AAPG Annual Convention & Exhibition, May 19-22, 2019 – San Antonio, TX

PANEL 1

Application of multiple hyperspectral imaging tools to the examination of submillimeter variability in geochemical reference materials from major U.S. shale plays

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ABSTRACT A variety of imaging and spectroscopic techniques are currently available for assessing geochemical and mineralogical properties of mudrocks at submillimeter scales. These non-destructive techniques fill an analytical niche at intermediate sizes between bulk and microscale analyses that have previously been examined using methods like thin section analysis but can now be examined more efficiently and definitively using spectral data. In this study, a combination of short-wave (SWIR, 1.0 to 2.5 µm) and mid-wave (MWIR, 2.5 to 5 µm) infrared spectroscopy and micro-X-ray fluorescence (µ-XRF) was applied to shale pieces (several centimeters long and across) from outcrops and roadcuts of several important U.S. shale plays. Samples included mudrocks from the Eocene Green River (Colorado), Late Cretaceous Niobrara (Colorado), Late Cretaceous Boquillas (Texas), Devonian-Mississippian Woodford (Oklahoma), and Middle Devonian Marcellus (New York) formations. These samples contained variably laminated structures, some of which have been examined by submillimeter Fourier transform infrared (FTIR) spectroscopy (2.5 to 25 µm) in previous work, and showed variable mineralogical composition and organic content. Bulk analyses of mineralogy and total organic carbon (TOC) content show that the shales vary from carbonate-rich (Green River, Niobrara, and Boquillas) to clay mineral-rich (Marcellus) to highly siliceous (Woodford). TOC contents for the analyzed shales range from 1 to 20 wt. %. Elemental and mineral maps were generated and compared to results from previous geochemical and spectral analyses. Lamina in the calcareous samples show alternating carbonate- and organic-rich compositions, while the more siliciclastic samples show differences in clay minerals, quartz, and pyrite content. In general, the elemental associations identified using the XRF maps agree with the mineralogical interpretations. Multivariate curve resolution was applied to SWIR and MWIR spectral datasets for each sample to better differentiate mineralogical features into millimeter-scale lithologies. The results show the utility of hyperspectral imaging for examining significant submillimeter variability in source rocks from both siliciclastic and carbonate-rich petroleum systems.

U.S. Geological Survey Reference Material Project – Shale Standards Task

Statement of Work: Develop shale (mudrock) Geochemical Reference Materials relevant to unconventional petroleum systems.

Rationale: Shale GRMs can be used as quality control and assurance standards for mineralogy and organic and inorganic geochemistry. They may also be useful to experimenters as control or test materials for method development and other research.

Goals: Obtain ~1000 lbs. or more of five shales from various basins around the United States with relevant mineralogies and a range of organic content, kerogen type, and thermal maturity.

Analyses: Standard organic and inorganic methods

- Major, minor and trace elements (ICP-MS/AES, WDXRF, etc.)
- Mineralogy (X-ray diffraction, XRD)
- Total organic carbon (TOC) analysis
- Programmed pyrolysis

Status: Five materials have been collected, three have been processed and bottled; two have been processed and will be bottled during summer FY2019.

Collection Locations: Between 700 and 1600 lbs. of rock were collected at the following locations:

(1) ShBOQ-1: Road cut off of US-90 west of Del Rio in Val Verde County, Texas, representative of the Late Cretaceous (Cenomanian-Turonian) Boquillas Shale of the Gulf Coast Basin;
(2) ShMCO-1: Outcrop off of US-50 in Delta County, Colorado, representative of the Late Cretaceous Mancos Shale of the Piceance Basin;
(3) ShWFD-1: Road cut off of I-35 near Ardmore and Springer in Carter County, Oklahoma, representative of the Devonian-Mississippian Woodford Shale in the Anadarko Basin;
(4) ShNIO-1: CEMEX Quarry near Lyons in Boulder County, Colorado, Late Cretaceous Niobrara Shale in the Denver–Julesburg Basin;
(5) ShMAR-1: Oatka Creek outcrop (exposed creek bed) in the village of Le Roy in Genesee County, New York, representative of the Middle Devonian Marcellus Shale in the Appalachian Basin
(6) ShPYR-1: Mahogany zone oil shale (Unocal Mine near Rifle, CO) from the Eocene Green River Formation, Piceance Basin. This GRM is not the same Mahogany sample discussed in the hyperspectral work.

