32 samples shows that the Frasnian/Famennian stage boundary interval is dominated by solid bitumen (92.2 %), whereas the intervals above and below the stage boundary are either a mix of two or three macerals (69% solid bitumen, 22.4% *Tasmanites* and 8.6% inertinites; 67.1% *Tasmanites* and 32.9% solid bitumen; 79.5% *Tasmanites* and 20.5% solid bitumen).

A recent study by Cumming et al. (2012) suggests that variable sedimentation conditions (a proximal lake margin setting during a time of fluctuating lake-levels producing variation in the sedimentation rates) together with heterogeneous organic matter content results in organic matter in sediments being variably enriched in Re and Os, possessing a diverse range in $^{187}\text{Re}/^{188}\text{Os}$ values that correlate with $^{187}\text{Os}/^{188}\text{Os}$ that yield a very accurate and precise age. Whereas homogeneous sedimentation (a distal lake centre when lake-levels were at their maximum and sedimentation rates are slow and steady) with the same flux of organic matter results in very similar Re and Os enrichment and subsequently almost identical $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ values that yield accurate, although imprecise dates. A previous study also finds that a mix of terrestrial and marine organic matter is related to a greater spread in $^{187}\text{Re}/^{188}\text{Os}$ values (Harris et al., 2013).

The previous studies coupled with the preliminary results of this study suggest that organic matter type and its variable abundance is likely to control the Re-Os fractionation in organic rich sedimentary rocks. As such, strata intervals bearing heterogenous organic matter may provide excellent targets for sample selection for precise Re-Os geochronology, if the interval has identical or near identical initial $^{187}\text{Os}/^{188}\text{Os}$ compositions.

Thermal history of Resolution Guyot using paired clumped isotopes and radiogenic isotopes in Cretaceous carbonates

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The reconstruction of a temperature-time evolution for sedimentary basins is essential to understand diagenetic processes and thermal maturation. This largely impacts porosity, permeability distribution, organic matter maturation, and the migration of hydrocarbons from source rocks to reservoirs. However, constraining the burial histories of carbonate lithologies is challenging: the most common methods for paleothermometry (vitrinite reflectance index, fluid inclusion thermometry, conodont alteration index, molecular indices, and standard oxygen isotope analysis) are limited by material availability, assumption inherent to each proxy, and the usable temperature/time range. At the same time, micropaleontology and fission track analysis – the most common age proxies- also depend on species abundance and dating within low temperature ranges.

In this presentation we combined two isotopic methods with the aim of constraining the temperature-time history of carbonate rocks: clumped isotope paleothermometry and U/Pb geochronology. The method of clumped isotope thermometry allows fingerprinting different diagenetic phases and constraining their formation temperature with a high level of confidence. In addition, the application of LA-ICP-MS U-Pb dating of carbonate cements on a <100µm scale allows the direct dating of diagenetic cements, potentially to quite high precision (+/- 4% of the age).

We focused on cores from Resolution Guyot, in the Western Pacific Ocean, which is a good facies analogue for major carbonate reservoir occurring on the Arabian plate. Our preliminary clumped isotope results for the deeper part of the core highlighted deposition in warm waters (24-32 °C) with positive oxygen isotope values (0.38 ‰ to 1.12 ‰), which suggests slightly evaporative lagoon conditions. The U/Pb measurements of the same samples revealed multiple phases of syn-sedimentary cement precipitation within an overall time interval ranging from 60 to 80 Ma. The upper part of the succession however exhibits much lower precipitation temperatures within cements (+4 °C) and more negative $\delta^{18}\text{O}$ of seawater (- 1.31 ‰). Our U/Pb dating of cements within the upper part of the atoll also reveals that cementation took place much later during the Cenozoic (30-40 Ma), most likely due to cold, deep-water current circulations within the atoll. Two types of dolomites (a brown and a white phase) are also present on the atoll. Our data reveal that the brown dolomite was formed at around 37 °C, during three major dolomitization pulses dating between 100-130 Ma. The dolomite of second pulse precipitated at much lower water temperatures (21 °C) from waters of slightly different isotopic composition (-1.7‰). Results for the white dolomite are still pending.

Our data demonstrates that pairing clumped isotopes and radiogenic isotopes is a powerful and effective tool to reconstruct diagenetic parasequence in carbonate rocks and to test geological models of deposition and diagenesis. We gratefully acknowledge funding from the NERC CDT Oil and Gas, and support from QCCSRC, funded by Qatar Petroleum, Shell, and the Qatar Science & Technology Park.

Shale Gas: Deciphering the Isotopic Code

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Understanding the fractionation of carbon isotopes within shale gases through time can help determine the history of a shale gas reservoir; from genesis through to residual gas. Current methods considering isotopic fractionation within shales focus on carbon capture and storage or use relatively simple methods which do not differentiate between diffusion fractionation of free gas and desorptive fractionation from gases in the adsorbed state. An added complexity is that often gases tested are extracted from cores meaning fractionation trends do not isolate primary (kerogen cracking), secondary (surface sorption/desorption and free gas movement) and tertiary (migration) isotopic fractionation mechanisms.

By combining a custom built sample cell which can be used to calculate gas capacity volumes with a Gas Chromatography – Combustion – Isotope Ratio Mass Spectrometer (GC-C-IRMS), an online system measuring isotopic fractionation of shale gas, gas sorption capacity and fractionation trends throughout a shale reservoirs life cycle can be measured. By injecting methane, representing shale gas, of a known isotopic composition into a sample and minimising migration, the secondary mechanism for isotope fractionation can be isolated. Focussing on this single component allows better understanding of isotope fractionation caused solely by free gas diffusion versus desorptive fractionation throughout shale gas production. Preliminary research using our unprecedented method suggests that isotopic fractionation trends from secondary fractionation are distinct for each shale components i.e. carbon isotope fractionation seen in a calcite sample with little to no adsorption capacity is far smaller than fractionation measured in kaolinite which is more adsorptive. Whilst more data must still be collected, the preliminary data does however, highlight the potential of this method for understanding changes in isotopic ratio through the life cycle of a shale gas reservoir. It also highlights the potential to test previously defined intrinsic links between various shale parameters including shale composition, poro-perm, maturity and pressure-temperature variations.

Our desorption method may provide the potential to upscale from core to reservoir scale and be universal across all basins. Ideally, by using isotope ratios through time, the lifecycle of a producing shale gas well can be calculated. Understanding the position of the well in terms of production time and volume of gas will provide the information required to work out a recovery factor. Knowing the recovery factor allows for volume of rock drained.

Registering Scanning Electron Microscopy (SEM) and X-Ray Tomography (XRT) images for pore-grain characterization of cross-laminated siliciclastic rock samples

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Significant variations in pore-grain structures within and across individual laminae are often observed in cross-laminated siliciclastic rock samples and they can greatly influence hydrocarbon fluid migration, retention and recovery. SEM instruments enable acquisition of 2D images on a large surface area (10's mm by 10's mm) at a resolution high enough to resolve sub-micron pores and grains. XRT instruments can acquire 3D images on a sample volume of 10's cm by 10's cm by 10's cm, capturing inter-lamina structures. We consider making use of a high-resolution SEM image to calibrate pore-grain structures within laminae that are observable in a low-resolution XRT image in this work. To do this, SEM and XRT images must be registered to the same locations on the same sample. Standard image registration methods work well if the resolution difference between SEM and XRT images are small (e.g. less than 1 order of magnitude) and both contain large grains/pores to serve as references. Unfortunately, neither of these two conditions holds for cross-laminated samples in general. To overcome this problem, we propose to upscale the SEM image to the resolution of the XRT image, prior to applying the image registration. With a fine-grained cross-laminated Triassic red sandstone sample, we show that a naïve image upscaling of a backscattered electron (BSE) image cannot guarantee to retain laminae features. Given that SEM with an energy-dispersive x-ray spectroscopy (EDX) enables to estimate elementary chemical composition, in proportion, for each pixel, we develop an upscaling procedure to calculate effective x-ray attenuation on each coarser grid cell from elementary chemical compositions of all its sub-pixels. We show this procedure retains adequate laminae features in the upscaled image to make subsequent image registration possible.

