Ion-beam analysis for non-destructive characterization of composition and structure of shale

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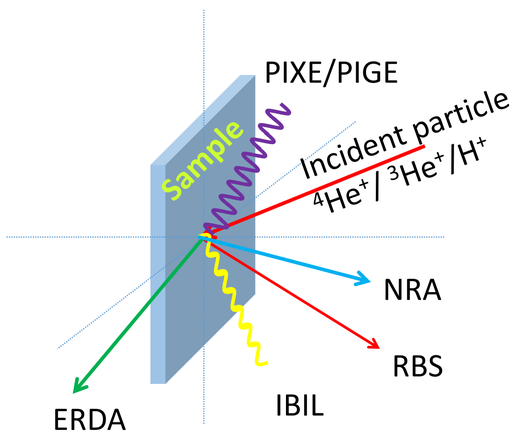
Objectives and Success Criterion

The U.S. has a large amount of hydrocarbon-rich shale deposits. However, in the current low-price environment, it is imperative to identify drilling locations which yield a high number of producing wells.

The current DoE SBIR project aims to demonstrate 'novel' analytical techniques to assist in these efforts. In particular, a suite of analytical methods (based upon ion-beam techniques) has been demonstrated. These methods encompass an effective and comprehensive set of tools for characterizing shale- one that may provide substantial benefits for identifying high-value shale deposits .

Introduction of Ion Beam Analysis (IBA)



A suite of Simultaneous Analysis Techniques

Rutherford Backscattering Spectrometry (RBS)
Sensitivity increases with Z^2
Elastic Recoil Detection (ERDA)
H and D profiling
Particle Induced X-ray Emission (PIXE)
Elemental analysis
Particle Induced γ-ray Emission (PIGE)
Elemental analysis
Nuclear Reaction Analysis (NRA)
Low-Z (C, N, O) profiling
Ion Beam Induced Luminescence (IBIL)
Molecular analysis

IBA doesn't require a standard for quantitative analysis and is mostly matrix independent.

Analytical Requirements	What IBA Can Offer?
Total Organic Carbon (TOC) for Maturity	Direct C measurement by NRA
Relative H, C, N, O Content for Kerogen Types	Direct measurement of H by ERDA, O and N by NRA
Brittleness: Elemental and Mineralogical Analysis	RBS and PIXE for elemental analysis Ionoluminescence for mineralogical analysis
Microstructural Analysis	Micro-beam scan, μ-PIXE, μ-IL

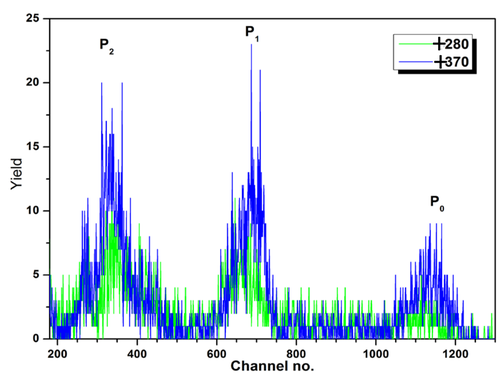
IBA of Shale

As received – drill cuttings

Sample prepared from powder

Samples can be fabricated from core cuttings of all sizes and shapes and require only minimum preparation time/effort. Shale samples from Utica and Woodford Plays were used for in the project.

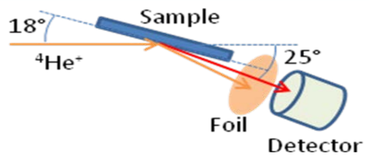
Carbon analysis-NRA using $^{12}C(^3He,p)^{14}N$



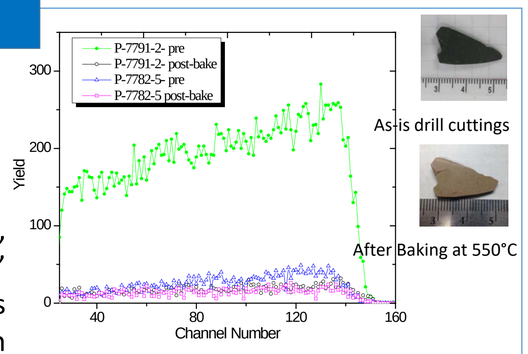
- ^{14}N in a ground state and first two excited stated results in 3 proton groups.
- Yield (ROI) ∝ C-content.
- Vitreous Carbon or Kapton used as reference.
- TOC is based on measurement of carbon levels before and after high-T baking (TOC = TC – TIC)

Proton spectra from NRA indicating the relative carbon content in the different samples

Hydrogen analysis by ERDA

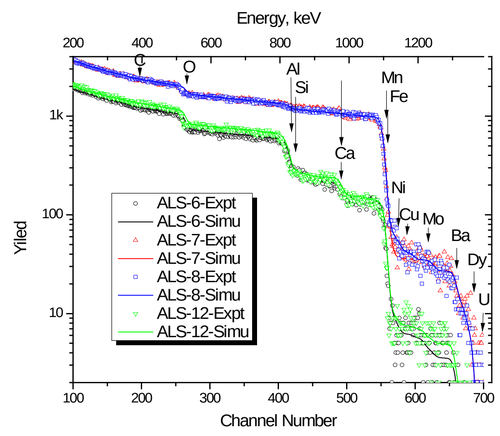


ERDA, *an IBA techniques for direct measurement of H*, involves the use of energetic ions to 'knock-out' hydrogen within the near-surface of a sample. This hydrogen is energy analyzed to yield the hydrogen composition within the sample. A foil is used to block the forward scattered ions, i.e. $^4He^+$.

