

Preliminary Characterization of Early Jurassic Source Rocks and Ocean-Redox Conditions Based on Trace-Metal and Organic Geochemistry of the Gordondale and Poker Chip Shale Members, Fernie Formation, Northeastern British Columbia

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Introduction

The Gordondale member (Asgar-Deen et al., 2004; previously the 'Nordegg Member' of Spivak, 1949) of the Lower Jurassic Fernie Formation in the subsurface of northeastern British Columbia (NEBC) has attracted interest for its hydrocarbon potential since the early 1990s (e.g., Creaney and Allan, 1990; Riediger et al., 1991). The Poker Chip Shale, another Lower Jurassic member in the Fernie Formation, overlies the Gordondale member in some areas and has also shown hydrocarbon potential (Riediger, 2002). With increasing oil and gas exploration in NEBC, especially in unconventional reservoirs, new source-rock plays like the Gordondale and Poker Chip Shale members may become viable targets for expansion of British Columbia's hydrocarbon resource base.

While there exists limited production from the Gordondale and Poker Chip Shale members in the Fort St. John area of NEBC, advancements in exploration and development activity may be achieved through a better understanding of geological and geochemical parameters of these formations. This study is designed to address this issue. Previous studies in NEBC and Alberta have included organic geochemistry and source-rock characterization (e.g., Riediger et al., 1991; Ibrahimbas and Riediger, 2004; Ross and Bustin, 2007; Kondla et al., 2017), biostratigraphy (e.g., Asgar-Deen et al., 2004; Them et al., 2017a), inorganic geochemistry (e.g., Ross and Bustin, 2006) and carbon-isotope geochemistry (e.g., Them et al., 2017a). This study examines in detail a 45.7 m core of the uppermost Pardonet Formation

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(Upper Triassic), Gordondale member and Poker Chip Shale (Lower Jurassic), and lowermost upper Fernie Formation shales (Upper Jurassic) from the Altares field (Figure 1) employing detailed organic and inorganic tracemetal geochemistry analyses.

The goal of this project is to identify spatial and temporal trends in paleoredox, paleoproductivity and paleohydrographic conditions during deposition of the Gordondale member and the Poker Chip Shale. This will help to constrain intervals that show the greatest potential for resource development in the study area, based on their potential for organic-matter deposition and preservation. The results of this study can hopefully be used to enhance prediction of reservoir parameters in these units in other parts of the Western Canada Sedimentary Basin. Another objective is to search for geochemical evidence of the Toarcian Oceanic Anoxic Event (T-OAE) in the Gordondale member or the overlying Poker Chip Shale. Identification of this event is necessary to constrain the impact of changes in global ocean-redox conditions on depositional geochemical signatures and thus aid with understanding geochemical differences between the two hydrocarbon source rocks in this region. Further analysis will include organic carbon-isotope $(\delta^{13}C_{org})$ geochemistry to test this hypothesis, as marine sedimentary rocks of Toarcian age worldwide contain negative $\delta^{13}C_{org}$ excursions that mark the T-OAE. This paper will highlight preliminary results of X-ray diffraction (XRD), major-element (CaO, P₂O₅, TiO₂ and Al₂O₃), molybdenum (Mo), uranium (U), rhenium (Re) and carbon content (organic and inorganic) analysis and the use of these results in identifying paleoredox and paleohydrographic trends. Future research directions are discussed.

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Figure 1. Location of study area in northeastern BC, with core and outcrop locations from previous studies. The red star indicates the location of the Progress HZ Altares c-B6-A/94-B-8 well (BC Oil and Gas Commission, 2018), core from which was examined in this study; empty stars indicate core and outcrop locations that have been examined by other authors (Asgar-Deen et al., 2004; Ross and Bustin, 2006; Kondla et al., 2017; Them et al., 2017a, b, 2018). Gordondale (formerly Nordegg) member coverage, transition to true Nordegg and subcrop are approximated from Asgar-Deen et al. (2004). The Poker Chip Shale can be found throughout the area covered by the Gordondale (blue) and Nordegg (grey) members, and the subcrop is inferred to coincide with that of the Gordondale member (Riediger, 2002).

Geological and Geochemical Background

Jurassic Strata of Northeastern BC

The basal Gordondale member of the Jurassic Fernie Formation in NEBC is an organic-rich, calcareous and variably phosphatic black shale. The unit is recognized petrophysically by its high gamma-ray log response with a 'doublet' (dual gamma-ray peak) feature. The gamma peaks correspond to units 1 and 3 of Asgar-Deen et al. (2004), or units B and D of Ross and Bustin (2006). The Gordondale member reaches thicknesses of up to 40 m over the depocentre (north-northwest trend) and thins to the west and east both depositionally and erosionally, although not equally in either direction (Poulton et al., 1994). The Gordondale member in NEBC ranges between 15 and 25 m in thickness (Asgar-Deen et al., 2004) and is underlain by the sub-Jurassic unconformity and truncated by progressively older strata from west to east (Poulton et al., 1994). The subsurface Gordondale member of NEBC is time

equivalent to the Red Deer Member, Poker Chip Shale and Nordegg Member cherty-carbonate facies of the Alberta foothills outcrop belt (Asgar-Deen et al., 2004). In NEBC, the Gordondale member is typically underlain by the dolomitic Triassic Pardonet Formation, which subcrops to the east where the Gordondale member immediately overlies the older Triassic Baldonnel Formation dolomite. The Gordondale member in NEBC is likely overlain by the Toarcian Poker Chip Shale (Riediger, 2002). Figure 2 outlines the Jurassic stratigraphy in NEBC.

