

Rock-Eval, lithogeochemistry, gamma ray spectrometry, thermal maturity and X-ray diffraction analysis of the Garbutt Formation, western Liard Basin (94N/11)

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Front Cover: Crumbly to fissile micaceous shale of the Garbutt Formation in the lower part of the formation. Thin beds of graded siltstone and fine sandstone containing current ripples can be traceable for over 10 metres and suggest deposition as turbidity currents. **Photo by Filippo Ferri**



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Introduction

Five stratigraphic sections of the Garbutt Formation were measured and systematically sampled along Toreva Creek and Scatter River in western Liard Basin (Figures 1, 2, 3). These sections are close to the standard section of the Garbutt Formation proposed by Stott (1982). Samples were analyzed for whole rock and Rock-Eval geochemistry, bulk mineral composition (X-ray diffraction) and thermal maturation (by reflective microscopy). In addition, gamma ray data were collected with a hand-held spectrometer. These sections and data sets will provide a reference for the Garbutt Formation type section for use in regional studies.

The UTM coordinates for the base of each section are: 1) 394932E 6612890N; 2)394286E 6612364N; 3) 394159E 6612554N; 4)389260E 6612795N; 5) 389021E 6612714N; Zone 10, NAD83; Figure 3). The measured sections are combined into one composite section (Figure 4). A compilation of all data sets can be found in Petroleum Geology Open File 2017-1_Data.xlsx. A summary and partial interpretation of the information are presented in this report; descriptions of the regional and local geology, are presented in Ferri et al. (2011).

Analytical Methods

The section was measured and described using a 1.5 metre staff. Semi-continuous chip samples for whole rock geochemistry and X-ray diffraction analysis were acquired across 2 m intervals and Rock-Eval samples were aggregated over 4 m intervals. These were crushed and homogenized before submission for analysis. Separate samples were also acquired for reflective light thermal maturation determination. In addition, a hand-held gamma ray spectrometer acquired data at a 1 metre spacing.

Gamma Ray Spectrometry

Natural gamma ray emissions from the outcrop were acquired with a RS-230 BGO Super-Spec hand held gamma ray spectrometer produced by Radiation Solutions Inc. Outcrop data were gathered at 1 m

intervals with the flat, front face of the instrument (containing the detector) placed against a flat rock surface. The attitude of the instrument was parallel to bedding surfaces and care was taken so that the measuring surface was not recessed. Data were acquired for 60 seconds after which the instrument converted measured gamma ray energy levels into concentrations of K (%), Th (ppm) and U (ppm). Average total counts were also recorded.

Rock-Eval Pyrolysis

Rock samples were pyrolyzed using a Rock-Eval 6 apparatus at the Geological Survey of Canada in Calgary, AB. This technique evaluates oil and gas shows, oil and gas generation potential, and thermal maturity, and identifies organic matter type (Espitalie et al. 1985a, b, 1986; Peters, 1986; Tissot and Welte, 1978, p. 443-447). This instrument uses a ramped temperature pyrolysis technique whereby a small amount of sample (70 -100 mg) is heated in an inert atmosphere (helium or nitrogen) and combusted with air to obtain several key geochemical parameters relating to the hydrocarbon potential of the rock: the total organic carbon (TOC), type or quality of organic matter and level of maturity (Peters 1986; Lafargue et al. 1998; Behar et al. 2001). Rock-Eval/TOC is a useful screen for recognizing hydrocarbon sources and stained rock types. The analysis gives five parameters: S1, S2, S3, TOC and Tmax. The S1 parameter measures free or adsorbed hydrocarbons volatilized at moderate temperatures (300°C). S2 measures the hydrocarbons liberated during a ramped heating (300-650°C at 25°C/min.). The S3 parameter measures organic CO₂ generated from the kerogen during rapid heating (300-390°C at 25°C/min.). Milligrams product per gram rock sample, the equivalent to kilograms per tonne, is the measure of all these parameters. Total organic carbon (TOC) is measured in weight per cent. Tmax, the temperature corresponding to the S2 peak maximum temperature, is measured in °C.