Day 2

Gas, salinity and temperature evolution of formation water in gas-rich basins

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Investigating the nature of palaeo-fluids in fluid inclusions can deliver critical information about the petroleum system in a basin. Palaeo-formation water trapped in cements in sandstone is typically of interest as palaeothermometers for cementation episodes and the presence of oil or gas inclusions can be taken as proof of charge and for active petroleum systems. Recent progress in developing spectroscopic methods for the assessment of fluid compositions has proved to be useful technology for both exploration and development of petroleum reservoirs. Salinity measurement, gas detection (CH₄, CO₂, N₂, H₂S) and fluid modelling, combining conventional microthermometry techniques with Raman spectroscopy, provides a new understanding of formation water evolution in gas-bearing basins. It provides pressure and temperature constraints of gas emplacement, salinities of the associated formation water, and the presence of undesirable gases such as N₂, CO₂ and H₂S.

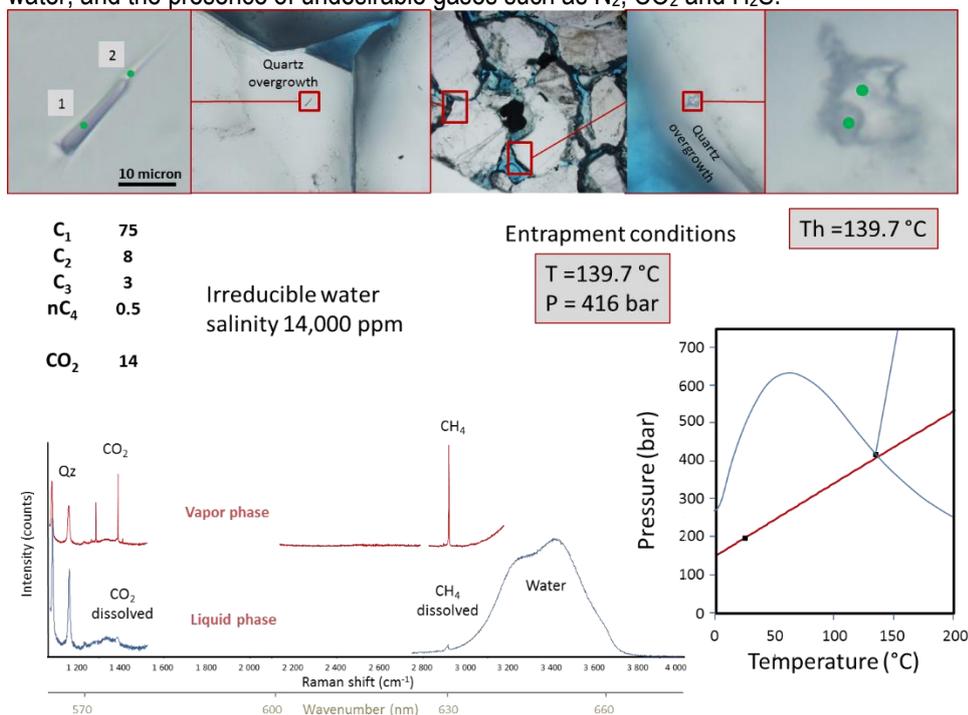


Fig.1 Gas and water inclusions PT reconstruction using Raman spectroscopy and microthermometry

A particular challenge was to deliver a reliable salinity measurement from fluid inclusions to assess irreducible water salinity in gas reservoirs. This data is essential to petrophysicists, but difficult to assess using conventional techniques. Calibration using the Raman signal of water has been used to overcome the recurrent metastability of water inclusions that are an issue when relying on microthermometry alone. Pressure measurements in CH₄-bearing water inclusion at melting of methane hydrate at low temperature also provide an alternative to refine salinities. The ability of Raman spectroscopy to detect and quantify methane in vapour and dissolved in water provides an additional control on the timing of entrapment relative to the establishment of a gas column and can provide further insight on the evolution of water salinity in the reservoir.

Gas composition, pressure and density measurements of gas inclusions can also be achieved using Raman spectroscopy, but require calibration efforts. In the example, Figure 1, a gas inclusion from a dry gas reservoir, yielded compositions of 14/75/8/3/0.5 mol% CO₂/C₁/C₂/C₃/C₄. The associated water salinity in the gas inclusion, as derived by Raman spectroscopy, was 14,000 ppm, equal to the salinity measured by the conventional thermometric technique of a water inclusion observed in nearby quartz cement. The density and the composition of the gas inclusion, derived from Raman data, enabled the calculation of an isodensity line using fluid modelling software and is shown in the PT diagram. The water inclusion composition, homogenisation temperature and density were used

to calculate its bubble point curve and an isodensity line. The gas inclusion isodensity line crosses the water inclusion isochore at its bubble point, constraining PT conditions of entrapment to 139.7 °C and 416 bar, and at gas saturation.

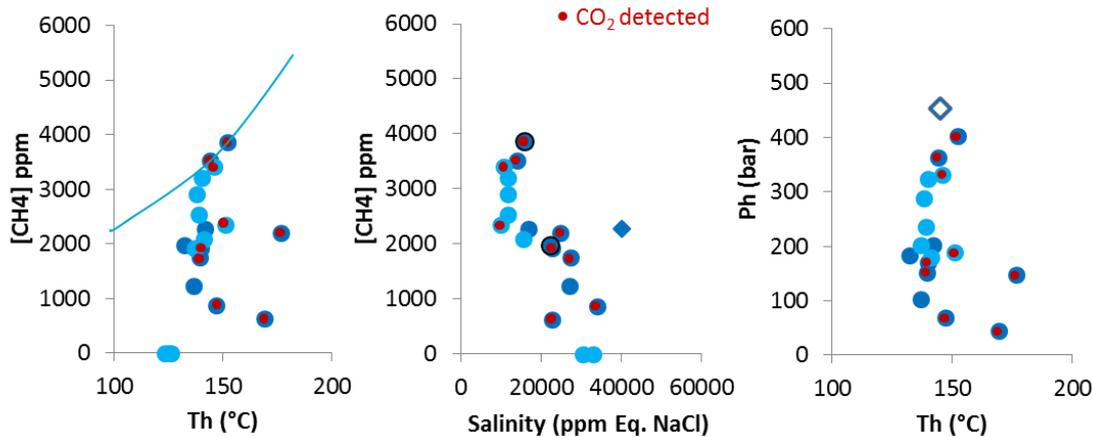


Fig.2 Water inclusion dataset for a single reservoir aquifer, showing the methane content, salinity and minimum pressure and temperature of entrapment.

The gas-prone Browse Basin, Australia, provided an opportunity to test these new techniques at a basin scale, by assessing the aquifer underlying the many large gas accumulations. Palaeo-temperature, salinity and gas content of water inclusions from core samples in the Plover Formation and Brewster Member, below the Torosa, Calliance, Ichtys and Poseidon gas fields, and from dry wells at Buffon-1, Yampi-2 and Caswell-2, were measured (Figure 2). The fluid inclusion data show that the salinity of the palaeo-formation waters decrease with increasing methane content, and that the salinities associated with water reached methane saturation (contemporaneous with free-gas) at salinities between 11,000 to 24,000 ppm (1.1 to 2.4 wt%). Water inclusions with dissolved CO₂, often in association with CH₄, do not follow the same trend with salinity, and in some cases show an opposite trend. They are also often associated with higher temperatures. Water inclusions from wells located inboard of the Caswell sub-basin (including Dinichthys North-1, Caswell-1 and Yampi-2) have characteristics in salinity, gas content and temperature that differ from those located outboard (Torosa-5, Kronos-1, Calliance-1, Buffon-1), and suggests a difference in fluid circulation. While the origin of inferred low-salinity formation water, at distances of about 200 km from the coast remains enigmatic, the influx of meteoric water is not supported by the location of the lowest palaeo-water salinities. The common association of methane and low salinity water might suggest this water accompanied migration in the gas phase and exsolved in the reservoir. Experimental data using a high pressure-temperature cell, combined with in-situ Raman measurements, supports this hypothesis.