Deposition of the Gordondale member occurred during a major marine transgression (Creaney and Allen, 1990). Eustatic lowstand caused periods of restriction in the Gordondale basin (Poulton et al., 1994) due to the presence of physical sills, thus promoting the development of anoxic or euxinic bottom-water conditions (Riediger et al., 1990; Riediger and Bloch, 1995). Convergent tectonism (Columbian orogeny) may have led to decreased ocean circulation



by the development of a foreland basin. However, the timing of tectonic activity on the western margin of the basin is still unclear. Middle Jurassic rock units exhibit signs of convergent tectonism, but there is some speculation that initiation of orogenesis may have occurred in the Early Jurassic (e.g., Poulton et al., 1994; Pană et al., 2017). Riediger and Coniglio (1992) suggested the emergence of a westward landmass and development of a foreland basin in the late-Early to Middle Jurassic, based on oxygen-isotope evidence of westerly sourced meteoric water inflow to the Gordondale basin. These restricted conditions promoted the accumulation of large quantities of organic matter and thus bacterial sulphate reduction, which provided excess dissolved sulphide (with respect to Fe) to form pyrite and sulphurized organic matter during deposition and early diagenesis, particularly during periods of bottom-water euxinia (Riediger and Bloch, 1995). Although support for basin restriction has been demonstrated, Os- and Tl-isotope data from Alberta foothills outcrop suggest that water exchange between the basin and open ocean occurred during deposition of most of the Gordondale member and the Poker Chip Shale (Them et al., 2017b, 2018), implying that restriction was likely not severe.

Ross and Bustin (2006) noted a thin conglomerate at the contact between the Gordondale member and the overlying Poker Chip Shale in a NEBC core. In a review of the Poker Chip Shale, Riediger (2002) described two units: Poker Chip Shale A and Poker Chip Shale B. Poker Chip Shale A is a calcareous black shale with total organic carbon (TOC) content greater than 1%. Where it overlies Gordondale member shales, the contact is conformable. Poker Chip Shale B is not thought to be equivalent to the Poker Chip Shale as described in its type area and has been noted to disconformably overlie Gordondale member shales north of Township 60. Poker Chip Shale B is a noncalcareous, pyritic shale with occasional bentonites and TOC usually less than 1%, and was interpreted to be deposited in a more oxygenated setting, with anoxic conditions restricted to below the sediment-water interface (Riediger, 2002).

Consensus on Poker Chip Shale units and boundaries has not been achieved by previous investigators. For example, Poker Chip Shale A (Riediger, 2002), Gordondale member subunit 3A (Asgar-Deen et al., 2003) and Gordondale member unit D (Ross and Bustin, 2006) may represent the same unit (Ross and Bustin, 2007). As a firm distinction between the Gordondale member and Poker Chip Shale units has not been established, this paper follows the correlations of Ross and Bustin (2006) because their core and study location in NEBC is relatively close to this study. The Gordondale member and Poker Chip Shale are herein defined as being separated by a coarser grained packstone unit and an abrupt change from calcareous (Gordondale) to noncalcareous (Poker Chip Shale) geochemistry.



Figure 2. Jurassic stratigraphy in northeastern BC (Poulton et al., 1994; Ross and Bustin, 2006). The Poker Chip Shale and the Gordondale member are highlighted in orange and blue, respectively. Grey areas represent hiatuses. Abbreviations: E, east; Fm., Formation; Gp., Group; K, Cretaceous; L, Lower; Mb., Member; MS, mudstone; PkSt, packstone; StSt, siltstone; W, west.

Organic geochemistry and source-rock analysis for the Gordondale member has yielded promising results. Creaney and Allen (1990) documented its source potential, citing type II sulphur-rich (II-S) kerogens and TOC content up to 27%. Additionally, they noted that the Gordondale member is within the oil window throughout much of the basin but becomes overmature to the west. It was also suggested that Gordondale hydrocarbons could be a constituent of updip accumulation (e.g., Creaney and Allen, 1990); however Riediger et al. (1991) argued that much of its hydrocarbons remain in situ. These characteristics are consistent with findings from recent high-resolution organic-geochemical analysis of the Gordondale member in northwestern Alberta (Kondla et al., 2017), with TOC values up to 13.6 wt. %, type I/II marine kerogens and diagenetic displacive calcite inhibiting vertical migration of free, oilprone hydrocarbons. Riediger (2002) studied the organic source-rock characteristics of the Poker Chip Shale through northwestern to west-central Alberta, describing the Poker Chip Shale A and B units. Subsurface Poker Chip



Shale A strata have TOC contents of 1.0–2.5% and contain oil-prone type II kerogens (Riediger, 2002).

Recent geochronology of the Gordondale member and equivalent units to the south has provided ages for the upper and lower contacts. Pană et al. (2018) performed Re-Os geochronology on cores in northwestern Alberta. Organicrich shales from the base of the Gordondale member yielded an isochron age of 192.0 \pm 1.4 Ma (near the Sinemurian–Pliensbachian boundary), whereas shales from the base of the Poker Chip Shale yielded an age of 182.0 \pm 2.5 Ma (approx. Pliensbachian–Toarcian boundary). These ages are in agreement with ammonite biostratigraphy (e.g., Asgar-Deen et al., 2004; Them et al., 2017a) and U-Pb zircon ages (e.g., Pană et al., 2017). The thickness of the dated interval was approximately 24.7 m, implying a minimum average sedimentation rate for the Gordondale member of 2.5 m/m.y.

Inorganic Geochemistry

Multi-element redox studies provide important information on ancient bottom-water O2 levels, porewater chemistry and extent of basin restriction in terms of water exchange with the open ocean. Bottom-water conditions are divided into oxic (>2.0 ml O₂ per L water), suboxic (0.2- $2.0 \text{ ml } O_2 \text{ per } L \text{ water}$) and anoxic ($0 \text{ ml } O_2 \text{ per } L \text{ water}$; after Tribovillard et al., 2006). Additionally, anoxic waters can be subdivided into ferruginous (0 ml O2 per L water, 0 ml H_2S per L water) or euxinic (0 ml O₂ per L water, >0 ml H_2S per L water). Modern oceans are widely oxic; however, there are several locations where anoxia and euxinia occur either seasonally or year-round. Extensively studied modern anoxic basins include the Black Sea (eastern Europe), Framvaren Fjord (Norway), Cariaco Basin (Venezuela), Saanich Inlet (British Columbia) and eastern tropical-Pacific open-ocean oxygen minimum zones along the California, Mexico and Peru continental margins. A shared feature of these basins is their restriction from consistent deep-marine circulation by seasonal changes in circulation, geographic configuration and/or submarine sills. Sedimentand water-column analysis in these basins has provided a catalogue of the chemistry defining these environments (e.g., Algeo and Lyons, 2006; Algeo and Tribovillard, 2009), which can now be compared with geochemical data from ancient anoxic marine strata, such as the Gordondale member, to identify similar past depositional settings.

