Gas Generation Reactions in Highly Mature Gas Shales*

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Search and Discovery Article #80162 (2011)
Posted June 30, 2011

*Adapted from oral presentation at AAPG Annual Convention and Exhibition, Houston, Texas, USA, April 10-13, 2011

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Abstract

As a new and abundant energy resource, gas shales have already impacted worldwide energy supply. Currently, worldwide exploration activities are drastically increasing. This unconventional gas resource constitutes complex self-contained source-reservoir systems, in which three distinct processes together result in the formation of thermogenic gas: (1) the decomposition of kerogen to gas and bitumen; (2) the decomposition of bitumen to oil and gas; and (3) the secondary cracking of oil to gas and a carbon-rich coke or pyrobitumen residue. While the basic stoichiometries and source-sink relationships are understood, the chemical and structural variability of gas shales at the submicrometer scale is still poorly documented. Consequently, hydrocarbon generation and retention processes occurring within such unconventional systems are still poorly constrained.

As part of the European GASH project (GAs SHales) coordinated by the GFZ-Potsdam, organic-rich calcareous mudstone samples from Northern Germany at varying stages of thermal maturation have been characterized using an original combination of compositional organic geochemistry and spectromicroscopy techniques, including synchrotron-based STXM (scanning transmission X-ray microscopy) allowing in situ imaging of organic-rich samples with a chemical-based contrast at a 25-nm spatial resolution while providing spatially-resolved information of organic constituent speciation.

Within the selected gas shale samples, we document multi-scale chemical and mineralogical heterogeneities, from the bulk scale down to the nanometer scale. Different types of bitumen, very likely genetically derived from thermally degraded organic precursors, have been detected in close association with authigenic minerals. Macroscopic fracture-filling bitumen with the same organic chemical signatures as one family has been documented. Chemical rock-fluid interactions could be inferred in the case of another family. The porosity evolution with thermal maturation has also been documented using TEM at the nanometer scale. Our observations provide

key constraints on the thermal history of this gas shale formation and shed new light on the influence of the organic precursor chemistry on the thermal generation and retention of the various organic moieties which can be encountered in gas shales.

Selected References

Bernard, S., B. Horsfield, H.-M. Schultz, A. Schreiber, R. Wirth, T.T. Vu, F. Perssen, S. Konitzer, H. Volk, N. Sherwood, and D. Fuentes, 2010, Multi-scale detection of organic and inorganic signatures provides insights into gas shale properties and evolution: Chemie der Erde-Geochemistry, v. 70/S3, p. 119-133.

Heaney, P.J., E.P. Vicenzi, L.A. Giannuzzi, and K.J.T. Livi, 2001, Focused ion beam milling: A method of site-specific sample extraction for microanalysis of Earth and planetary materials: American Mineralogist, v. 86, p. 1094-1099.

Hill, R.J., E. Zhang, B.J. Katz, and Y. Tang, 2007, Modeling of gas generation from the Barnett Shale, Fort Worth Basin, Texas: AAPG Bulletin, v. 91/4, p. 501-21.

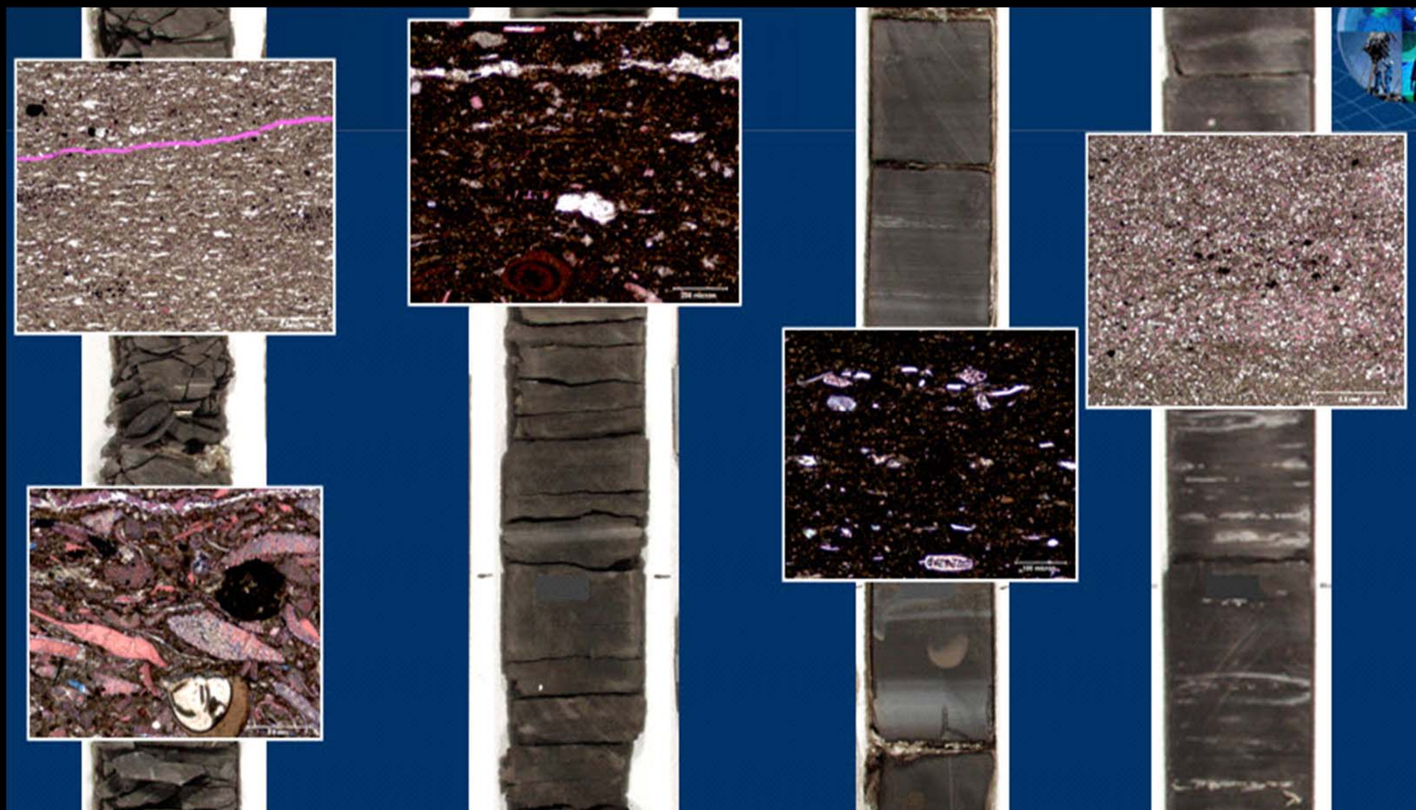
Jarvie, D.M. R.J. Hill, T.E. Ruble, and R.M. Pollastro, 2007, Unconventinal shale-gas systems; the Mississippian Barnett Shale of North-Central Texas as one model for thermogenic shale-gas assessment: AAPG Bulletin, v. 91/4, p. 475-499.

Loucks, R.G., R.M. Reed, S.C. Ruppel, and D.M. Jarvie, 2009, Morphology, genesis, and distribution of nanometer-scale pores in siliceous mudstones of the Mississippian Barnett Shale: JSR, v. 79/12, p. 848-861.

Petmecky, S., L. Meier, H. Reiser, and R, Littke, 1999. High thermal maturity in the Lower Saxony basin: intrusion or deep burial?: Tectonophysics, v. 304, p. 317-344.

Rullkotter, J., and R. Marzi, 1988, Natural and artificial maturation of biological markers in a Toarcian shale from northern Germany: Organic Geochemistry, v. 13, p. 639-645.

Gas generation reactions in highly mature gas shales

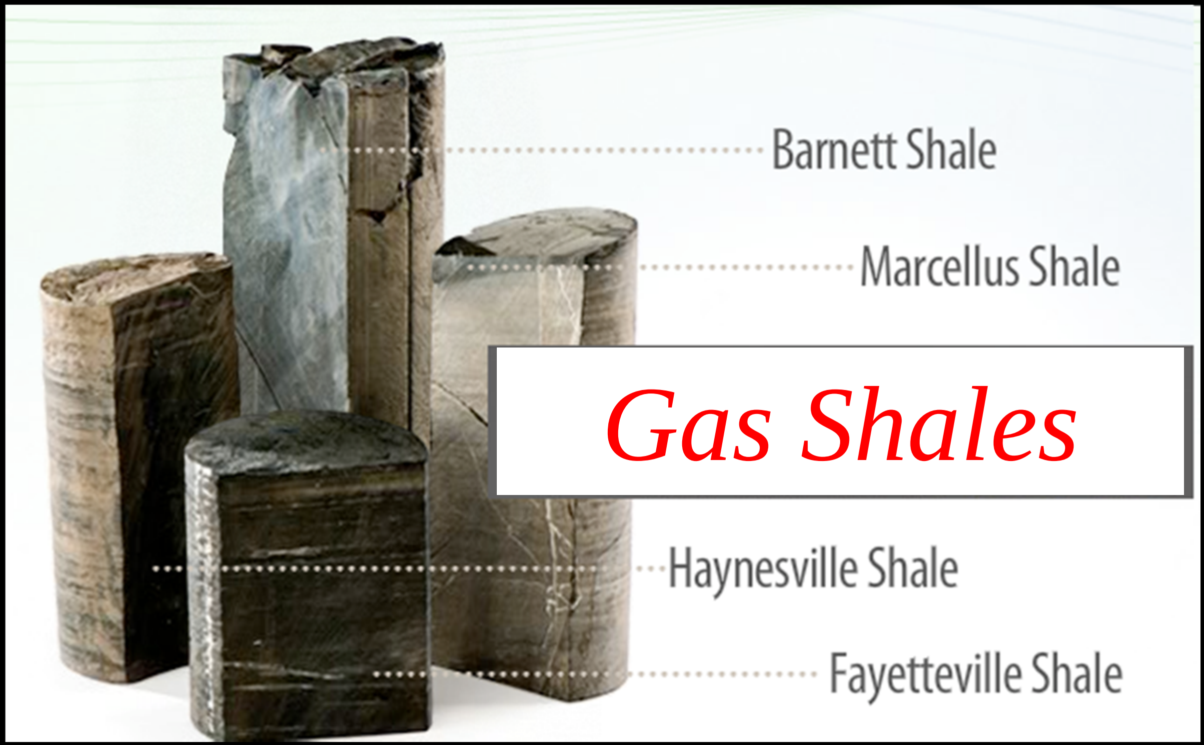


GFZ
Helmholtz Centre
POTSDAM

Sylvain Bernard - Brian Horsfield
Hans-Martin Schulz - Richard Wirth - Anja Schreiber

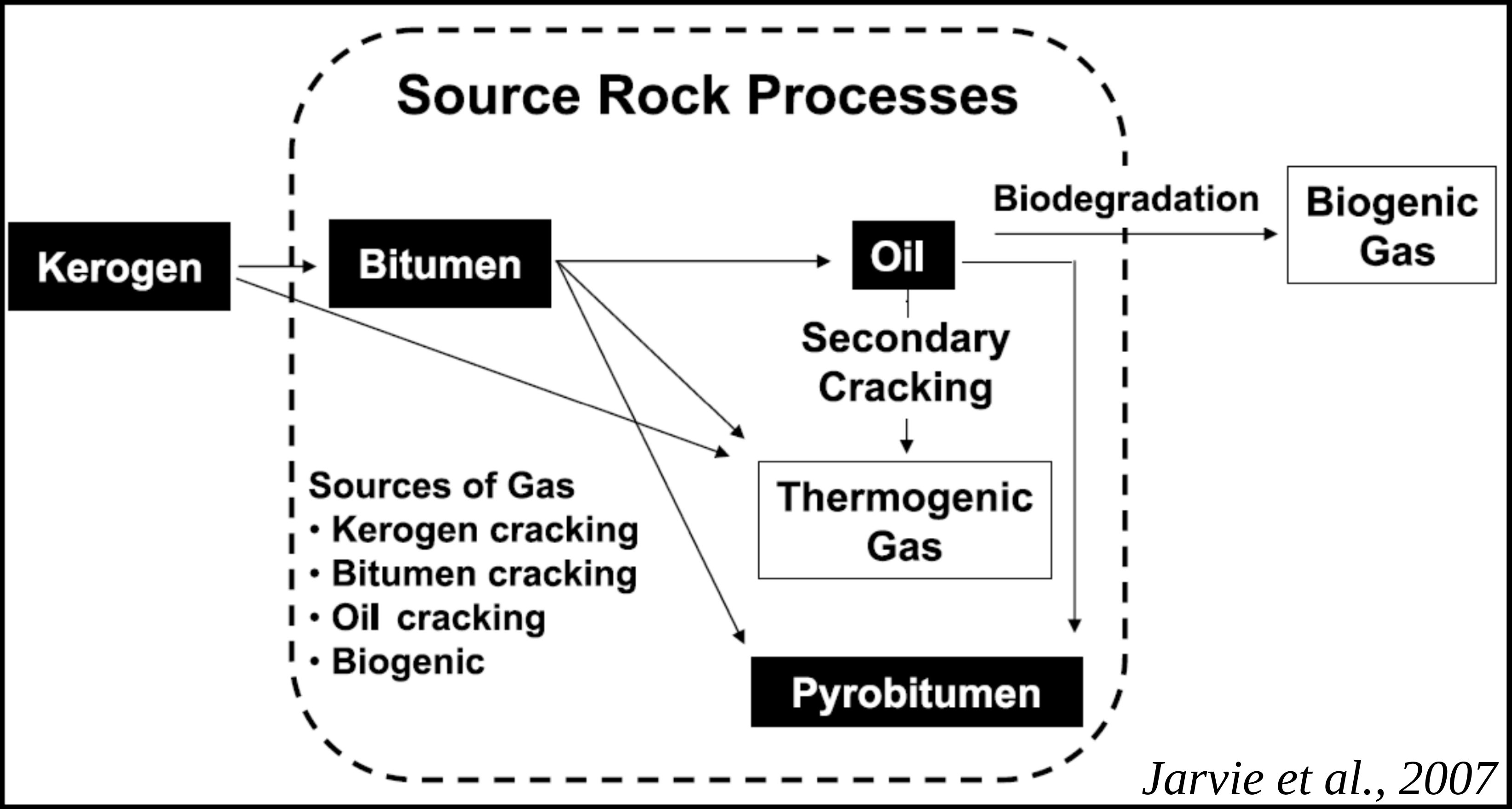
GASH
Gas Shales in Europe

Gas generation reactions in highly mature gas shales



Gas shales constitute self-contained source-reservoir systems of large and continuous gas accumulation

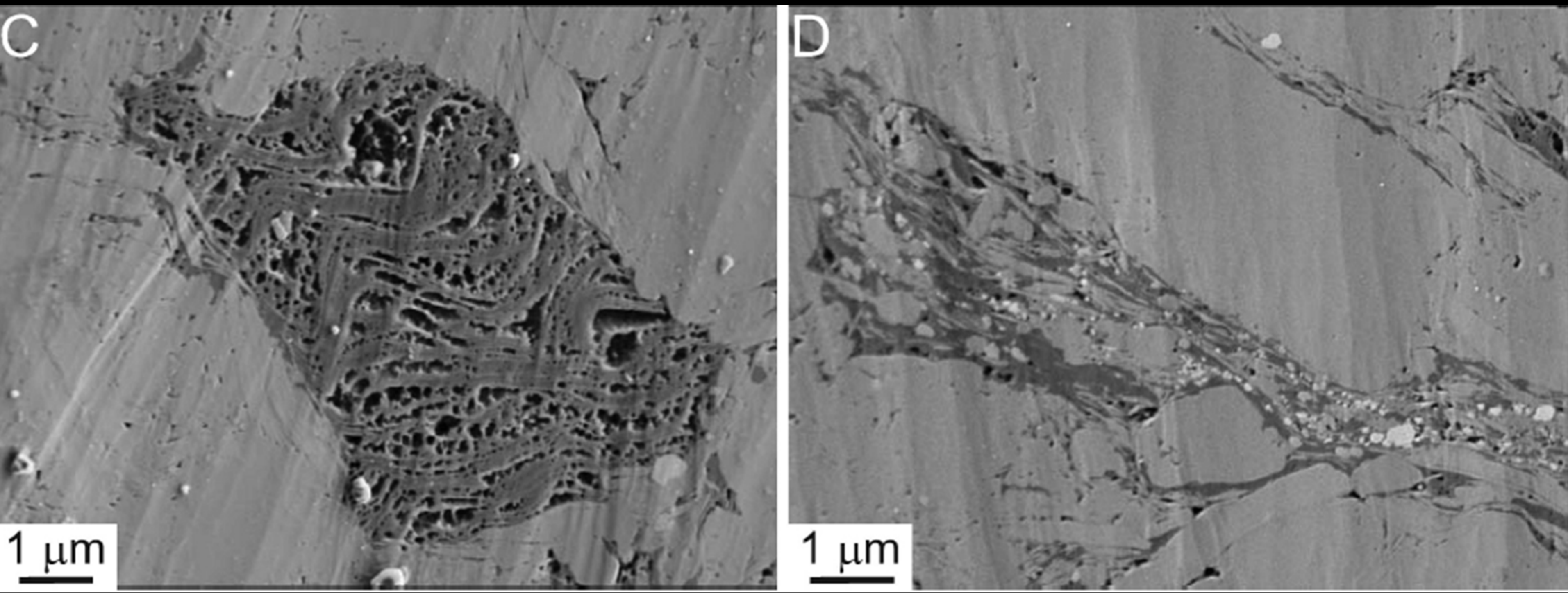
Different processes may lead to thermogenic gas formation