Making oil from Magma

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While the tectonic histories of rifted margin basins, emplacement mechanics of intrusions and possible effects on hydrocarbon kinetics and migration have been closely scrutinized (Dalziel, 1991; Galushkin, 1997; Muirhead *et al*, 2012; Rateau *et al*, 2013) there is currently very little work on the impact (either beneficial or detrimental) of igneous intrusions on the potential volume of recoverable or migrated hydrocarbons. A significant factor on such understanding is the pre-intrusion maturity of the host rocks and the extent of organic matter alteration. Here we present a model to predict possible source rock maturation volumes within intrusive igneous systems in rifted margin basins as a factor of pre-intrusion maturity. Initial work on extractable organic matter from sediments adjacent to three intrusions suggest that in fact, two of these regimes have the potential to generate commercial volumes of hydrocarbons. Applying this regime to frontier basins west of the UK suggests the emplacement of large sills in rifted basins could be of benefit to otherwise immature source rocks.

A Multidisciplinary Re-assessment of Calcite Cement in Brent Reservoirs, Heather Field, Northern North Sea

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Across the Heather Field, calcite cement varies significantly in concentration within the five formations that comprise the Brent reservoir. Cement ranges from localised nodules to massive beds in excess of 10ft thick. Where extensive, poikilotopic calcite cement almost completely occludes porosity and leads to low permeability. Stratiform calcite-cemented horizons act as impermeable barriers to fluid flow. Crestal areas of the field are largely free of carbonate cement, whereas downdip areas are, at many sites, heavily cemented. However there is no simple relationship between present day structural depth and calcite abundance. Calcite also has a complex stratigraphical distribution; the Broom is the most cemented layer followed by the Broom-Rannoch Transition, the Rannoch and the Eive Formations.

Calcite cement in the Brent Group has been ascribed to both depositional and early diagenetic processes and late diagenetic processes associated with elevated temperatures. Understanding the origin of calcite is important since the correct model can help lead to predictive models to help understand reservoir quality distribution and compartmentalisation. Calcite cement within the Heather field has been studied previously but major uncertainty still remains about the distribution of the cement across the field, away from well control. The timely re-assessment, presented here, comprises a multi-disciplinary approach focussing on a detailed diagenetic and geochemical evaluation of the calcite, together with observations from cores, well logs and seismic data, in order to develop a practical, predictive model for calcite cement distribution.

Calcite-cemented zones exhibit up to 40% calcite by volume, 30-40% minus cement porosity, loose apparent grain arrangements and floating- to point-grain contacts. Petrographic evidence for post-compactional calcite cementation and growth after quartz cement, coupled with the significant number of fluid inclusion homogenization temperatures between 80 and 125°C, suggests that the majority of calcite cement in the Heather Field is of late diagenetic, deep-burial origin. The dominance for strongly negative $\delta^{13}\text{C}$ compositions implies that a significant proportion of the carbon used in calcite cementation was sourced from CO_2 derived from the decarboxylation of kerogen in the Kimmeridge Clay Formation source rock. Abundant oil inclusions in calcite cement indicate growth during oil emplacement. Increasingly negative $\delta^{18}\text{O}$ values confirm calcite growth at elevated temperatures.

The new model of calcite growth will directly assist in reservoir modelling and enable risk assessment for future infill drilling targets.

Dates through the ages: mineral fertility and bias in sedimentary provenance studies and some examples of how these may be identified and reduced

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Sand composition prior to diagenetic alteration is a primary control on sandstone reservoir quality. Many factors influence sand composition during its transfer from source to sink, most notably climate, alluvial storage, weathering and depositional environment. The most fundamental influence is arguably inherited from the lithologies that were eroded within the sedimentary source region. In an effort to constrain the geographical position of the sedimentary source region, the rock types it contained, how sand was dispersed and how these factors have evolved with time, various sedimentary provenance techniques are commonly adopted. An improved understanding of these parameters increases confidence in seismic, reservoir prediction and regional tectonic models.

Although there is consensus that multi-proxy sedimentary provenance studies are most advantageous for accurate interpretations, the combination of techniques used is highly variable. Nevertheless, most researchers adopt detrital zircon U-Pb geochronology because this method is widely accepted as being the most informative despite known issues surrounding fertility and sedimentary recycling. An overreliance on zircon dating and failure to satisfactorily address its shortcomings has compromised provenance interpretations. Using case studies from the southwest Barents Shelf, the impact of zircon recycling and fertility on provenance interpretations are explored through the application of recently established techniques, specifically the Pb isotopic composition of detrital K feldspar and combined U-Pb dating and geochemistry of detrital apatite and rutile.

This exercise has been valuable because it has highlighted cases where pronounced and unexpected mineral fertility variations existed within the sedimentary source regions for Mesozoic sandstones deposited on the southwest Barents Shelf. In the most extreme cases, where the geology of the sedimentary source region was diverse and consisted of approximately equal proportions of crystalline granitoid basement and sedimentary cover, most detrital zircon was reworked from the sandstone overburden and relatively few grains were sourced directly from the crystalline granitoid rocks. The reverse situation is apparent for rutile and K feldspar, most of which were sourced from the crystalline basement.

Misinterpretations surrounding sand transport directions and the intensity of compositional modifications during source to sink transport are inevitable without additional data from emerging provenance techniques to complement detrital zircon patterns.

Detailed characterisation of deepwater reservoir heterogeneity using automated core mapping tools

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A suite of analytical tools are now available that allow detailed measurement and mapping of a range of interdependent physical attributes possessed by new and historical core. These include mineralogy (eg. clay type and relative abundance), permeability, P & S-wave velocity, elastic properties and rock strength. These automated or semi-automated devices allow for rapid acquisition of data from both whole and slabbed core, and can be run within a time frame that is typically much shorter than that for more traditional point source analyses. The study presented here is from a single slabbed 3ft core stick from a North Sea deepwater reservoir. This section of core had previously been described in detail both sedimentologically and structurally, but was then subsequently imaged using plain light photography, a 3D CT scanner, short and long wave infrared reflectance systems, and physically tested using an automated system to produce detailed maps of permeability and rock strength. The study of this highly heterogeneous section of core demonstrates that effective integration of multiple imaging and mapping data sets is critical if their value is to be optimised, and informed decisions are to be made with regard to the position, meaning and significance of subsequent point source data more traditionally used to characterise deepwater reservoirs.

Zircon Geochronology, Improving the Understanding of the Provenance of the Upper Carboniferous / Lower Permian Sandstones in the Sns

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Provenance studies are critical to understanding sediment input pathways for clastic material from source to sink. This allows for an increased understanding and improved prediction of reservoir distribution / extent with potential implications for reservoir quality.

This study demonstrates how zircon geochronology has been employed, as part of a larger multi-disciplinary study, to investigate the provenance of the Upper Carboniferous successions of the Southern North Sea. The study area spans from quad 44 (UK sector), through quad K (Dutch sector) to quad L (German sector), and incorporates previously published data from Morton *et al.* (2001) and Finlay *et al.*, (2013).

This study builds upon the work of Morton *et al.* (2001, 2005), Pearce *et al.* (2005, 2010) and Finlay *et al.*, (2013). And also utilises work done by Olivarius *et al.* (2014) and Linnemann *et al.* (2008), these authors providing zircon age distributions for candidate source terrains.

Analysed samples from the Carboniferous Boulton Fm, Upper Ketch Mbr and Cleaver Mbr intervals all have similar zircon age distributions, with a strong preponderance toward Variscan aged grains. Cadomian aged grains are also common, and this Variscan/Cadomian signal suggests a southerly source.

Samples analysed from the Lower Ketch Mbr and Caister Fm typically contain little Variscan or Cadomian age material and Caledonian aged grains are common as well as those derived from the Svenconnorwegian and Gothian orogenies. These zircon populations are consistent with sediment derived from the north.

