SEDIMENTARY ORGANIC MATTER IN THE COLORADO GROUP (CRETACEOUS), ALBERTA

by

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Abstract

The transgressive interval between the top of the Viking Formation and the top of the Second White Speckled Shale in south-central Alberta consists predominantly of mudstones with varying organic richness. The section has been divided into six lithologic "zones" named A through F in ascending stratigraphic order. Existing informal names are used for Zone B (the Fish Scale Zone) and Zone F (the Second White Speckled Shale or Second White Specks). The organic matter in all zones is largely of marine origin. Low TOC values characterize Zone A as a result of destruction of organic matter in a relatively oxidizing environment. All zones above Zone A were deposited under mainly oxygen-deficient conditions caused by constriction of the basin due to tectonic movements and by a sea level drop at the onset of Fish Scale Zone time. At peak transgression during deposition of Zone E and the Second White Speckled Shale episodic oxygenation of bottom waters occurred. Relatively high TOC values characterize the Fish Scale Zone, Zone C, Zone D and the Second White Speckled Shale. Low TOC values in Zone E resulted from destruction of organic matter at the sediment/water interface, and possibly as a result of low productivity. The high TOC levels in the Second White Speckled Shale occur in spite of episodic oxygenation of bottom waters and may reflect a global productivity increase at about the Cenomanian-Turonian stage boundary. The present
distribution of organic matter in all zones is influenced by a westward increase in thermal maturation. Clay mineralogy is unrelated to organic content. Coarse-grained beds contain less and more refractory organic matter than the finer-grained rocks. The amount of silt in mudstones and argillaceous siltstones is unrelated to TOC in all zones except the Fish Scale Zone, in which a increasing silt content correlates to lower TOC. Silt content and oxygen index are related only in Zone D; the correlation is positive. Variations in sedimentation rate derived from thickness variations are correlated in a positive sense for Zone A, the Fish Scale Zone and Zone E. Zone D exhibits a negative correlation, suggestive of dilution. Potential oil exploration targets exist in sandstones in the Fish Scale Zone, at the base of Zone D, and in fractured shales of the Second White Speckled Shale.
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Acknowledgment

In too many acknowledgments spouses are late-finishers. Not so here. My wife Cathy is responsible for my having undertaken this work, and for her assistance, advice, encouragement and faith I am deeply grateful. My daughter Rosemary provided invaluable help by putting the world in proper perspective. My supervisor, Dr. Marc Bustin, was a constant source of suggestions and vigorous encouragement. I appreciate having had the chance to learn from him. The work was improved by suggestions from committee members Dr. W. Barnes and Dr. J. Murray. Among others I must thank are Doni Jacklin, Stanya Horsky and numerous other staff and students in the UBC Departments of Geological Sciences, Oceanography and Soil Science. Dr. T. Lewis at the Pacific Geoscience Centre kindly provided the gamma ray spectroscopy data. This work would not have been possible without the assistance of the many oil companies who provided samples of drill cuttings, and without the cooperation and assistance of the staff of the Core Research Centre in Calgary. Funding was provided by NSERC (to R. M. Bustin), Texaco Canada and the University of British Columbia. Husky Oil provided funding and gave me the opportunity to return to university by allowing me to take a leave of absence. I am most grateful.
1. Introduction

This study is primarily concerned with the organic constituents of the rocks of a portion of the Colorado Group (Cretaceous) of Alberta, a thick transgressive section dominated by mudstones and an important petroleum source rock interval (Allan and Creaney, 1988 and 1991). The objective of this research was to describe the organic matter in these rocks, to document lateral and stratigraphic variations in organic content, to attempt to account for some of the observed variations and to evaluate some possible controlling factors on organic deposition and preservation. The study has implications for the determination of volumes of oil and gas generated. It is also relevant to interest within the oil industry about the possibility of exploiting unconventional reservoirs ('fractured shale') in this interval by horizontal drilling. It is hoped the data concerning the influences on organic matter distribution will be useful additions to the search for predictive models of source rock deposition.

The study interval was deposited in a transgressive setting, as were many organic-rich shales (Wignall, 1987), and another objective of the study was to determine what effects differing depositional conditions during the progress of the transgression had on the organic character of the rocks. The study interval contains beds laid down
during an 'Oceanic Anoxic Event' and a further objective was an examination of the effects of this worldwide phenomenon.

The study area in southwestern Alberta (Figure 1) was selected primarily because of the availability of a relatively large number of cores. The area is triangular, bounded arbitrarily by Township 46 to the north, the Fifth Meridian on the east, and on the west by the foothills thrust belt of the Rocky Mountains. Within the study area, the strata of the Colorado Group are, as will be shown later, within the oil window. This level of thermal maturity presents some difficulty in interpretation due to the effects of maturation on organic matter, but it allows study of these effects and provides an opportunity to study the source rocks which have probably generated oils reservoired in the Colorado Group, and not just their immature equivalents.

In this study, the rocks hosting the organic matter are described in terms of their sedimentary structures and lithology, major element geochemistry and radioactivity. The organic matter contained within these rocks is characterized by organic petrography, pyrolysis and stable carbon isotope analysis. A number of potential influences on organic matter distribution, specifically thermal maturity, depositional oxygenation conditions, grain size, sedimentation rate and clay mineralogy, are then evaluated. Finally the available data is synthesized in an attempt to construct a model for the deposition of organic matter in the Colorado Group seas.
Location Map

Northwest Territories

Alberta

British Columbia

Saskatchewan

Study Area

U.S.A.

Figure 1.
2. Methods

This study is based largely upon the analyses of about 2500 core and drill cuttings samples from forty eight petroleum exploration and development wells (Figure 2), together with examination of wireline logs. Formation tops were picked from the logs. Cores from 41 wells were examined at the Core Research Centre, a facility in Calgary, Alberta operated by the Energy Resources Conservation Board, an agency of the Alberta Government. Cores were described and small samples were removed at approximately 0.75 metre intervals. Samples of drill cuttings from 38 wells (many of which were also cored) were supplied by the oil companies which operated the wells. Approximately 2 grams of sample were taken from each vial in the study interval. The sample interval was generally 5 metres. A subsample, used for pyrolysis, was subsequently picked by hand in order to obtain material representative of the fine-grained fraction, and to avoid cavings. Coarse-grained material was not present in drill cuttings in sufficiently large volumes to permit a sample to be taken. All analytical work was done in the Department of Geological Sciences at The University of British Columbia (UBC) unless otherwise indicated.

All samples were analysed by Rock-Eval pyrolysis, using a Rock-Eval II with TOC module. Samples were crushed by hand with an agate mortar and pestle. The average sample size was 74 mg. The pre-programmed Cycle 1 heating program of the
### WELL LOCATIONS

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<td>48</td>
<td>9-11-28-2W5M</td>
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25 kilometres

Figure 2.
Rock-Eval instrument was used. In the pyrolysis phase of this cycle, the temperature is increased from 300°C to 600°C at a rate of 25°C/minute. In the oxidation phase, required for TOC determination, the temperature is raised almost instantly to 600°C, and held at that level for seven minutes. Details of Rock-Eval analyses are contained in Peters (1986).