Rock-Eval results correlate to other techniques (Espitalie et al., 1985a, b, 1986; Tissot and Welte, 1978). Source rock potential is sensitive to lithology, TOC and S2 values (Tables 1 and 2). It is common practice to rate carbonate rocks with lower TOC comparable with richer clastic rocks. Extractable HC yields from leaner carbonate rocks are comparable to richer clastic rocks (Tissot and Welte, 1978, p. 430; Gehman, 1962). The organic matter associated with carbonate rocks is often more hydrogen-rich and thermally labile than that in fine-grained clastic rocks. As a result, more TOC in carbonate rocks may be transformed into bitumen compared with average clastic source rocks of comparable maturity.

Rock-Eval/TOC parameters have significance only above threshold TOC, S1 and S2 values. If TOC is less than < 0.3 wt. % then all parameters have questionable significance and the experiment suggests no potential. Oxygen Index (OI), S3/TOC, has questionable significance if TOC is < 0.5 wt. %. Both Tmax and Production Index (PI = S1/(S1+S2)), have questionable significance if S1 and S2 values are < about 0.2 mg HC/g rock. Results can be affected by mineral matrix effects. These either retain generated compounds, generally lowering the S1 or S2 peaks, while increasing Tmax, or by liberating inorganic CO₂ and increasing S3 and OI. These effects are important if TOC, S1 and S2 are low. OI values greater than 150 mg/g TOC suggest either low TOC or a mineral matrix CO₂ contribution during pyrolysis.

Rating	Wt. %TOC	Wt. %TOC
	In shales	In carbonates
Poor	0.00 - 0.50	0.00 - 0.12
Fair	0.50 - 1.00	0.12 - 0.25
Good	1.00 - 2.00	0.25 - 0.50
Very Good	2.00 - 4.00	0.50 - 1.00
Excellent	>4.00	>1.00

Table 1: Standard criteria for rating potential source socks based on TOC values.

Table 2: Standard criteria for rating potential source rocks based on S2 values.

Rating	S2 mg HC/g	
Poor	Less than 2.00	
Fair	2.00 - 5.00	
Good	Greater than 5.00	

Results reported in this open file were obtained from one of several Rock-Eval 6 apparatus at the Geological Survey of Canada. This instrument is an improvement over the Rock-Eval 2 apparatus and provides greater sensitivity and more parameters on rock composition (see Behar et al. 2001 and Lafargue et al. 1998). For comparison purposes, OI as reported by the Rock-Eval 2 instrument is equitable to the $OICO_2$ as obtained by the Rock-Eval 6 machine.

Lithogeochemistry

Samples were cleaned, crushed and split at the BC Ministry of Energy and Mines. All samples, duplicates, and standards were analyzed at Acme Analytical Laboratories Ltd. in Vancouver, BC for major, trace, and rare earth element abundances. Every twentieth sample analyzed was a duplicate; the USGS SDO-1 Devonian Ohio shale (Kane et al., 1990) was used as a geochemical standard. Samples were pulverized at Acme Analytical Laboratories Ltd. in a mild steel mill and sieved to 200 mesh. Quartz was processed through the mild steel mill prior to the milling of each sample. Major element (Si, Al, Fe, Ca, Mg, Na, K, Mn, Ti, P, Cr and Ba) concentrations were determined on a 0.2g sample by inductively coupled plasma emission spectroscopy (ICP-ES) following a lithium metaborate – tetraborate fusion and dilute nitric acid digestion. Rare earth and refractory element abundances (Ba, Be, Co, Cs, Ga, Hf, Nb, Rb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) were determined from a 0.2g sample by induced coupled plasma mass spectroscopy (ICP-MS) after a lithium metaborate - tetraborate fusion and nitric acid digestion. Precious and base metals (Au, Ag, As, Bi, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Se, Tl, and Zn) concentrations were determined from a 0.5 g split digested in nitric-hydrochloric acid solution and analyzed by ICP-MS. Total carbon and sulphur were determined by a Leco Carbon/Sulphur analyzer whereby a 2g sample was combusted in an oxygen atmosphere and liberated CO₂ and SO₂ were measured via an infrared detection cell.

Vitrinite Reflectance

Due to the rate of coalification reactions and percent reflectance in oil (%Ro) of huminite, vitrinite and bitumen (Jacob, 1989) increase with increasing temperature, these macerals provide an indirect geothermometer for evaluating the thermal conditions during sediment burial.