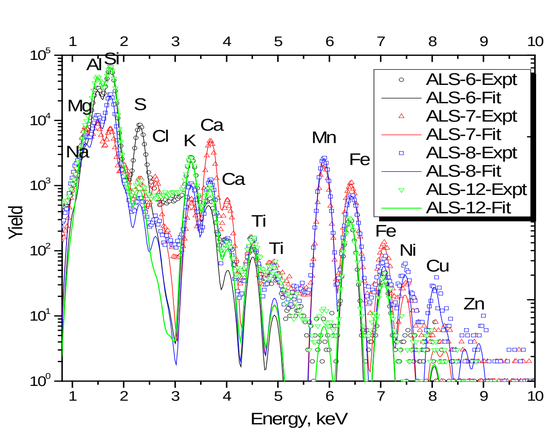


ERDA analysis of H before and after sample baking at 550°C

Non-destructive Elemental Analysis by RBS and PIXE



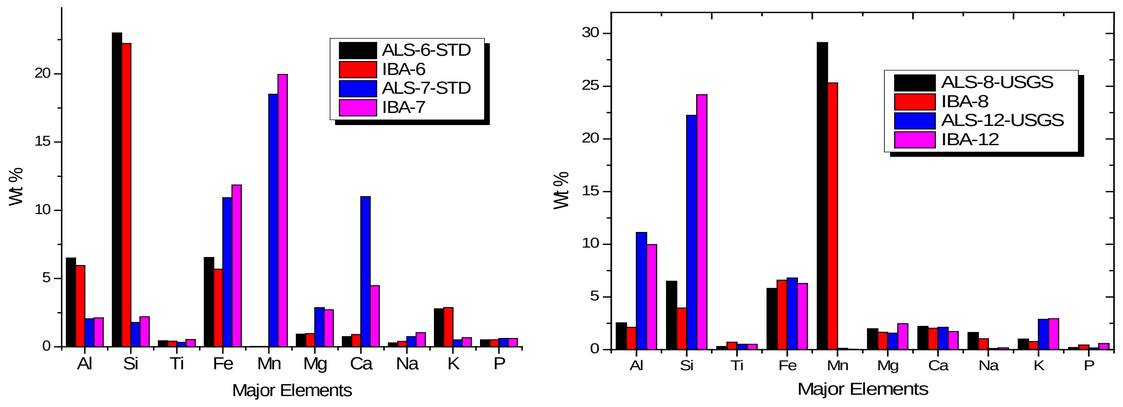
Experimental and simulated RBS spectra with arrows inserted to locate different elements within the shale.



Experimental and fitted PIXE spectra annotated with the different elements within the analyzed sample.

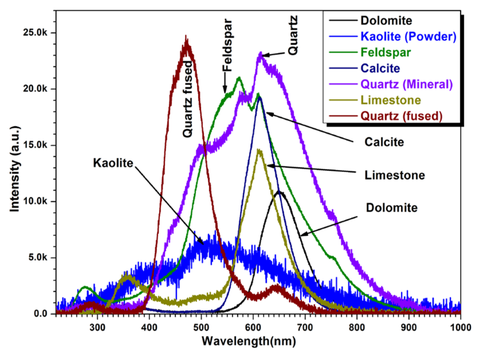
Verification of IBA with USGS Standards

Measurement of elemental concentrations by IBA (RBS/PIXE, NRA) techniques agrees typically to within 5% with USGS Standard values.



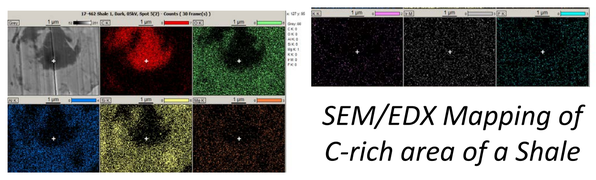
Comparison of USGIS (ALS std) values with IBA of samples ALS-6, ALS-7 ALS-8 and ALS-12

IBIL Spectroscopy and imaging



Ion-beam Induced Luminescence (IBIL) spectra of typical minerals in Shale:

IBIL is used to identify detects, mineralogical types and variations, and nano-porosity.

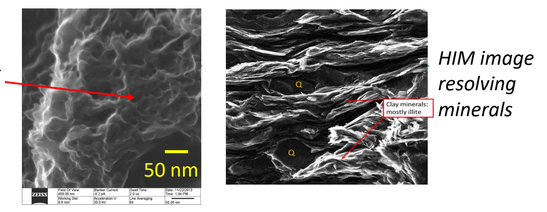


SEM/EDX Mapping of C-rich area of a Shale

Efforts are in-progress to simultaneously use IBIL for mineralogical imaging and PIXE for elemental mapping.

Synergy Opportunities

Collaboration is ongoing to develop He-ion microscopy (HIM)–based pore imaging and elemental mapping.



HIM images of Shale. HIM does not require sample preparations e.g., FIB cut or conductive coating

Project Summary

Lessons Learned

- IBA is non-destructive and requires only small samples, e.g. drill cuttings. As such, its use reduces sampling cost and turn-around time.
- Direct measurement of C, H (in hydrocarbons) and O, N (in oxygen and nitrogen containing compounds) provides key information on major constituents of shale .
- IBA methods are reliable and repeatable due, in part, to their simplicity.

Plans

- Simultaneous mineralogical and elemental mapping through μ-beam scanning using PIXE and IBIL.
- He-ion microscopy enhancement though simultaneous elemental mapping.
- Direct measurement of N in addition to C, H and O to establish hydrocarbon and productivity modeling.

Collaborators

Rutgers University | New Brunswick; Cerium labs – Bringing the Elements Together; Oklahoma State University; ALS Oil & Gas