Molybdenum is a trace metal with a low upper-crustal concentration of 1.5 ppm (McLennan, 2001) but is found in abundance in oxic seawater (105 nmol/kg; Tribovillard et al., 2006). Sediments deposited from well-oxygenated bottom waters have low authigenic Mo enrichments that approach crustal concentrations. Modern sediments and sedimentary rocks deposited from euxinic waters have pronounced Mo enrichments (several tens to hundreds of parts per million; Scott and Lyons, 2012) because molybdate converts to thiomolybdate and to particle-reactive polysulphides that are removed to the sediments (Dahl et al., 2013). Mild authigenic Mo enrichment can occur in marine environments where bottom waters are mildly oxygenated to ferruginous and the sediment pore fluids just below the sediment-water interface contain dissolved sulphide. Molybdenum enrichment in sediments is further enhanced if Fe-Mn oxyhydroxides are delivered to sediments. Adsorption of molybdate to Fe-Mn oxyhydroxides can occur in the oxic upper-water column and, upon deposition in anoxic settings, the Mo species are desorbed once the Fe-Mn particulates are dissolved. The released Mo can be captured by organic matter and sulphide minerals, thus enhancing Mo enrichments in anoxic sediments (Tribovillard et al., 2006).

Scott and Lyons (2012) compiled Mo concentration data for modern marine sediments. Sediments deposited under non-euxinic bottom waters with active Fe-Mn oxyhydroxide shuttles and porewater H₂S have Mo concentrations above crustal values but below 25 ppm. Sediments deposited under year-round Mo-replete euxinic bottom waters have Mo >100 ppm. Intermediate concentrations (25-100 ppm) were linked to four possible nonexclusive conditions: 1) seasonal euxinia, 2) high sedimentation rates (dilution effect), 3) depletion of aqueous Mo in restricted marine settings, and 4) pH effects. Alternatively, Scholz et al. (2017) stated that intensely suboxic (i.e., nitrogenous) conditions of the Peruvian margin oxygen-minimum zone have Mo enrichments (~70-100 ppm) in sediments similar to those found in euxinic basins. Hardisty et al. (2018) also demonstrated that significant overlap in sediment Mo concentrations may occur under various redox conditions, which may confuse interpretation of paleoredox environments. In all cases, alternative proxies should be used to further strengthen interpretations in constraining the local redox environment.

Uranium is a redox-sensitive trace metal that, like Mo, has a low upper-crustal concentration (2.8 ppm; McLennan, 2001) and is present as dissolved uranyl carbonate complexes in seawater with an average concentration of 13.4 nmol/kg (Tribovillard et al., 2006). Oxic sediments have low U concentration, typically near crustal concentrations. Unlike Mo, enrichment of U in anoxic environments does not require the presence of free H2S (although enrichment is not deterred by its presence) in the water column and typically occurs within the sediment rather than at the sediment-water interface (Tribovillard et al., 2006). Once U is diffused into sediments, enrichment under anoxic conditions is facilitated by abiotic or microbial reduction (e.g., sulphate/iron-reducing or fermenting bacteria; Stylo et al., 2015) of U(VI) to U(IV), resulting in sedimentary U >10 ppm (Partin et al., 2013). Uranium adsorption to Fe-Mn particulates is much weaker than that of Mo (Algeo and



Tribovillard, 2009). Uranium enrichments can correlate with organic-matter content in sediments (McManus et al., 2006). Other factors influencing U enrichments in sediments are the depth of O_2 penetration below the sediment-water interface, sedimentation rate and oxic remobilization.

Like Mo and U, Re is a redox-sensitive trace metal with very low upper-crustal abundance (0.4 ppb; McLennan, 2001; Sheen et al., 2018) but high seawater concentrations $(39.8 \pm 0.1 \text{ pmol/kg} \text{ at } 1\sigma^1$; Anbar et al., 1992). Oxic sediments do not show Re enrichments, but retain concentrations near the crustal average. The main Re sink is anoxic sediments, with Re typically >5.0 ppb (Sheen et al., 2018). Euxinic sediments are a sink for Re, but its enrichment is independent of H₂S availability, so no threshold for euxinia is defined in terms of Re concentration (Sheen et al., 2018). Rhenium adsorption to Fe-Mn oxyhydroxides is weak and therefore not an important control on delivery of Re to sediments, and enrichment is thought to occur below the sediment-water interface (Crusius et al., 1996).

In combination, Mo and U covariations show a relationship with basin restriction and sediment trace-metal enrichment mechanisms (Algeo and Tribovillard, 2009). Algeo and Tribovillard (2009) examined this relationship by observing Mo_{EF}/U_{EF} ratios (EF, enrichment factor; see 'Methods' section for calculation) in three anoxic-euxinic locations: 1) the eastern tropical Pacific (California, Mexico and Peru margins), 2) the Cariaco Basin, and 3) the Black Sea. The eastern tropical Pacific is a productive upwelling zone of predominantly open-ocean characteristics but with localized sills leading to partially restricted, euxinic deep-water masses. Along these coasts, sediments exhibit a range of redox environments from suboxic (marginal) to anoxic and euxinic (basinal). The Cariaco Basin is a tectonic depression located off the coast of Venezuela in the Gulf of Mexico with a sill at 120-150 m that weakly restricts deep-water exchange with the open ocean, creating a mildly euxinic bottom-water layer. An Fe-Mn-oxyhydroxide particulate shuttle operates in the Cariaco Basin, delivering Mo to the sediment-water interface and producing pronounced Mo enrichments relative to U (because U removal to particulates is less efficient) and thus increased Mo_{EF}/U_{EF} ratios in sediments. The Black Sea is a highly restricted, pervasively anoxic, intensely stratified basin with a shallow sill connecting it to the Mediterranean Sea that limits O₂ penetration in deep waters. High sulphate and organic-matter fluxes lead to sustained microbial sulphate reduction and scavenging of reactive iron by sulphide, resulting in euxinic bottom waters. Renewal times of deep-water masses in the Black Sea are long (500-2000 years) compared to those of the Cariaco Basin (50-100 years), which limits the replenishment of aqueous chemical species. As drawdown of redox-sensitive metals into euxinic Black Sea sediments occurs, the water-mass trace-metal chemistry evolves to lower aqueous concentrations. Due to the faster rate of reduction and removal of Mo from euxinic waters to sediments compared with U, the Mo_{EF}/U_{EF} decreases over time until steady-state conditions are achieved or aqueous species are replenished (Algeo and Tribovillard, 2009).