Previous work

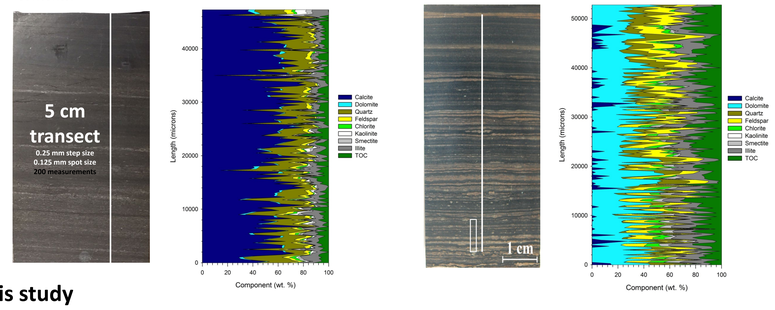
Attenuated Total Reflectance (ATR) infrared microscopy (Washburn et al., 2015. *Energy & Fuels*, v. 29, 4264-4271)

Samples: Boquillas Shale, Green River Formation Mahogany zone oil shale

ATR µ-IR : Bruker Lumos FTIR Microscope in ATR mode (photo on right), spectral window 600 – 4000 cm^{-1} with 4 cm^{-1} resolution and a 125 µm spot size.

Chemometrics Analysis: Infrared spectral features used to predict mineralogy and total organic carbon content based on a Partial Least Squares Regression model calibrated with 96 homogenized whole rock samples analyzed by X-ray diffraction and Leco TOC.

Below: Boquillas Formation shale collected from a roadcut near Del Rio, TX and Green River Formation Mahogany zone oil shale from the Anvil Points Mine (Piceance Basin). Results of an ATR µ-IR transect across the rock is shown to the right of the sample photo and demonstrates the variability in mineral and organic carbon contents. Boquillas: Calcite and quartz content show the highest variability. Green River: High variability is observed in dolomite, quartz and organic carbon contents.



Methods applied in this study

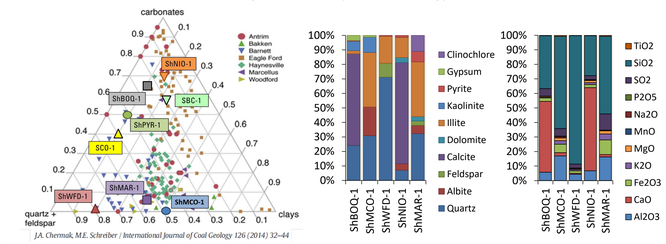
Micro XRF: M4 Tornado MicroXRF instrument (Bruker Nano GmbH, Berlin, Germany)

Hyperspectral imaging (HSI; SWIR, MWIR): Via-Spec™ Geo 5 Series multi-range hyperspectral scanner (Middleton Spectral Vision)

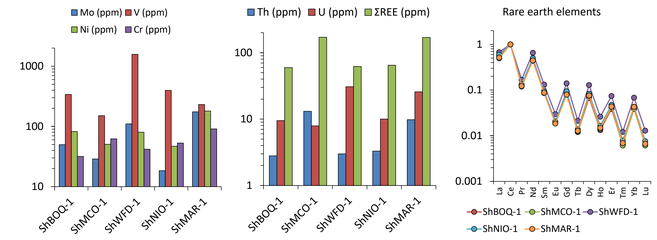
Multivariate curve resolution (MCR) analysis: Middleton Spectral Vision KemoQuant™ hyperspectral analysis software package.

Background information and bulk geochemical and mineralogical data for Geochemical Reference Materials

Inorganic Chemistry and Mineralogy

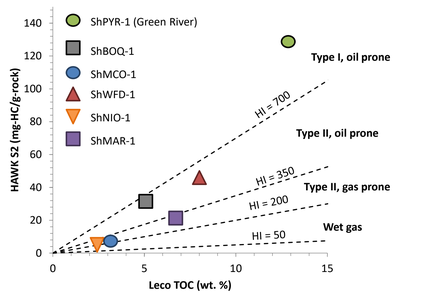


Major inorganic phases: Range of shale mineralogies in the U.S. (left), mineral speciation in GRMs (center), and WD-XRF major oxides (right); results on an organic-free basis.

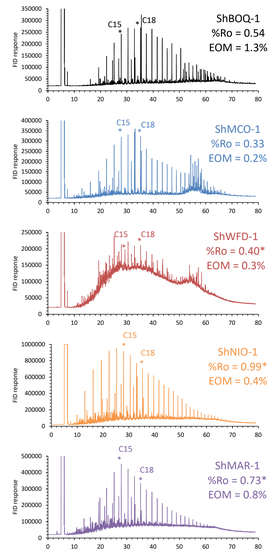


Trace elements: Concentrations (mg/kg, ppm) of redox-sensitive trace elements, lanthanides (rare earth elements, REEs) and actinides (U, Th), and REE distributions (normalized to Ce concentration).