✓ *Chemical heterogeneities of gas shales at the submicrometer scale ?*

✓ *Structural organic/inorganic relationships at the nanometer scale ?*

Identification of nanoscale pores within Barnett Shale samples



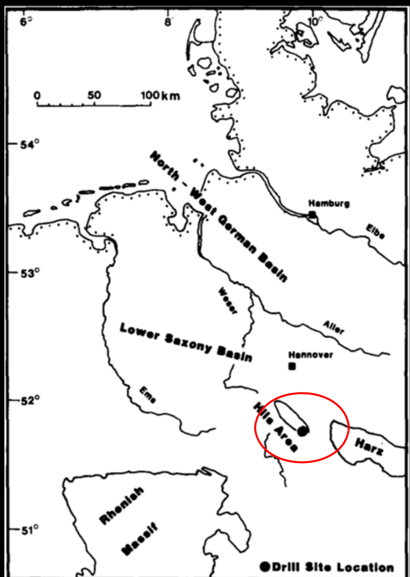
Loucks et al., 2009

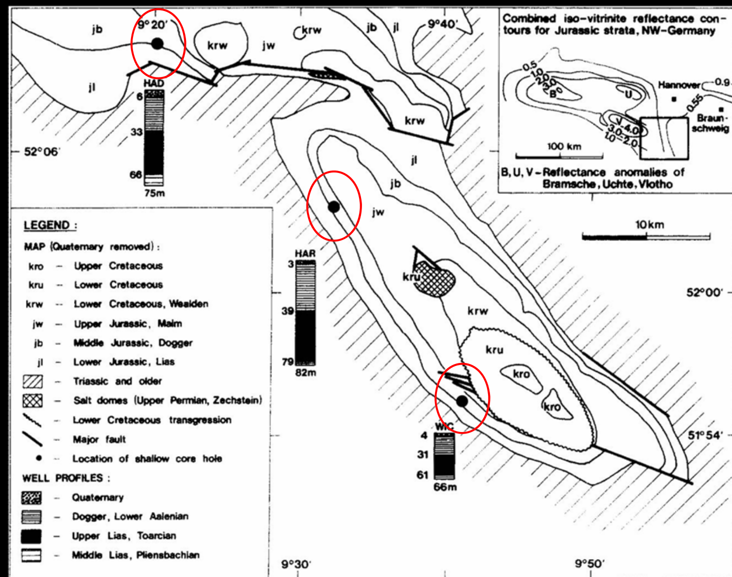
✓ *Origin of such nanoscale porosity : gaseous hydrocarbon generation ?*

→ *Multiscale characterization of a maturation series using TEM + STXM*

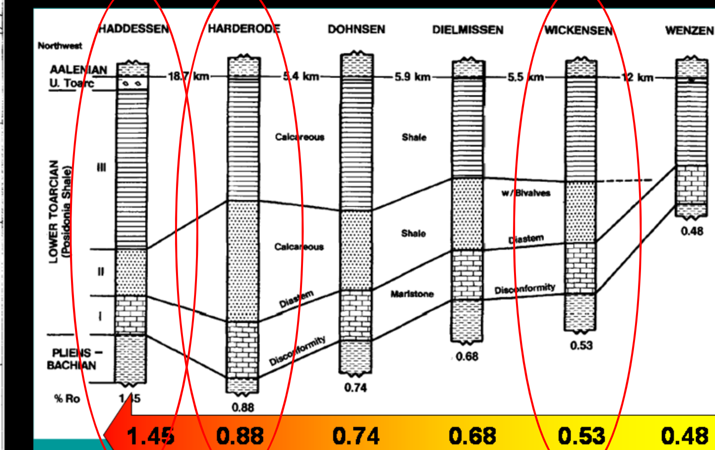
Posidonia Shales : Location and Maturity

Lias ε level of the Lower Toarcian Posidonia Shales from the Hils syncline area



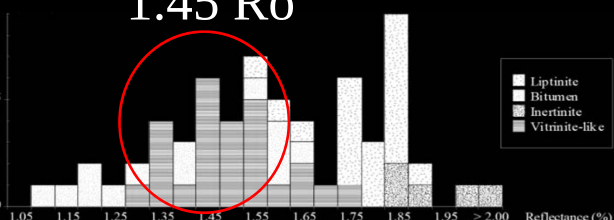


Haddessen Wickensen



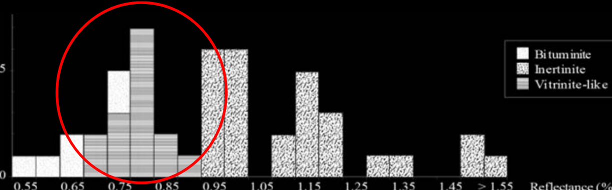
Harderode

1.45 Ro



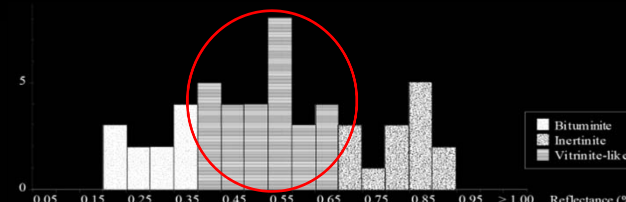
Haddessen Well

0.85 Ro



Harderode Well

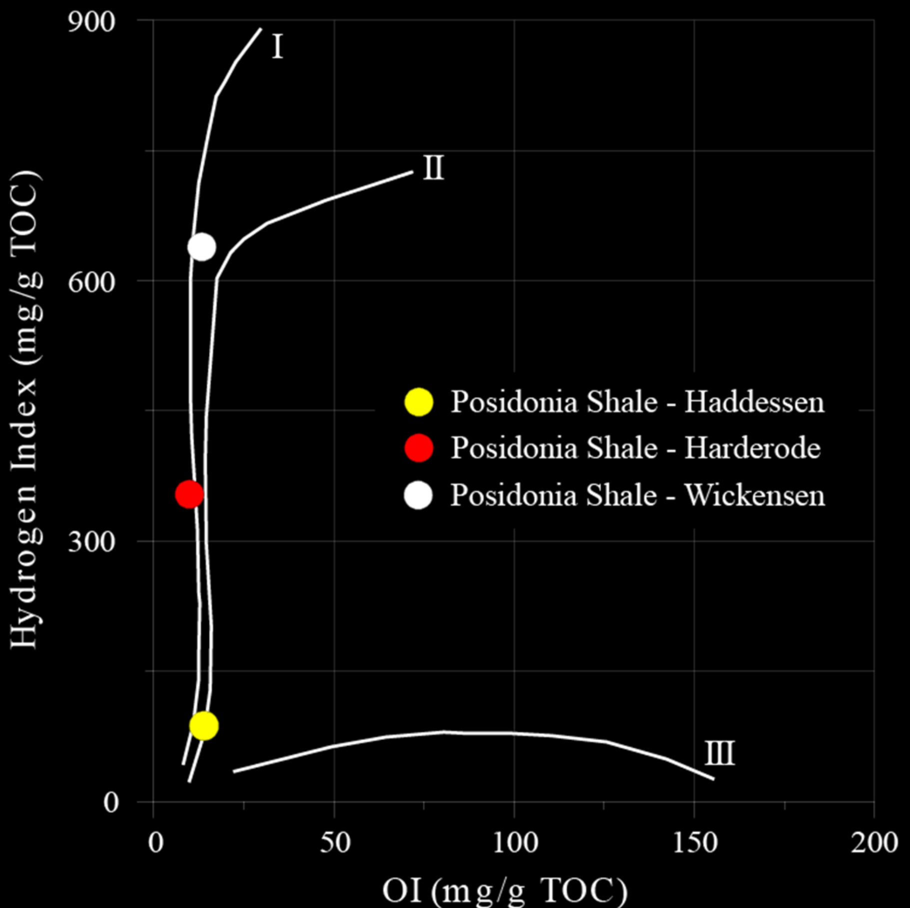
0.55 Ro

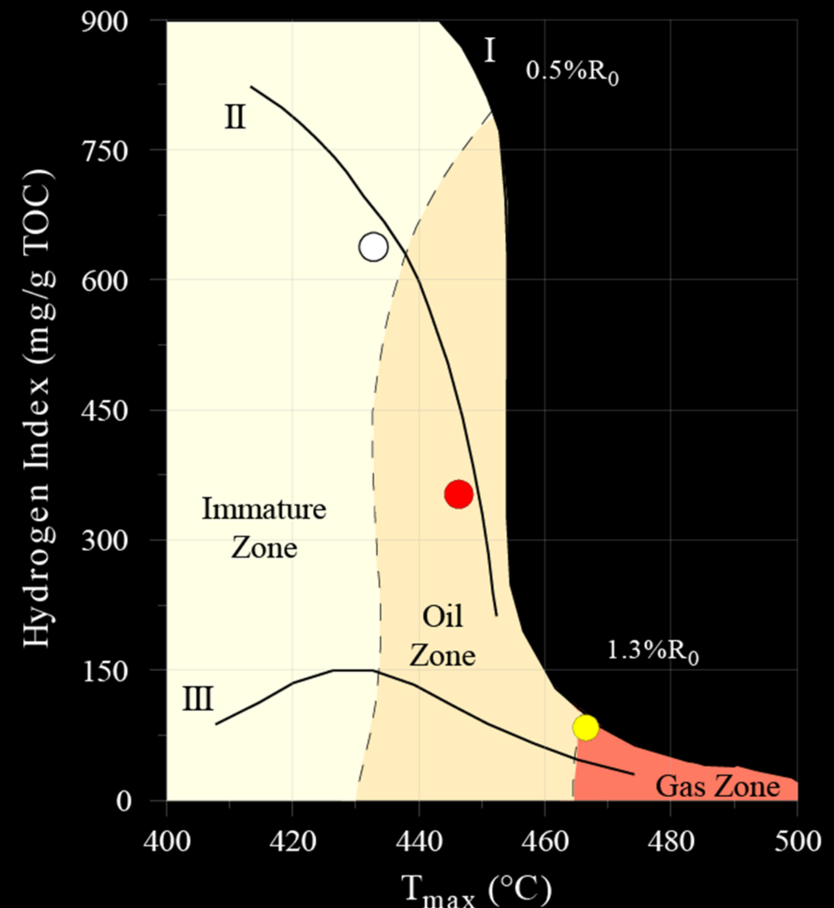


Wickensen Well

Maturity increases

Posidonia Shales : Rock-Eval Pyrolysis Data





Haddessen Well = Overmature gas shale

Bernard et al., Chemie der Erde, 2010
Bernard et al., Marine and Petroleum Geology, 2011

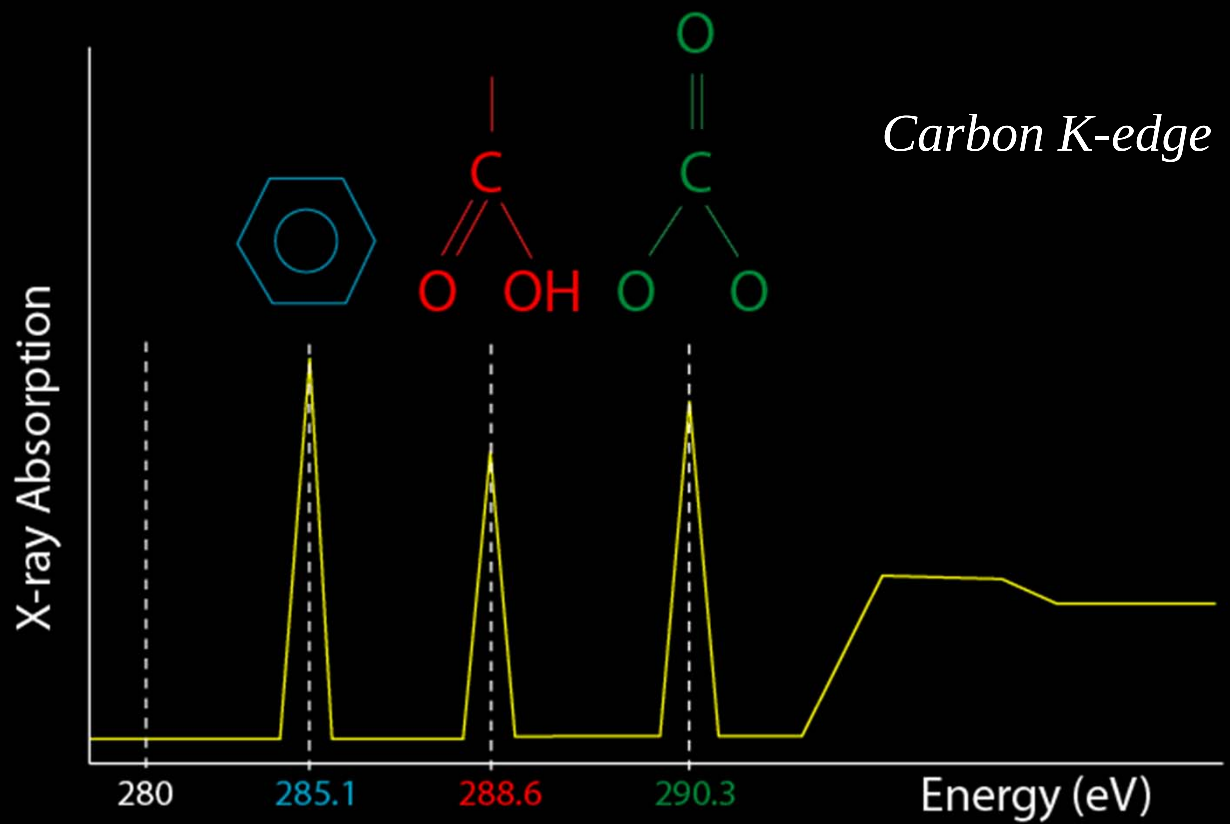
Soxhlet extraction of the soluble fraction

Solvent extraction and fractionation of the :

- *Aliphatic fraction*
- *Aromatic fraction*
- *Polar NSO compounds*
- *Asphaltenes*