The extent of basin restriction can be inferred from organicrich mudrocks deposited in restricted basins by the degree of Mo enrichment normalized to TOC content (Algeo and Lyons, 2006). Based on Mo and TOC concentrations from four modern anoxic basins, Algeo and Lyons (2006) illustrated that the slope (m) of a Mo–TOC covariation trend infers the relative extent of basin restriction, where a steep slope (higher Mo/TOC) implies weaker restriction than a shallow slope (lower Mo/TOC). Their study examined four anoxic marine basins with varied water-exchange restriction, from least to most restricted: 1) Saanich Inlet (m =45 ppm/wt. %), 2) the Cariaco Basin (m = 25 ppm/wt. %), 3) Framvaren Fjord (m = 9 ppm/wt. %), and 4) the Black Sea (m = 4.5 ppm/wt. %). Saanich Inlet is a small, seasonally euxinic (annual renewal of deep-water mass) and silled fiord located on Vancouver Island, connected to the Georgia and Haro straits. Framvaren Fjord is a redox-stratified basin with a very long and shallow sill (2.5 m depth) connecting it to the ocean via Helvikfjord and Lyngdalsfjord (Algeo and Lyons, 2006).

Methods

Two sample sets have been collected and analyzed from the 45.7 m Progress HZ Altares c-B6-A/94-B-8 Jurassic cored well drilled 75 km west of Fort St. John. The first sample set $(n_1 = 45)$ was collected in 2016 and included XRD analysis, which guided initial stratigraphic correlation and selection of the second sample set $(n_2 = 46)$ in 2018. This second set has been analyzed for major and minor elements, redoxsensitive trace-metal concentrations and carbon content. The cored well contains (from base to top): uppermost Pardonet Formation, Gordondale member, Poker Chip Shale and lowermost upper Fernie Formation shales. The samples included rocks from the Pardonet Formation $(n_1 =$ 2; $n_2 = 3$), Gordondale member ($n_1 = 21$; $n_2 = 22$), Poker Chip Shale ($n_1 = 15$; $n_2 = 19$) and upper Fernie Formation shales $(n_1 = 7; n_2 = 2)$. The black shales of the Gordondale member and Poker Chip Shale are the focus of the analysis.

X-ray Diffraction (XRD)

Analysis of the first sample set, including the XRD analysis, was completed at Argile Analytica (Calgary, Alberta). Bulk-analysis XRD was conducted on 1.5 g samples that were crushed for 3 minutes in a Retsch ball mill and subsequently by hand in an agate mortar to homogenize grain size. Sample powder was packed into a sample holder to

¹one standard deviation



avoid preferential orientation and scanned from 4° to 60° 2θ (where θ is the angle of the incident X-ray beam with a crystallographic plane; Stefani, 2016).

Sample Collection and Preparation for Elemental Analysis

The second set of core samples was collected at Weatherford Labs (Calgary, Alberta) in January 2018. Sampling was completed at ~1 m intervals, targeting black shales where lithology was consistent; if rock type varied over short intervals, each lithology was sampled. Several features were avoided during sampling, including veins (calcite or quartz), macroscopic pyrite nodules, fossils and bedding contacts, to reduce the influence of diagenetic and biological effects on depositional geochemical signals. Samples were mainly black shales (i.e., dark, finely laminated, fissile, organic-rich mudstone); however, other rocks such as turbidites, ash beds and siltstones were collected to derive geochemical information about background detrital sedimentation and volcanogenic contributions.

Bagged samples were photographed, catalogued and returned to the University of Waterloo for analytical preparation. Samples were cut to remove unwanted material (e.g., core paint, chisel marks), manually crushed using a rubber mallet and powdered using an automated ball mill with agate grinding jars to avoid metal contamination. Powdered samples were separated into multiple aliquots for elemental and carbon analysis.

Elemental Analysis

Powdered samples were weighed $(100 \pm 20 \text{ mg per sample})$ and ashed overnight at 550°C to oxidize organic matter. Ashed powders were digested through iterative dissolution in trace-metal grade HCl-HNO3-HF in a clean room at the Metal Isotope Geochemistry Laboratory, Department of Earth and Environmental Sciences, University of Waterloo. Aliquots of sample solutions were diluted by factors of 6000 (for major, minor and most trace elements) and 400 (for Cd, Re and heavy rare-earth elements) for analysis on an Agilent 8800 triple-quadrupole inductively coupled plasma-mass spectrometer (QQQ-ICP-MS). An internal standard solution of Sc, Ge, In and Bi was employed to monitor and correct for instrument signal drift. A set of multi-element calibration standards, designed to be representative of black shale chemistry, was used to define calibration curves for each element undergoing analysis. Each element for a single sample was analyzed three times per QQQ-ICP-MS session, providing an averaged concentration and relative standard deviation (RSD), which was typically less than 4%. Three shale standards (USGS SBC-1, SDO-1 and SGR-1b) were prepared and analyzed in the same manner as the core samples. During each analytical session, these standards were analyzed multiple times to

verify instrument accuracy, which was determined to be 90–110% calculated as percent recovery compared to certified standard values. Procedural blanks were prepared with the samples during dissolution to monitor background elemental contamination levels. Blanks were typically less than 0.01% of sample-element content. Replicate analysis was completed for eight samples from splits of un-ashed powder to monitor analytical precision. Reproducibility was typically better than 5% on all elements; however, Re was an exception with a mean reproducibility of 8%.

Enrichment Factors

Normalization of trace-element concentrations to a detrital proxy was completed by calculating enrichment factors (EF) to account for dilution by chemical/biochemical components (e.g., opal and carbonate; equation 1). To avoid spurious correlations, Van der Weijden (2002) outlined requirements for using Al for EF normalization, including 1) the need for low Al RSD compared to the RSD of the trace metal, 2) exclusion of samples with very low detritalmineral content, and 3) limited excess Al in relation to other detrital elements such as Ti. The EF normalization compares the ratio between a given trace-metal (X) and the Al content in a sample to that ratio in a standard material or rock type:

$$X_{EF} = (X/AI)_{sample} / (X/AI)_{standard}$$
(1)

An X_{EF} of ~1 indicates negligible enrichment, values between 1 and 10 show slight enrichment, and values greater than 10 show substantial enrichment relative to the standard. This scaling is also used to determine relative depletion, where X_{EF} between 1 and 0.1 indicates slight depletion in the trace metal and values of less than 0.1 indicate substantial depletion. Two standard values were used for normalization: 1) average upper continental crust (UCC) concentrations of McLennan (2001), and 2) Post-Archean Australian Average Shale (PAAS) for direct comparison with the Mo_{EF}–U_{EF} covariation trends identified by Algeo and Tribovillard (2009). Table 1 presents the UC and PAAS values for the elements of interest in this paper.

