Task 1: Character and development of porosity in organic-rich rocks

Objective and Methods: Better understanding of the evolution and nature of porosity in shales is needed for predicting gas sorption capacities and gas-in-place volumes. We explore the multi-modal pore structure in shales to clarify the roles that organic matter content and thermal maturity play in porosity development. In this part of our study, we examine a suite of New Albany Shale samples spanning a maturity range from immature (vitrinite reflectance \( R_o \) 0.35%) to post-mature (\( R_o \) 1.41%). Devonian to early Mississippian New Albany Shale samples from the Illinois Basin contain marine Type II kerogen and a total organic carbon contents from 1.2 to 13.0 wt. %. Organic petrology, CO\(_2\) and N\(_2\) low-pressure adsorption, and mercury intrusion capillary pressure (MICP) techniques are used to quantify pore volumes, pore sizes, and pore size distributions.

Preliminary results #1:
Increasing maturity of New Albany Shale is paralleled by large changes in the characteristics of porosity. Total porosity of 9.1 vol. % in immature New Albany Shale decreases to 1.5 vol. % in the late mature sample, whereas total pore volumes decrease from 0.0365 cm\(^3\)/g to 0.0059 cm\(^3\)/g in the same sequence. Reversing the trend at even higher maturity, the post-mature New Albany Shale exhibits higher porosity and larger total pore volumes compared to the late mature sample (we have a manuscript in review in the AAPG Bulletin).

Relationships between total pore volume (as determined by MICP and helium porosimetry) and (A) vitrinite reflectance, and (B) total organic carbon (TOC).

(C) Absolute micro-, meso-, and macropore volumes, and (D) percentages of micro-, meso-, and macroporosities with increasing maturity based on gas adsorption data.
Preliminary results #2:
With increasing maturity, changes in total porosity and total pore volumes are accompanied by changes in pore size distributions and relative proportions of micropores, mesopores, and macropores. Porosity-related variances are directly related to differences in the amount and character of the organic matter and mineralogical composition, but maturity exerts the dominant control upon these characteristics. **We conclude that organic matter transformation owing to hydrocarbon generation and migration is a pivotal cause of the observed porosity differences in these organic-matter rich shales.**

Overall interpretation of trends in porosity observed in organic-rich shales with increasing maturity (in review for *AAPG Bulletin*). Circles in the last column indicate the positions of measured samples along maturation history.
Task 2: Natural methane outgassing from shales

**Objective and Methods:** In order to constrain natural emission of shale gas into the atmosphere, we conducted field work in New York, Pennsylvania, Kentucky and Indiana targeting shale outcrops, soil overlying shale, caves and basements above shales (caves and basements are natural reservoirs of seeping gas). We employed three independent analytical techniques to quantify concentrations of hydrocarbons and CO₂ in the field; (i) a *Boreal* open-path laser for large-scale CH₄ surveys across distances of up to 100 m; (ii) a *West Systems* (Italy) laser- and infrared-based system for measurements of CH₄ and CO₂; and (iii) a *Gasmet* FTIR system for quantification of a wide range of gases, including CH₄ and CO₂. All 3 methods proved to be compatible.

**Preliminary results #1:** Shale quarries and roadcuts through shale failed to yield unambiguous data for elevated methane, not even a freshly blasted large shale roadcut in Kentucky. Our finding can be explained by the absence of strong faulting in these sampled areas, thus deeper shale gas has no seepage system to reach the surface.
Preliminary results #2: Strong natural shale gas emission into the atmosphere was documented in Chestnut Ridge County Park in New York State where a spectacular “eternal flame” marks a gas macroseep of dominantly thermogenic origin emanating through faults directly from deep shale source rock. Diffuse outgassing from faults was evident in the area. We have a manuscript in review for the journal *Marine and Petroleum Geology*.

**Left:** Dr. Giuseppe Etiope measured the flux of shale gas emanating through exposed faults in a creek bed in Chestnut Ridge County Park. Some of the seeps in the flat creek bed can be temporarily ignited, but flames are extinguished during occasional flooding.