X-ray Absorption Near Edge Structure (XANES) Spectroscopy

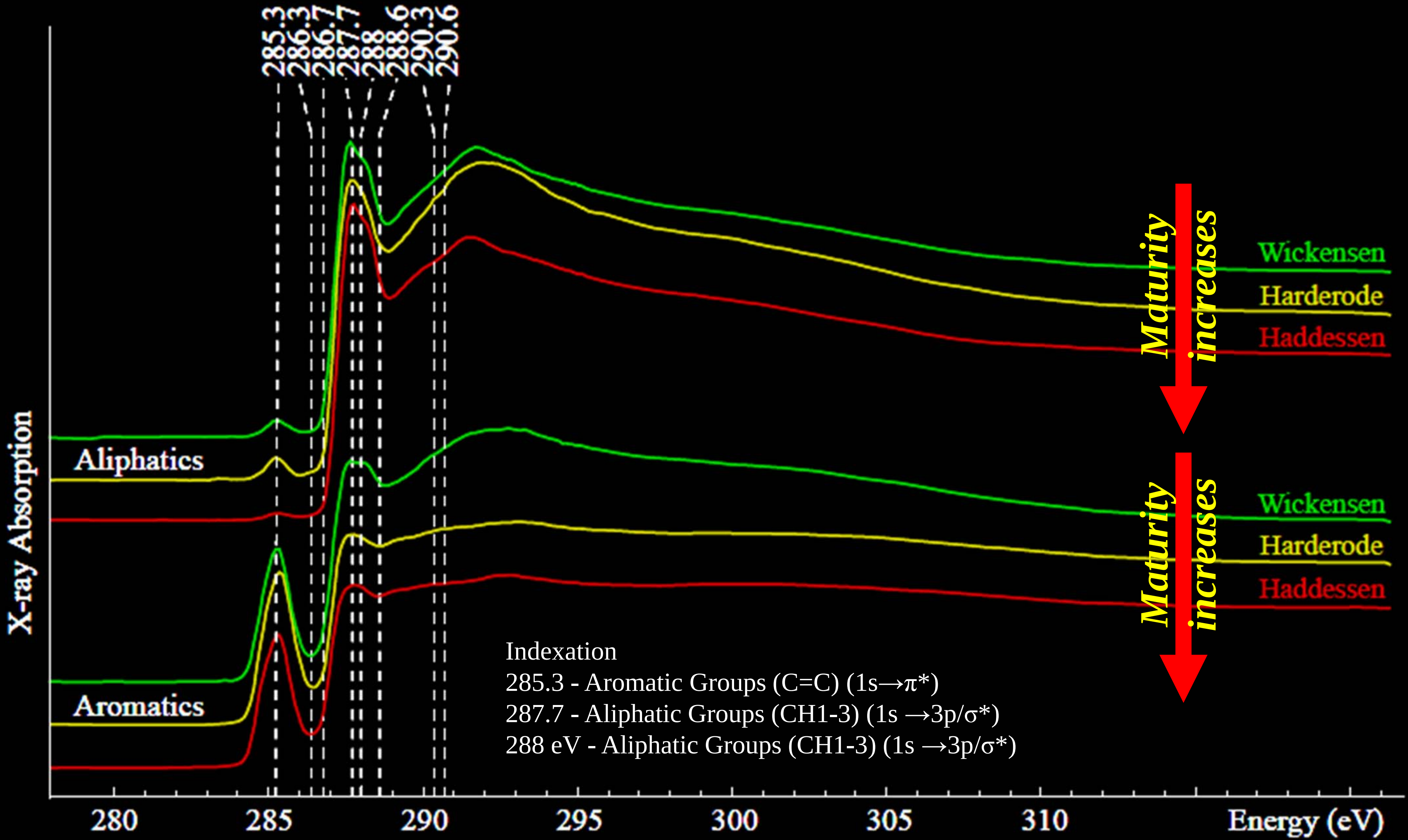
or Near Edge X-Ray Absorption Fine Structure (NEXAFS)



Very high spectral resolution (0.1 eV) → information on the bonding environment

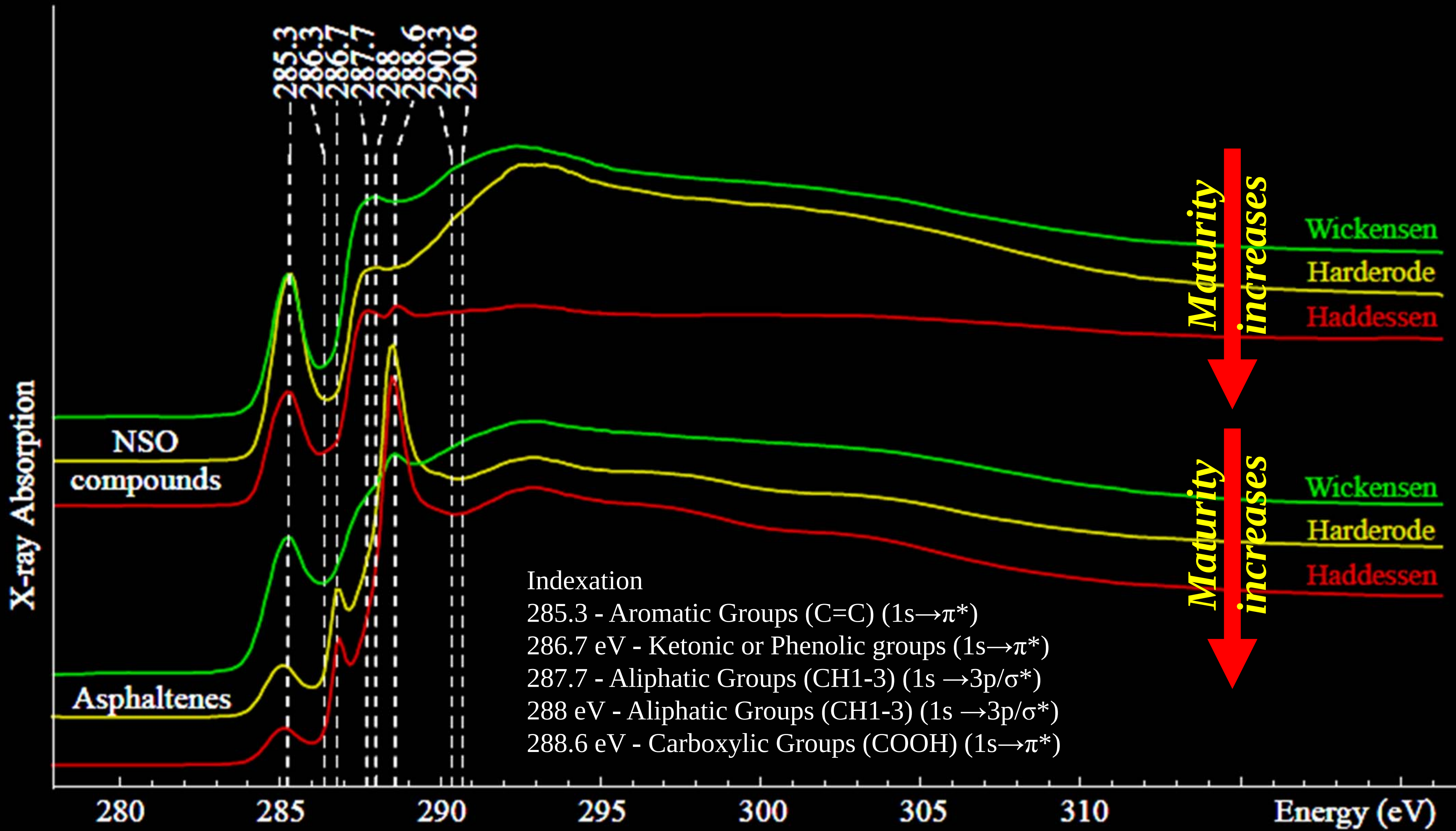
XANES spectrum = information on speciation with a Beer's Law response

Evolution of XANES signatures with increasing maturity:
Aliphatic and Aromatic Fractions



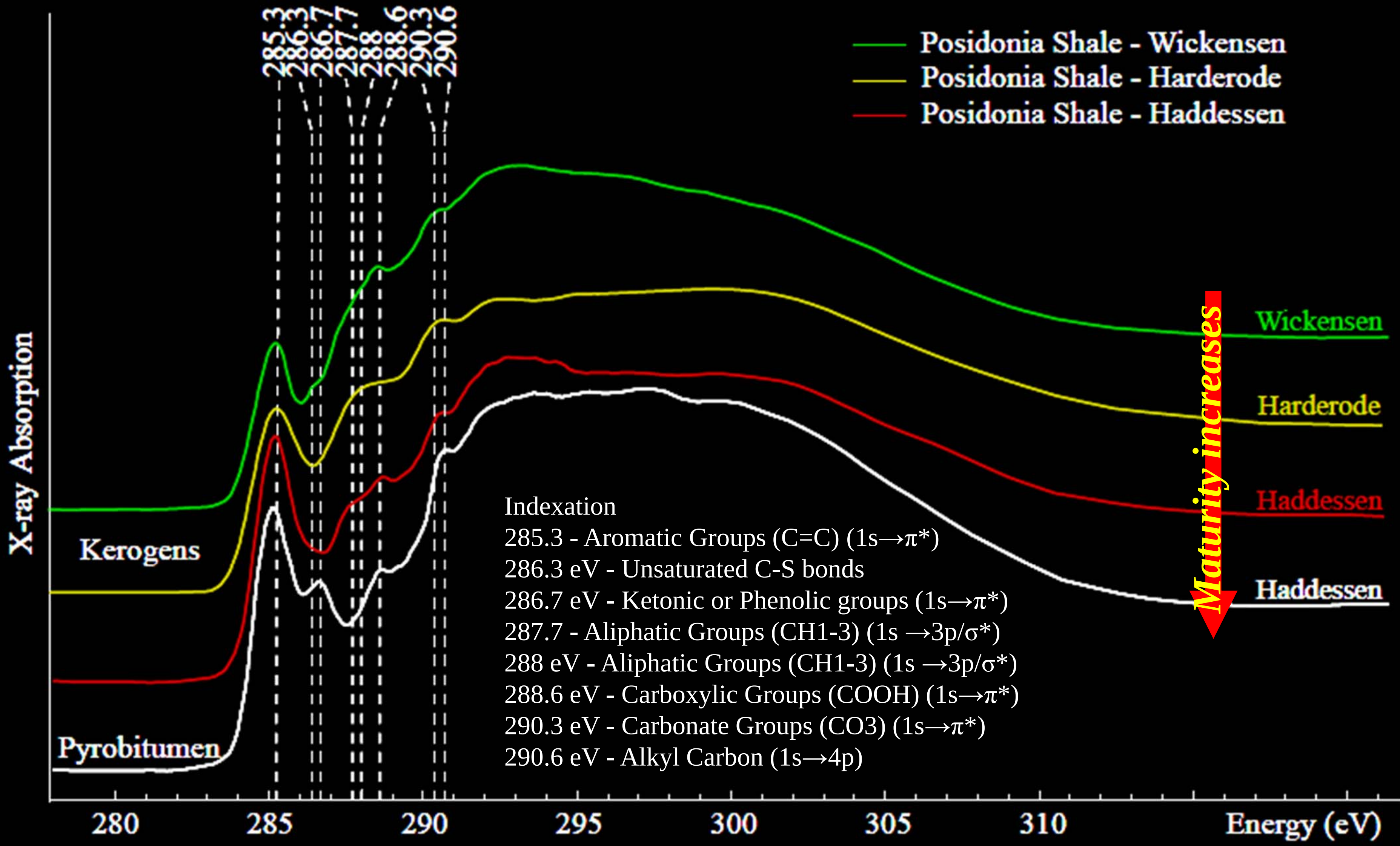
Indexation
285.3 - Aromatic Groups (C=C) (1s→π*)
287.7 - Aliphatic Groups (CH1-3) (1s →3p/σ*)
288 eV - Aliphatic Groups (CH1-3) (1s →3p/σ*)

Evolution of XANES signatures with increasing maturity:
Polar NSOs and Asphaltenes



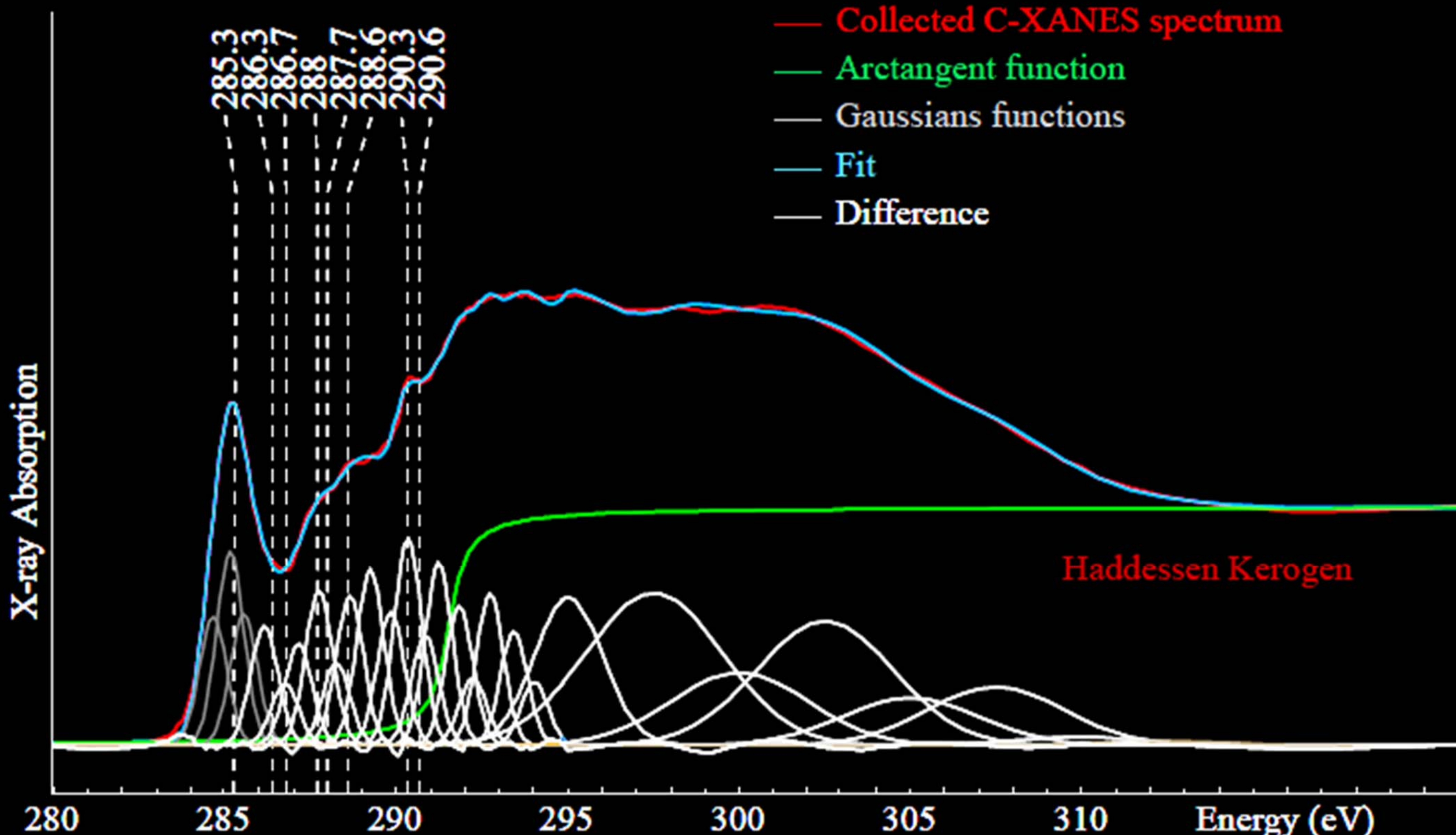
Indexation
285.3 - Aromatic Groups (C=C) (1s→π*)
286.7 eV - Ketonic or Phenolic groups (1s→π*)
287.7 - Aliphatic Groups (CH1-3) (1s →3p/σ*)
288 eV - Aliphatic Groups (CH1-3) (1s →3p/σ*)
288.6 eV - Carboxylic Groups (COOH) (1s→π*)

Evolution of XANES signatures with increasing maturity:
Insoluble Kerogen and Pyrobitumen



Indexation
285.3 - Aromatic Groups (C=C) (1s→π*)
286.3 eV - Unsaturated C-S bonds
286.7 eV - Ketonic or Phenolic groups (1s→π*)
287.7 - Aliphatic Groups (CH1-3) (1s →3p/σ*)
288 eV - Aliphatic Groups (CH1-3) (1s →3p/σ*)
288.6 eV - Carboxylic Groups (COOH) (1s→π*)
290.3 eV - Carbonate Groups (CO3) (1s→π*)
290.6 eV - Alkyl Carbon (1s→4p)

Deconvolution Procedure



Posidonia shale kerogen: Chemical and structural evolution with increasing maturity