CFM study of brine effect on adhesion of silica face kaolinite

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The interaction between oil, clay, and brine plays a crucial role in increasing the oil yield from low salinity enhanced oil recovery (LSEOR) in sandstone reservoirs. LSEOR is driven by a change in the wettability state of the reservoir (from oil to water wet), but the underpinning mechanisms behind it are not fully understood. It has been hypothesized, however, that the reduction in “adhesion” of oil to clay minerals present in the reservoir is one of the main drivers in the change of wettability. We have set to study the adhesion of representative oil molecules to clay surfaces at the nanoscale by means of chemical force microscopy using at various brine concentration and pH conditions. In our experiments, the polar crude oil is represented by functionalized tip which are carboxylic acid (-COOH), amide (-NH₂), and alcohol (-OH) terminated Kaolinite is selected as a representative clay mineral (silica face). Adhesion measurement is performed in NaCl and CaCl₂ with concentrations of 0.001 M, 0.01M and 1 M, and with pH ranging 5 to 9. Results show that the concentration effect produced three different trends for the three functional group categories. At pH close to neutral, changes from low to high CaCl₂ concentration resulted in an inverse low salinity effect for -COOH tips (i.e. adhesion increased at lower concentrations), whereas the opposite was true when the pH of the solution was 8 (i.e. adhesion decreased with decreasing concentration).

Maturity and facies effects on the abundance of acidic compounds in Upper Visean black shales from the Dniepr-Donets Basin (Ukraine): Source rock characterization via electrospray ionization fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR-MS)

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Knowledge about thermally-controlled variations in the molecular composition of hydrocarbons that are progressively generated from a source rock during thermal maturation is of great importance for petroleum geosciences. New requirements for source rock studies particularly arouse from the progressing exploration for unconventional hydrocarbons. Detailed knowledge about maturity and facies variations are key factors for economic success, considering that these control the type and amount of hydrocarbons that are actually generated to later form the unconventional deposit. As unconventional production is performed directly from the artificially fractured source rock, a maximum of free hydrocarbons, as well as a detailed understanding about their composition, is critical. Therefore, the progressing exploration for unconvensionals triggered the development of a multitude of analytical methods, particularly in the field of organic geochemistry.

Pyrolysis-gas chromatography (Py-GC) is an important method, allowing a detailed assessment of the generative potential of a source rock sample with advancing (artificial) thermal maturation. With this technique, the bulk composition of oil or gas/condensate that a source rock sample produces can be anticipated and maturity- and facies-induced variations of the hydrocarbon potential can be described. However, this technique is subject to certain limitations, as the analytical window of conventional Py-GC is restricted to a mass range of m/z 50-300, covering mainly low-polarity compounds. In contrast, electrospray ionization combined with Fourier Transform ion cyclotron resonance mass spectrometry shifts the analytical window to considerably higher masses (up to $\sim m/z$ 2000), for the first time allowing the detection of highly polar compounds (e.g. acidic NSO's). Within the last years, ESI FT-ICR-MS was successfully applied to crude oils, bitumens and source rock extracts from various locations, providing valuable insights for reservoir exploration (such as new maturity or biodegradation proxies; Pötz et al., 2014; Li et al., 2010). During this study, ESI FT-ICR-MS was used to characterize the acidic NSO compounds of 10 Upper Visean source rock samples ("Rudov Beds") from the Ukrainian Dniepr-Donets Basin (DDB), an important hydrocarbon province of Eastern Europe (>220 conventional fields) and, recently, major target for unconventional exploration.

Misch et al. (2015) used combined isotopic and biomarker data as well as pyrolysis experiments to evaluate the contribution of various potential source intervals to the prevailing conventional deposits. They proved, that Upper Visean Rudov Beds and adjacent organic-rich Upper Visean intervals are likely the most important source for gas, but also oil, despite prevailing type III/II kerogen. However, apart from their relevance as a source for conventional hydrocarbons, high thickness and average TOC, especially in the central part of the northwestern DDB ("Srebren Bay"), make them a potential target for unconventional production (Misch et al., 2016). Besides an obvious maturity trend, pyrolysis experiments revealed a predominantly gas-prone facies in marginal areas, whereas basinal samples hold a potential to create low-wax P-N-A oils (Misch et al., 2016). Based on these results, a sample set covering both different facies zones and a maturity range from ~ 0.6 to 1.2 %Rr was chosen for further ESI FT-ICR-MS measurements.

Similar as described by Pötz et al. (2014), a rapid decrease in O_x class compounds and increase in N_y class compounds can be referred to ongoing thermal maturation (Fig. 1). While N_1 compounds dominate over N_{2+} compounds in both early and late mature samples, a clear maturity trend to predominating N_1O_1 and N_1S_1 over N_1O_{2+} and N_1S_{2+} , respectively, is evident. While in basinal samples, O_x class compounds almost disappear at higher maturities, they are still present in equally mature samples from more distal positions, suggesting a facies-related overprint (see Fig. 1). Similarly, the total amount of O_xN_y compounds might be controlled both by facies and thermal maturation. Although their abundance generally increases from 0.6 to 0.8 %Rr and decreases again at higher maturity levels, varying contributions were obtained for comparable maturity levels especially in the range >1.0 %Rr. In summary, ESI FT-ICR-MS offers a great opportunity to verify and refine maturity assessment based on

established maturity parameters and to reveal changes in the molecular composition of polar high mass-compounds, either caused by facies changes or other processes (e.g. biodegradation).

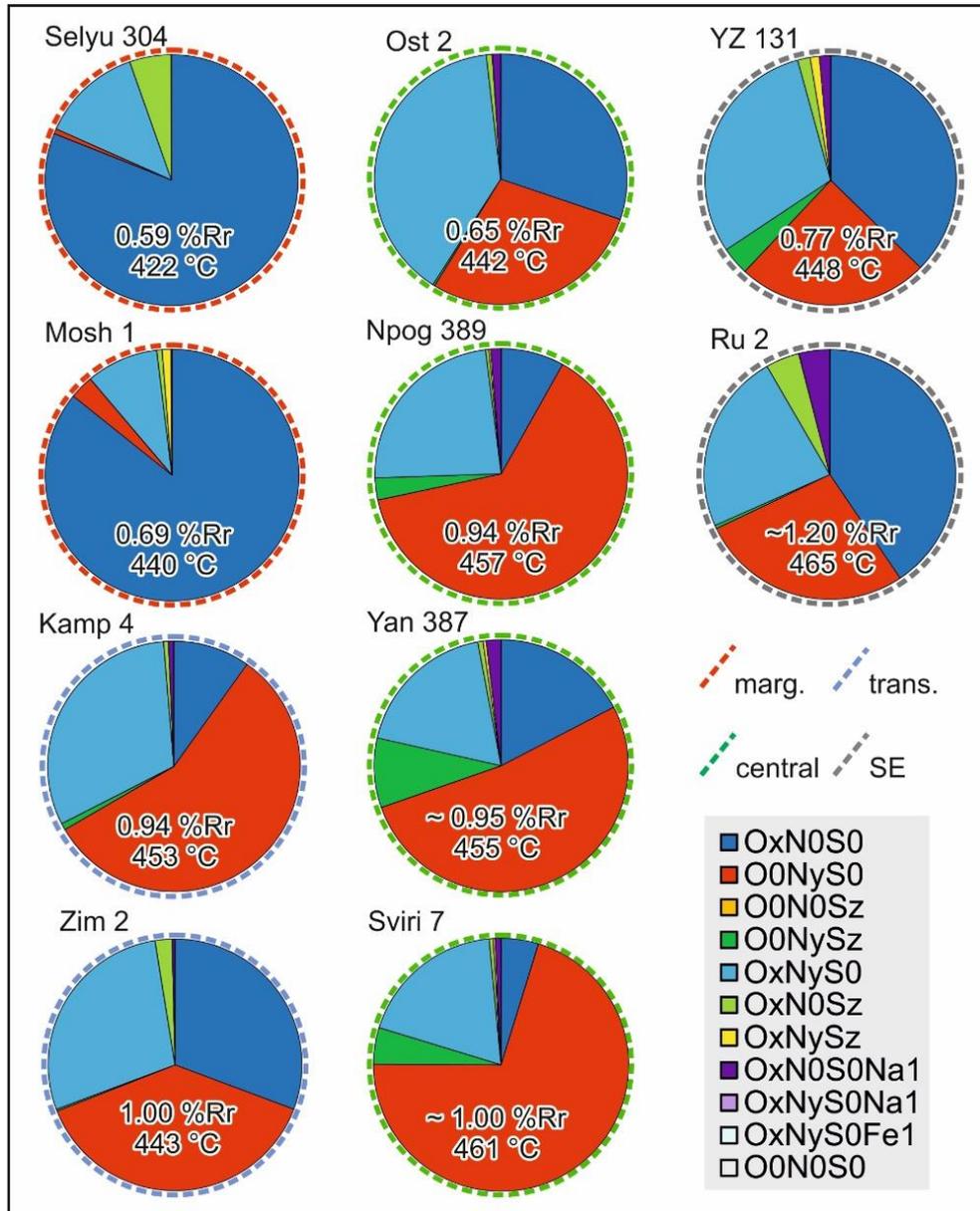


Fig. 1: Pie charts showing the bulk elemental distribution of acidic NSO compounds in the investigated Upper Viséan black shales based on peaks from ESI FT-ICR-MS spectra. Dashed circles represent the position of wells in relation to the so-called Srebren Bay, a vast syncline hosting Rudov Beds with the highest oil potential according to previous pyrolysis measurements (e.g. Misch et al., 2016). Marg. – marginal; trans. – transitional; SE – south east