Reflected light and fluorescence microscopy was done using a Leitz Orthoplan MPV2 microscope with photomultiplier. All reflected light microscopy was done with oil immersion lenses. Polished samples were prepared by mounting the sample in epoxy, then polishing the resulting pellet as described in Bustin et al. (1983). Reflected light examinations were carried out using unpolarized white light. Fluorescence microscopy was performed using incident blue light with Leitz BG12 excitation and K530 barrier filters. The majority of the petrographic work was done using small samples of whole rock from core. Core samples too friable to permit cutting a sufficiently large piece were coarsely crushed. Several samples of drill cuttings were also examined. Selected samples were studied using a Semco Nanolab 7 scanning electron microscope.

Random reflectance measurements of vitrinite were made in oil using unpolarized light. The samples were of crushed core material and drill cuttings.

Conventional thin sections were examined using a transmitted light petrographic microscope.
Stable carbon isotopes of organic matter were determined in the Department of Oceanography at UBC. Crushed rock samples were treated with warm dilute HCl to remove carbonates, then air dried. The samples were introduced into a VS Isogas Prism Mass Spectrometer from a Carlo Erba Strumentazione Elemental Analyser 1106. The results are expressed in conventional °/oo notation with reference to the Peedee Belemnite standard (PDB).

Major element geochemistry was determined by x-ray fluorescence using a Philips PW 1400 x-ray spectrometer, also housed in the Department of Oceanography at UBC. The analyses were carried out on fused glass disks prepared by melting the sample with a dilithium tetraborate/lithium carbonate/lanthanum oxide flux, then rapidly cooling the glass in a mold.

Total sulphur was determined using a Fisher Sulfur Analyser Model 475 in the UBC Department of Soil Science.

Reactive iron was determined by atomic absorption spectrometry using the method of Berner (1970). Approximately 100 mg of sample was digested in boiling concentrated HCl for one minute. The reaction was quenched with distilled water, and the volume made up to 250 ml in a volumetric flask. After allowing the suspension to settle for about one hour, about 150 ml was decanted into a polyethylene bottle. These samples were then aspirated directly into Techtron SI-RO-SPEC Atomic Absorption Spectrophotometer with a Varian hollow cathode lamp. Iron
concentrations were determined from standard curves for wavelengths of 248.3 and 271.9 nm produced using prepared solutions of known concentrations.

Acid digestion was used to determine the calcite content of some samples. The samples were treated with cold dilute HCl and the calcite content calculated from the weight loss.

Clay mineralogy was determined by X-ray diffraction using a Siemens D5000 diffractometer, scanning from 3° to 15° 2θ and using Cu Kα radiation. Each sample was crushed and the fraction finer than 2 μm separated by settling in water. A small amount of the resulting suspension was pipetted onto a glass slide and air dried in order to produce an oriented mount. All samples were analysed on the diffractometer three times: 1) air dried samples; 2) after having been left for about 24 hours in a desiccator over ethylene glycol; and 3) after heating to 550°C for one hour.

Additional oriented slides were made from some samples after following digestion of the crushed samples in hot 6N HCl to dissolve any chlorite (Brindley, 1972). Others were treated by the addition of a concentrated KCl solution to determine if the commonly observed broad diffraction peak indicating a basal peak of about 100 nm was due to potassium deficiency in the illite lattice ('degraded illite'). All these treated samples were analysed after air-drying.

Maps were computer-contoured using GeoGraphix PC software.
3. Geological Setting

The Colorado Group was deposited in a large mid-Cretaceous epeiric sea (Figures 3 and 4) which covered much of what is now the American midwest and southwest, and the prairie provinces of Canada (Kauffman, 1977). The sea was oriented approximately north to south between the rising cordillera to the west and the Canadian Shield to the east. The basin was formed by isostatic subsidence in response to tectonic thickening of the crust along the western margin of North America during the Columbian orogeny (Porter et al., 1982). At times of peak transgression the seaway extended from the present Arctic Ocean to the Gulf of Mexico. The deposits of the eastern basin margin have been removed by erosion, and the western shoreline deposits of many of the units in the Canadian portion of the basin are buried beneath the thrust sheets of the Rocky Mountains (Stott, 1984).

Sedimentation was influenced by a number of transgressive-regressive cycles (Figure 5). Despite fairly intensive studies, however, there is still disagreement over the relative importance of tectonism and global sea level change in controlling some of the cycles. Even the definitions of the cycles are unresolved; compare, for example, Kauffman (1977), Caldwell (1984) and Stott (1984).

The study interval, between the top of the Viking Formation and the top of the Second White Speckled Shale,
Late Late Albian Seas

Neogastropiltes cornutus time

Figure 3. Extent of the Colorado Sea during deposition of Mowry-equivalent Zone A. From Williams and Stelck (1975).
Late Early Turonian Seas
Watinoceras time

Figure 4. Extent of the Colorado Sea during late Early Turonian time (at about maximum transgression). From Williams and Stelck (1975).
Figure 5. Transgressive-regressive cycles of the Cretaceous. Stratigraphic position of the study interval indicated by arrows at extreme right. From Caldwell (1984).
constitutes the deposits of the transgressive and earliest regressive phases of the Albian to Turonian Greenhorn Cycle (Kauffman, 1977; McNeil and Caldwell, 1981). This cycle is relatively well-defined and eustacy is considered to have been the major controlling factor (Kauffman, 1977; Caldwell, 1984). During deposition of the lowermost strata within the study interval there was no connection between the Boreal (northern) and Gulfian (southern) seas (Figure 3). With continued transgression a continuous seaway eventually formed (Figure 4) which was in existence by the time of deposition of the Fish Scale Zone (latest Albian) (Ananyorke and Stelck, 1978). During peak transgression, southwestern Alberta may have been directly connected to the Pacific Ocean to the west through gaps in the cordillera (Lang and McGugan, 1988).

The climate was temperate (Kauffman, 1977), as the global Cretaceous climate was considerably warmer than that of the Recent (Barron, 1983). The computer simulations of Ericksen and Slingerland (1990) suggest circulation in the basin was largely controlled by storm events.

The faunal diversity of the Colorado Group is relatively low. There are abundant molluscs (particularly ammonites and bivalves) and planktonic foraminifera, however there is little or no record of other invertebrate macrofauna (Kauffman, 1977; McNeil and Caldwell, 1981).
4. Description of the Rocks of the Study Interval

Although the focus of this study is on the organic matter contained in the rocks of the study interval, it is necessary to examine the nature of the rocks as well in order to more fully understand the organic facies. To that end the rocks are described based on core, drill cutting and thin section examination, thickness data derived from well logs and major element geochemistry. Results are presented below; the interpretations can be found in Section 9 in which all relevant data are gathered in an attempt to synthesize a depositional model.