Carbon Content

Forty-two of the 46 samples were analyzed for carbon content at the Agriculture and Food Laboratory, University of Guelph. Excluded samples were the three volcanic-ash beds and one Pardonet Formation sample that had inadequate sample-powder mass for analysis. Following the procedure described in Wang (2018), 1 g of powdered sample was divided into two splits to determine total inorganic carbon (TIC) and total carbon (TC) contents. To measure TIC, sample splits were ashed at 475°C for 3 hours to oxidize organic matter. They were then combusted in an Elementar Vario Macro Cube CN catalytic combustor at 960°C; resulting gases were measured using a thermal-conductivity detector. Total carbon was measured in the same manner, but the splits were not ashed before analysis. Total organic carbon is calculated as the difference between the TC and TIC contents. Two shale standards (USGS SBC-1 and SGR-1b) and two replicate samples were included for analysis to verify accuracy and precision.

Table 1. Normalization standards for enrichment-factor calculations: **PAAS**, Post-Archean Australian Average Shale (PAAS) concentrations from Tribovillard et al. (2006); **UCC**, upper continental crust concentrations from McLennan (2001).

Parameter	UCC	PAAS			
Maior elements (wt.%):					
CaO	4.2	-			
P_2O_5	0.3	-			
TiO ₂	0.7	-			
AI_2O_3	15.2	15.9			
$TiO_2/AI_2O_3^*$	0.045	-			
Trace metals:					
Mo (ppm)	1.5	1			
U (ppm)	2.8	0.91			
Re (ppb)	0.4	-			

*wt.%/wt.% ratio

Results

The majority of the samples analyzed (n = 34) are black shales of the Gordondale member (n = 18) and the Poker Chip Shale (n = 16). Samples from the underlying Pardonet Formation dolomitic siltstones (n=3), upper Fernie Formation fissile shales (n = 2), and volcanic ash beds (n = 3), turbidites (n = 2) and siltstones (n = 2) within the Gordondale member and Poker Chip Shale were also analyzed. This paper focuses on the black shales of the Gordondale member and Poker Chip Shale; interpretations for other samples will be integrated with future work and will enable identification of geochemical changes associated with stratigraphic boundaries (Pardonet, upper Fernie), volcanic inputs (volcanic ash beds) and local detrital composition (turbidites and siltstones).

XRD Mineralogy and Major Elements

The first set of samples was analyzed for XRD mineralogy. The analysis revealed an abrupt change approximately midway in the core (~1575 m) from calcareous (high calcite content) and variably phosphatic (variable apatite content) below the contact to virtually calcite and apatite free and siliceous (quartz rich) above the contact. Based on the con-

Table 2. Average XRD calcite, apatite and quartz mineralogy; concentrations of major elements CaO, P_2O_5 , TiO₂ and Al₂O₃, and TiO₂/Al₂O₃ ratio; trace-metal concentrations and enrichment factors (EF); and total inorganic (TIC) and organic (TOC) carbon content in the black shales of the Gordondale member and Poker Chip Shale.

Parameter	Poker Chip Shale	Gordondale Member	All black shale samples	
XRD mineralogy (wt.%):				
Quartz	49.1 ± 9.8	35.5 ± 29.8	41.2 ± 24.3	
Calcite	0.2 ± 0.4	44.1 ± 32.5	25.8 ± 32.9	
Apatite	0 ± 0	7.2 ± 11.7	4.2 ± 9.6	
Major-element concentrations (wt.%):				
CaO	1.4 ± 0.7	20.7 ± 9.5	11.6 ± 11.9	
P_2O_5	0.2 ± 0.1	2.0 ± 2.5	1.2 ± 2.0	
TiO ₂	0.5 ± 0.1	0.2 ± 0.1	0.4 ± 0.2	
AI_2O_3	12.4 ± 2.0	5.1 ± 2.3	8.5 ± 4.3	
$TiO_2/AI_2O_3^*$	0.038 ± 0.004	0.048 ± 0.008	0.043 ± 0.008	
Trace-metal concentrations:				
Mo (ppm)	14.6 ± 11.0	120.4 ± 95.7	70.6 ± 87.5	
U (ppm)	4.4 ± 2.2	14.4 ± 7.9	9.7 ± 7.7	
Re (ppb)	122.5 ± 85.1	220.5 ± 92.9	174.4 ± 101.0	
Trace-metal enrichment factors:				
Mo _{EF} (UC)	11.9 ± 9.5	333 ± 355	182 ± 302	
U _{EF} (UC)	2.0 ± 1.0	20.1 ± 16.0	11.6 ± 14.7	
Mo _{EF} (PAAS)	18.6 ± 14.9	521 ± 556	285 ± 474	
U _{EF} (PAAS)	6.4 ± 3.1	64.5 ± 51.3	37.2 ± 47.2	
Mo_{EF}/U_{EF} (PAAS)	3.2 ± 1.8	7.5 ± 4.7	5.5 ± 4.2	
Re _{EF}	346 ± 250	1811 ± 1122	1122 ± 1108	
Carbon content (wt.%):				
TOC	4.2 ± 0.8	6.2 ± 2.0	5.3 ± 1.8	
TIC	0.5 ± 0.3	4.9 ± 2.2	2.8 ± 2.7	

*wt.%/wt.% ratio

tact ages given by Pană et al. (2018) and the position of the Gordondale member interval in the core, from approximately 1595.8 to 1575.0 m (thickness of 20.8 m), Gordondale member sedimentation occurred at a minimum average rate of 2.1 m/m.y.