Hydrocarbon and noble gas geochemical survey in a mud volcano province: Insights into oil-water-gas interactions and gas hydrate occurrences in the subsurface

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We present the results of a survey of the molecular and isotopic composition of hydrocarbon and noble gases in active mud volcanoes (MVs) of the Gulf of Cadiz, NE Atlantic (Fig. 1). The study area is located in an active convergent tectonic setting covered by sediments up to 14 km thick (Thiebot & Gutscher, 2009). Source rocks include organic-rich Jurassic shales and limestones and Cretaceous black shales. Oil fields are exploited on the Spanish margin and MVs are widespread (> 50 identified to date) across the region. Mud breccia samples were collected for the analysis of noble gas concentrations and isotopic compositions in pore fluids using the methodology of Brennwald *et al.* (2003, 2013) and Tomonaga *et al.* (2011, 2013, 2014). This method involves sub-sampling core sediment in noble gas-tight copper tubes prior to opening the core, thus enabling the measurement of their concentration and isotope composition in pore fluids. It is relatively simple to apply and has proven robust (Tomonaga *et al.*, 2013; this work) and we present here an example of its application to a regional hydrocarbon (HC) seepage survey in which the combined HC and noble gas geochemistry provide insights into fluid interactions in the subsurface and on gas hydrate stability. This can be highly valuable to survey a frontier HC province such as the Guf of Cadiz. All the MVs depicted in Fig. 1 vent deep-sourced thermogenic hydrocarbon gases except for the deep-water “ATI MVs” in which methane has a microbial origin (Fig. 2). The wetness (C₂₊ content) of the thermogenic gases is highly variable, whereas $\delta^{13}\text{C-CH}_4$ values are comparable and C₂₊ variations cannot be accounted for by migration or maturity. The presence of disseminated gas hydrates has been observed in most of these MVs, whether they vent wet (e.g., Bonjardim MV; CRMV) or dry (e.g., CAMV, Porto MV) gases.

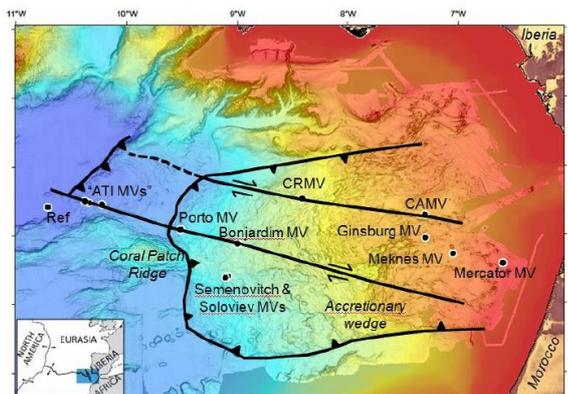


Fig.1: Bathymetric map of the broad Gulf of Cadiz area SW of Iberia and NW of Morocco, with locations of main Mud Volcanoes (MVs) and major tectonic structures (after Hensen *et al.*, 2015).

All MVs fluids are highly oversaturated with respect to Helium (He) produced by the buried Cenozoic sediments as indicated by the enrichment in 4He over 3He (Figure 3A). This anomalous excess in He is interpreted as an indication for desorption of adsorbed gas from

the buried sediments due to pressure changes along the faults (above which the MVs are located).

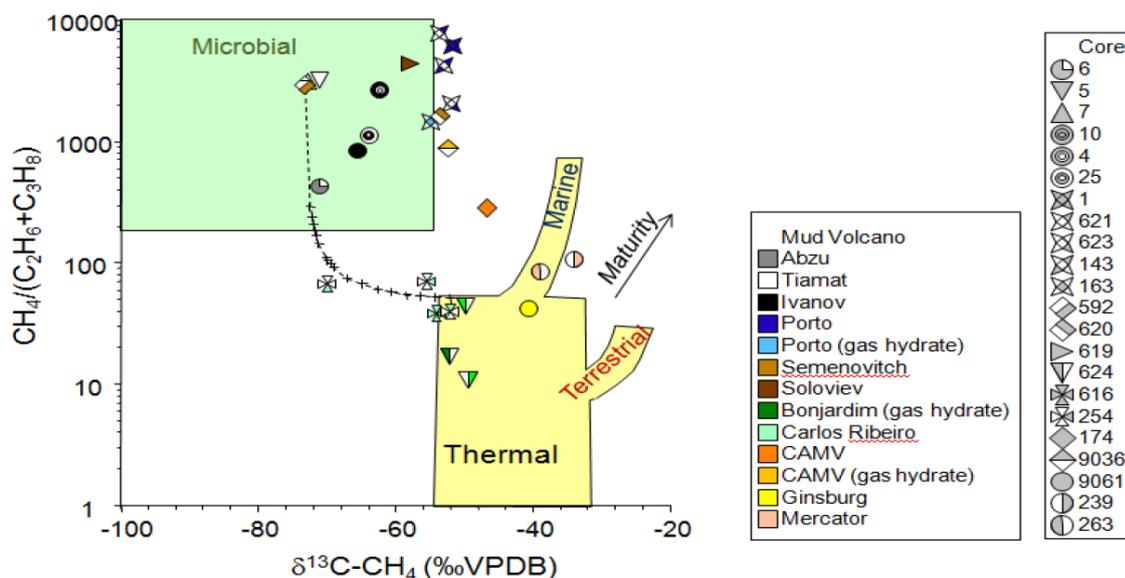


Fig.2: “Bernard diagram” showing immature/microbial gas in the deep-water MVs near Coral Patch Ridge [“ATI MVs” (Abzu; Tiamat & M. Ivanov MVs) & Semenovitch MV] and thermogenic gases of highly variable wetness [$\text{CH}_4/(\text{C}_2\text{H}_6+\text{C}_3\text{H}_8)$] in the other MVs (after Bernard *et al.*, 1976).

We relate the variable wetness of HC gases to the same desorption process and suggest that advection of the large volumes of interstitial clay water released from buried sediments (Hensen *et al.*, 2007) is responsible for focussed gas transport to the seafloor. In this hypothesis, the seep fluids are highly enriched in methane when the input of desorbed gas is predominant and in C2+ when the faults also tap a reservoir or an active source rock (e.g., CRMV).