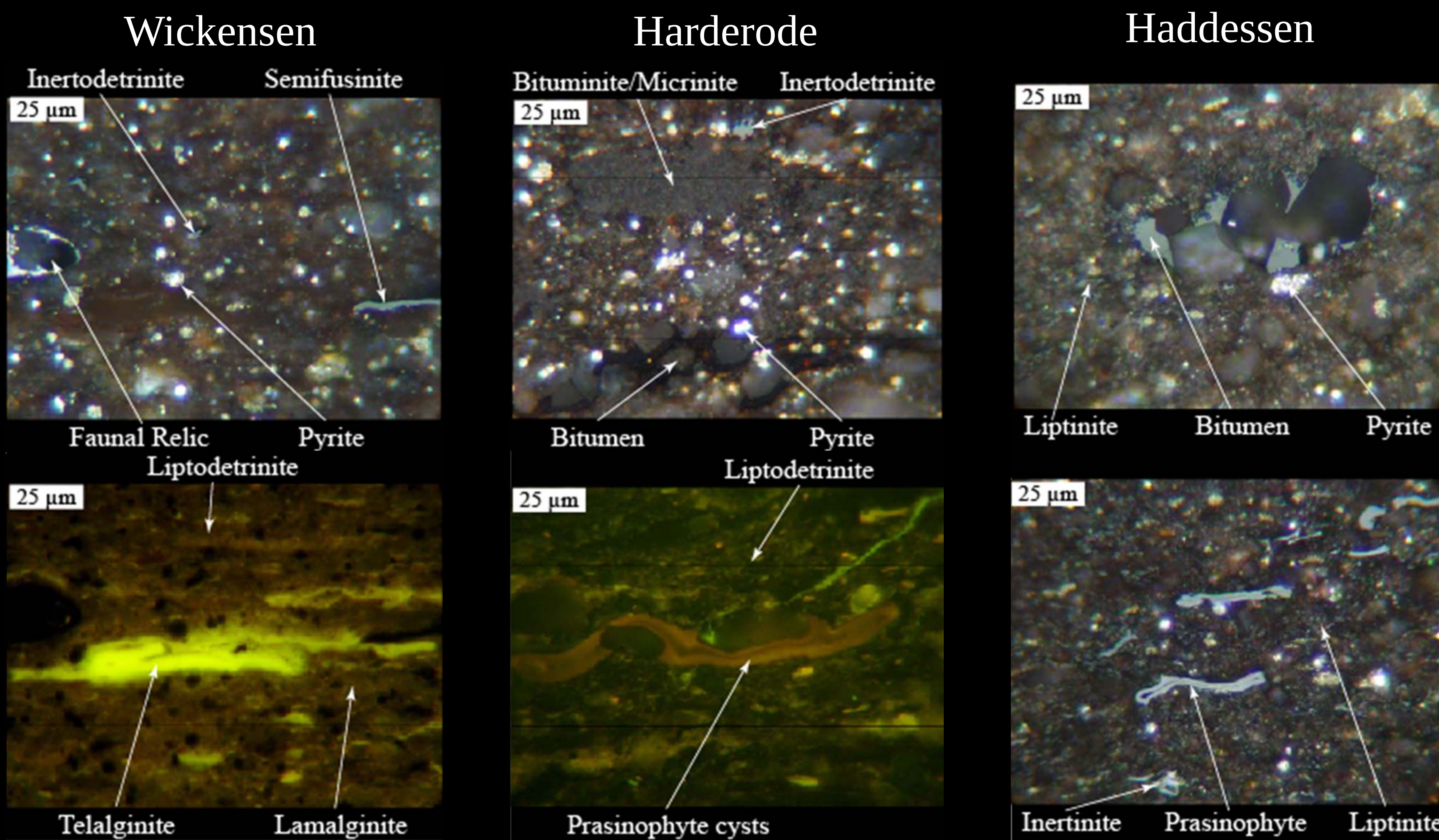
Parameters extracted from XANES spectra	Kerogen		
	Wickensen	Harderode	Haddessen
Aromaticity - S_A	1.25	1.56	1.90
Ratio Alipatics/Aromatics - R_{Aliph}	0.96	0.76	0.52
Ratio (Phenols+Ketones)/Aromatics	0.62	0.49	0.36
Ratio Carboxylics/Aromatics	0.62	0.43	0.33
Ratio Oxygen/Aromatics - R_{Oxygen}	1.24	0.92	0.69

Maturity increases

With increasing maturity :

1. The aromaticity of the kerogen increases
2. The relative concentration of aliphatic carbon drastically decreases
3. Sulfur and oxygen-containing functional groups are progressively lost

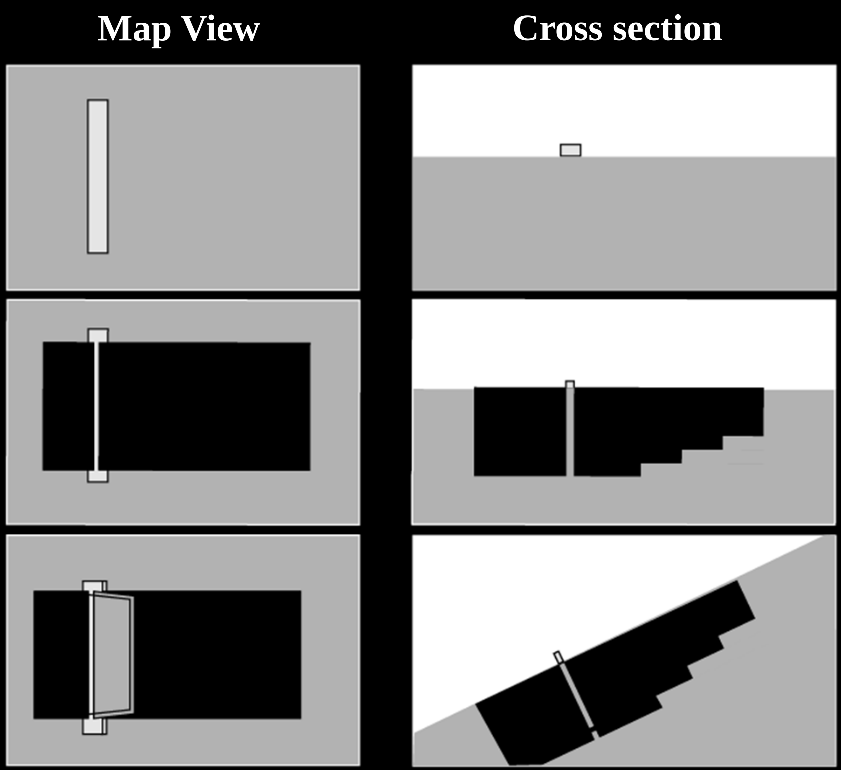
Microscope observations - Organic Petrography

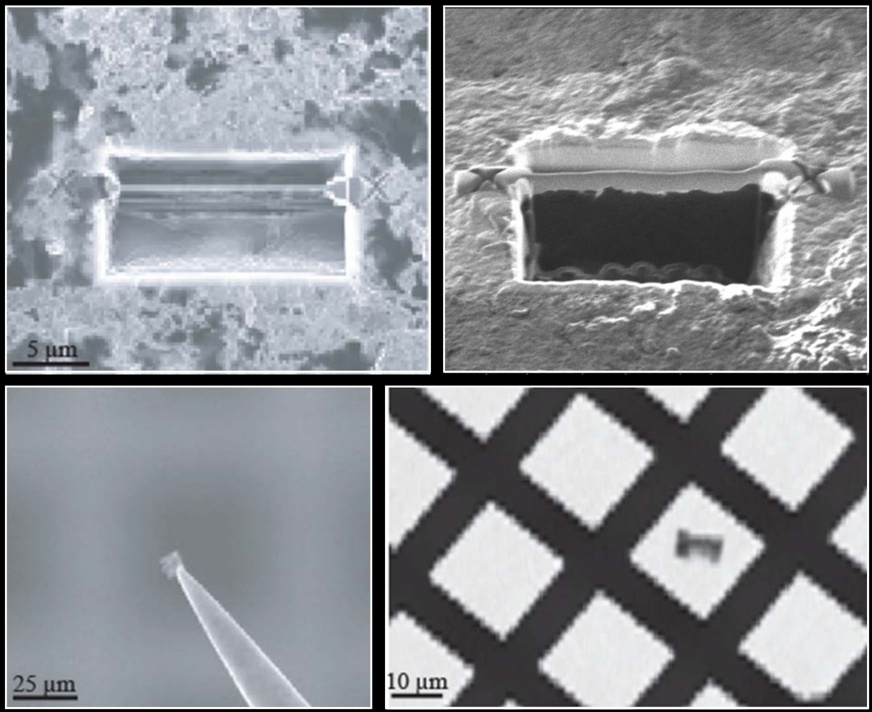


Maturity increases

Organic and inorganic heterogeneities at the micrometric scale.

Preparation of FIB sections for TEM and STXM characterization





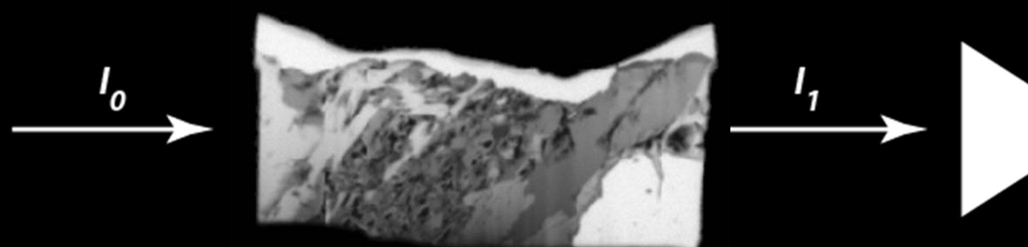
Heaney et al., 2001

In situ extraction of a ~10 µm x 5 µm x 100 nm slice of sample for TEM and STXM characterization

STXM = Scanning Transmission X-ray Microscopy

Synchroton radiation - Spatial Resolution: ~25 nm - Spectral Resolution: 0.1eV

Monochromatic X-ray at a single energy E



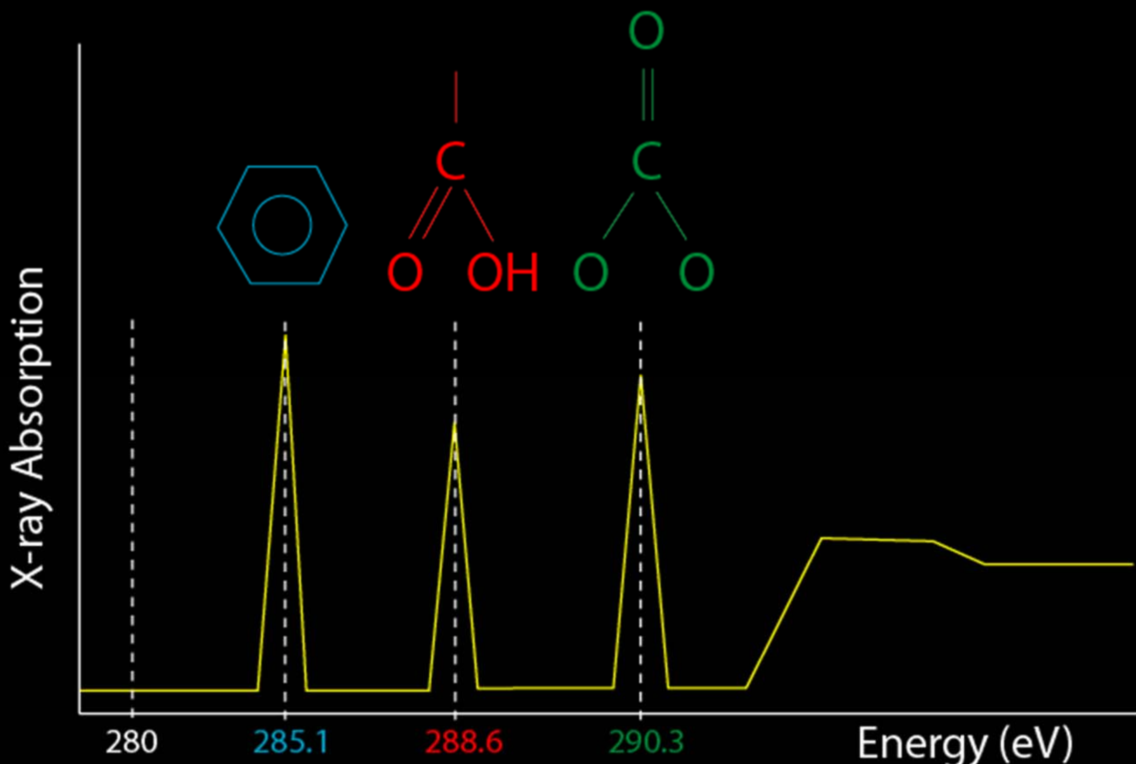
Absorption Measurement

$$A = -\ln\left(I_1/I_0\right) = f(E)$$

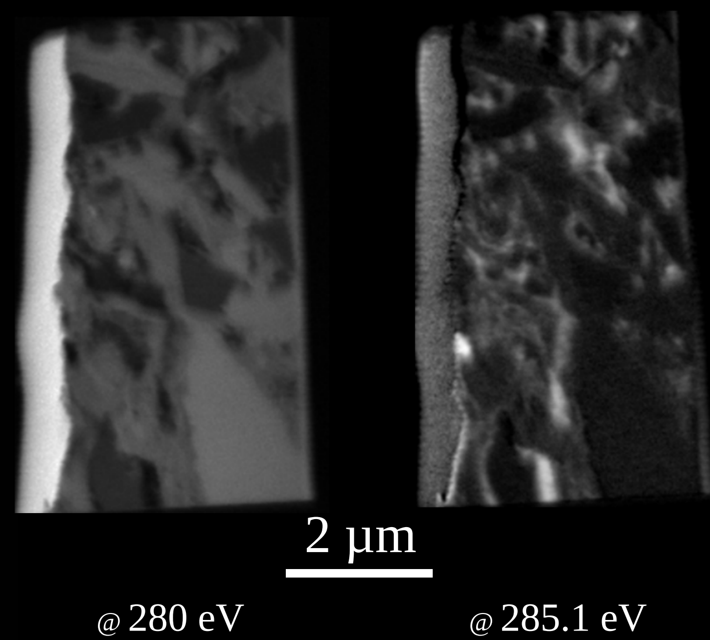
Spectromicroscopy = Both spectroscopy and microscopy at high spatial and spectral resolutions

STXM = Scanning Transmission X-ray Microscopy

Synchroton radiation - Spatial Resolution: ~25 nm - Spectral Resolution: 0.1eV



XANES spectrum : bonding environment of the compound

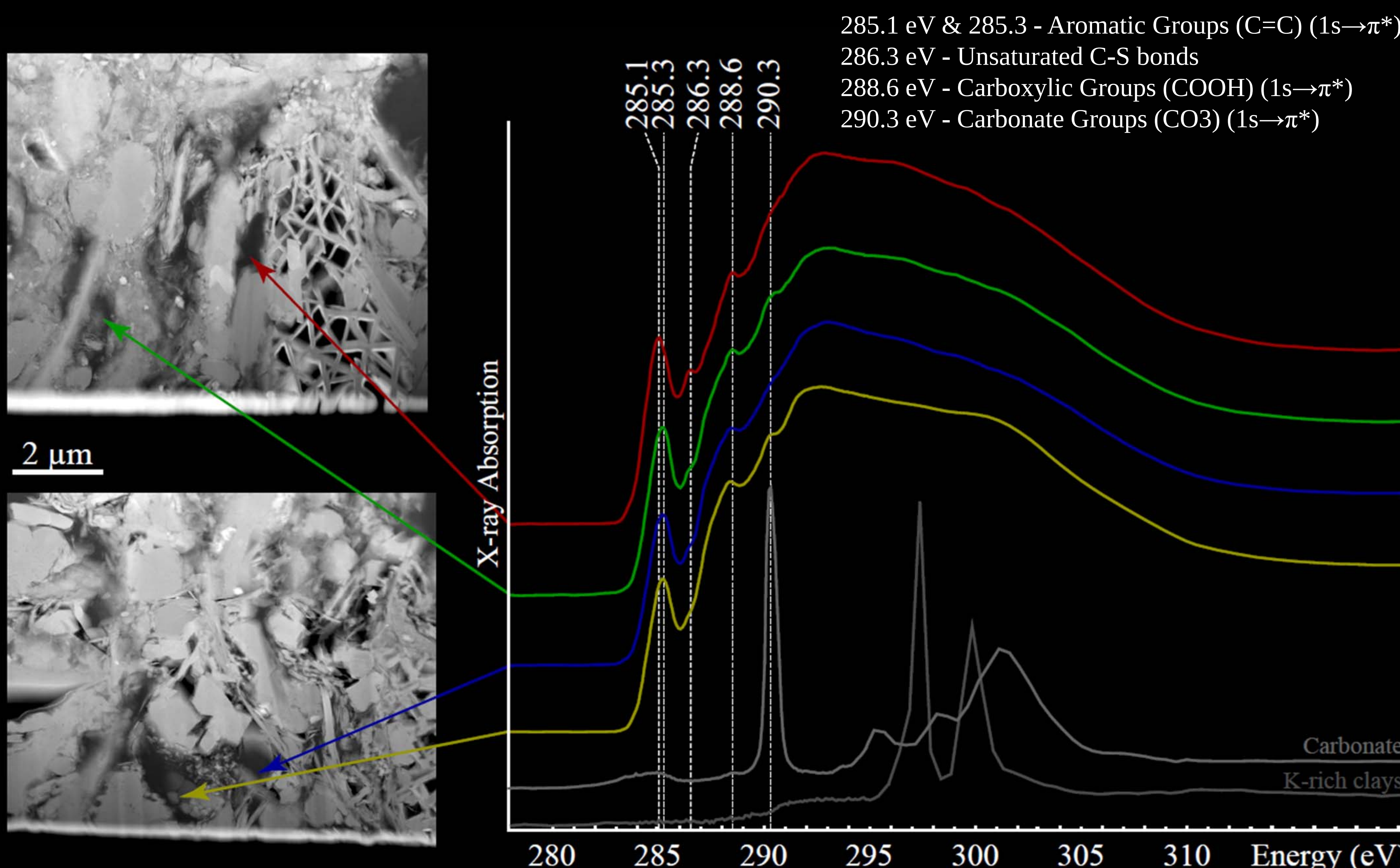


STXM image contrast = f (speciation)

