



## Full Length Article

# Correlation of zooclast reflectance with Rock-Eval T<sub>max</sub> values within Upper Ordovician Cape Phillips Formation, a potential petroleum source rock from the Canadian Arctic Islands



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## ABSTRACT

The lower part of the Cape Phillips Formation (Upper Ordovician, Canadian Arctic) is an ideal unit to test the correlation of graptolite and chitinozoan reflectance, and to compare zooclast reflectance with Rock-Eval pyrolysis T<sub>max</sub>. The Cape Phillips Formation is an organic-rich limestone and shale containing abundant zooclasts, bitumen, and amorphous organic matter, and has biomarker characteristics consistent with a carbonate depositional environment and organic matter derived from marine algae.

Random graptolite reflectance on thirty-seven samples in the Ro<sub>grap</sub> range of 0.58%–1.02% (T<sub>max</sub> range of 424–441 °C) were examined. The correlation between random reflectance of graptolite and chitinozoan reflectance was determined to have the following linear model:

$$(Ro_{grap}) = 0.11 + 0.814 \times (Ro_{chi})$$

whereas the linear correlation between Rock-Eval T<sub>max</sub> (converted to vitrinite reflectance equivalent VRo<sub>eqv</sub>) and Ro<sub>grap</sub> and Ro<sub>chi</sub> were determined to be:

$$VRo_{eqv(T_{max})} = 0.232 + 0.499 \times (Ro_{grap}) \text{ for random reflectance of graptolites.}$$

$$VRo_{eqv(T_{max})} = 0.231 + 0.482 \times (Ro_{chi}) \text{ for chitinozoan.}$$

Graptolite and chitinozoan reflectance are generally greater than vitrinite reflectance equivalent, but the difference between the equations to convert graptolite and chitinozoan reflectance to VRo<sub>eqv(T<sub>max</sub>)</sub> are so small that the equations could be used interchangeably and may represent a general solution to the conversion of zooclasts reflectance to VRo<sub>eqv(T<sub>max</sub>)</sub> in Lower Paleozoic rocks.

The correlation between zooclast reflectance and Rock-Eval T<sub>max</sub> improves in samples that have undergone solvent extraction, indicating that hydrocarbons affect T<sub>max</sub>. Sample that has asymmetrical S2 peak on Rock-Eval pyrolysis also has very high total extract yield with resins and asphaltenes as the dominant extracted fractions. Rock-Eval analysis of samples before and after solvent extraction demonstrates that some portion of the soluble hydrocarbon is pyrolysed in the temperature range that overlaps the S2 peak. In extracted samples S2 peaks become more symmetrical and the T<sub>max</sub> value shifts compared to the unextracted samples.

## 1. Introduction

Thermal maturity studies typically rely on optical proxies, such as carbonization of palynomorphs or vitrinite reflectance, to estimate maximum thermal stress experienced by a rock sample [23,49]. Thermally altered kerogen reflects a higher percentage of light due to the loss of functional groups, hydrogen and oxygen, and reorganization of carbon bonds. Hence the benchmark technique in optical thermal maturity studies is percentage of light reflected off vitrinite particles [49].

Vitrinite reflectance (VRo) measurement is a widely used and robust thermal maturity indicator (e.g., [26]).

Vitrinite originates from woody tissue of land plants, which only became common in Early Devonian time. Due to the absence of vitrinite in pre-late Silurian rocks, reflectance measurements have been carried out on organic-walled zooclasts such as graptolites, chitinozoans, and scolecodonts [4,6,9,16,17,19,20,18,27,33,37,41,51] and solid bitumen [29,32,44,46]. There is a direct relationship between the reflectance of graptolites and chitinozoans and the thermal maturity of the rock.

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Goodarzi and Norford [19,20] correlated the reflectance of graptolites to conodont colour alteration index (CAI) and established that graptolites become more reflective with increasing CAI. Subsequent studies have supported and refined the use of zooclasts as thermal maturity indicators, as recently reviewed by Hartkopf-Fröder et al. [23].

Thermal maturity is also commonly determined using programmed pyrolysis methods, such as Rock-Eval which involves heating a sample under an inert atmosphere [13,31]. In this technique, thermal maturity is quantified using the temperature ( $T_{max}$ ) at which the maximum generation of hydrocarbons from indigenous kerogen takes place [31]. Studies by Teichmüller and Durand [47] and Jarvie et al. [28] indicated a strong relationship between vitrinite reflectance and  $T_{max}$  obtained from Rock-Eval of Type II marine kerogen. This relationship allows  $T_{max}$  to be converted to vitrinite reflectance equivalent ( $VR_{0eqv}$ ; [28,40]).

Samples from Upper Ordovician strata in the Canadian Arctic Islands that contain abundant graptolites and chitinozoans are used in this study to evaluate the correlation between zooclast reflectance and Rock-Eval  $T_{max}$ . Using the previously established correlation between  $T_{max}$  and  $VR_{0eqv}$  [28,40], conversions from graptolite and chitinozoan reflectance to  $VR_{0eqv}$  are proposed and the limitations of Rock-Eval  $T_{max}$  in organic-rich rocks at low thermal maturity are discussed.

## 2. Geological setting

The Franklinian Margin of the Canadian Arctic Islands records deposition from the latest Neoproterozoic to Late Devonian. The succession was deposited on an extensive shallow water platform in the (present day) south and east, with a deep-water basin in the north and west. Siliciclastic strata dominated in the early Cambrian, followed by carbonate-dominant sedimentation until Middle Devonian and a return to siliciclastics in the Middle and Late Devonian. These successions are estimated to be up to 15 km thick. The Franklinian Basin was tectonically deformed between Late Silurian and Late Devonian time, first by localized deformation in the central Arctic Islands, then by a widespread Late Devonian fold and thrust event [50].

