Geochemical characterization of the Upper Ordovician Macasty shale gas and oil Anticosti Island, Gulf of St, Lawrence, Quebec

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Abstract

Lower Ordovician to Lower Silurian marine sedimentary rocks are extensively distributed along the Appalachians, as they were deposited during the Taconic orogeny. These sedimentary rocks
are limestones and fine-grained siliciclastic rocks. Among them, black shale with abundant organic matter is the host of oil and gas. We examined such organic-rich black shale of the Upper Ordovician age from the Anticosti Island in the St. Lawrence River, Quebec. The shale is quartz cemented by calcite (8-17 vol %), organic matter (7-9 wt %TOC) and pyrite (0.68-1.57 wt % S). It contains abundant animal fossils, such as cephalopods and graptolites.The compositions of shale samples are similar to those of North American Shale Composite.
Our black shale is enriched in redox-sensitive elements, such as U (up to 13 ppm), As (~ 9.4 ppm), Se (up to 3 ppm), Cu (up to 71 ppm), Sb (up to 1.5 ppm), and Pb (up to 21 ppm). Considering high pyrite contents, chalcophile elements (As, Cu, Pb, and Se) are likely in the sulphide phase. Sulphur isotope compositions for pyrite range from -2 ‰ to + 0.1 ‰, suggesting that the depositional environment had a slightly restricted supply of ocean water.
Calcite has $^{13}C_{PDV}$ values ranging from -2.8 ‰ to -2.5 ‰ and $^{18}O_{PDV}$ from -10.4 ‰ to -8.6 ‰, suggesting that marine carbonate values were slightly modified during the diagenesis at temperatures around 50-70 °C or at low temperatures under the influence of surface waters. Carbon isotope compositions of organic carbon (-29.3 ‰ to -22.1 ‰) are similar to typical values found in the Ordovician sedimentary
rocks of the area. Bulk rock eNd values range -13 to -14 at present time and-7 to -9 at 450 Ma. The model ages based on the Bulk Earth are ~ 1300 to 1390 Ma, suggesting that the provenance of the black shale is likely derived from Grenvillian granitic rocks. The ages coincide with those of abundant granitic igneous rocks in the Grenville Province.

Introduction

Upper Ordovician Macasty shale in the Anticosti Island, Quebec, is organic-rich black shale and hosting oil and gas. It is equivalent to the Ithaca shale in northeastern US.
We conducted a geochemical study of the black shale to characterize the compositions, and to evaluate the depositional environment and the provenance of the sediments.

Objectives

- Determine the mineralogy of the black shale,

- Measure the concentrations of major, minor and trace elements including organic carbon and sulphur

- Measure the stable isotope compositions of sulphur and carbon

- Evaluate the provenance of the black shale.

- Evaluate the depositional environments

Location and Geology

We studied eight samples from Anticosti Island, in the Gulf of St. Lawrence in Quebec, Canada. The Island,> 220 km x 56 km, has a total surface area of 7943 km^2 and relatively flat topography with a mean elevation of 126 m.

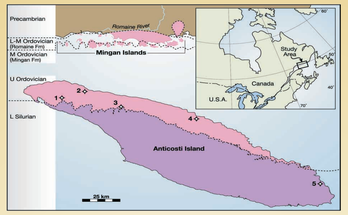

Fig 1. The Macasty black shale in the Anticosti Island in the Gulf of St Lawrence.

The Anticosti Island is underlain by Lower Ordovician to Lower Silurian sedimentary rocks. Lower Ordovician rocks have ~ 2200 m in thickness, but not exposed. Upper Ordovician to Lower Silurian rocks are exposed with the total stratigraphic thickness of ~ 1000 m. They form gently dipping NW-trending monoclinal beds.

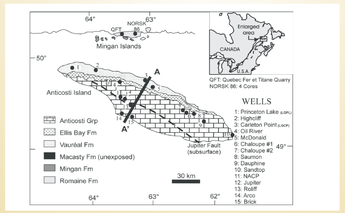

Figure 2.General geology of Anticosti Island and the nearby Mingan Islands with the location of wells (solid circles) on Anticosti. Line AA' shows the cross-section on Figure 3. After Lavoie et al., (2005)

Lithology and Stratigraphy

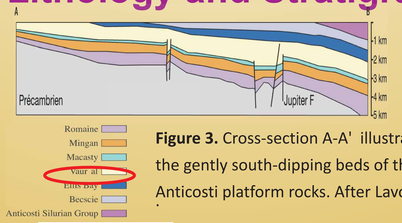

Figure 3. Cross-section A-A' illustrates the gently south-dipping beds of the Anticosti platform rocks. After Lavoie et al.(2005)

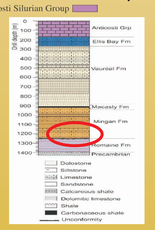

Fig 4. Ordovician-Silurian succession on Anticosti Island reported by Shell et al., 2000 based on Chaloupe well. After Lavioe et al. (2005)

Lithology

The black shale are composed of fine-grained quartz cemented by calcite.