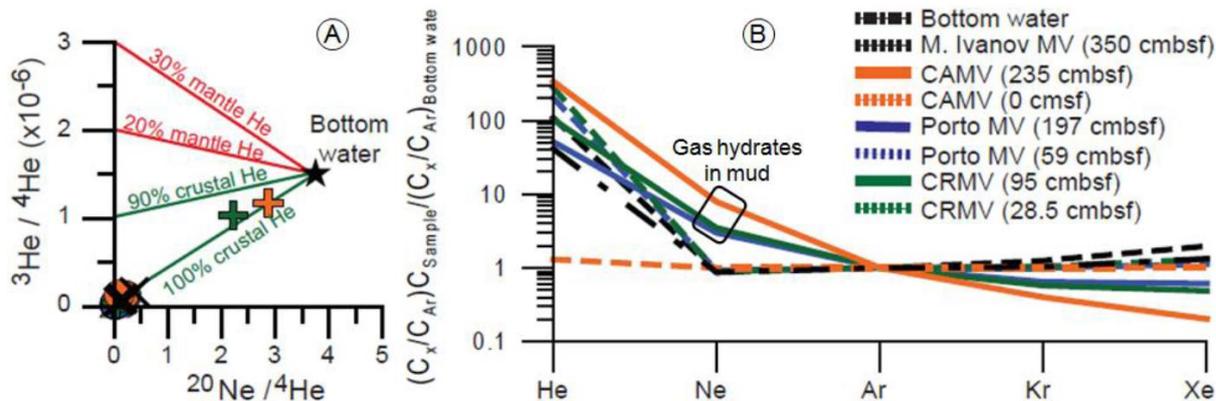


Fig.3: A) He and Ne isotope ratios: crustal vs radiogenic origin of noble gases; B) Fractionation of noble gases relative to Ar in MV fluids compared to bottom water (after Winkler *et al.*, 2002).

Additionally, partitioning of noble gases between the pore water and the free gas in the clathrates is indicated by the enrichment in the light He and Neon (Ne) and depletion of the heavy Krypton (Kr) and Xenon (Xe) relative to Argon (Ar) in gas hydrate-bearing sediments (Figure 3B). It is observed in sites in which a significant flux of thermogenic gases can stabilize gas hydrates deposits. By contrast, in MVs venting microbial gas (*i.e.*, no focussed flux of thermogenic gas), noble gas partitioning becomes similar to that reported by Winkler *et al.* (2002) for gas hydrates: the dissociation of clathrates drives seepage at the seafloor. The isotopic composition of noble gases also points to oil-water-free gas interactions in the most active “thermogenic MVs”. These results can contribute to evaluate the presence of HC reservoirs, a main concern in such a tectonically active frontier area.

OG analytical methods in the Petroleum industry - Enhanced data density and method flexibility by multiple detector GC coupling

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Organic geochemical analyses performed in the petroleum industry cover a wide range of methods and applications. The aim is most often the analysis and interpretation of naturally occurring petroleum and organic matter in source rock samples to determine the origin of oil and gas and delineate the state of maturation and expulsion, as well as to detect and quantify alteration processes.

To serve the needs of the industry, it is crucial to setup methods that allow for fast but comprehensive geochemical analyses. To enhance data density "per injection" and to meet the high requirements for analyses, especially when handling different sample types and matrices, we integrated different instruments into an online workflow. A gas chromatograph (GC) (Agilent 7890B) was coupled to a Q-TOF (Agilent 7200) and to a combustion GC (GC 5, Isoprime) which are linked to an IRMS (Isoprime 100). In addition, the GC was equipped with a TCD and a FID detector, which are coupled in sequence. Two multipurpose samplers (Gerstel MPS) and two inlets (Gerstel CIS 6 with TDU and Pyrolyser and an Agilent Split/Splitless) expand the flexibility of this system. The GC column configuration consist of a 50 m x 0.33 µm (Film) x 0.200 mm i.D.HP - 5 column for the analyses of liquid samples and pyrolysates as well as a J&W PoraPlot column (25m x 0.10 µm (Film) x 0.32 mm i. D.), which is mounted in a heated valve box to allow isothermal separation of gases up to nC-5. Together with a custom made solvent vent and peak cutting device as well as purged splitters, the GC system presented here offers uncompromising possibilities and robustness for organic geochemical analyses of hydrocarbon liquids and gases.

Examples from applications will be presented for both gas range as well as heavier compounds using natural gas, petroleum and as well as extracts obtained from a well in the Tertiary basin in Svalbard.

Using old analytic techniques to generate new ideas: Satal Formation, Sirt Basin, Libya

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The Satal Formation of the western Sirt, Libya is an isolated reef-bounded carbonate platform of Late Maastrichtian-Danian age. The Satal and carbonates units directly above, harbor a prolific petroleum system comprised of several large oil fields sourced from a common generative area. A variety of conventional analytic technologies and techniques have been used to describe primary and secondary reservoir distribution and charge history of oil accumulations in the central and northern part of the platform. Core and log based facies analysis supported by SEM, bulk XRD and thin section petrography helped to describe the distribution of primary reservoir facies and subsequent development of secondary porosity and permeability. The nature and distribution of fracturing and fracture porosity was tentatively assessed from cores, wireline logs and seismic based structural maps and used to build predictive stress models. Oil geochemistry identified one distinctive oil family with two possible sub-groups. Finally, a well-based regional tectono-stratigraphic analysis provided a robust framework in which to synthesize this information within in a general hydrocarbon charge model (*Fig 1*).

The Satal Platform initially developed on a rifted basement high. As this subsided and base level rose, several highstand aggrading sequences built up and out to form the isolated reef ringed platform, interrupted by occasional exposure/meteoric dissolution events. Open marine marls interdigitating with lowstand Hagfa shales pass laterally into Upper Satal coccolithic chinks and reef margin facies characterized by bryzoa, corals and lagoonal/inner platform miliolid bearing lime mudstones and dolomites. Early burial was associated with micritization, calcite cementation, neomorphism and dolomitization. Increasing burial during the late Paleocene and Eocene was marked by solution seams/stylolitization, blocky ferroan calcite and dolomite cements. Porosity is predominantly secondary dominated by intercrystalline porosity developed during dolomitization and local vuggy dissolution. Towards the end of the Eocene and continuing intermittently into the Plio-Pleistocene, the western part of the Sirt Province was uplifted and partially unroofed tilting the Satal Platform to the east, reactivating old basement faults and locally fracturing the reservoir. This episodic tilting encouraged long distance lateral oil migration from the Marada generative area to the east into the Satal carbonate and overlying reservoir units. With continued unroofing and tilting, meteoric waters flooded through the western part of the platform with some dissolution locally.