Organic Geochemistry



Above: Programmed pyrolysis (S2) and TOC (Leco method) values for GRMs. Plot shows trendlines indicating kerogen types. Tmax (temperature of S2 max) values range from 420 (Mancos) to 455 °C (Niobrara).



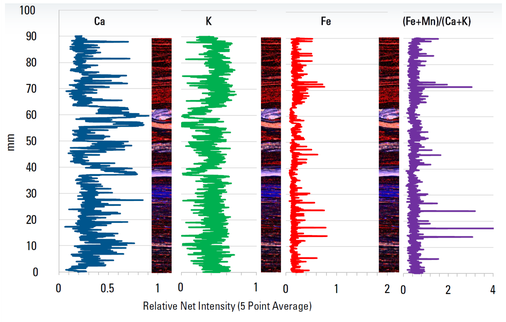
Right panels: GC-FID traces for saturate fractions from EOM samples (retention time in **minutes**). C-15 and C-18 HC peak identified on each trace. %Ro values provided by Paul Hackley (USGS-Reston). In some cases, macerals are true vitrinite, in others the maceral identified was bituminite (indicated by a *). Biomarker content (GC traces, between 50 – 60 minutes) indicates ShMCO-1 less mature than petrographic analysis shows. Total extractable organic matter (EOM) content also shown on traces.

Micro X-ray Fluorescence Mapping (Green River shale)

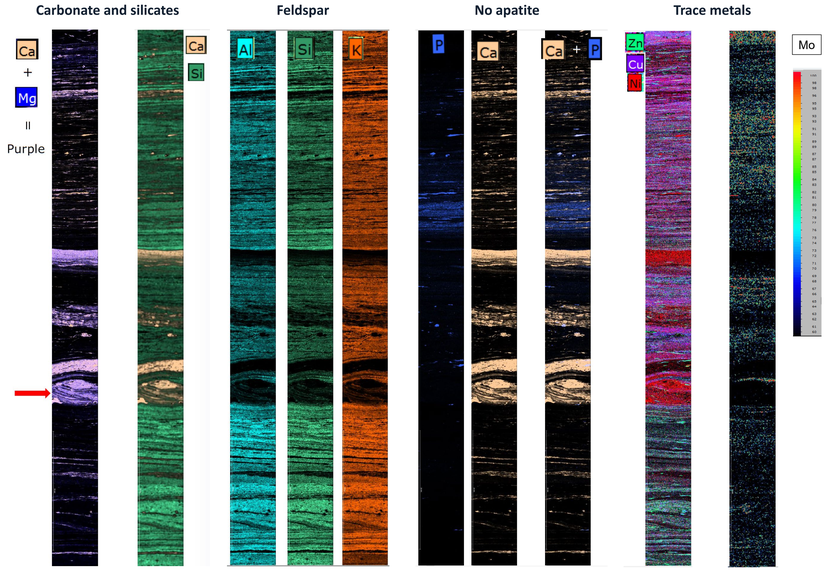
Micro-X-ray fluorescence (micro-XRF) is a non-destructive technique that can be used to map elemental distributions across the surface of geologic samples. This method complements hyperspectral imaging analyses, providing compositional information to compare with mineral phase identifications determined from spectral data.

Results for the Green River Mahogany zone sample (right and below) show substantial spatial heterogeneity across a small piece of oil shale (< 10-cm long) similar to what was observed in previous work using ATR-FTIR microscopy. The fluctuations in the abundances of elements associated with carbonate (calcium, magnesium) and silicate (feldspar, quartz) minerals indicate variability in detrital inputs and depositional environment over time.

Elemental maps showing multiple diagnostic components (Si and Ca, Ca and P, etc.) can provide insights into the distribution of particular mineral phases to guide interpretation of hyperspectral features.



Above: Major element and elemental ratio logs for a piece of Green River Mahogany zone oil shale derived from micro-XRF.



Above: Elemental (single and multi-element) maps of Green River Mahogany zone oil shale (Anvil Points Mine, CO), from Piceance Basin. Major element maps show that carbonate- and silicate-rich (mostly quartz and feldspar) laminae are spatially segregated. Trace metal distributions show some mineralogical associations.