The second set of samples was analyzed for Ca, P, Fe, Ti, Al, Mg, Na, K and Mn. Presented in this paper are the concentrations of the major elements CaO, P₂O₅, TiO₂ and Al_2O_3 as well as the TiO₂/Al₂O₃ ratio (Table 2). The observation that all black shales have MnO concentrations well below the crustal average concentration (0.08 wt. %); McLennan, 2001) implies that the samples were exposed to an anoxic water column and/or pore waters during and/or following deposition (Tribovillard et al., 2006). Profiles of the XRD mineralogy and major-element distributions are illustrated in Figure 3. Calcium and P vary strongly through the black shales in this core, where mean CaO content is 11.6 \pm 11.9 wt. % (1 σ) and mean P₂O₅ content is 1.2 \pm 2.0 wt. % (1 σ). Mean CaO and P₂O₅ contents in the Gordondale member are 20.7 \pm 9.5 wt. % (1 σ) and 2.0 \pm 2.5 wt. % (1 σ), respectively. Variability in P₂O₅ content of the Gordondale member is still apparent, with two peaks at 1590.25 m $(P_2O_5 = 9.1 \text{ wt. }\%)$ and 1582.14 m $(P_2O_5 = 7.0 \text{ wt. }\%)$ and a minimum at 1584.18 m ($P_2O_5 = 0.05$ wt. %). Mean CaO and P_2O_5 contents in the Poker Chip Shale are 1.4 ±0.7 wt. % (1σ) and 0.2 ± 0.1 wt. % (1σ) , respectively, which are both more than an order of magnitude lower compared to the Gordondale member. Additionally, both Al₂O₃ and TiO₂ show a steady uphole increase in concentration that corresponds to the decrease in CaO and P2O5 and increase in quartz content.

To evaluate the appropriateness of using Al for EF normalization of redox-sensitive trace-metal contents, the RSD of Al and the trace metals was calculated. The RSD for Al in the black shale sample set is 50%, while trace metals reported in this paper have RSDs ranging from 58% (Re) to 123% (Mo). Additionally, a cross-plot of TiO₂ versus Al₂O₃ for the black shale samples shows a strong correlation ($r^2 =$ 0.91) and a mean of 0.043 ±0.008 (1 σ ; n = 34) that is near the crustal average of 0.045 (McLennan, 2001). The criteria noted in Van der Weijden (2002) for working with EFs are met for this sample set.

Redox-Sensitive Trace-Metal Content

The elemental content and enrichment (X_{EF}) of Mo, U and Re were examined in detail (Table 2). The Mo_{EF}, U_{EF}, and Re_{EF} values for the Gordondale member (Figure 4) are high with respect to upper continental crust (EF >1) and typically strongly enriched (EF >10), with mean Mo_{EF} of 332.7 ±354.9 (1 σ ; range = 22.4–1002.8), U_{EF} of 20.1 ±16.0 (1 σ ; range = 4.0–57.6) and Re_{EF} of 1810.7 ±1122.2 (1 σ ; range = 501.4–4456.0). The magnitude of trace-metal enrichments in the Gordondale member is highest at the base of the member and steadily decreases toward the upper contact with the Poker Chip Shale at ~1575 m. Trace-metal enrichments in the Poker Chip Shale are smaller than in the Gordondale member and do not vary as greatly, with mean Mo_{EF} of 11.9 ±9.5 (1 σ ; range = 3.9–35.8), U_{EF} of 2.0 ±1.0 (1 σ ; range = 0.9–4.0) and Re_{EF} of 346.3 ±250.1 (1 σ ; range = 110.9–1032.3). The interval in the Poker Chip Shale containing samples 1562.93 m, 1563.90 m and 1564.28 m shows a slightly increased enrichment (Mo_{EF} = 12.8–35.8, U_{EF} = 2.7–4.0, Re_{EF} = 432.9–1032.3).

Carbon Content

The TOC and TIC contents were determined for the black shales of the Gordondale member and Poker Chip Shale (Table 2). The TOC contents for all black shale samples ranged from 2.5 to 10.9 wt. %, with a mean of 5.3 ± 1.8 wt. % (1σ ; n = 34; Figure 4). The TIC content ranged from 0.2 to 8.8 wt. % with a mean of 2.8 ± 2.7 wt. % (1σ ; Figure 3) and is strongly and positively correlated with Ca content ($r^2 = 0.96$) throughout the core, indicating that much of the TIC is associated with Ca in carbonate. Mean TOC and TIC contents for the Gordondale member are 6.2 ± 2.0 wt. % (1σ) and 4.9 ± 2.2 wt. % (1σ), respectively. The Poker Chip Shale has mean TOC and TIC contents of 4.2 ± 0.8 wt. % (1σ) and 0.5 ± 0.3 wt. % (1σ), respectively.

Mo-U and Mo-TOC Covariance

Using a cross-plot of PAAS-normalized Mo_{EF} versus U_{EF}, ancient black shales can be compared to sediment data from modern marine environments to infer the basin-restriction regime, local redox conditions and presence/absence of an Fe-Mn particulate shuttle. Figure 5 depicts the $Mo_{EF}-U_{EF}$ covariation for the Gordondale member and Poker Chip Shale. A strong correlation between Mo_{EF} and U_{EF} exists for all samples from both the Gordondale member and Poker Chip Shale ($r^2 = 0.80$; n = 34). Individually, Gordondale member samples show moderate correlation ($r^2 = 0.55$; n =18), whereas Poker Chip Shale samples show poor correlation ($r^2 = 0.10$; n = 16) between Mo_{EF} and U_{EF}. When compared to the modern environments studied by Algeo and Tribovillard (2009), the black shales have a covariation trend similar to that of sediments from the eastern tropical Pacific. The Gordondale member is more enriched in both Mo and U, and the mean Mo_{EF}/U_{EF} is 7.1 ±4.5 (1 σ), more than two times greater than the weight average of 3.1 for Mo/U in modern Pacific seawater. The Poker Chip Shale is less enriched in Mo and U, and has a lower mean Mo_{EF}/U_{EF} of $3.8 \pm 3.1 (1\sigma)$.

Covariation between Mo and TOC (Figure 6) for the Gordondale member yields a moderate slope (m = 24 ppm/wt. %), whereas the Poker Chip Shale defines a shallow slope (m = 4.9 ppm/wt. %). However, neither the Gordon-dale member nor the Poker Chip Shale shows good correla-





Figure 3. Stratigraphic and lithological units; gamma-ray (GR) log; quartz (Qz), calcite (Cal) and apatite (Ap) XRD mineralogy; TiO_2 , Al_2O_3 , CaO and P_2O_5 concentrations; Ti/Al oxide ratio; and total inorganic carbon (TIC) in black shale samples of the Gordondale member and Poker Chip Shale in the Progress HZ Altares c-B6-A/94-B-8 core. Average upper continental crust concentrations for the major-element oxides are denoted (red dashed lines; McLennan, 2001). Other abbreviations: MS, mudstone; Pard, Pardonet Formation; PkSt, packstone; StSt, siltstone; UFS, upper Fernie shales.