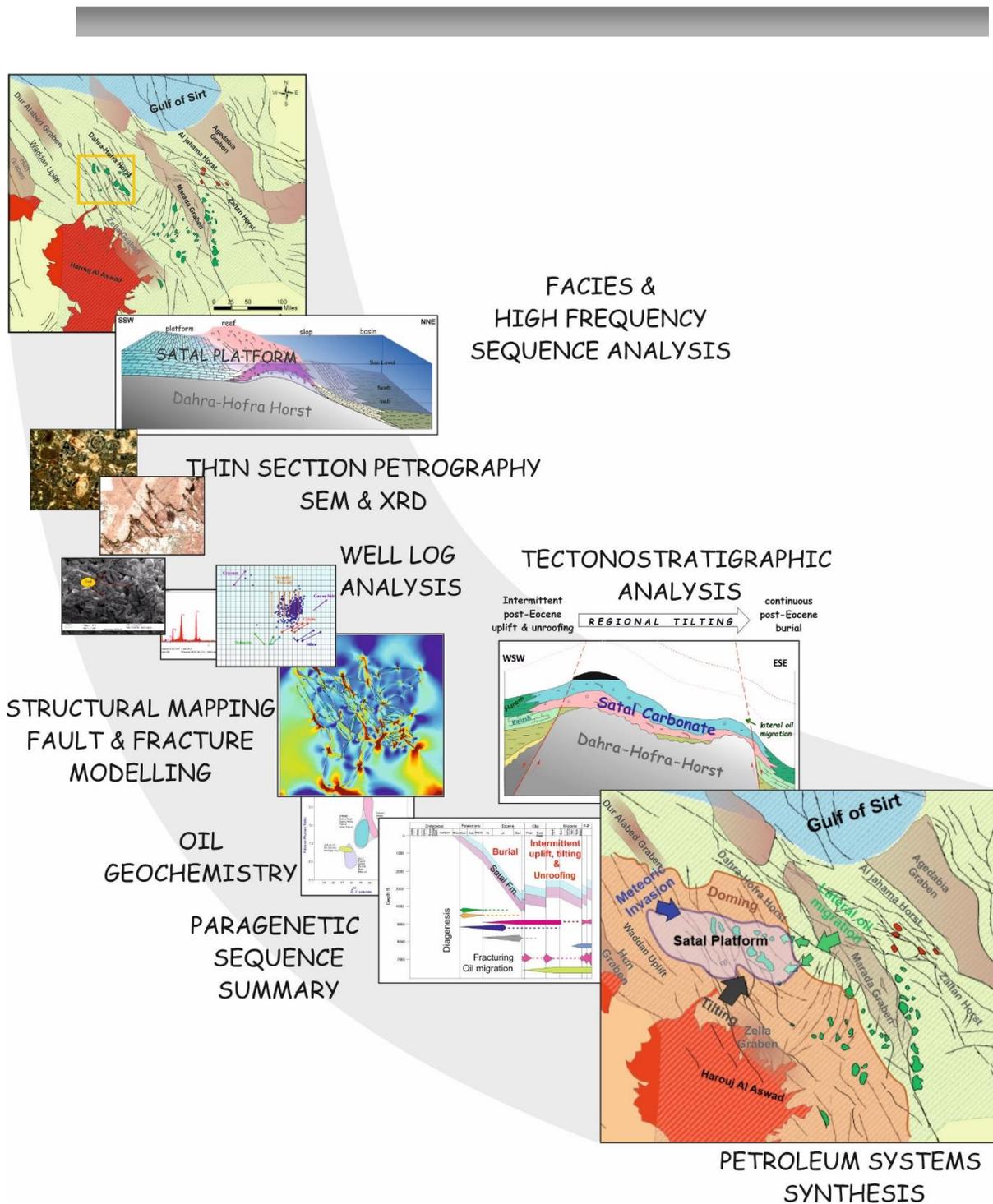


Fig 1: Progression of analytic techniques used to reconstruct petroleum systems reservoir and charge history of the Satal Platform, Western Sirt Rift Province.

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Exit via Piccadilly entrance or main reception entrance.

Lecture Theatre

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All accidents should be reported to Reception and First Aid assistance will be provided if necessary.

Facilities

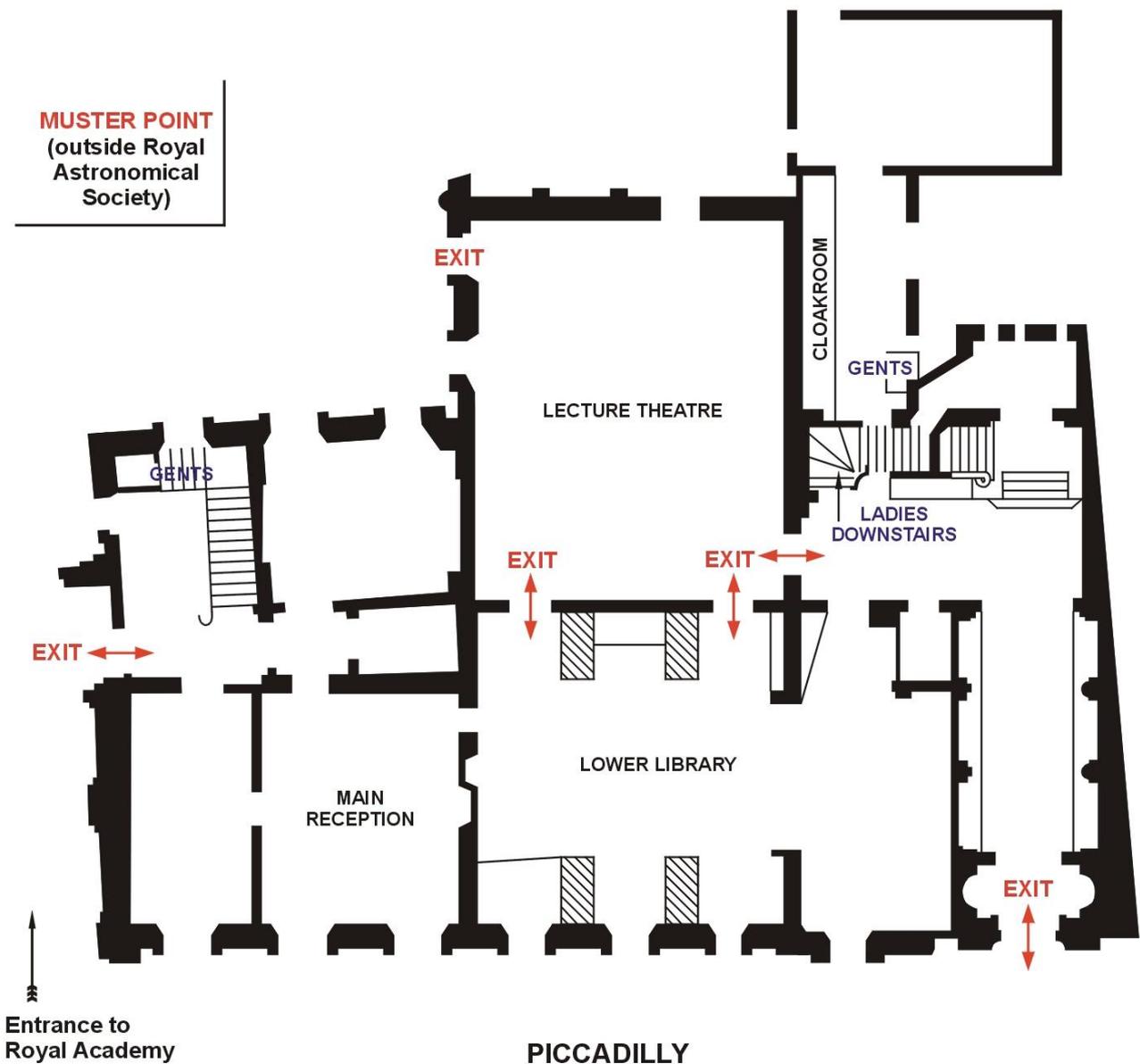
The ladies toilets are situated in the basement at the bottom of the staircase outside the Lecture Theatre.

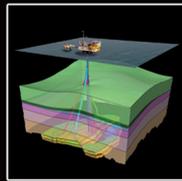
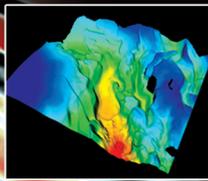
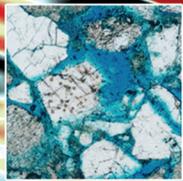
The Gents toilets are situated on the ground floor in the corridor leading to the Arthur Holmes Room.

The cloakroom is located along the corridor to the Arthur Holmes Room.

Ground Floor Plan of the Geological Society, Burlington House, Piccadilly

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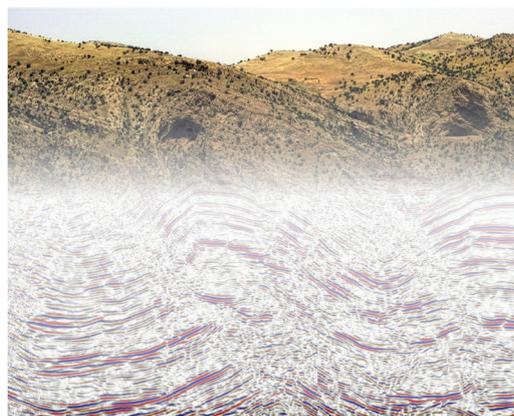
Fernando Alegria
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Call for Abstracts – Deadline: Friday 30 June 2017

Fold and Thrust Belts: Structural style, evolution and exploration

31 October – 2 November 2017

The Geological Society, Burlington House, Piccadilly, London



Fold and thrust belts have formed in all eras of geological time and, represent some of the planet's most complex geological environments. Deformation styles may evolve spatially and temporally according to the type of sedimentary sequence involved, the presence of main detachment zones, and the orientation and evolution of the stress field with respect to the plate boundaries. At the same time, fold and thrust belts contain many substantial producing fields and some of the world's largest remaining hydrocarbon reserves. The complex interaction of fold and thrust processes, and their effects on potential reservoir quality and deliverability makes accurate characterization of such fields and reserves extremely difficult. New technologies and approaches

developed in the last 10 years are helping to advance understanding of fold and thrust belts, opening new exploration opportunities in these systems.

This three-day meeting aims to bring together leading academic and industry geoscientists to discuss new techniques and case studies, and to capture an up to date assessment of our understanding of fold and thrust belts globally.