The grain size discussed in the following section refers to visual estimates of the silt content of the fine-grained fraction. The results are expressed in map form using a numerical scale (Table 1) explained more fully in Section 7.4. Larger values correspond to higher percentages of silt.

4.1 Stratigraphy and Sedimentology

The stratigraphic framework of the study interval is shown in the stratigraphic column, Figure 6. The strata sampled extend from the top of the Viking Formation to the top of the informally designated Second White Speckled Shale, and comprise a portion of the Colorado Group. The study interval ranges in age from late Albian to early Turonian. A detailed discussion of the stratigraphy of the
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<th>Numeric Designation</th>
<th>Lithology</th>
<th>Approximate Silt Content</th>
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<td>Claystone</td>
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<tr>
<td>2</td>
<td>Mudstone</td>
<td>30%-40%</td>
</tr>
<tr>
<td>3</td>
<td>Silty Mudstone</td>
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<td>12</td>
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<td>13</td>
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Table 1. Numeric grain size scale.

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<td>Albian</td>
<td>Cenomanian</td>
<td>Turonian</td>
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<td>Belle Fourche Shale</td>
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<tr>
<td>Peacey Formation</td>
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<td>Blairmore Gp.</td>
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<td>Blackstone Formation</td>
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<td>Marcelle Fm</td>
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<tr>
<td>Pfaff Moon</td>
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Colorado Group and correlative strata can be found in Caldwell et al. (1978).

The stratigraphic nomenclature is complicated by a number of informally designated intervals and unnamed zones. For the purposes of this thesis subdivisions of the interval are given simple letter designations and existing informal names are used where appropriate. The division of the interval into six zones is based upon lithologic changes defined by their electric log signatures. Typical resistivity logs are shown on an east-west cross section through the study area (Figure 7).

The section is composed largely of mudstones and argillaceous siltstones, with subsidiary siltstones, sandstones, bioclastic limestones and volcanic ash beds. There is, in general, an upward decrease in the amount of silt in the fine-grained fraction throughout the section. The upper portion of the section is calcareous. The composition of the clay mineral fraction (discussed in more detail in Section 7.3) is quite uniform throughout the entire interval, with the dominant clay mineral being illite. The average whole rock major element composition is shown in Table 2.

The total study interval varies in thickness between 91 and 182 metres, thickening to the northwest (Figure 8), although individual subunits have different isopach patterns, discussed later. The overall isopach pattern reflects westward thickening of the section towards the
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Normalized to Calcium-free Basis

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Table 2. Major element data, averaged by zone.

FSZ= Fish Scale Zone
2WS  = Second White Speckled Shale
Figure 7. East-west stratigraphic cross section. Datum: Base Fish Scale Zone
Figure 8. Isopach map of the interval between the top of the Viking Formation and the top of the Second White Speckled Shale.
basin axis. The thin area in the southeast probably results from the influence of the Sweetgrass Arch, a northeast-trending positive basement feature (Cant, 1989).

Macrofossils are rare, with the exception of fish debris (generally scales) and shell fragments of inoceramid bivalves, the latter being particularly common in the upper part of the section.

Each zone within the study interval is discussed below. Short descriptions of the strata overlying and underlying the study interval are also included.

COLORADO GROUP

VIKING FORMATION

The Viking Formation underlies the study interval. It is a predominantly sandstone unit, important as a hydrocarbon reservoir in western Canada (Reinson et al., 1983). The depositional environment of the Viking Formation has been the subject of much work and controversy, however it is generally interpreted to be largely marginal to shallow marine (Cant, 1989).

ZONE A

Zone A, the lowermost portion of the study interval, lies between the top of the Viking Formation and the base of the Fish Scale Zone. On well logs Zone A is a low radioactivity interval as compared to the overlying Fish
Scale Zone. Its thickness across the study area ranges between 9 and 39 metres and it thickens to the northeast (Figure 9). The map of the average grain size of the fine-grained fraction (Figure 10) shows areas of coarse material in the western central part of the map area and along the strike of the basin in the south.

Zone A consists largely of laminated dark grey pyritiferous mudstones and argillaceous siltstones. The silt content of these fine-grained lithologies decreases upwards. Up to 30% laminae to lenses (and rarely beds) of light grey siltstone to sandstone occur intercalated with the mudstones and fine-grained siltstones. The thickness and frequency of the coarser layers decreases upsection. The siltstones and sandstones are generally lensoid to continuous and many are ripple cross-laminated. The bases of these coarser units are generally sharp and some show small loading features. Most are normally graded although rarely are reverse graded or have sharp tops. Small horizontal burrows are often associated with the coarser-grained layers, and thicker silty or sandy intervals may be intensely bioturbated (Figure 11).

Secondary components include minor fish debris and volcanic ash beds. Bedded siderite occurs as well, and a number of these siderite beds exhibit small locally pyritized bioturbation traces (Figure 12). Minor pyritiferous concretions are present. Pyrite occurs disseminated throughout the section, within some burrows and
Figure 9. Isopach map of Zone A.
Figure 10. Grain size map, Zone A.
Figure 11. Intensely bioturbated interval of sandstone and argillaceous siltstone from the lower portion of Zone A. Scale is 3 cm long.
Figure 12. Trace fossils in a siderite bed, Zone A. Scale is 3 cm long.
in some siltstone or sandstone laminae, apparently replacing quartz.

Subvertical clastic dykes, filled with medium grey siltstone to very fine grained sandstone, occur in Zone A in two wells, 8-12-35-5W5M (Figure 13 a and b) and 6-10-37-8W5M. Leckie and Potocki (1988) have described similar clastic dykes from Zone A in cores from wells 1-35-35-7W5M and 2-25-35-7W5M. They interpret these dykes to have been injected at burial depths between 150 and 300 metres, possibly as a result of earthquakes.

The mudstones and argillaceous siltstones are variably fissile. The lamination within the mudrocks is on a 1 to 5 mm scale in most of the area, and is defined by the presence of slightly coarser laminae (Figure 14). These silty layers are generally less than 1 mm thick, sharp based, discontinuous and often graded. In the extreme western part of the study area, in the 14-31-45-15W5M well, clearly-defined normally graded sequences occur (Figure 15), with the distance between the bases of successive sequences decreasing upward from 5 or 6 cm to 1 or 2 cm. The grading becomes indistinct toward the top of the core.

Foraminifera within Zone A suggest a depositional water depth of 25 to 100 metres (personal communication, P. Sherrington in Leckie and Potocki, 1988).