Spectromicroscopy = Both spectroscopy and microscopy at high spatial and spectral resolutions

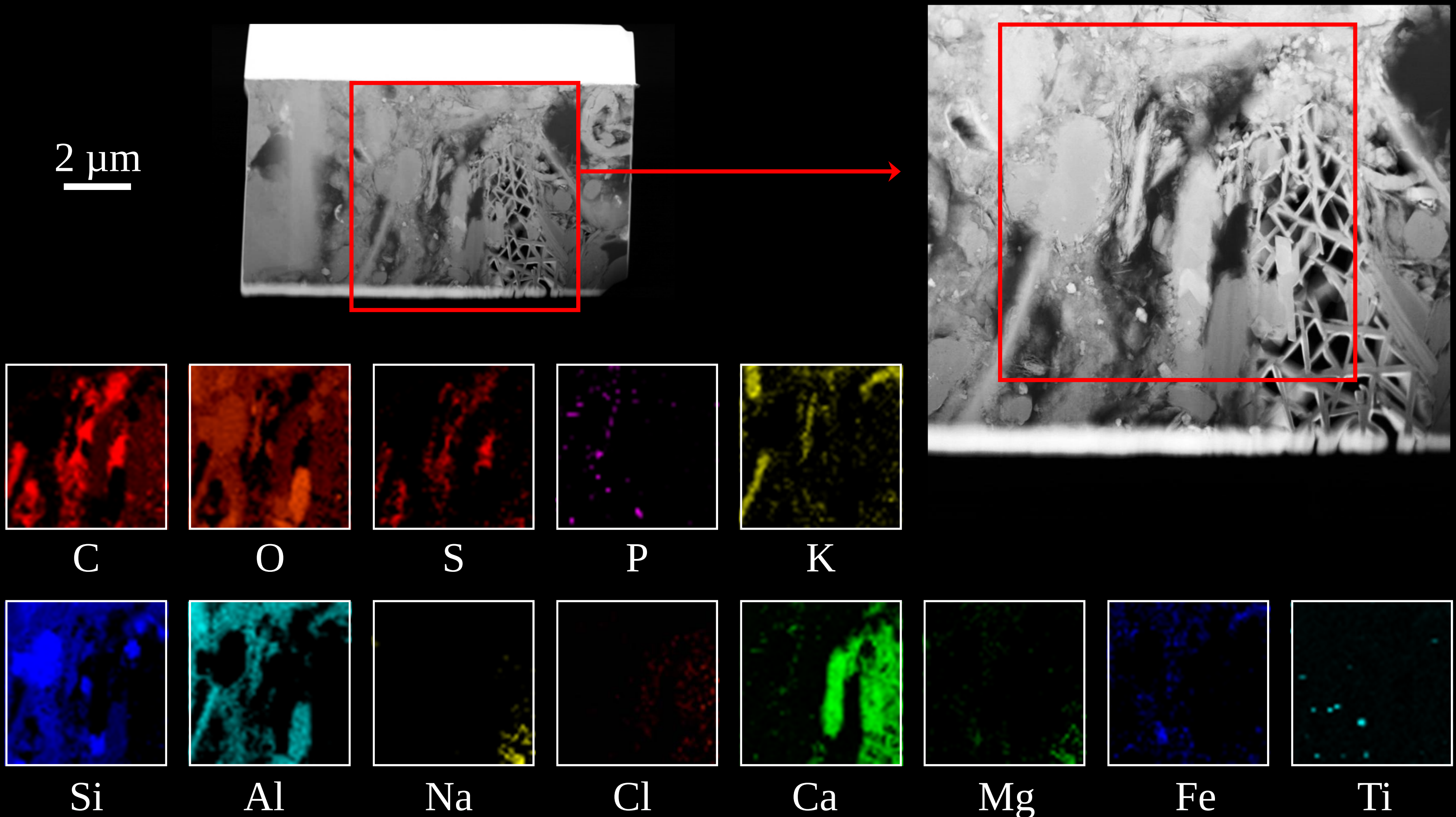
→ Organic Geochemistry at the nanoscale

XANES Spectroscopy : FIB sections - Wickensen Well - 0.5 Ro



Bernard et al., Marine and Petroleum Geology, 2011

EDXS Mapping : FIB section - Wickensen Well - 0.5 Ro

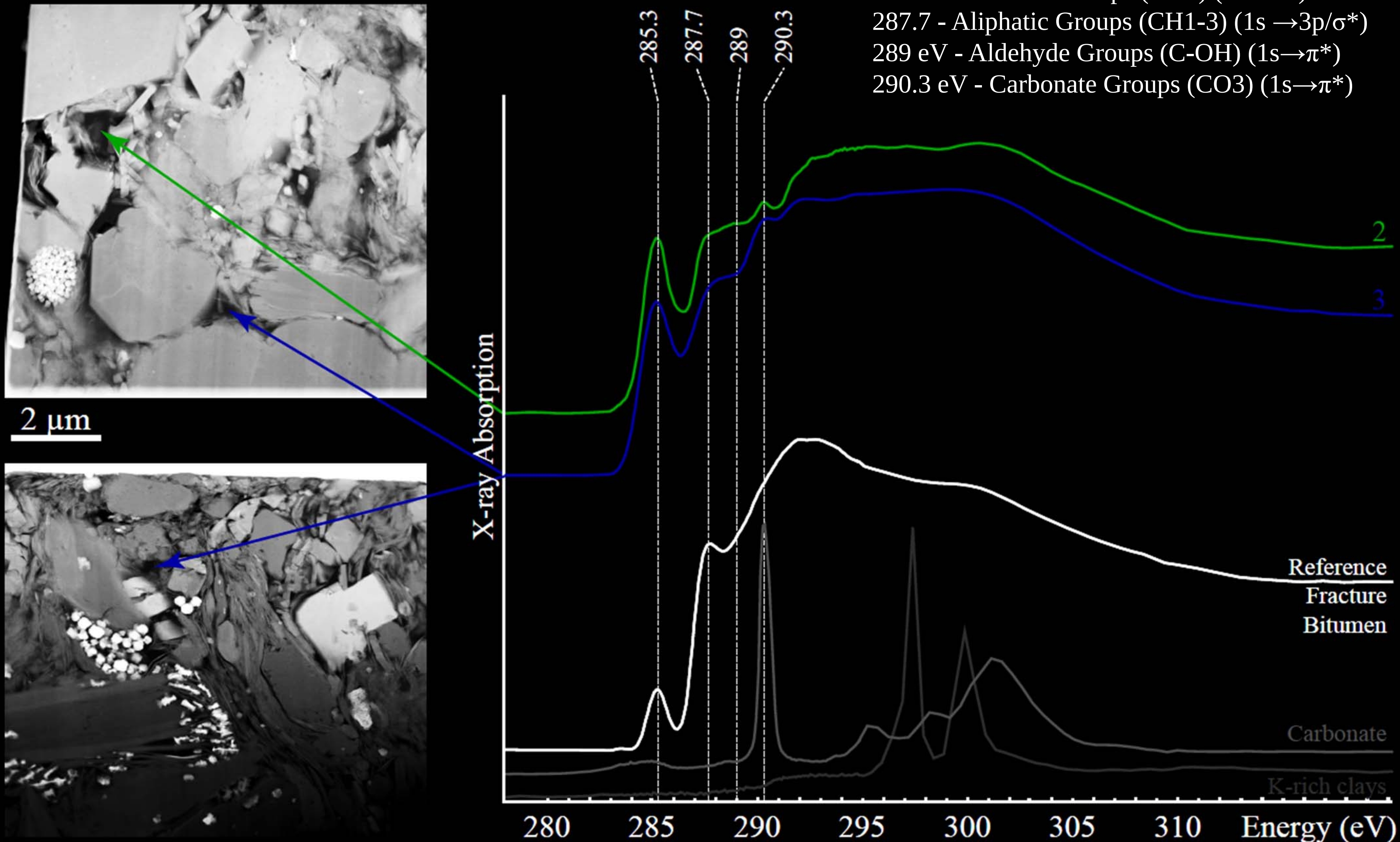


Nanoscale mineralogical heterogeneities - Complex organic/inorganic relationships

Bernard et al., Marine and Petroleum Geology, 2011

XANES Spectroscopy : FIB sections - Harderode Well - 0.85 Ro

285.3 - Aromatic Groups (C=C) (1s→π*)
287.7 - Aliphatic Groups (CH1-3) (1s →3p/σ*)
289 eV - Aldehyde Groups (C-OH) (1s→π*)
290.3 eV - Carbonate Groups (CO3) (1s→π*)



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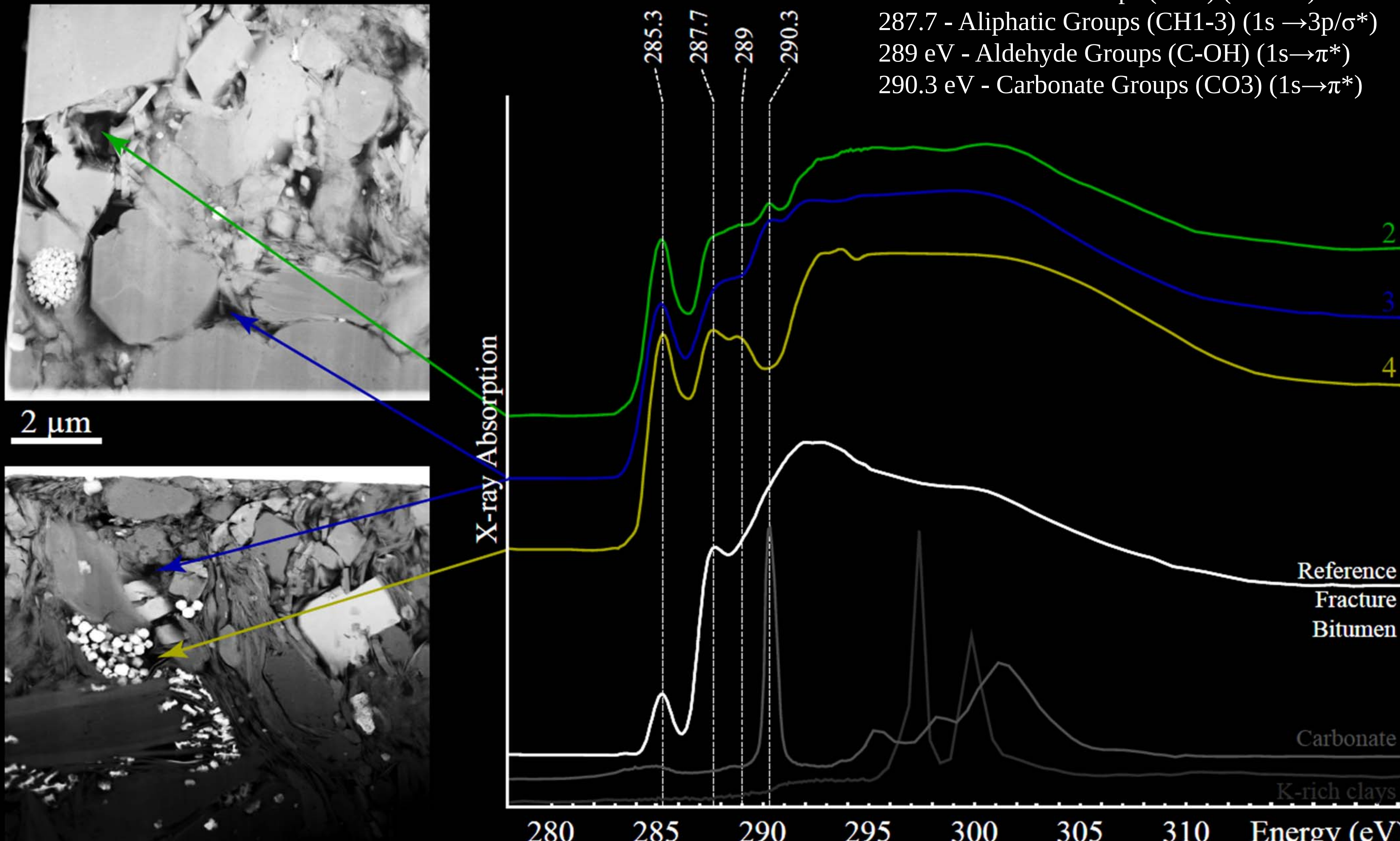
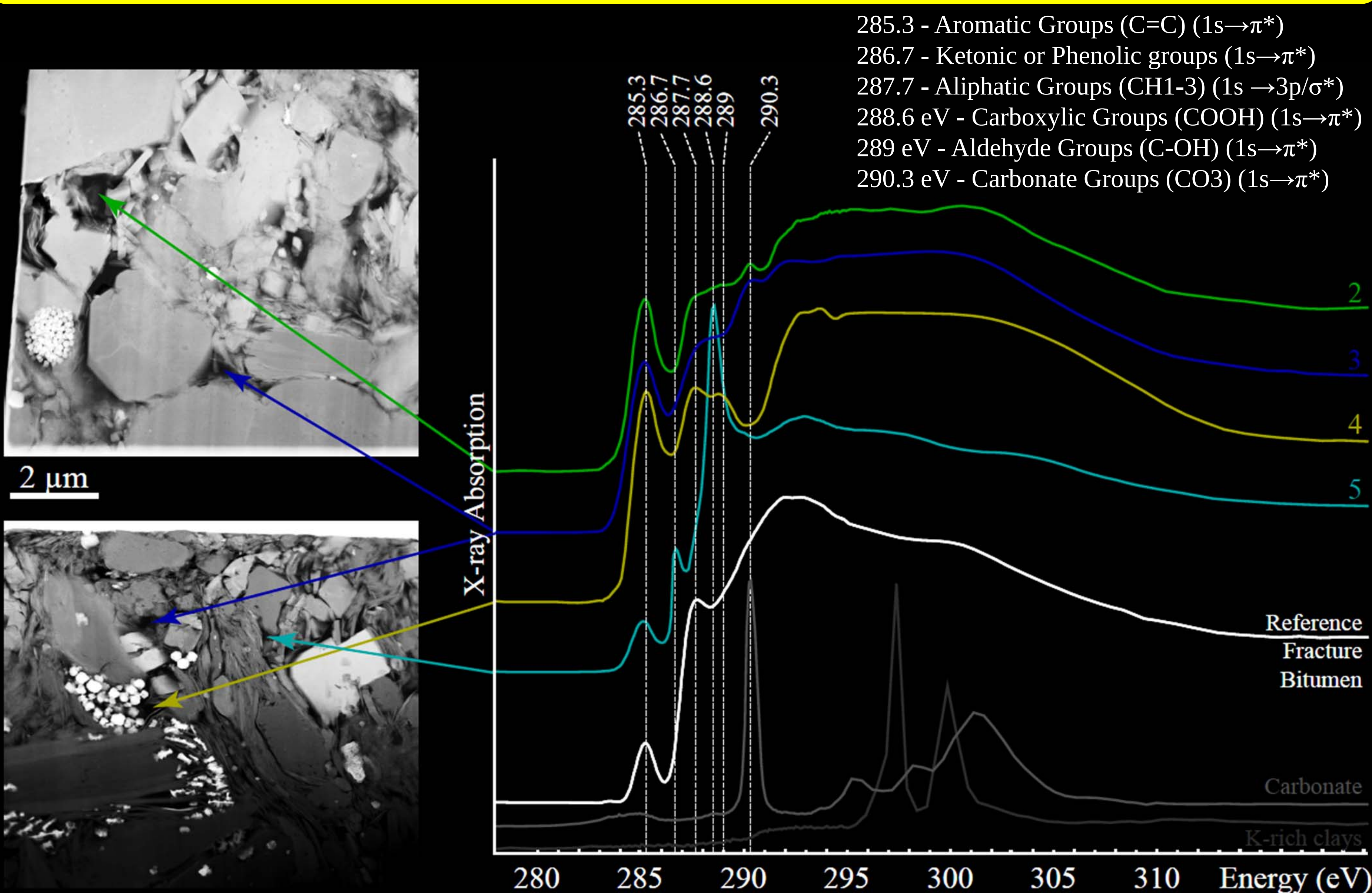