**Above:** The spectacular “eternal flame” in Chestnut Ridge County Park burns in a small, recessed cove under a natural waterfall. The flame consumes about 1 kg of methane per day.

**Below:** The geochemical and isotopic composition of the emanating shale gas (black filled triangle) matches published data on shale gas in the area (in review for *Marine and Petroleum Geology*).

Preliminary results #3: Absence of elevated methane concentrations was found above soils and waters in areas overlying horizontal, non-tectonized shales when there was no fault system providing conduits for a seepage system. Soil is known to be an active sink for atmospheric methane due to methanotrophic microbial consortia in soil.

Sensitive flux data from many locations, like soil, at natural springs (left) and a well house (right), yielded no evidence for shale gas.
Preliminary results #4: Caves in limestone above shale would serve as natural conduits and intermittent reservoirs for shale gas on its way through fractures to the surface. Kentucky and Indiana are rich in caves above shales. Curiously, five visited caves showed the lowest concentrations of methane in all measured natural environments, with typical concentrations far below atmospheric methane concentrations. Our hypothesis is that microbial methanotrophy on moist cave walls serves as a highly active sink for methane, similar to soils. We are testing our hypothesis in a microbiology lab at Indiana University (PhD student Kevin Webster chose this topic for his doctoral research). A consequence of methanotrophy in caves would be elevated CO$_2$ with isotopic depletion of $^{13}$C. In fact, several caves feature elevated CO$_2$, which will be analyzed isotopically. Also, elevated radon levels would be expected in affected caves. Both radon and elevated CO$_2$ would be the result of shale gas emissions combined with microbial methanotrophy converting hydrocarbon to CO$_2$.

Preliminary conclusions and working hypotheses relating to Task 2:
(1) Unfractured, horizontally stratified (i.e. not affected by tectonics) shales apparently do not provide effective seepage systems for shale gas to naturally migrate upward into the atmosphere where methane can function as a greenhouse gas.
(2) Fractured, bended, tectonized shales (e.g., via basin uplift) may offer seepage systems through which shale gas from deep reservoirs can naturally move upward along geological fractures from shale through roof rocks, and ultimately release CH$_4$ into the atmosphere. The natural release of shale gas can potentially be spread over large regions.
(3) We hypothesize that during its ascent, shale gas will normally encounter vibrant methanotrophic consortia of microbes that biodegrade hydrocarbons and convert the flux of shale gas to a flux of carbon dioxide before hydrocarbons can reach the atmosphere. Only a strong and focused upward flux of shale gas along geological fractures can outpace biodegradation and deliver methane to the atmosphere. Additional surveys of regions with naturally fractured shales are needed to evaluate whether our findings from Chestnut Ridge County Park in New York State are an isolated occurrence or indicate a widespread phenomenon that would be responsible for considerable natural emissions of shale gas methane into the atmosphere.
Task 3: Isotopic testing of shales’ ability to generate catalytic gas

Objective and Methods: Our experiments test the influence of three temperatures (60°C, 100°C, 200°C) and three pressures (ambient pressure, 1000 bar, 3000 bar) on the ability of source rocks to generate natural gas over months to years. We sealed different types of immature source rocks (Wilcox lignite, Springfield Coal, Mowry Shale, New Albany Shale, Mahogany Shale) with isotopically defined waters under argon into gold cells. Batches of 5 gold cells were loaded into steel reactors flushed with water. Some loaded reactors were capped at ambient pressure, whereas others were connected to a high-pressure booster pump supplying pressures of 1000 or 3000 bars. Batches of steel reactors were bundled to keep them isothermal in one of three heated chambers. Our 60°C laboratory experiments test the hypothesis that shales can generate significant amounts of catalytic gas at low temperature, whereas the 100°C and 200°C experiments explore the transition towards traditional hydrous pyrolysis conditions beyond 300°C (which is typically not encountered in nature). Our array of gold tube experiments includes duplicates that differ only with regard to the deuterium concentration in the added water. Any newly generated methane will partially adopt the hydrogen isotopic signal from the ambient water and thus provide unambiguous evidence for methanogenesis. The first batch of gold tubes has been heated for 6 months and is currently being analyzed (January 2013).