The base of Zone A (the top of the Viking Formation) is placed at the top of the uppermost major Viking Formation sand body and is usually marked by a significant electric
Figure 13 a) (top) and b) (bottom). Clastic dyke of very fine sandstone to coarse siltstone intruding mudstone of Zone A. Scale is 3 cm long.
Figure 14. Thin section photograph of laminated mudstone from Zone A showing thin laminae of quartz siltstone. Magnification 31.25X. Uncrossed polars.
Figure 15. Graded bedding in siltstone and mudstone of Zone A in the western part of the study area (well 14-31-45-15W5M). Scale is 3 cm long.
log deflection. The contact is sharp and irregular (Figure 16) and may be marked by an intensely bioturbated interval. Regionally the contact is erosional (Downing and Walker, 1988; Boreen and Walker, 1991). The contact with the overlying Fish Scale Zone is gradational.

**FISH SCALE ZONE**

The Fish Scale Zone is a widespread marker horizon in the Western Canada Sedimentary Basin, with characteristic high resistivity and gamma ray responses on geophysical logs. Similar beds at approximately the same stratigraphic level are found over a very large area of the western interior of North America from Oklahoma to the Mackenzie Valley (Reeside and Cobbin, 1960, and references therein; McNeil and Caldwell, 1981; Simpson, 1984; Stott, 1984). The thickness of the Fish Scale Zone in the study area ranges from 6 to 14 metres, but it does not exhibit any particular isopach pattern (Figure 17). The grain size distribution map (Figure 18) shows a general westward increase in silt content consistent with the regional westward coarsening noted by Caldwell (1984). There is also a slight increase in silt content in the west-central portion of the map area where coarser material is also found in Zone A. The grain size of the coarser lithologies within the Fish Scale Zone
Figure 16. Erosional surface at the contact between the Viking Formation and Zone A. Scale is 3 cm long.
Figure 17. Isopach map, Fish Scale Zone.
also increases slightly to the west and decreases up section.

The Fish Scale Zone is a relatively silty to sandy interval encased in underlying and overlying strata composed largely of mudstone. It consists of ribboned intercalations of dark gray mudstone and argillaceous siltstone, and coarser layers of light gray siltstone and very fine-grained sandstone (Figure 19).

The coarser-grained material within the Fish Scale Zone occurs as laminae to beds ranging in thickness from a few grains to a maximum of 3.5 cm. The coarser-grained layers are generally sharp-based and commonly wavy-bedded to rippled with ripple cross-lamination. Locally they exhibit small-scale loading features. The tops of the coarser layers are usually sharp, although thicker layers may have gradational tops. The very thin coarser layers define the lamination in the mudstones and argillaceous siltstones. Contorted laminae are locally present in the thicker intervals (Figure 20).

The mineralogy of the coarser layers is dominated by quartz with minor amounts of plagioclase and chert. The grains are angular to sub-angular, moderately to well sorted and cemented by calcite.

Bioturbation in the Fish Scale Zone is rare. Only minor small burrows were noted in the core from the westernmost well in the study, 6-10-39-9W5M.
Figure 19. Cross-bedding in sandstone of the Fish Scale Zone. Scale is 3 cm long.
Figure 20. Contorted bedding in the Fish Scale Zone. Scale is 3 cm long.
Fish debris (mainly scales, but with some bones as well) is a common accessory component. They occur scattered throughout the zone, but more particularly as concentrations on bedding surfaces.

Pyrite is scattered throughout the section. Minor pyritized siltstone and sandstone laminae are present as are pyritiferous concretions.

The lower contact of the Fish Scale Zone is gradational over about 2 to 2.5 metres, with alternations of laminated silty mudstone characteristic of the underlying Zone A and typical Fish Scale Zone lithology. The base of the Fish Scale Zone in this study is placed at the base of the lowermost occurrence of the characteristic lithology. No cores over the upper contact were available, however well log response indicates a relatively sharp contact.

ZONE C

Samples of Zone C come only from drill cuttings and one core, from the 7-19-45-6W5M well, which covers only the uppermost 5.5 metres of the zone. On geophysical logs Zone C is characteristically radioactive. At the base of the zone the level of radioactivity is less than that exhibited by the Fish Scale Zone, however it increases upwards. The thickness of Zone C ranges between 22 and 43 metres and increases to the west-northwest (Figure 21). There is also a
Figure 21. Isopach map, Zone C.
thin area in the southwest portion of the map area, perhaps reflecting positive movement of the Sweetgrass Arch. The silt content of the fine-grained fraction ('grain size') decreases to the southeast (Figure 22).

The core from the 7-19-45-6W5M well consists of dark gray, finely laminated, slightly calcareous, pyritiferous mudstone. Zooplankton fecal pellets are relatively common and generally occur concentrated in laminae about 0.5 to 1 mm thick. Individual fecal pellets are calcareous lensoid bodies ('white specks') less than 1 mm long, in most cases a very pale brown colour. Calcareous foraminifera are locally common. Relatively uncommon are Inoceramus bivalve shell fragments, 5 to 8 centimetres long. The slightly calcareous nature of the zone (and some of the overlying zones) probably results from the presence of calcareous nannofossil material.

Lamination is defined by often subtle laminae of calcareous siltstone, laminae of mudstone only slightly siltier than the adjacent rock, laminae rich in 'white specks', and by variations in calcite content. The coarse laminae are generally less than 1 mm thick and many are only the thickness of one or two silt grains. They are generally spaced 1 to 4 mm apart. Many are at least partly pyritized. In the basal 0.5 m of the core the calcareous siltstone laminae reach thicknesses of 2 millimetres, and are sharp-based. Thin sections show the calcareous siltstones to be composed of angular quartz fragments and common fragments of
Figure 22. Grain size map, Zone C.
calcareous foraminifera; calcite cement is pervasive. Examples of the same lithology from the Second White Speckled Shale are shown in Figure 23a and 23b.

The lower contact of Zone C is probably sharp, based on log response. The upper contact is gradational.

ZONE D

Zone D is a somewhat coarser grained and more calcareous interval than either the overlying or underlying units. The major element geochemistry (Table 2) reveals a higher calcium content that in Zones C and E. Based on its stratigraphic position relative to the Fish Scale Zone, Zone D is correlative to the Dunvegan Formation of northern Alberta, a progradational deltaic sequence attributed to a eustatic sea level fall by Bhattacharaya and Walker (1991).

Zone D is easily recognized on geophysical logs by an increased resistivity response. In addition, it is marked by a sharp upward reduction in radioactivity. Zone D varies in thickness from 14 to 46 metres and thickens to the WNW (Figure 24). The grain size map (Figure 25) does not reveal any obvious patterns.