Samples used in this study are from the Upper Ordovician to Upper Silurian (Pridoli) Cape Phillips Formation, a stratigraphic unit consisting of bituminous carbonate rocks and calcareous shale, and is widespread in the Canadian Arctic Islands (Fig. 1). Samples for this study were chosen from the lowermost 50 m interval of the formation. This lower unit consists of interbedded organic-rich, black argillaceous carbonate and shale that were deposited in a deep shelf setting [34,35,48]. The signature of bacterial sulphate reduction (BSR) and methanogenesis in early diagenetic carbonates of the lower Cape Phillips Formation was documented by Coniglio and Melchin [11].

Graptolites found in the lower 50 m span the Upper Ordovician *fastigatus* to *pacificus* zones [34]. Trilobites, chitinozoans, and rare scolecodonts are also common in this lower unit [24]. The Cape Phillips Formation contains exceptionally well-preserved fossils and a record of continuous sedimentation across the Hirnantian—Llandovery and Wenlock—Ludlow boundaries. These characteristics have made it the subject of numerous paleontological studies, including research on graptolites, trilobites, chitinozoans, radiolarian, sponges, algae, and brachiopods.

The lower unit of the Cape Phillips Formation is one of many organic-rich units of latest Ordovician to early Silurian age occurring worldwide. These include, amongst others, the Red Head Rapids Formation in Hudson Bay Basin [53], the Macasty-Utica formations in Québec and New York, Mudawwara Formation in Jordan and the Tayyarat Formation in Saudi Arabia [3]. In common with these units, organic matter in the Cape Phillips Formation is dominated by Type II kerogen with initial average hydrogen index (HI) value of about 550 mg HC/g TOC inferred from the slope of the S2—TOC line of best fit (see Rock-Eval methodology below). The Cape Phillips Formation is considered the primary source rock for crude oil produced from the only oil field in the Canadian Arctic Islands at Bent Horn [36].

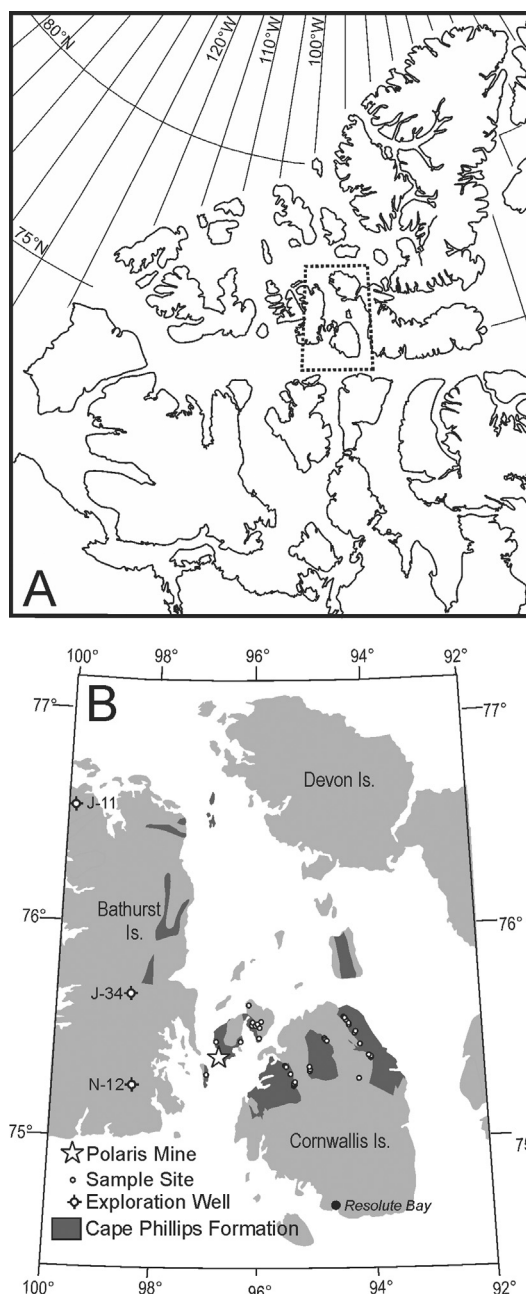


Fig. 1. (A) Location of the study area in the central Canadian Arctic Archipelago; (B) map inset shows location of Cape Phillips Formation outcrops, with sample study sites.

## 3. Methodology and sampling

Samples were collected from the central Canadian Arctic Islands in Nunavut, Canada by geologists working for the mining company Cominco Ltd. Randell et al. [43] demonstrated that a large thermal anomaly is present in the Cape Phillips Formation overlying the giant Polaris carbonate-hosted Zn-Pb deposit. In an effort to discover new Zn-Pb deposits, hundreds of samples across Little Cornwallis and Cornwallis islands were collected for thermal maturity analysis (Fig. 1; [24]). Forty-two samples from mining core and outcrop were selected for this study from both Cornwallis and Little Cornwallis islands (Fig. 1, Table 1). Using data collected by Héroux et al. [24], samples were chosen to cover thermal maturity values with a range as wide as possible. Samples are numbered by both the original INRS number assigned by Cominco Ltd and Geological Survey of Canada catalogue number (C-

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