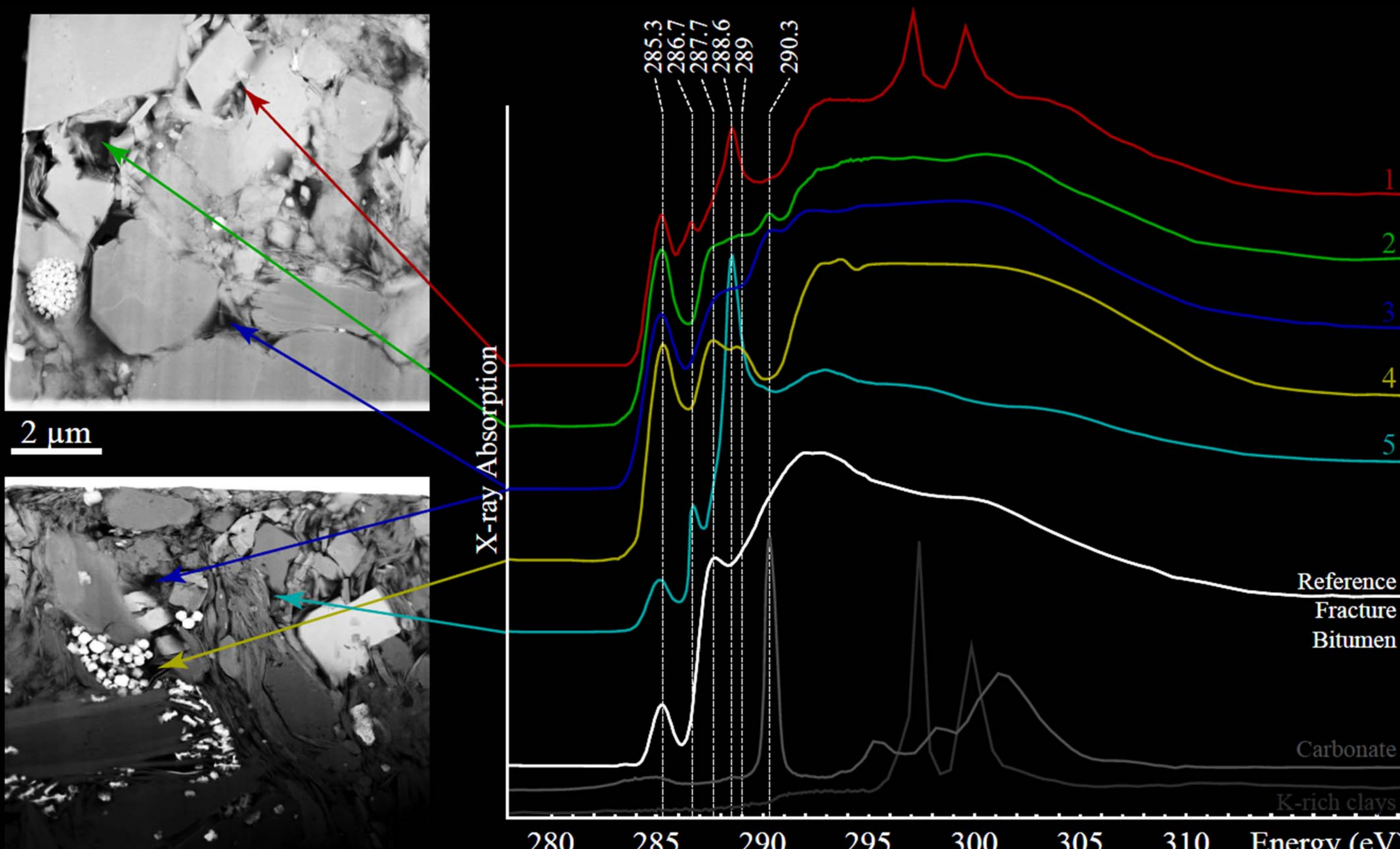
Bernard et al., Marine and Petroleum Geology, 2011

XANES Spectroscopy : FIB sections - Harderode Well - 0.85 Ro



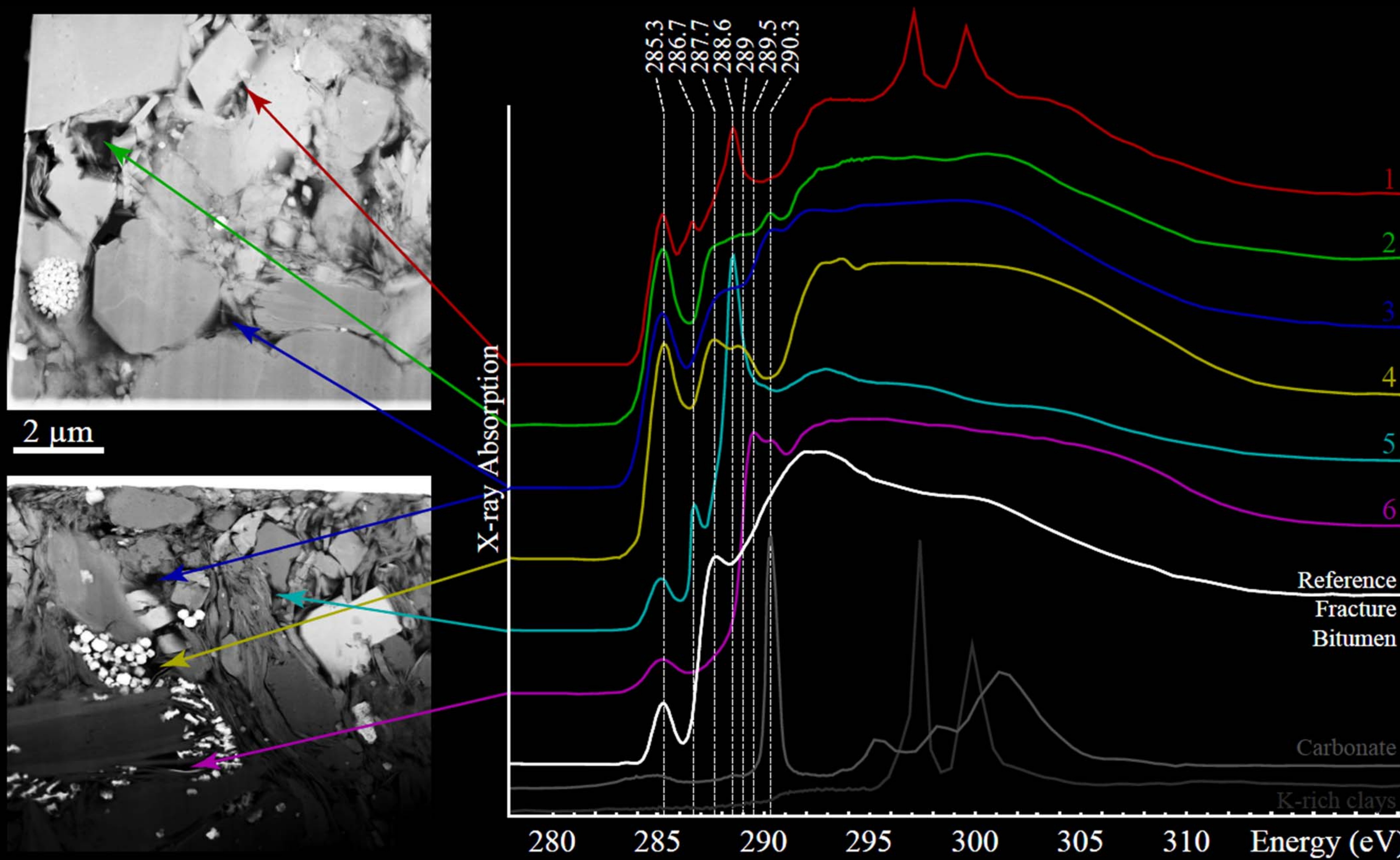
Bernard et al., Marine and Petroleum Geology, 2011

XANES Spectroscopy : FIB sections - Harderode Well - 0.85 Ro



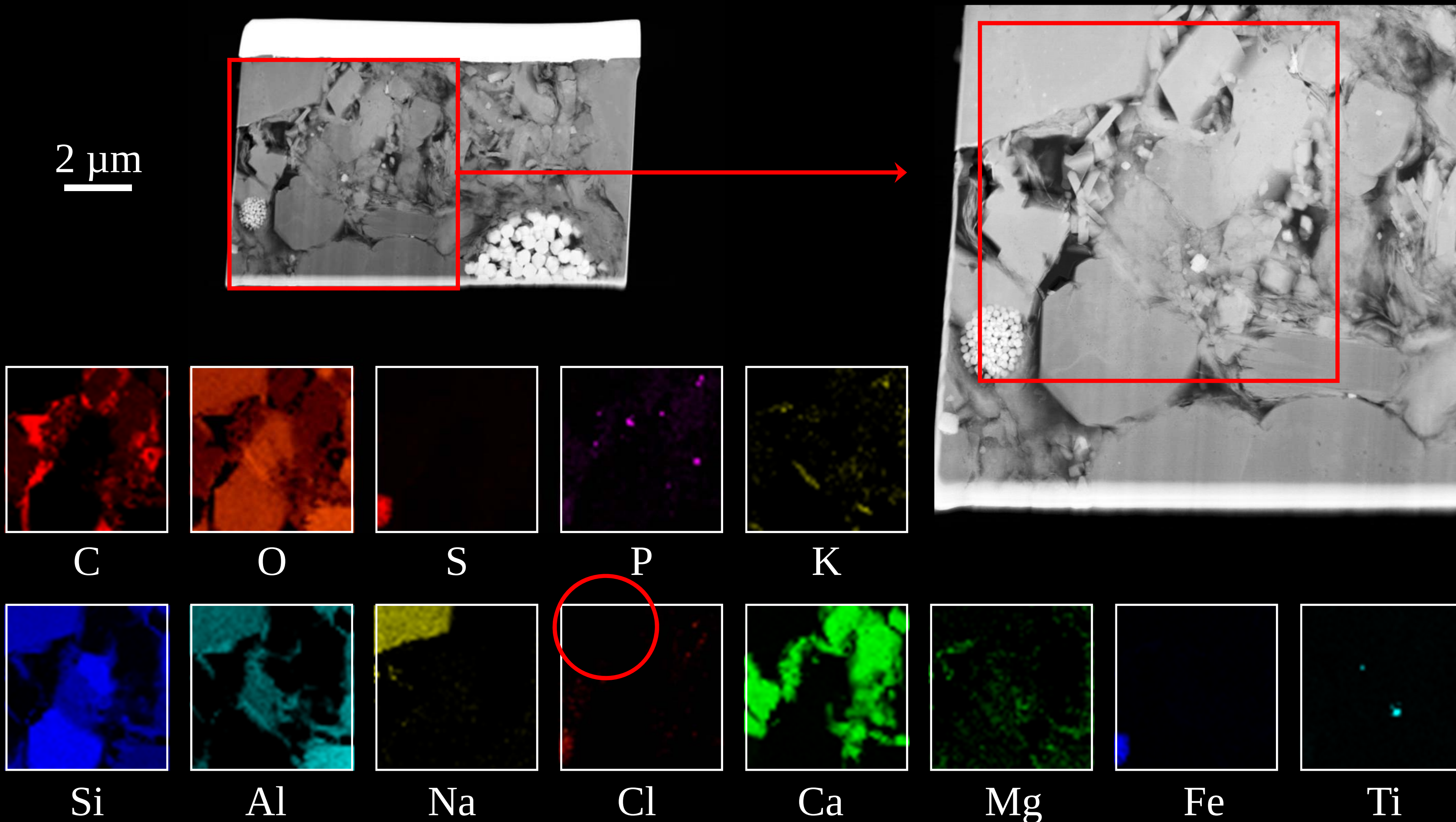
Bernard et al., Marine and Petroleum Geology, 2011

XANES Spectroscopy : FIB sections - Harderode Well - 0.85 Ro



Bernard et al., Marine and Petroleum Geology, 2011

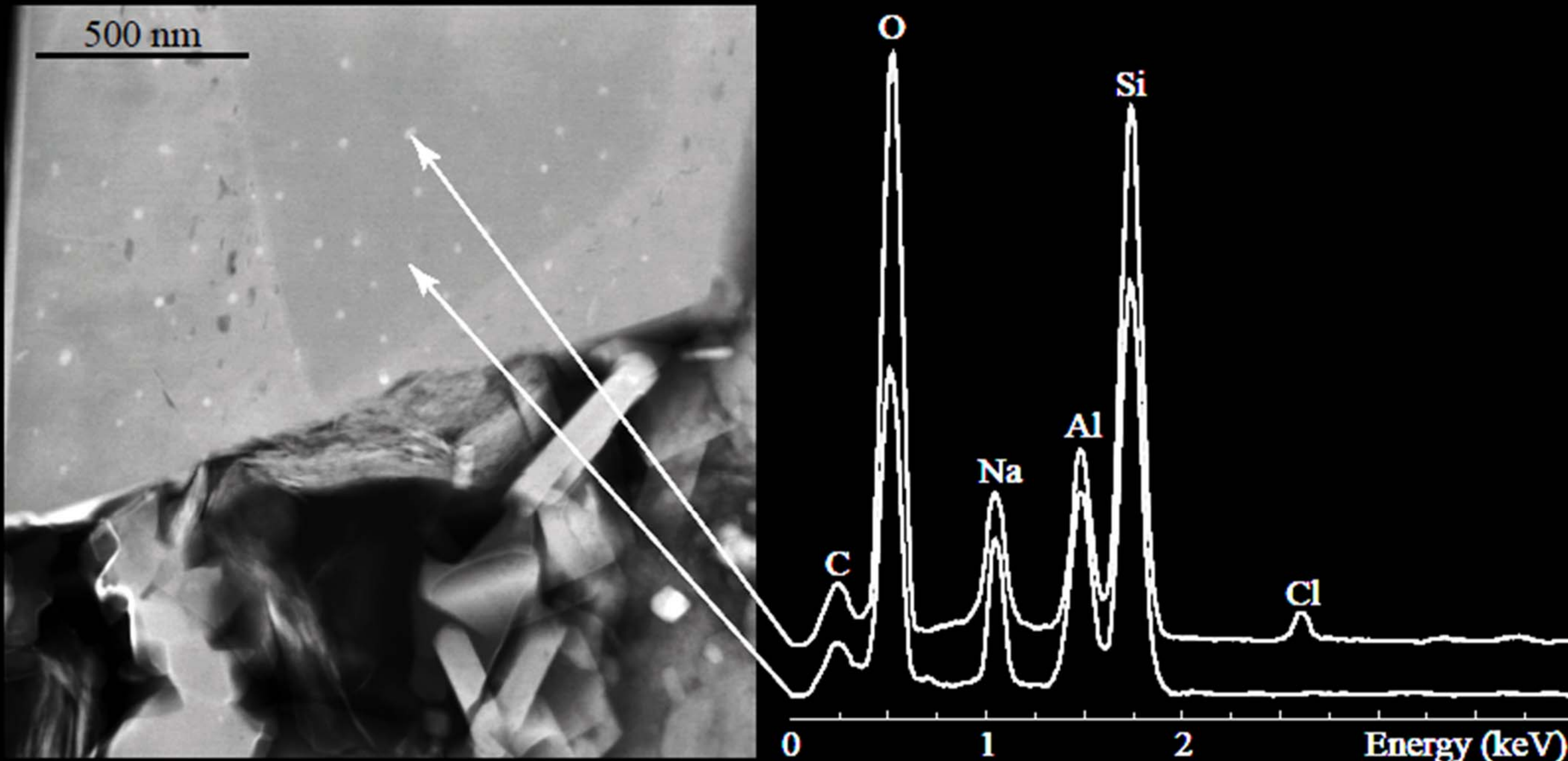
EDXS Mapping : FIB section - Harderode Well - 0.85 Ro