All of Zone D was cored in the 7-19-45-6W5M well. In this core Zone D is composed of finely laminated calcareous and pyritiferous mudstone. The lamination is defined by calcareous siltstone laminae and by variations in calcite and pyrite contents. The more calcareous laminae are
Figure 23 a) (top) and b) (bottom). Thin section photographs of calcareous siltstone from the Second White Speckled Shale. Note fish debris in Figure 23a and brachiopod fragment in Figure 23b. Magnification 31.25X. Crossed polars.
Figure 24. Isopach map Zone D.
Figure 25. Grain size map Zone D.
characterized by higher concentrations of 'white specks'. Minor bioturbation is present only in the lowermost portion of the interval, associated with thin zones with abundant *Inoceramus* shell fragments. Calcareous siltstone laminae are generally about 1 mm thick and decrease in concentration up the section. Many show some degree of replacement by pyrite. One 0.7 m thick interval in the lower portion of the zone contains about 30% laminae to lenses of calcareous siltstone, 0.1 to 4 mm thick, some of which show cross-lamination. Minor *Inoceramus* shell fragments, some of which are pyritized, are present and become less common and smaller up the section. Fecal pellets (white specks) occur throughout and in a very concentrated 0.8 cm thick layer near the top. Rare fish debris is also present. Radiolaria are moderately common. A calcareous concretion containing large *Inoceramus* fragments and having a pyritized rim occurs near the base of the zone (Figure 26).

Both upper and lower contacts of Zone D are gradational over very short intervals.

**ZONE E**

On geophysical logs Zone E is less resistive than either the overlying or underlying strata. The thickness of Zone E ranges from 18 to 36 metres. The isopach map of the zone (Figure 27) shows thickening to the west, with the exception of the southwestern area where thickening to the
Figure 26. Calcareous concretion with pyritized rim and associated *Inoceramus* shell fragments. Scale is 3 cm long.
Figure 27. Isopach map, Zone E.
east suggests the influence of the Sweetgrass Arch. The grain size distribution map shows an increase in silt content size to the northwest (Figure 28).

Zone E consists of finely laminated, dark grey, slightly to moderately pyritiferous mudstone with minor scattered siltstone laminae (1-0.1 mm thick) and laminae of bioclastic limestone composed almost entirely of calcite prisms derived from the shells of Inoceramid bivalves ('Inoceramite', McNeil and Caldwell, 1981). Minor fish scales, scattered isolated Inoceramus prisms and rare larger Inoceramus shell fragments are present within the mudstones. A few bentonite beds occur. At 7-19-45-6W5M some small probable pyritized cephalopods are present (Figure 29). Fecal pellets (white specks) are generally uncommon, although more abundant in the lower portion of the core from the 14-7-36-5W5M well.

Both upper and lower contacts are gradational, with the overlying and underlying zones characterized by more abundant laminae of calcareous siltstone.

SECOND WHITE SPECKLED SHALE

The informally named Second White Speckled Shale is more commonly referred to simply as the Second White Specks. On geophysical logs the Second White Speckled Shale is recognized by its relatively low gamma ray response and high resistivity, both effects probably the result of the high
Figure 28. Grain size map, Zone E.
Figure 29. Probable small pyritized cephalopod. Scale is 3 cm long.
calcite content. High resistivities were ascribed to high calcite content for the correlative Pavel Formation of Manitoba (McNeil and Caldwell, 1981).

The thickness of the Second White Speckled Shale ranges across the study area from 5 to 31 metres (Figure 30) and thickens to the north and west. The grain size (Figure 31) does not change in any predictable way across the study area, although there is a suggestion of coarse input from the west-southwest in the central part of the area.

The Second White Speckled Shale consists of dark grey laminated, pyritiferous, calcareous mudstone with common laminae to beds of both calcareous siltstone and 'Inoceramite' bioclastic limestone (Figure 32 a and b). The number of Inoceramite laminae and beds increases up the section, and they are locally extensively bioturbated (Figure 33). Calcareous siltstone layers are also more common in the higher part of the zone, up to 30% in the upper portion at some well locations. Scattered fish debris occurs throughout the section (Figure 32b) and minor radiolaria are present. Volcanic ash beds are a secondary constituent. The 'white specks' of the zone name are small (<1 mm) lensoid calcareous bodies which occur scattered throughout the interval, but occurring most notably in concentrated bands less than 1 centimetre thick. They were first recognized as aggregates of coccoliths by Dawson (1874), and later again by Goodman (1951). Hattin (1975) identified them as zooplankton fecal pellets. Scanning
Figure 30. Isopach map, Second White Speckled Shale.
Figure 31. Grain size map, Second White Speckled Shale.
Figure 32 a) (top) and b) (bottom). "Inoceramite" bioclastic limestone. Note the large fish bone in Figure 32 b). Magnification 31.25X. Polars uncrossed (Figure 32a); crossed (Figure 32b).
Figure 33. Bioturbated "inoceramite" limestone, Second White Speckled Shale. Scale is 3 cm long.
electron microscopy of the specks illustrates the fragmental nature of the material within the pellets (Figure 34). Although in most samples the material is not clearly identifiable, a few probable coccolith fragments can be recognized.

The lower contact of the Second White Speckled Shale is gradational and marked by an upward increase in the number of coarse interlaminae. Both gradational and sharp upper contacts occur. At a few locations the sharp upper contact is marked by an intensely bioturbated bed of Inoceramite limestone.

ZONE G

Only the basal portion of the interval overlying the Second White Speckled Shale was examined. It consists of dark grey, calcareous laminated mudstone with scattered thin laminae of calcareous siltstone which are generally discontinuous and some of the thicker of which are rippled. Rare fish debris also occurs, along with scattered fragments of Inoceramus shells, the amount of which decreases upwards. Minor radiolaria are locally present.
Figure 34. SEM photograph of a fecal pellet ("white speck") showing its fragmental nature.
4.2 Major Element Geochemistry

As a consequence of iron determinations required for an analysis of iron-sulphur-carbon relationships (Section 7.5), major element geochemical compositions were acquired for 54 samples. It is assumed that variations in levels of silicon and aluminum reflect variations in amounts of quartz and clay minerals present in the samples, and that variations in calcium content result from differing amounts of biogenic calcite. Relationships between silicon, aluminum and calcium, and between these components and organic carbon (Section 7.2) were examined in order to determine if compositional (i.e. mineralogical) data could add to the interpretations of depositional processes or of the controls on organic matter distribution.

The major element compositions were determined by x-ray fluorescence of fused glass disks. The results are summarized in Table 2. Graphs are shown using both raw and zone-average data, the latter used to illustrate compositional variations between zones.

Calcium content is highest in Zone D and the Second White Speckled Shale. The strong correlation between calcium determined by x-ray fluorescence and calcite determined by weight loss after digestion of finely-crushed sample in cold, dilute (0.6N) hydrochloric acid (Figure 35) suggests the calcium occurs largely as calcite. The 'calcite' determined by acid treatment is in excess of that determined
Figure 35. Calcite content of samples calculated from XRF data vs. calcite content determined by acid digestion.
by x-ray fluorescence, suggesting the presence of small amounts of other carbonate minerals.