Themes / Thematic sessions:

- Case studies documenting the temporal and spatial evolution of structural style
- New techniques and approaches to understanding fold and thrust belts
- New Exploration discoveries in fold and thrust belts, and their impact on understanding and prospectivity
- Understanding and predicting fold and thrust belt geometries
- Evolving stress fields and their impact on fault and fracture networks
- Hydrocarbon modelling in fold and thrust belts

Call for Abstracts:

Please email paper and poster contributions to abstracts@geolsoc.org.uk and copy to raffaele.dicua@geplan.it by Friday 30 June 2017.

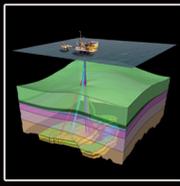
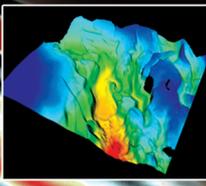
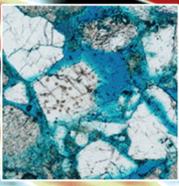
For further information please contact:

Sarah Woodcock, The Geological Society, Burlington House, Piccadilly, London W1J 0BG.
Tel: +44 (0)20 7434 9944, sarah.woodcock@geolsoc.org.uk



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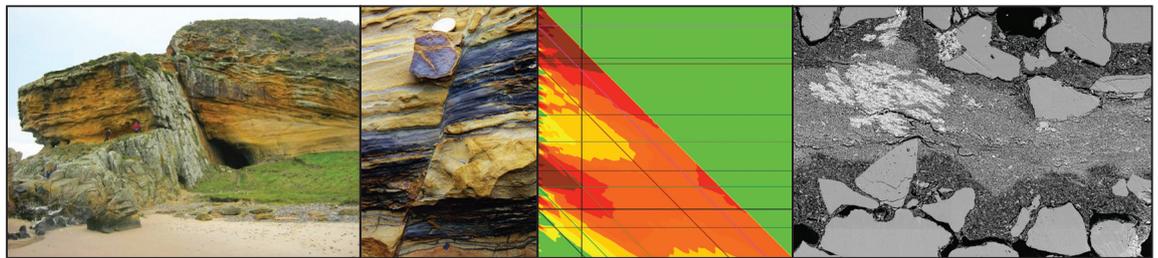
Call for Abstracts – Deadline: 1 May 2017

Handling Fault Seals, Baffles, Barriers and Conduits

Cost Effective & Integrated Fault Seal Analysis

15-17 November 2017

The Geological Society, Burlington House, Piccadilly, London



Faults are a key component of heterogeneity in reservoirs. They can trap/seal hydrocarbons or be barriers/baffles to fluid flow in a producing field. Whether or not they seal or act as a barrier to fluid flow is crucial in every part of the petroleum value chain – from prospect generation to development well planning. Characterizing the fluid flow properties of faults is often seen as a specialist subject, requiring dedicated software, and is often overlooked. However, most aspects of fault seal analysis draws upon the skills of an integrated geoscientist who can utilize all available data (e.g. seismic, well log, core, thin-section, outcrop, laboratory, PVT, and dynamic data) and assess uncertainty in both input data and interpretation. There are relatively simple and well established workflows (i.e., juxtaposition analysis, shale gouge calculations, which may or may not work depending on reservoir architecture and geomechanical conditions) that a geoscientist should follow that help characterize fault seal potential, but how to address more detailed challenges related to the intrinsic properties of fault rocks (i.e. other than shale gouge), fault geometries (i.e. segmentation) and setting (i.e. non-clastic lithologies, geomechanical effects, neotectonics) is not well established.

This meeting will build upon previous meetings to consider the most-cost effective ways of carrying out an integrated fault seal analysis in today's environment, in order to understand the uncertainties, risks and upsides associated with fault-related fluid flow. All parts of the petroleum value chain from exploration and appraisal to – development and production will be considered.

Themes/Thematic sessions

- Types of fault seal (processes, juxtaposition, reactivation) and established techniques
- Fault rock/zone architectures in core and outcrop
- Laboratory studies of fault rocks
- Fault slip modelling and simulation
- Reservoir geomechanics including coupled simulation modelling during production
- Fault seal in exploration and appraisal (i) workflows – seismic, juxtaposition diagrams, pre-and post-well scenarios, (ii) fault-controlled traps, (iii) basin modelling and migration, (iv) neotectonic settings
- Fault seal in development and production (i) workflows (as above but including more dynamic data, 4D Seismic, reservoir monitoring), (ii) baffles, barriers to flow, (iii) impact upon completion designs, depletion plans, (iv) fault reactivation, (v) uncertainty assessment.
- Novel approaches to handle issues where the basic workflow cannot address the key uncertainties e.g., self-juxtaposition seal in sands, fluid movement up and along faults.

Call for Abstracts:

Please submit paper contribution to sarah.woodcock@geolsoc.org.uk by 1 May 2017.

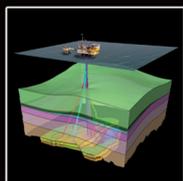
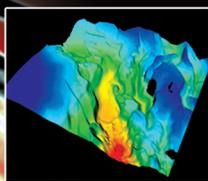
For further information please contact:

Sarah Woodcock, The Geological Society, Burlington House, Piccadilly, London W1J 0BG. T: 020 7434 9944

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Earth Science Analytics

Faroe Petroleum

IGI

OMV

Rystad Energy

Richmond Energy

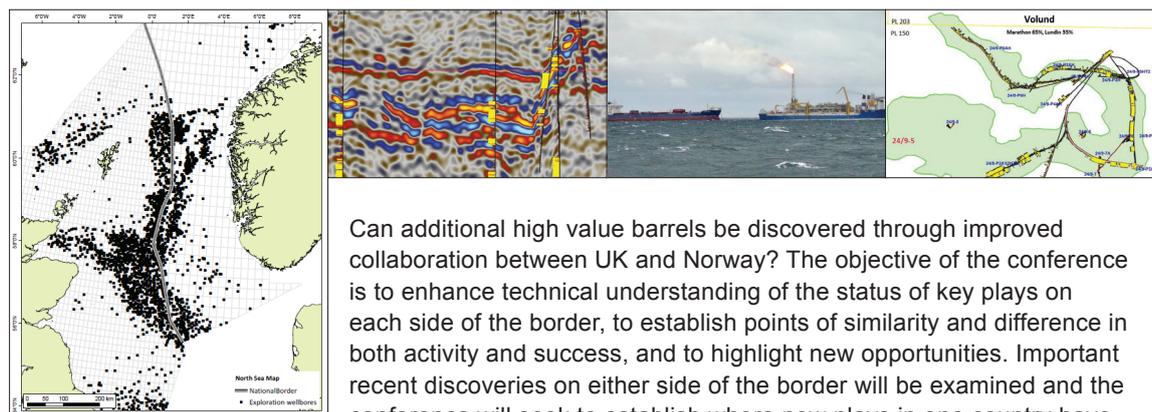
Statoil

Call for Abstracts – Extended deadline: 1 June 2017

Cross-border Exploration between UK & Norway – Comparisons, Contrasts and Collaborations

27-28 November 2017

The Geological Society, Burlington House, Piccadilly, London



Can additional high value barrels be discovered through improved collaboration between UK and Norway? The objective of the conference is to enhance technical understanding of the status of key plays on each side of the border, to establish points of similarity and difference in both activity and success, and to highlight new opportunities. Important recent discoveries on either side of the border will be examined and the conference will seek to establish where new plays in one country have

not yet been understood or exploited across the border. Key note presentations will be made by leading figures from both Norway and UK.

This two day international conference will bring together explorationists from UK, Norway and other European countries with the following themes:

- Play opening discoveries as yet unexploited cross border
- Differences in how competence is organised and technology adopted
- Examples of specific play knowledge being exploited cross border
- Challenges on median line including data continuity and differences in nomenclature
- How to build a geology-without-borders view
- Issues for service industry
- Differences in exploration performance
- Danish and Dutch (and other) cross border examples
- Impact of regulatory and fiscal frameworks

Call for Abstracts:

Please submit paper contribution to sarah.woodcock@geolsoc.org.uk by 1 June 2017.

For further information please contact:

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