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PANEL 2

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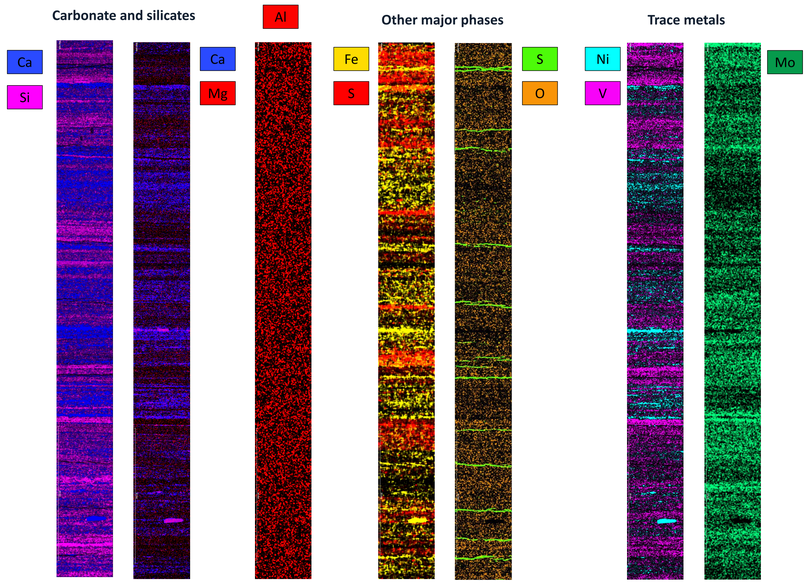
Micro X-ray Fluorescence Mapping (Boquillas shale)

Results for the Boquillas Formation shale sample (right) show substantial spatial heterogeneity again similar to observations by ATR-FTIR microscopy. Alternating calcium (carbonate) and silicon abundances shows variability in carbonate deposition but with nearly uniform aluminum concentrations. Magnesium enrichment in carbonate indicated by the purple color on the Ca-Mg plot.

Sulfur and iron distributions show that iron is more widely distributed throughout the sample and sulfur is more localized. Oxygen content is fairly well distributed.

Nickel is enriched in areas with high iron concentrations while vanadium is somewhat more associated with sulfur. Molybdenum is enriched in some parts of the sample, mostly associated with silicon, indicating that organic content is diluted by carbonate.

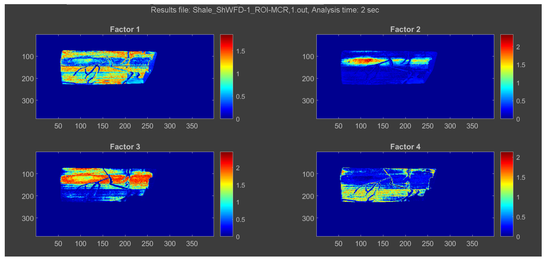


MCR component concentration maps

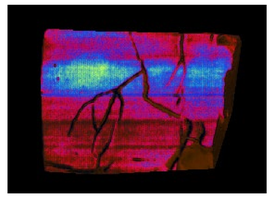
Sample images from Hyperspectral analysis

The Woodford Shale sample is a silicate rich, cherty mudrock with high organic carbon and trace metal content according to bulk analyses. The sample is thermally immature, with fine lamination and what appear to becarbonate cemented fractures.

Woodford Formation shale (Armore, OK outcrop)

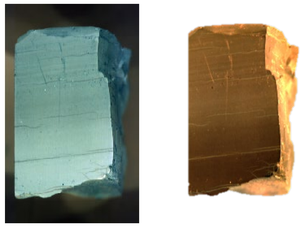


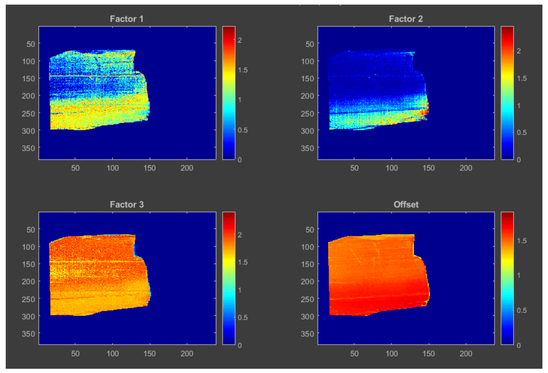
Rebuilt RGB images



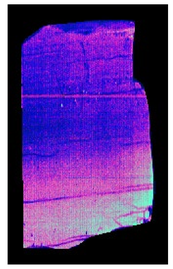
Factors 1,2,3

Marcellus Shale (Oatka Creek Member, Le Roy, NY)



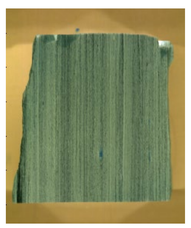


The Marcellus Shale sample is a laminated, pyrite-rich mudrock with high organic carbon content. It is marginally mature and clay mineral rich.