Figure 4. Stratigraphic and lithological units; gamma-ray (GR) log; trace-metal concentrations (black) and enrichment factors (EF; red) normalized to upper continental crust of McLennan (2001) for Mo, U and Re; and total organic carbon (TOC) content in the Progress HZ Altares c-B006-A/094-B-08 core. Grey fields represent sediment Mo concentrations where sulphidic porewater (PW H₂S) and bottom-water (BW) euxinia develop (Scott and Lyons, 2012), and sediment U concentrations for bottom-water anoxia from Partin et al. (2013). White field in Mo track represents a transition zone between PW H₂S and euxinia.Red dashed lines mark boundaries between slight depletion and slight enrichment (EF = 1), and slight enrichment and substantial enrichment (EF = 10). All Re samples are substantially enriched (Re_{EF} >10) and represent anoxia (Re >5 ppb; Sheen et al., 2018), so no fields or dividers are presented. See Figure 3 for core-lithology legend. Abbrevia-

tion (r^2 of 0.25 and 0.13, respectively), in contrast to data from modern anoxic basins (Algeo and Lyons, 2006).

Preliminary Interpretations

First-Order Variations in Gordondale–Poker Chip Shale Geochemistry

Geochemical analysis revealed that the Gordondale member black shales are more enriched in Mo, U and Re than shales in the overlying Poker Chip Shale. Hence, the Gordondale member was likely deposited in an environment conducive to trace-metal enrichment in sediments, such as lower bottom-water O₂ levels, higher H₂S levels or higher water-mass trace-metal concentrations compared to the Poker Chip Shale. This first-order trend to lower redoxsensitive metal enrichments upsection in the core corresponds to a decrease in calcite, apatite, TOC, CaO and P₂O₅ content from the Gordondale member to the Poker Chip Shale. Poker Chip Shale Mo concentrations fall into the lower (<25 ppm) and intermediate (25–100 ppm) bins of Scott and Lyons (2012), indicating that any of several factors may have influenced the degree of Mo enrichment. The contrast between the units implies major changes in the depositional environment, which may include one or more of the following conditions: enhanced detrital input or sedimentation, local bottom-water redox variation, basin restriction or global ocean-redox conditions.

The first possible explanation for the reduced enrichments in the Poker Chip Shale is the apparent increase in the input of siliciclastic material. This is observed through 1) a change from calcite to quartz enrichment in XRD profiles, 2) an increase in Al_2O_3 and TiO₂ contents upsection, and hence 3) a potentially enhanced sedimentation rate for siliciclastic material. All three may have had a dilution effect on the concentration of trace metals and TOC, resulting in muted enrichments.

A strong correlation between the Mo_{EF} - U_{EF} covariation trend for the Gordondale member and Poker Chip Shale (Figure 5) indicates that there may have been a stable and





Figure 5. Covariation diagram for Mo_{EF} and U_{EF} of the Gordondale member (blue) and Poker Chip Shale (orange). Enrichment factors (EF) are normalized to Post-Archean Australian Average Shale (PAAS; Tribovillard et al., 2006). There is moderate correlation between Gordondale member samples ($r^2 = 0.55$) and poor correlation between Poker Chip Shale samples ($r^2 = 0.10$) independently (trends not depicted), but a strong correlation ($r^2 = 0.80$) exists between all black shale samples from both members (solid black line). Modern marine redox trends for weakly restricted (e.g., Cariaco Basin), open-marine (e.g., eastern tropical Pacific) and strongly restricted (e.g., Black Sea) basins are approximated from Algeo and Tribovillard (2009). Modern Pacific seawater (SW) Mo/U (weighted average = 3.1) is depicted at factors of 0.1, 0.3, 1 and 3 (black dashed lines).

continuous redox transition from anoxic and/or euxinic (Gordondale) to suboxic (Poker Chip Shale), similar to the modern eastern tropical-Pacific margin (Algeo and Tribovillard, 2009). The mechanisms for the transition might include 1) a decrease in primary productivity, or 2) a transition from basinal to marginal deposition.

It is also possible that the aqueous chemistry began to evolve due to intense drawdown of trace metals into the sediments without replenishment from exchange between deep water and the open ocean, such as occurs in a strongly restricted basin like the Black Sea. A Mo-TOC covariation diagram (Figure 6) helps to illustrate the extent of restriction in the basin in which sediments were deposited. Whereas both the Gordondale member and the Poker Chip Shale have poor correlations between Mo and TOC contents, a shallowing between their covariation slopes is observed ($m_{Gordondale} = 24$ ppm/wt. %; $m_{Poker Chip} = 4.9$ ppm/ wt. %), suggesting that the basin may have transitioned from being weakly restricted, similar to the modern Cariaco Basin, to strongly restricted, like the modern Black Sea. If correct, this change toward strong restriction would pro-



Figure 6. Covariation diagram for Mo and TOC of the Gordondale member (blue) and Poker Chip Shale (orange), superimposed on trends for modern anoxic basins (Algeo and Lyons, 2006). The Gordondale trend slope of 24 ppm/wt. % is similar to that of the weakly restricted Cariaco Basin, whereas the Poker Chip Shale slope of 4.9 ppm/wt. % is similar to that of the Black Sea. Correlations are poor (Gordondale $r^2 = 0.25$, Poker Chip Shale $r^2 = 0.13$), so the trends depicted are not definitive.

mote intense drawdown of trace metals into anoxic seafloor sediments while depleting the water column. This process tends to lead to lower sediment Mo_{EF}/U_{EF} ratios. A decreased Mo_{EF}/U_{EF} ratio is evident between the Gordondale and Poker Chip Shale members, with the latter having a ratio less than half that of the former. If further evidence of increased basin restriction is identified, this may indicate a western landmass during the Early Jurassic through initiation of a foreland basin (Riediger and Coniglio, 1992; Pană et al., 2017) that inhibited communication between the Gordondale and/or Poker Chip Shale basins and the open ocean. However, the poor Mo-TOC correlation does not provide a robust justification for these interpretations. The low r^2 values may be a result of dynamic changes in the depositional environment or diagenetic processes (e.g., sedimentation rates, water-column pH, water-column Mo concentrations, bottom-water redox conditions and/or overmaturation).