Nanoscale mineralogical heterogeneities - Complex organic/inorganic relationships

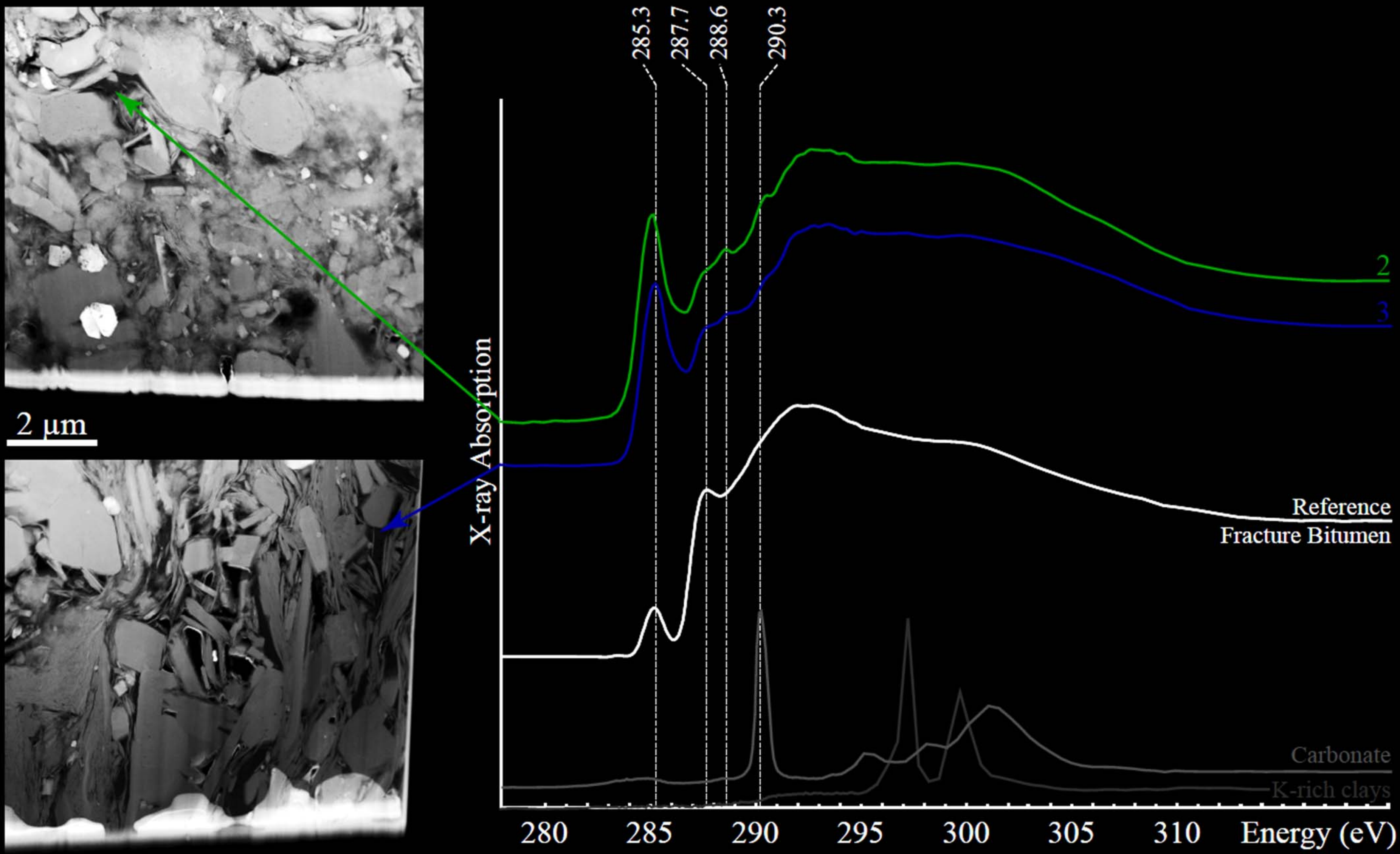
Bernard et al., Marine and Petroleum Geology, 2011

STEM Imaging and EDXS : Harderode Well - 0.85 Ro



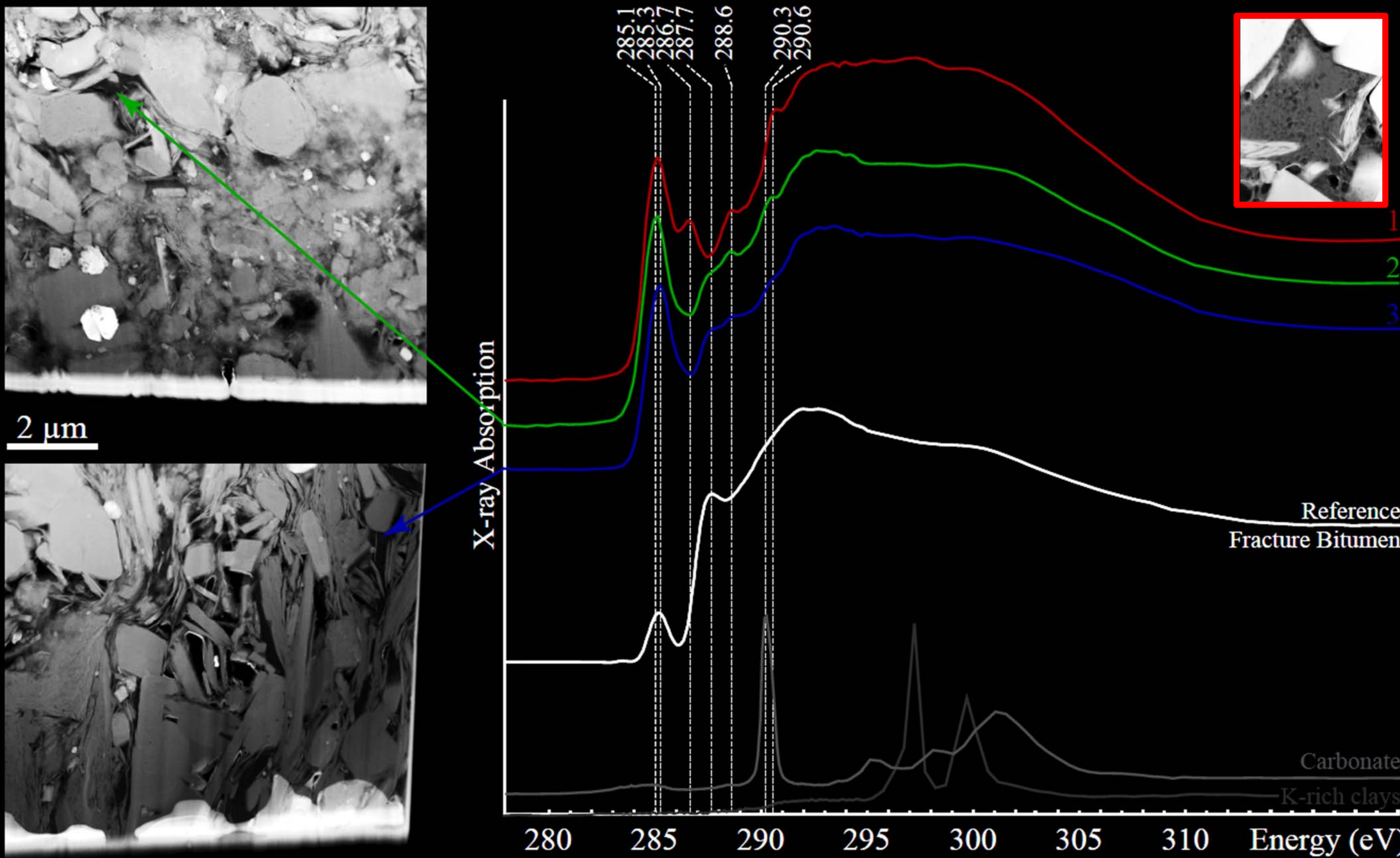
Authigenic Albite containing nano-inclusions of NaCl crystals

XANES Spectroscopy : FIB sections - Haddessen Well - 1.45 Ro



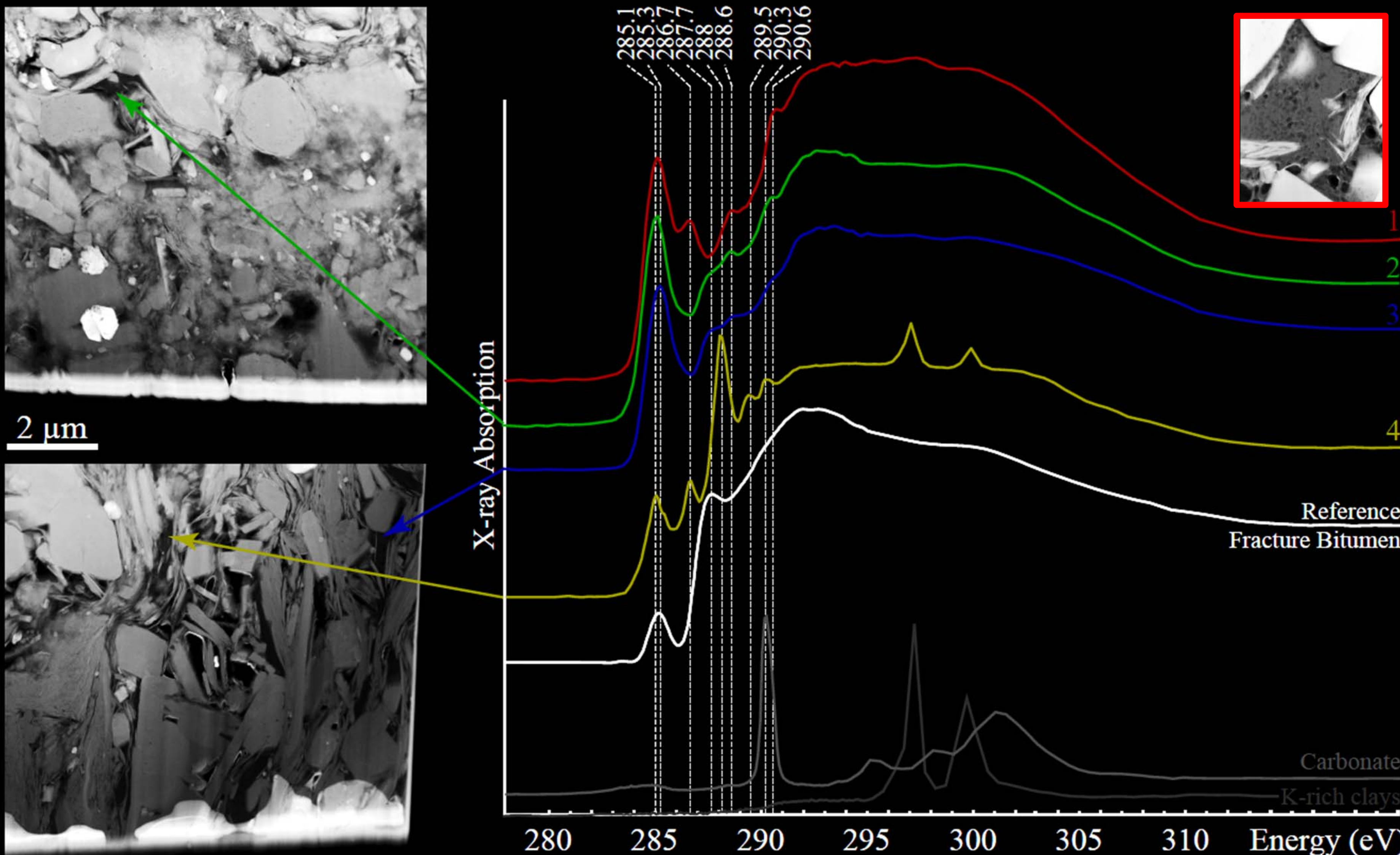
Bernard et al., Marine and Petroleum Geology, 2011

