Mineral and Organic Diagenetic Modifications in the Post Mature Marcellus Shale

Claudio Delle Piane[1], Julien Bourdet[1], Vladimir Luzin[2], David N. Dewhurst[1], and Mark Raven[3]

[1] CSIRO Energy Perth, Western Australia, Australia
[2] ANSTO Bragg Institute, Lucas Heights, New South Wales, Australia
[3] CSIRO Land and Water, Adelaide South Australia, Australia

ABSTRACT

Shale gas and shale oil have dramatically changed the hydrocarbon market in the USA and pushed the need for improved evaluation of unconventional resources worldwide. The Middle Devonian Marcellus Formation has attracted great attention as an important gas-producing unit in North America and is considered by the United States Energy Information Administration, as one of the main sources of natural gas in the United States, accounting for nearly one fifth of the country's total gas production. Since 2004, the formation has been perforated by around 9000 unconventional wells in Pennsylvania alone (data from Penn State Marcellus Center for Outreach and Research) spanning various degrees of thermal maturity organic content and burial/ diagenetic history.

Here we studied samples from the post-mature part of the Marcellus shale-gas play and, in particular, from an interval of high gamma-ray response of a well drilled in the high thermal maturity (Ro > 4%) part of the Appalachian Basin (see East et al. 2012). These samples offer the opportunity to study diagenetic effects on both minerals and organic matter in a context of deep burial at conditions close to incipient metamorphism.

We focused in particular on the mineral assemblage, organic content, porosity and crystallographic preferred orientation of this thermogenic shale-gas reservoir. 22 samples homogeneously distributed over a depth interval of 3 meters were used to quantify their mineralogy and total organic carbon (TOC). High resolution electron microscopy images were collected from ion milled samples of different organic content with particular focus on the presence of organic-hosted porosity and the characteristic features of detrital and diagenetic phases. Raman spectroscopy was used to quantify the degree of thermal alteration recorded in the organic matter. Finally, neutron diffraction was used on a representative sample to quantify the crystallographic orientation (bulk texture) of the rock-forming minerals averaging over large number of particles in a volume of 10 x 10 x 10 mm3• Multiple pole figures for different minerals (illite, calcite, dolomite and quartz) were measured to allow the reconstruction of the orientation state of all constituents in the samples.

The results indicate a relatively rich organic content (3-7 wt %) and mineralogical composition comprising quartz, illite, calcite, chlorite, albite, and pyrite. Over the three meter depth range of the 22 samples, there is a significant variation in relative content of the mineral phases and in all the samples, illite is identified as the high temperature polytype 2M 1 with crystallinity quantified by the Kubler index ranging between 0.34 and 0.43.

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

The organic fragments (i.e. pyrobitumen) are highly porous and their position with respect to the quartz overgrowth indicates that they were emplaced following quartz precipitation. Raman spectroscopy of the organic material show the presence of a number of bands in the first order region of the spectrum typical of thermally altered carbonaceous material. Quantification of the full width at half maximum for each of the bands allowed the use of a Raman geothermometer to assess the maximum temperature the sediment has been exposed to.

Neutron diffraction reveals a significant crystallographic preferred orientation in the diagenetic illite and calcite with poles to basal planes clustering in the direction perpendicular to the bedding plane; the texture of dolomite and quartz is essentially random. Overall the textural features of the Marcellus shale can be well modelled assuming transverse isotropy. The preferred orientation of two strongly anisotropic minerals like illite and calcite is certainly contributing to the anisotropic nature of the Marcellus shale and while the former is commonly linked to the re-orientation and nucleation of clay platelets during burial, the latter is not often reported and is possibly associated with the nucleation of diagenetic calcite in an anisotropic stress field. The orientation of calcite with c axes perpendicular to the bedding plane is consistent with low-temperature compression, suggesting that the orientation may be formed during compaction and diagenesis.

The Raman geothermometer, the analysis of illite cristallinity and legacy data on vitrinite reflectance ($R_o > 4.5\%$) indicate that the Marcellus Shale, in this part of the basin, has been exposed to maximum temperature of260-284°C consistent with the prehnite-pumpellyite metamorphic facies and a maximum burial depth of at least 6-8 km followed by uplift to its current depth.

The diagenetic history ofthe Marcellus shale encompassed an early stage of mechanical compaction at shallow burial depth followed by diagenetic alterations at greater depth represented by quartz overgrowth, clay mineral transformations, calcite and pyrite nucleation. Organic porosity likely developed during petroleum (catagenesis) and methane (metagenesis) expulsion and was preserved to the maximum burial depth.