Fig. 5. Pyritized fracture

Fig. 6. Massive black shale

Fig. 7. Graptolite in black shale

Fig. 8. Pyritized graptolite

Reflected light photomicrographs

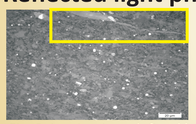

Fig. 9. Laminations defined by organic matter

Fig 10.Aggregate of pyrite

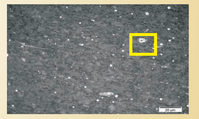

Fig 11. Cubic pyrite.

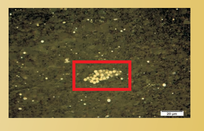

Fig. 12. Framboidal pyrite

Analytical Results

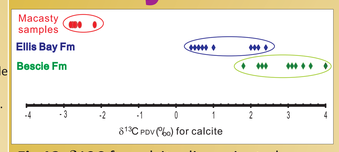

Fig 12. δ13C for calcite disseminated in the black shale range from 2.6 to 2.8 °/$_{oo}$. The values are lower than those for calcite in the Ordovician-Silurian limestones in the island reported by Jones et al. (2011).

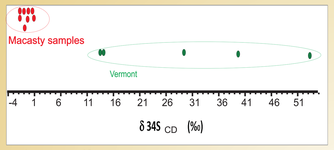

Fig. 13. Sulfur isotope compositions of pyrite in the black shale range from -2.41 °/$_{oo}$ to 0.11 °/$_{oo}$. The values are lower than those for pyrite in the Ordovician black shale in Vermont reported by Thompson (2001).

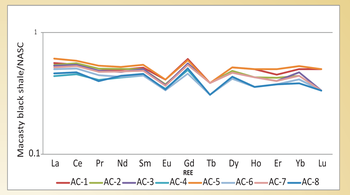

Fig. 16. Anticosti Shale have similar REE abundance as the North-America Shale Composite with more pronounced negative Eu anomalies. NASC after Gromet et al. (1984).

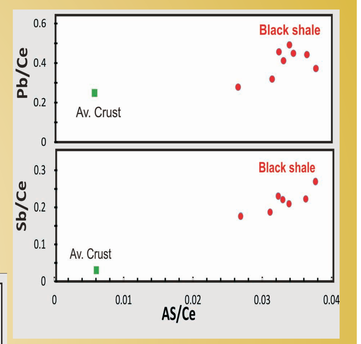

Fig 18. Macasty black shale are enriched in As, Pb, Sb, compared to the Bulk Continantal crust vaues (Taylor & McLennan,1985).

Fig 14. δ13C for organic C range from -29.3to -22.2 °/$_{oo}$ The values are similar to those of the Silurian formations (Jones, 2011) and those of the M. Ordovician shales in the Mid-Continental and East-Central US (Hatch, 1987)

Fig 15. Oxygen isotope compositions of calcite in the Macasty black shale show a narrow range from from -10.4 ‰ to -8.1 ‰. The values for Ordovician-Silurian limestones in the island are shown in the purple circle

Fig 17. Macasty black shale Nd isotopic evolution (red line) compared to the chondritic uniform reservoir (CHUR; black line) and the depleted mantle (purple line). The parameters of CHUR and depleted mantle (Allegre et al., 1983)

Summary

The negative $\delta_{13}C$ for organic carbon indicate that there was an active marine life during the sediment deposition.
The values of $\delta_{18}O_{PDB}$ suggest elevated temperatures, or incursion of meteoric waters during the diagenesis. $\delta_{34}S$ isotopic data reveals that the depositional environment had a mildly restricted supply of ocean water, allowing the fixation of redox-sensitive metals into the sediments in a reduced form.
Overall major and minor element abundance of the Anticosti black shale is similar to that of NASC, suggesting that the shales reflect the exposed upper crust.
Neodymium isotope compositions suggest the model age of ~ 1400 Ma, suggesting that the provenance of the sediments has Proterozoic ages. These coincide with the granitic rocks of the Grenville basement.

Acknowledgements

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