Average sodium content decreases upsection. The anomalously high average phosphorus content of the Fish Scale Zone results from one sample only, which probably contains phosphatic fish debris.

Calcium and silicon concentrations vary inversely (Figures 36 and 37). There is only a very weak positive correlation between silicon and aluminum (Figures 38 and 39). However, on a calcium-free basis (reflecting the composition of the detrital minerals, unaffected by autochthonous biogenic calcite) there is a strong negative correlation between zone-average SiO₂ and Al₂O₃ values (Figure 40). The dataset as a whole does not reflect this relationship, however (Figure 41). Highest aluminum concentrations, and lowest silicon concentrations, on a calcium free basis, are in Zone E, while the highest SiO₂ and lowest Al₂O₃ levels are found in the Fish Scale Zone (Table 2).

The relationships between chemical composition and total organic carbon contents were also examined, and are considered in the discussion of the possible influences on organic content (Section 7.2), which follows the presentation of the data on the organic matter.
Figure 36. SiO$_2$ vs. CaO.
Figure 37. SiO₂ vs. CaO using mean values for each zone.
Figure 38. SiO₂ vs. Al₂O₃.
Figure 39. SiO$_2$ vs. Al$_2$O$_3$ using mean values for each zone.
Figure 40. SiO$_2$ vs. Al$_2$O$_3$, both calculated on a calcium-free basis. Mean values for each zone plotted.
Figure 41. SiO₂ vs. Al₂O₃, calculated on a calcium-free basis.
5. **Description of the Organic Matter**

Disseminated organic matter is present within the Colorado Group mudrocks in sufficient quantity to have been an important hydrocarbon source. The organic matter has been characterized by organic petrography in both white and blue light, by Rock-Eval pyrolysis and by stable carbon isotope analysis.

5.1 **Organic Petrology**

5.1.1 **Introduction**

In addition to the bulk geochemical parameters derived from isotope ratios and pyrolysis, important information about the organic constituents of rocks can be obtained from petrographic examination of samples in reflected white light and under blue or ultraviolet light excitation (fluorescence microscopy). Under such illumination hydrogen-rich liptinitic kerogen exhibits characteristic autofluorescence (Bustin et al., 1983).

5.1.2 **Previous Study**

The organic petrology of the Colorado Group and equivalent rocks outside of the present study area has been studied by several workers. Creaney (1980) in a study of dispersed organic matter in the mudrocks of the Boundary Creek Formation (Second White Speckled Shale equivalent) of
the Beaufort-Mackenzie Basin noted the predominance of amorphous organic matter, or fluorescing groundmass, which he termed matrix bituminite. Also present is bituminite I (terminology of Teichmuller and Ottenjann, 1977). This is a yellow to dark brown fluorescing kerogen, which tends to occur in wispy or stringy forms and which contains abundant inclusions of yellow-fluorescing liptodetrinite. Examples of a similar material but with few inclusions also occur. The observed inverse relationship between the relative abundances of matrix bituminite and discrete bituminite I was interpreted to suggest that the former resulted from increased dilution by mineral matter of the same material that made up the latter.

The dominant liptinites in the Boundary Creek Formation, other than the bituminites, are various types of alginite. Liptodetrinite was also reported. Sporinite and resinite are rare. The non-fluorescing constituents included vitrinite, inertinite (mainly inertodetrinite) and faunal (vertebrate bone) fragments.

The work of Stasiuk and Goodarzi (1988) concerning the Second White Speckled Shale in Saskatchewan showed the dominant fluorescing organic constituent to be amorphous material 'adsorbed into the mineral fraction' (fluorescing groundmass). The particulate fluorescing components include *Tasmanites* algae, small alginite (considered possibly to be *Nostocopsis*), dinoflagellates and spores. Their 'Bituminite III' (terminology of Teichmuller and Ottenjann, 1977) is
commonly the most abundant organic constituent. This non-fluorescent material occurs in small, poorly defined elongate to lensoid bodies and is characterized by a granular to pitted appearance. It is often associated with faunal remains. They also noted a variety of bituminite which fluoresces brown to dark brown with a fluorescence spectrum similar to that of degraded *Tasmanites* algae.

Stasiuk and Goodarzi (1989) also note the presence of rare (never more than 1% by volume) of ‘stringy’ huminite (Ro 0.26-0.27) along with relatively minor inertinite. The section also contains fish scales, which commonly show lamination and a poorly defined fibrous structure and which fluoresce from yellow to brown.

The lower part of the Shaftesbury Formation in the Peace River area of Alberta contains abundant amorphous organic matter along with leiospheres, dinoflagellates, tasmanitids, *Botryococcus* algae and liptodetrinite. Minor wood fragments (presumably huminite/vitrinite) and fragments of tracheids and leaf cuticle are also present (Leckie et al., 1990).

Several palynological studies of Colorado Group rocks recorded the presence of angiosperm pollen, acritarchs, dinoflagellates and ‘phytoplankton debris’ along with recycled Carboniferous and Permo-Triassic pollen and spores (Norris et al., 1975; Singh, 1975; Anan-Yorke and Stelck, 1978).
In the present study forty samples were examined petrographically. Because of the abundance of liptinite and because of the importance of the hydrogen-rich material to the petroleum source characteristics of the rocks, the majority of the microscopy was done using blue light excitation. Blue light is preferable to ultraviolet because of the more intense fluorescence colours which result. The samples were chosen to provide examples of rocks with a range of TOC contents and Hydrogen and Oxygen Indices within each stratigraphic interval. The majority of the samples were pieces of core, cut perpendicular to bedding. Some core samples were coarsely crushed, if too friable to cut, and some drill cuttings samples were also examined. Each major particle type is discussed below.

5.1.3 Results

Fluorescing Groundmass

All samples, except limestones, are characterized by a fluorescing groundmass, with the colour of the fluorescence under blue-light excitation ranging from yellow through green to brownish-green. Figure 42a shows a typical example of a fluorescing groundmass. Limestone samples exhibit an overall fluorescence (Figure 42b), however this is very probably mineral fluorescence. The fluorescence intensity of actual fluorescing groundmass generally decreases as a function of increasing thermal maturity. The weakest
Figure 42. a) (top) Typical example of fluorescing groundmass. b) (bottom) Limestone exhibiting mineral fluorescence. Photographed under blue light. Magnification 160X.
fluorescence observed was in a sample from the 6-10-39-9W5M well. This nearly non-fluorescent sample is characterized by low TOC (0.92%) and high Tmax (447°C). Brownish green-fluorescing groundmass was noted only in Zones A and C (Figures 43 a and b). The brownish-green fluorescing groundmass occurs in the richest samples (TOC > 4% in Zone C; TOC>1.25% in Zone A) and appears to be related to the presence of large amounts of brown-fluorescing bituminite (discussed below).