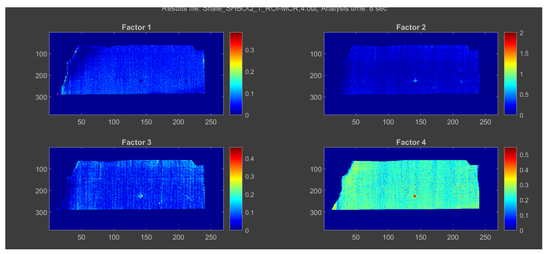
Factors 1,2,3

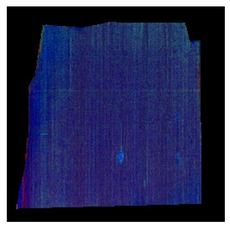
Sample images from Hyperspectral analysis



The Boquillas Formation sample is another well laminated, mineralogically variable mudrock with alternating carbonate and silicate-rich lamina. Organic matter content, according to micro-ATR-FTIR, is also highly variable, with the highest organic carbon contents in the less carbonate-rich lamina.

Boquillas Formation shale (Del Rio, TX)

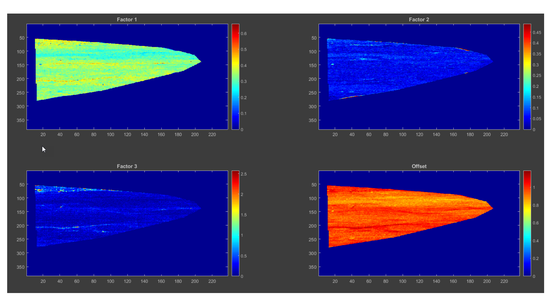


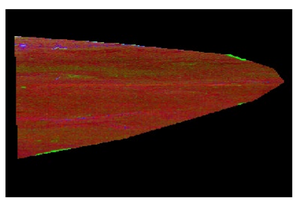


Factors 1,3,4

Niobrara Formation shale (C-Marl, CEMEX quarry, Lyons CO)

The Niobrara Formation sample (C-marl) is a thermally mature (Ro ~1%) calcite-rich mudrock with low residual organic matter content (~2%).

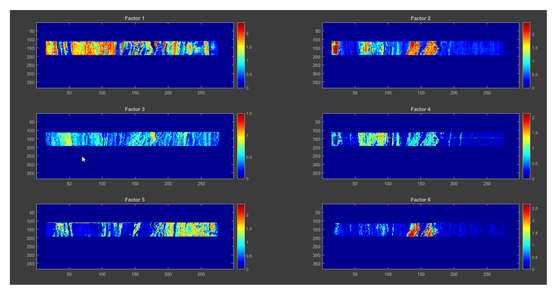


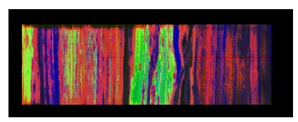


Factors 1,2,3

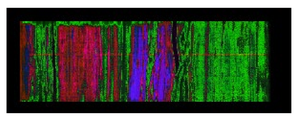
Green River Mahogany zone oil shale (Piceance Basin, near Rifle, CO)

The Green River oil shale sample is a highly laminated mudrock with substantial lamina-scale mineralogical variability, as illustrated by the HSI and micro-XRF results. Multiple mineral components are distinguished by chemometric (MCR) analysis (right).



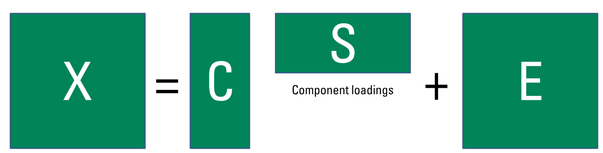


Factors 1,2,3



Factors 4,5,6

Multivariate curve resolution (MCR) is a chemometric tool for examining spectral or chromatographic datasets in order to resolve multicomponent mixtures or identify latent features. Different models yielding different number of components can be generated with different degrees of explained variance.



Raw data
Set of spectra, pyrograms, diffractograms, etc.

Component character

Model residuals

U.S. Department of the Interior
U.S. Geological Survey