Standard procedures for organic petrology based on Mackowsky (1982) were generally followed. Washed core cuttings, core, and outcrop samples were prepared in a similar way by crushing them into 1-5 mm particulates, with many also sized to ~ 1 cm cubes. The samples were then mounted in a oneinch mold using two parts epoxy, and were then polished using four types of polishing material. Random reflectance (Rom) measurements were determined using a Leitz reflected light microscope with a 50X oil immersion objective and white (halogen; 546nm) and fluorescent (HBO 100W) light sources. The actual %Ro measurements were taken by the Leitz MPV II – COMBI photometer system mounted on top of the microscope (and attached to a pc-controller system) for %Ro data collection. Reflectance was calibrated using Schott precision glass standards with 0.506, 1.025, and 1.817 %Ro refractive index. The microscope was calibrated before and mid-way through each analysis in accordance with standard procedures outlined in Mackowsky, (1982), ICCP (1975) and Bustin et al. (1983). The oil used is halogen free/low fluorescence with a refractive index of ne = 1.518 at 23°C. Reflectance measurements were made on vitrinite, bituminite, and bitumen macerals together with identified alginite and sporinitederived macerals. In the absence of vitrinite, vitrinite equivalent (%Roequivalent) was calculated using the measured reflectance of primary bitumen (%RoBitumen) and Jacob's (1989) equation (if applicable). For vitrinite; huminite, eu-ulminite B and telovitrinite A are the preferred macerals for reflectance measurement.

X-Ray Diffraction

The mineralogy of bulk materials and clay-size separates was determined by X-ray powder diffraction analysis (XRD) at the Geological Survey of Canada in Ottawa, ON. Suspensions (in water) of the samples were pipetted onto glass slides and air-dried overnight to produce oriented mounts. X-ray patterns of the air-dried samples were recorded on a Bruker D8 Advance Powder Diffractometer equipped with a Lynx-Eye Detector, Co Kα radiation set at 40 kV and 40 mA. The samples were also X-rayed following saturation with ethylene glycol and heat treatment.

Initial mineral identification was made using EVA (Bruker AXS Inc.) software and comparisons to reference mineral patterns using Powder Diffraction Files (PDF) of the International Centre for Diffraction Data (ICDD) and other available databases. Quantitative analysis was carried out using TOPAS (Bruker AXS Inc.), a PC-based program that performs Rietveld refinement (RR) of XRD spectra. This is based on a whole pattern fitting algorithm. It relies on having particular mineralogical structure files (.cif) such that the reference minerals are as close a match as possible to the unknown.

All samples were further pulverized in a McCrone mill to reduce the grain size to about 5-10 μ m, which is more appropriate for RR. All the samples were then prepared as pressed powder, randomly oriented mounts. Samples FF10-313 was also run as a smear mount to verify if swelling clays were present.

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References:

- Behar, F., Beaumont, V., and De B. Penteako, H.L. 2001. Rock-Eval 6 technology: Performances and developments. Revue de L'institut Francais du Petrole, volume 56, pages 111-134.
- Bustin, R.M., Cameron, A.R., Grieve, D.A., and Kalkreuth, W.D. 1983. Coal petrology, its principles, methods and applications. Geological Association of Canada short course notes, Geological Association of Canada, volume 3, 273 pages.
- Espitalié, J., Deroo, G., and Marquis, F. 1985a. Rock-Eval pyrolysis and its applications (Part Two). Institut Français du Pétrole, Oil & Gas Science and Technology Review, volume 40, pages 755-784.
- Espitalié, J., Deroo, G., and Marquis, F. 1985b. Rock-Eval pyrolysis and its applications (Part One). Institut Français du Pétrole, Oil & Gas Science and Technology Review, volume 40, pages 563-579.
- Espitalié, J., Deroo, G., and Marquis, F. 1986. Rock-Eval pyrolysis and its applications (Part Three). Institut Français du Pétrole, Oil & Gas Science and Technology – Review, volume 41, pages 73-89.
- Ferri, F., Hickin, A. S. and Huntley, D. H. 2011. Geochemistry and shale gas potential of the Garbutt Formation, Liard Basin, British Columbia (parts of NTS 094N, O; 095B, C); in Geoscience Reports 2011, BC Ministry of Energy and Mines, p. 19–36.
- Gehman, H. M. Jr., 1962. Organic matter in limestones; Geochimica et Cosmochimica Acta, volume 26, pages 885-897.
- International Committee for Coal Petrology (ICCP), 1995. Vitrinite classification, ICCP System 1994. Aachen, Germany, 24 p.
- Jacob, H., 1989. Classification, structure, genesis, and practical importance of natural solid bitumen ("migrabitumen"): International Journal of Coal Geology, v.11, p.65-79.
- Kane, J.S., Arbogast, B.F. and Leventhal, J.S., 1990, Characterization of Devonian ohio Shale SDO-1 as a USGS geochemical reference sample: Geostandards Newsletter, volume 14, pages 169-196.
- Mackowsky, M. –Th., 1982. Methods and tools of examination; in Stach's textbook of coal petrology, (ed.) E. Stach, M.-Th. Mackowsky, M. Teichmüller, G.H. Taylor, D. Chandra, and R. Teichmüller; Gerbruder Borntaeger, Berlin, p. 295-299 (third edition).