Liptodetrinite

In the majority of samples the particulate (i.e., non-amorphous) fluorescing kerogen is dominated by liptodetrinite (Figures 42a and 43a). This material could be *Nostocopsis* algae as suggested by other workers for similar material (e.g.. Stasiuk and Goodarzi, 1988), however liptodetrinite from other sources is impossible to distinguish from *Nostocopsis* in polished sections (Teichmuller, 1986). Liptodetrinite is especially abundant in leaner samples. In organically richer samples the liptodetrinite is relatively less important due to the larger proportions of other fluorescing kerogen types.

Brown-Fluorescing Bituminite

Another important kerogen type is stringy, brown-fluorescing bituminite, which is brown and somewhat granular in appearance in reflected white light. It occurs as diffuse
Figure 43. a) (top) and b) (bottom). Examples of brownish-green fluorescing groundmass. Photographed under blue light. Magnification 160X.
bodies, elongate parallel to bedding, although it is
difficult to define the extent of some occurrences which
grade into the fluorescing groundmass (Figure 43a, 43b and
44a). It contains abundant inclusions of yellow-fluorescing
liptodetrinite, characteristic of bituminite type I
(Teichmuller and Ottenjann, 1977). The liptodetrinite
inclusions are also usually oriented parallel to the
bedding. In some examples the inclusions are elongate and
constitute the maceral lamalginite (Figure 45a), discussed
further below. There are also examples of brown fluorescing
bituminite with few or no inclusions of liptodetrinite
(Figures 44b and 45b); however, this material is much less
common than that which does contain the inclusions. The
fluorescence colour of the bituminite ranges from orange-
brown to dark brown. Bituminite of this type is present in
all zones except Zone E, but occurs only rarely in Zone A.
Bituminite is more common in samples with higher TOC
contents and lower levels of thermal maturity. Less intense
fluorescence and darker fluorescence colours characterize
more thermally mature samples. Some very mature samples
(from the Fish Scale Zone in 6-10-39-9W5M with an average
Tmax of 447°C) contain none of this bituminite, although it
may be present but not recognizable due to lack of
fluorescence. A non-laminated (bioturbated) sample (from
well 4-19-39-5W5M, 7060 ft.) from Zone C, with a high OI of
29 mg CO₂/g TOC contains only very weakly fluorescing
bituminite of this type, while more intensely fluorescing
Figure 44. a) (top) and b (bottom). Examples of brown-fluorescing bituminite. Photographed under blue light. Magnification 160X.
Figure 45. a) (top) Brown-fluorescing bituminite with common lamalginite inclusions. b) (bottom) Brown-fluorescing bituminite with less abundant inclusions, consisting of liptodetrinite. Photographed under blue light. Magnification 160X.
examples were noted in laminated samples from the same zone in the same well.

Alginite

Fluorescing structured algal forms and thin filamentous algal material (lamalginite) occur in many samples. Both varieties exhibit yellow fluorescence and are reddish brown in reflected white light. Lamalginite is much more abundant than the structured algal bodies and is a relatively major component of the fluorescing organic fraction. It consists of relatively featureless, elongate thread-like yellow-fluorescing material oriented parallel to bedding (Figure 44a). In general there is a direct qualitative relationship between increasing amounts of lamalginite and increasing sample TOC and HI. Maturation also plays a role in the distribution of lamalginite. Samples from the Second White Specks in the 7-19-45-6W5M well (with an average Tmax value over the interval of 444°C) contain little or no lamalginite, whereas it is present in other, less mature samples from the same interval. The other quite mature strata from which samples were examined were sampled from the 6-10-39-9W5M well. These samples from the Fish Scale Zone also contain no lamalginite, however lamalginite is abundant in less mature samples of the same interval at 14-32-31-2W5M (Tmax=436°C).

Included with the structured algal bodies are yellow-fluorescing Tasmanites-type algae which occur at all
stratigraphic levels, except Zone A. Two typical examples are shown in Figures 46a and 46b. The tasmanitids are relatively minor components, and occur more commonly in more organic-rich samples. They are recognized by their thick-walled nature, punctae (although these are only very rarely visible) and morphology.

Leiosphere-type algae, similar to those described from the Shaftesbury Formation by Leckie et al. (1990), are present at all stratigraphic levels. They are thin-walled and may be ornamented (Figures 47a and b). There is an anomalous occurrence of moderately abundant small algal bodies in a sample from Zone A in 6-15-28-2W5M (Figures 48a and b). This sample is from the thinnest section of Zone A in the study area, presumably close to the western paleoshoreline, and the unusual concentration of small algae may represent a community influenced by the paleogeography.

Of presumed algal origin are also very large, generally tabular bright-yellow fluorescing objects, unique within the study interval to the Fish Scale Zone. Examples are shown in Figures 49a and 49b. In reflected light they are reddish-brown in colour, similar to the recognized algal forms.

Dinoflagellates

Dinoflagellates, in most examples relatively formless but more rarely well-preserved, are present throughout the section as accessory components. Their occurrence is
Figure 46. a) (top) and b) (bottom). Examples of *Tasmanites* algae. Photographed under blue light. Magnification 160X.
Figure 47. a) (top) and b) (bottom). Examples of leiosphere algae. Photographed under blue light. Magnification 160X.
Figure 48. a) (top) and b) (bottom). Small leiospheres from well 6-15-28-2W5M. Photographed under blue light. Magnification 160X.
Figure 49. a) (top) and b) (bottom). Large, brightly fluorescing bodies unique to the Fish Scale Zone. Photographed under blue light. Magnification 160X.
unrelated to the TOC or HI of the samples. Figure 50a shows an example of an unusual form.

**Bituminite**
Small, irregular masses of intensely yellow-fluorescing but essentially formless material occurs throughout the section. The origin of this material is unclear. Stasiuk and Goodarzi (1988) refer to similar objects as concentrations of bituminite. Alternatively, this material may have originated from the mechanical destruction of larger fluorescing bodies, possibly algal.

**Sporinite**
Probable sporinite was noted from samples throughout the section except for the Second White Specks; however, it is a very minor component. The sporinite from Zone A shown in Figure 50b is an exceedingly rare occurrence.

**Carbonate Fossil Material**
Also recognizable under blue light are fossil fragments and some fluorescing mineral material. Carbonate grains occur in a number of samples. Shell fragments of *Inoceramus* bivalves are present both as scattered prisms (fragments of the prismatic palisade structure of the shell) and as fragments of bioclastic limestone composed largely of such prisms and called 'inoceramite' (McNeil and Caldwell, 1981). The shell fragments can be recognized by their columnar
Figure 50. a) (top) an unusual form of dinoflagellate. b) (bottom) a rare occurrence of sporinite. Photographed under blue light. Magnification 160X.
habit and by the hexagonal outline of the individual prisms in cross-section (Figures 51a, 51b and 52a). None occur in Zone A samples, and they constitute only rare components of samples from the Fish Scale Zone. They are relatively minor in samples from Zones C through E, but more abundant in samples from the Second White Speckled Shale.