XANES Spectroscopy : FIB sections - Haddessen Well - 1.45 Ro



Bernard et al., Marine and Petroleum Geology, 2011

XANES Spectroscopy : FIB sections - Haddessen Well - 1.45 Ro



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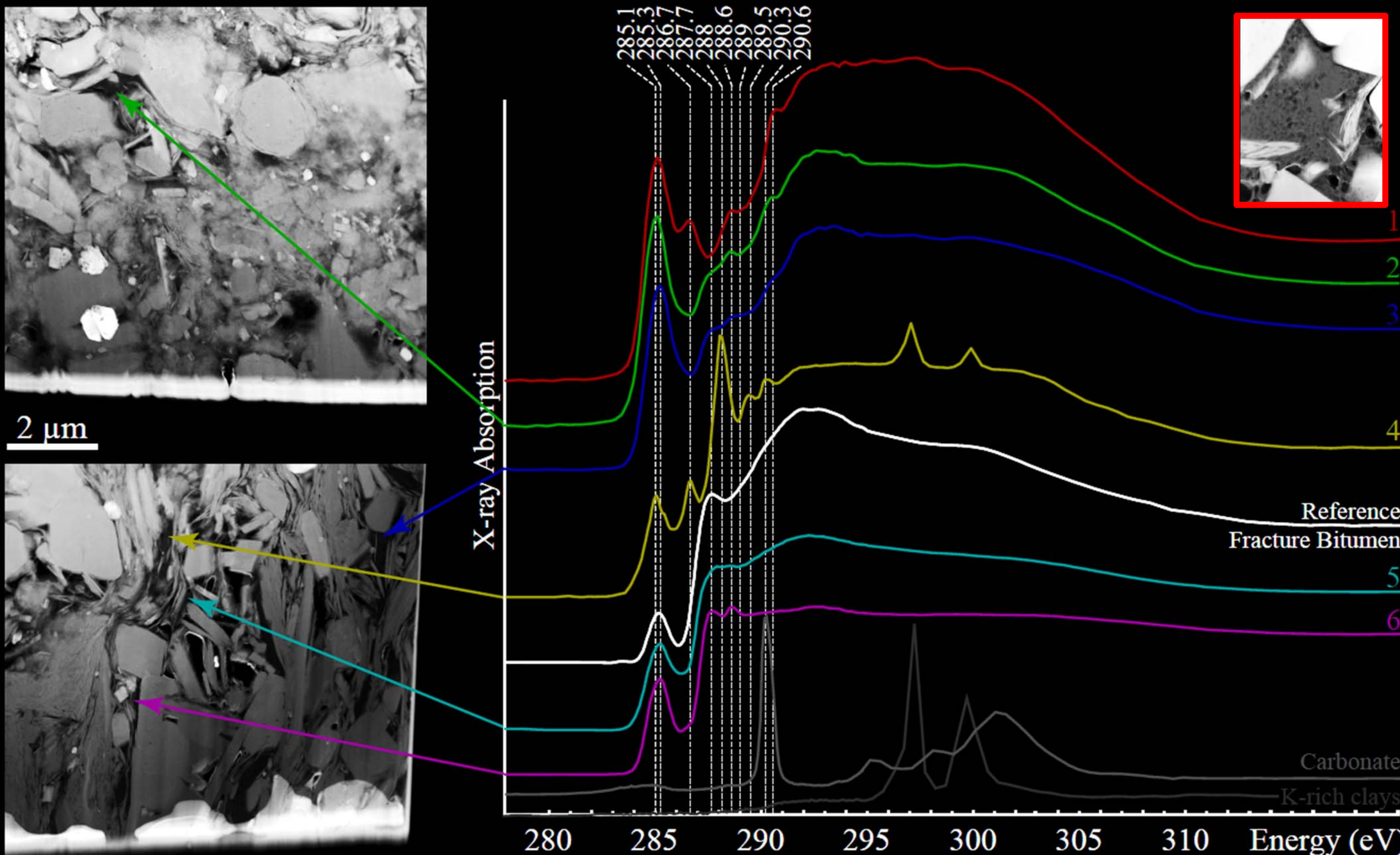
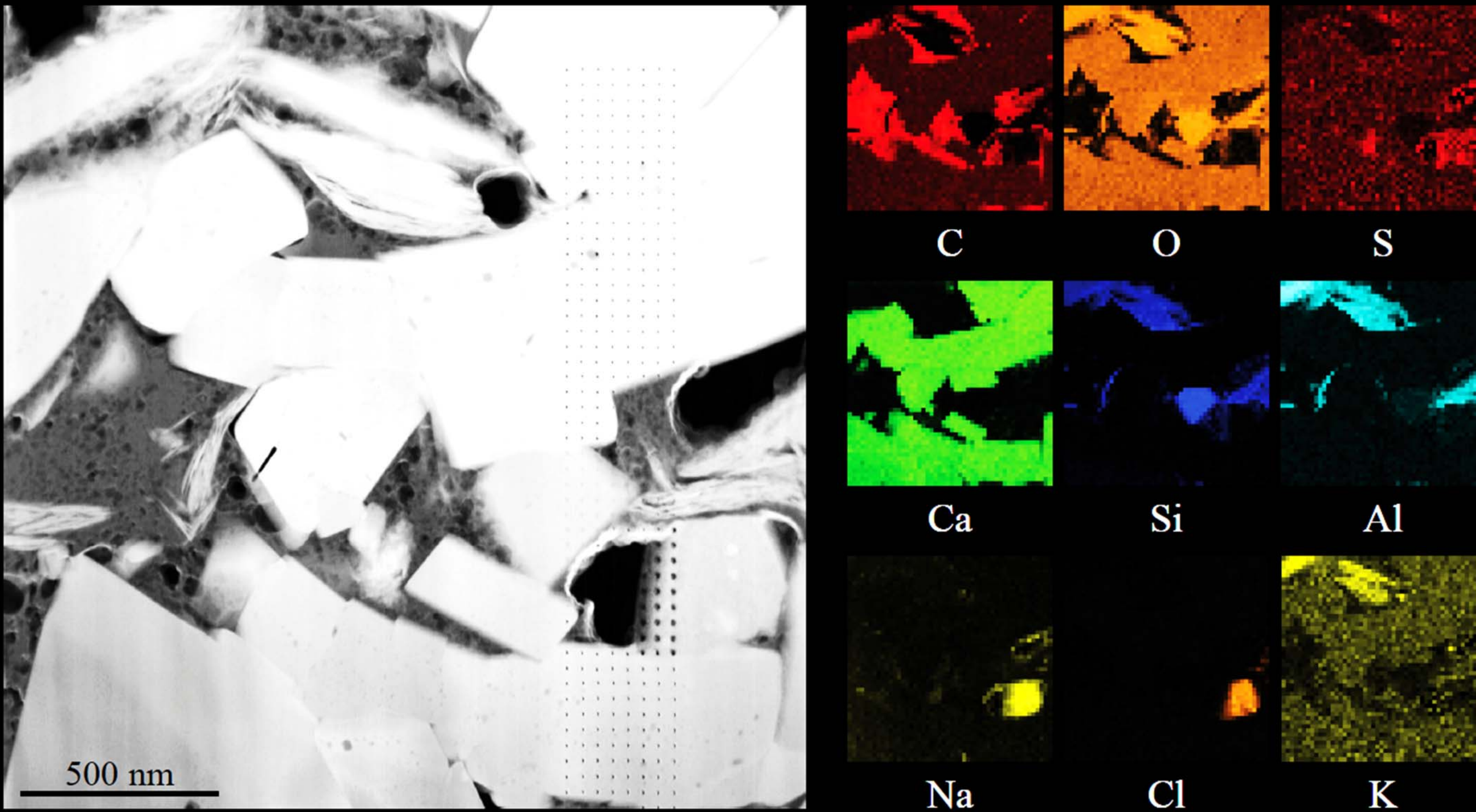
XANES Spectroscopy : FIB sections - Haddessen Well - 1.45 Ro



Bernard et al., Marine and Petroleum Geology, 2011

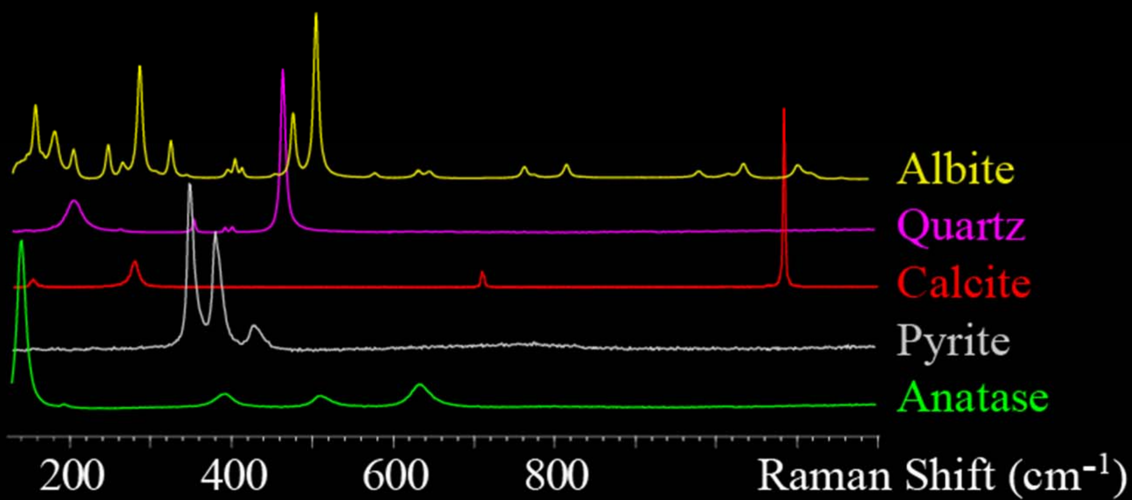
EDXS Mapping : FIB section - Haddessen Well - 1.45 Ro

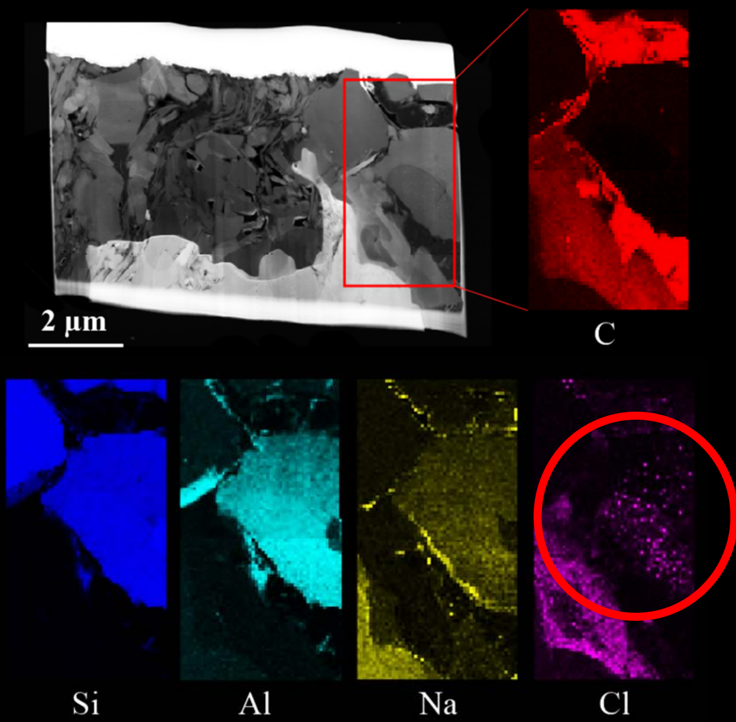


Intra-pyrobitumen nanoporosity: Evidence of gas formation

Thermal maturation scenario of Posidonia Shale

Authigenic Albite containing NaCl-inclusions
= tracer of brine/carbonate interactions *(Spötl et al., 1999)*





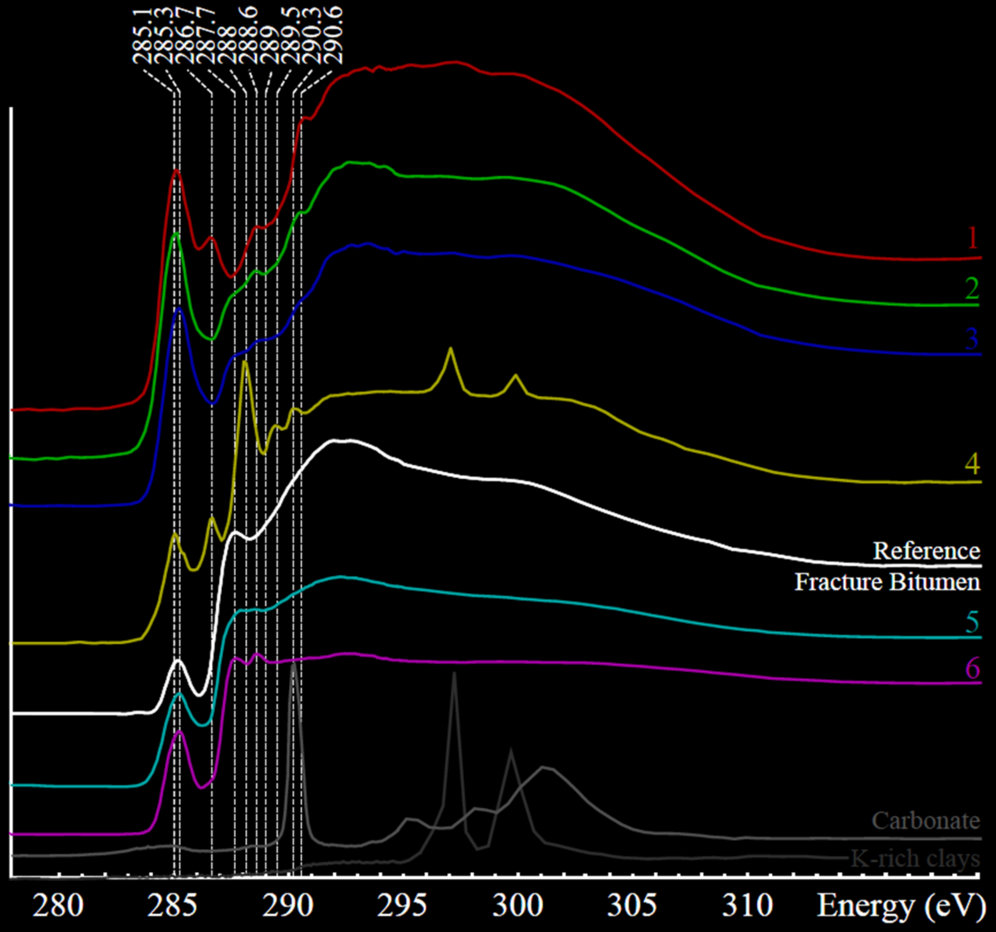
Crystallisation of authigenic albite from evaporite-derived brines-carbonates interactions

Implications for the thermal maturation scenario of Posidonia Shales:
Intrusive body *(Rullkötter et al., 1988)* *vs* Deep burial + Hydrothermalism *(Petmecky et al., 1999)*

Bernard et al., Marine and Petroleum Geology, 2011

Identification of different generations of bitumen and pyrobitumen

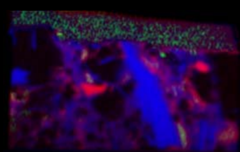
(Mastalerz and Glikson, 2000; Hill et al., 2003)



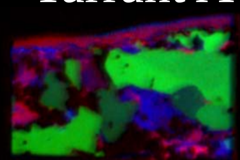
→ New insights on gaseous hydrocarbon generation processes

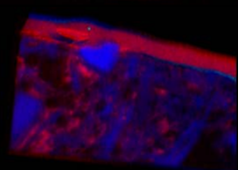
Ongoing Research = to be continued...

Fuller #1
Frank Wolf #1

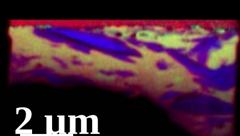


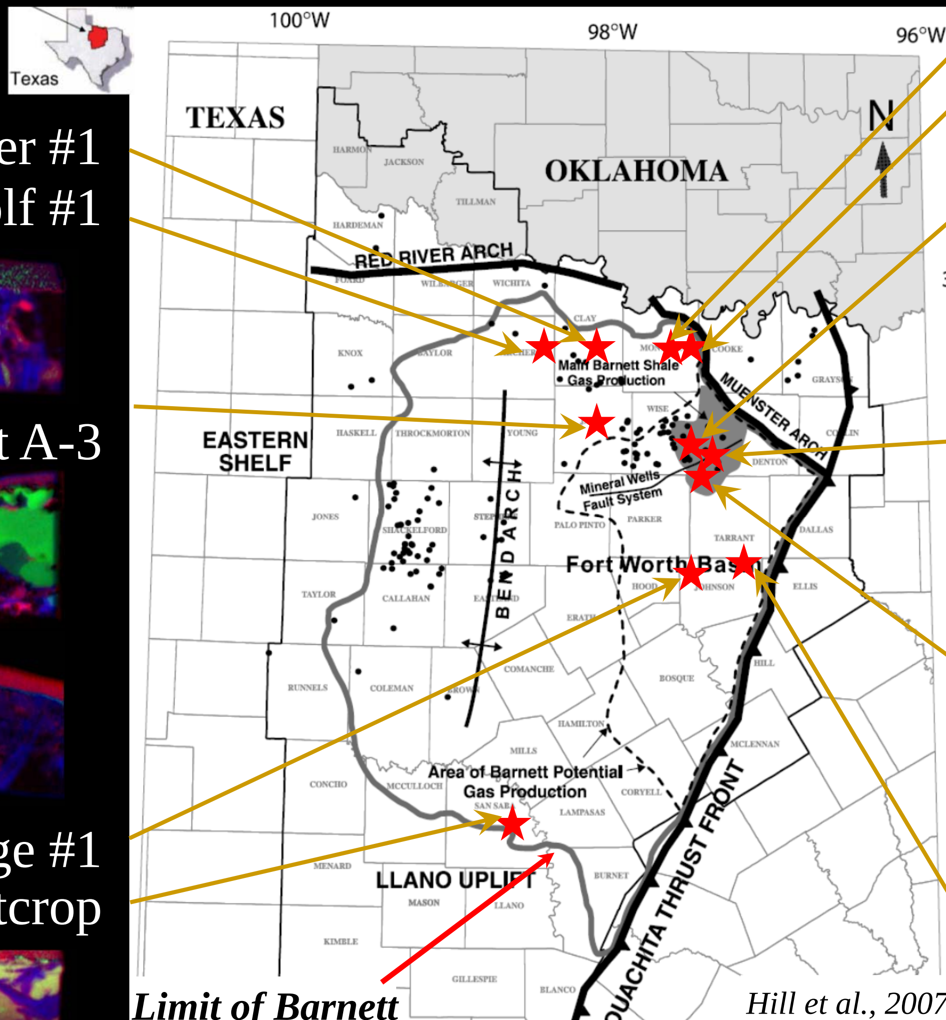
Tarrant A-3





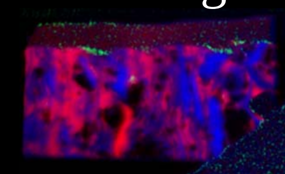
Savage #1
Outcrop



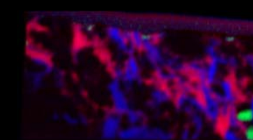


Braun Clint 2H
Ron Cheek 1H

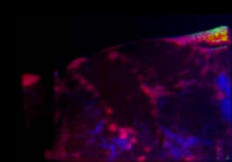
WC Young #2



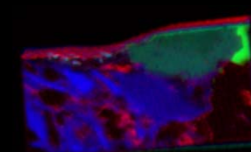
TP Sims #2



Oliver #1



Raam 3H



Ongoing Research = to be continued...

Advanced Light Source synchrotron (Berkeley, CA) from outside

Future alloted STXM beamtime:

- *June 2011*: ALS, Berkeley, USA
- *June 2011*: CLS, Saskatoon, Canada
- *July 2011*: Bessy II, Berlin, Germany

Gas Shales in Europe

GASH
Gas Shales in Europe

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Physical, chemical and biological processes contributing to shale gas formation are examined by experiments, monitoring, surveying and modelling.