Another factor to consider is the Toarcian Oceanic Anoxic Event (T-OAE), which may have resulted in a global areal increase in anoxic bottomwater conditions (Them et al., 2018). The T-OAE is readily identified in core and outcrop sections globally based on a distinct negative $\delta^{13}C_{org}$ excursion, but there are currently no C-isotope data available for this core. This event may coincide with Poker Chip Shale deposition in NEBC, given that the C-isotope expression of the T-OAE was found in the lower Poker Chip Shale in Alberta (Them et al., 2017a, b, 2018). During the T-OAE, a global drawdown of trace metals into an expansive area of anoxic and euxinic sediments may have occurred. Hence, the lower redox-sensitive metal enrichments observed in



the Poker Chip Shale may not reflect strong basin restriction, but rather a lower global oceanic reservoir of these metals, if the T-OAE occurred during deposition of the Poker Chip Shale (e.g., Owens et al., 2016).

Implications for Source-Rock Potential

From the geochemical analysis and preliminary interpretations completed thus far, the following can be said regarding possible implications for the Gordondale and Poker Chip Shale source-rock potential:

- The TOC contents in the black shales of both the Gordondale member and the Poker Chip Shale support enhanced source potential. The Gordondale member is the more attractive unit, based on higher mean TOC of 6.2 wt. % (maximum of 10.9 wt. %), compared to the Poker Chip Shale (mean TOC of 4.2 wt. %).
- Increased sedimentation rates may have occurred in the Poker Chip Shale, thus diluting organic-matter concentrations.
- Open or weakly restricted basin conditions during deposition of the Gordondale member suggest that anoxia/ euxinia was driven by increased primary productivity, implying an enhanced nutrient supply (consistent with higher TOC and P contents);
- Global expansion of anoxia and/or euxinia during the T-OAE may have resulted in widespread conditions for organic-matter preservation, potentially including the Poker Chip Shale.

Some limitations in this study area are the indication of thermal overmaturity (Creaney and Allen, 1990) and extensive structural deformation due to its proximity to the Rocky Mountain deformation front. Additionally, type II-S kerogens in the Gordondale member that have resulted from euxinic conditions could pose a hazard during drilling operations due to the presence and release of sour gas (H_2S) .

Conclusions

A preliminary examination of XRD mineralogy and majorelement (CaO, P₂O₅, TiO₂, Al₂O₃), trace-metal (Mo, U, Re) and carbon (TOC, TIC) data was presented for one of the very few continuous, full-diameter, Early Jurassic cores in NEBC. The core covered the Gordondale member and Poker Chip Shale of the Fernie Formation. The calcite/CaO and apatite/P₂O₅ concentrations showed a significant decline from the Gordondale member to the Poker Chip Shale, indicating substantial changes to the depositional environment, specifically increased siliciclastic and decreased carbonate sedimentation. Redox-sensitive tracemetal concentrations suggest the Gordondale member experienced periodic water-column euxinia based on peaks of Mo (>100 ppm) and anoxia (U >10 ppm and Re >>5 ppb). The Poker Chip Shale did not exhibit such high metal concentrations. Four scenarios are proposed to explain the lower metal enrichments in the Poker Chip Shale:

- Sedimentation rates increased with the input of siliciclastic material, which had a dilution effect on the tracemetal and TOC concentrations in the Poker Chip Shale.
- A transition of local bottom-water redox state from intensely suboxic-anoxic and periodically euxinic (Gordondale member) to dominantly suboxic (Poker Chip Shale) conditions would be accompanied by less efficient burial of redox-sensitive trace metals in sediments.
- Strong basin restriction with slow rates of deep-water renewal depleted the stock of aqueous trace-metal species following intense drawdown into euxinic sediments.
- Global drawdown of the trace-metal inventory from seawater to sediments occurred during the T-OAE, when the area of bottom-water euxinia was expansive.

Paleoenvironmental factors such as primary productivity and bottom-water redox conditions are linked to current source-rock potential of the Gordondale and Poker Chip Shale members. Gordondale member TOC indicates excellent source-rock potential (up to 10.90 wt. %), while the Poker Chip Shale has moderate source potential with TOC up to 5.74 wt. %, mirroring the decreasing trace-metal content. Environmental changes likely had an effect on source potential and may include an increased sedimentation rate diluting organic matter/TOC, a shift in bottom-water redox conditions from euxinic/anoxic to suboxic decreasing organic-matter preservation, or an extinction event due to ocean anoxia (T-OAE) leading to the widespread decline in primary productivity and organic-matter deposition. These factors occur at local, regional and global scales, respectively. Deduction of paleoenvironmental conditions from detailed organic and inorganic geochemistry will aid in hydrocarbon exploration efforts, having implications for the areal extent, quantity and quality of the source potential in the Early Jurassic of NEBC.

Future Work

This paper focused on preliminary interpretation of geochemical data for black shales of the Gordondale member and Poker Chip Shale intersected in a core within the Altares field of NEBC (Progress HZ Altares c-B6-A/94-B-8 well). Analyses of these samples included more minor and trace metals (including rare-earth elements) than are discussed in this paper; these will be examined in the future to provide a full picture of the paleoredox, paleoproductivity and paleohydrography of the stratigraphy covered in the core. Sedimentary Fe-speciation data (Raiswell et al., 2018) may also be acquired to provide independent constraints on local bottom-water redox conditions during deposition. Additionally, organic carbon-isotope data will be collected at the University of Waterloo's Environmental



Isotope Laboratory to search for the presence of the Toarcian Oceanic Anoxic Event (T-OAE), which is marked by a strong negative organic C-isotope excursion in sedimentary rocks at other localities worldwide, including the Poker Chip Shale in Alberta (e.g., Them et al., 2017a, b, 2018). This will not only provide information in the context of the T-OAE but will also further constrain the age of the core in NEBC if the excursion is present. Once C-isotope analyses are completed, intervals of interest will be chosen from which to complete higher resolution sampling and geochemical analysis in early 2019.

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