- Massey, N.W.D., MacIntyre, D.G., Desjardins, P.J. and Cooney R.T. 2005. Digital Geology Map of British Columbia; British Columbia Ministry of Energy, Mines and Petroleum Resources; Open File 2005-2.
- Lafargue, E., Marquis, F., and Pillot, D. 1998. Rock-Eval 6 applications in hydrocarbon exploration, production, and soil contamination studies. Revue de L'institut Francais du Petrole, volume 53, pages 421-437.
- Peters, K. E., 1986. Guidelines for evaluating petroleum source rock using programmed pyrolysis. American Association of Petroleum Geologists, Bulletin, volume 70, pages 318-329.
- Stott, D.F. 1982. Late Cretaceous Fort St. John Group and Upper Cretaceous Dunvegan Formation of the Foothills and Plains, Alberta, British Columbia, District of Mackenzie and Yukon Territory; Geological Survey of Canada, Bulletin 328, 124 p.
- Tissot, B. P., and Welte, D. H., 1978. Petroleum formation and occurrence; Springer-Verlag, Berlin, 538 pages.
- Wheeler, J. O. and McFeely, P. 1991. Tectonic assemblage map of the Canadian Cordillera and adjacent parts of the United States of America; Geological Survey of Canada, Map 1712A.

Yukon Geological Survey, 2010. Yukon Digital Bedrock Geology. http://www.geology.gov.yk.ca/update_yukon_bedrock_geology_map.html, accessed: [Oct., 2010]



Figure 1: Regional geological setting of the study area. Red box indicates coverage of Figure 2. Geological base map is from a digital version of Wheeler and McFeely (1991).



Figure 2: Geology near the measured sections. Red box shows approximate coverage of Figure 3. Geological base map is from Massey et al. (2005) and Yukon Geological Survey (2010).



Figure 3: Detailed location map of the measured sections showing topographic elements and geology. Geological base is from Stott (1982).

Figure 4: Garbutt Formation, near the confluence of the Scatter River and Toreva Creek, western Liard Basin, northern British Columbia (94N/11).

UTM Coordinates for base of sections, NAD 83. Section 1: 394932E 6612890N. Section 2: 394286E 6612364N. Section 3: 394159E 6612554N. Section 4: 389260E 6612795N. Section 5: 389021E 6612714N.



1 cm = 5 m

current ripples present. Micaceous, calcareous, authigenic pyrite locally.



E Laminaations ----- Load casts Soft sediment deformation

Bentonite VVVVVV

Current ripples Worm burrows ne

Tool marks

Fault

*Grain size is averaged within interbedded sections sh: shale; sls: siltstone; fs: fine sandstone

Figure 4: Garbutt Formation, near the confluence of the Scatter River and Toreva Creek, western Liard Basin, northern British Columbia (94N/11).UTM Coordinates for base of sections, NAD 83. Section 1: 394932E 6612890N. Section 2: 394286E 6612364N. Section 3: 394159E 6612554N. Section 4: 389260E 6612795N. Section 5: 389021E 6612714N.