The discrete *Inoceramus* fragments commonly exhibit pale yellow fluorescence. Non-fluorescing examples occur as well. *Inoceramus* limestones are almost invariably fluorescent (Figure 42b), probably due to mineral fluorescence, although it is not clear why some shell fragments do not fluoresce.

Foraminifera, commonly yellow-fluorescing probably as a result of mineral fluorescence, occur in Zone D and especially in the Second White Speckled Shale, scattered in mudstones and in laminae of calcareous siltstone. In some samples the fluorescence is a uniform pale yellow (Figure 52b), however more commonly it has a net-like appearance (Figures 53a and b). Some specimens are non-fluorescent.

Probable ostracods, exhibiting yellow fluorescence, occur in the coarser-grained portions of two samples from the Second White Specks. An example is shown in Figure 54a.

**Fecal Pellets**

Non-fluorescent, granular, flattened-ovoid bodies occur in Zones C (rare), D and the Second White Speckled Shale, often associated with faunal remains (particularly foraminifera). Scanning electron microscope inspection of
Figure 51. a) (top) and b) (bottom) Examples of *Inoceramus* shell fragments. Photographed under blue light. Magnification 160X.
Figure 52. a) (top) *Inoceramus* shell fragment. b) (bottom) Foraminifer. Photographed under blue light. Magnification 160X.
Figure 53. a) (top) and b) (bottom) Examples of foraminifera showing typical net-like fluorescence. Photographed under blue light. Magnification 160X.
these objects shows them to be composed of small fragments, some of which are recognizable as fossil (coccolith?) debris (see Figure 34). They are soluble in cold, dilute hydrochloric and acetic acids, as shown by the results of etching of polished surfaces, confirming that they are composed primarily of carbonate. These bodies are interpreted as fecal pellets based on their similarity to those described by McNeil (1984) and O’Brien and Slatt (1990, p.34-35). In fact these are 'white specks', as originally described by Dawson (1874) in the outcrop of the Favel Formation.

Oil

In several samples bright green fluorescing material was observed, commonly within Inoceramus fragments, presumably in microvugs (Figures 51b and 52a). Less commonly it is present in small fractures in fish fragments (bone and scale) and in small fractures in the rock matrix. In one example it appeared to exude from a fracture and cloud the immersion oil. This material, although rare, occurs in the Fish Scale Zone, Zones D and E and the Second White Speckled Shale. In reflected light some Inoceramus prisms with inclusions of this substance exhibit internal prismatic effects ('rainbows'). The green fluorescing material is interpreted to be generated oil, based on its mode of occurrence and on its similarity to other known examples (Robert, 1984; Teichmuller 1986).
Fluorescing Micaceous Material

In many of the coarse grained samples examined the principal particulate fluorescing constituent is fine-grained micaceous material, which displays a yellow fluorescence (Figures 54b, 55a and b). The colour of the mica in reflected light changes from almost transparent to black with increasing maturation. However there is no obvious change in the fluorescence colour or intensity with increases in maturation.

Fish Debris

Fish debris, largely scale fragments but also some bone, is found as a minor constituent throughout the study interval. It is characteristically laminated in appearance and may display weak brown fluorescence (Figure 56a). Figure 56b shows a view of a scale showing growth rings. In both this example and the fish bone fragment shown in Figure 57 the pores are filled with yellow-fluorescing exudatinite.

Vitrinite, Semi-Fusinite and Fusinite

Amongst the non-fluorescing organic constituents are vitrinite, semi-fusinite and fusinite. The vitrinite occurs both as small discrete fragments, and as irregular 'stringy' material, apparently the more mature equivalent of the stringy huminite of Stasiuk and Goodarzi (1988). Other discrete particles, superficially similar to the vitrinite but with significantly higher reflectance, also are present
Figure 54. a) (top) Ostracod. b) (bottom) fluorescing mineral grain. Photographed under blue light. Magnification 160X.
Figure 55. a) (top) and b) (bottom) Fluorescing mineral matter. Photographed under blue light. Magnification 160X.
Figure 56. a) (top) Cross section of fish scale. b) (bottom) Fish scale showing growth rings. Photographed under blue light. Magnification 160X.
Figure 57. Fish bone. Note yellow-fluorescing exudatinite in pores. Photographed under blue light. Magnification 160X.
and may be semi-fusinite or recycled vitrinite. Some obvious semi-fusinite is present, with well-defined cell structure. Highly reflecting fusinite also occurs, and very rare sclerotinite. These terrestrial materials are minor constituents of the rocks, although more common in coarser lithologies. Vitrinite is much less common than semi-fusinite (recycled vitrinite?) and fusinite.

5.2 Pyrolysis Data

5.2.1 Introduction

Rock-Eval pyrolysis is a standard technique for characterization of sedimentary organic matter (Peters, 1986). The Rock-Eval instrument records the volumes of gases evolved during a pre-programmed heating cycle carried out first under an inert and then an oxidizing atmosphere. The chart-recorder output of the measurements is known as a pyrogram (Figure 58).

The first peak output, S1, represents light hydrocarbons (generated oil) present in the sample. S2 results from the hydrocarbons evolved by thermal degradation of the kerogen. S3 represents carbon dioxide generated from oxygen-rich organic matter. S4 is the result of CO₂ produced by oxidation of whatever organic matter survives the pyrolysis phase. S4 is not output on the pyrogram, but is used along with S2 and S3 to calculate total organic carbon content (TOC).
Figure 58. Typical pyrogram (Rock-Eval output). Significance of peaks explained in text. From Peters (1986).
The temperature of peak generation of hydrocarbons during the S2 phase is called Tmax and varies directly with the sample’s level of thermal maturity.

Using S1 to S4 the instrument calculates a number of parameters in addition to TOC. Hydrogen Index (S2/TOC) can be correlated to the elemental hydrogen/carbon ratio of the kerogen. Oxygen Index (S3/TOC) is related to the oxygen/carbon ratio. Hydrogen Index and Oxygen Index are commonly abbreviated as HI and OI, respectively. HI and OI can be used to characterize kerogen as Type I, II or III by plotting the values on what is known as a modified van Krevelen diagram (see, for example, Figure 59).

5.2.2 Results

5.2.2.1 General

The following discussion is concerned with the mudstones and argillaceous siltstone rock types which dominate the study interval. Data concerning the much less common coarser-grained lithologies is discussed in Section 7.4.

The vast majority of the samples from all zones plot in the Type I/Type II field on a modified van Krevelen diagram (Figures 59 to 64). TOC values in the entire data set range up to 6.02%, and HI values reach a maximum of 581. Oxygen Indices are low, mainly less than 25.
Figure 59. Modified Van Krevelen diagram for fine-grained fraction samples, Zone A. Position of Zone A is indicated on the resistivity log.
Figure 60. Modified Van Krevelen diagram for fine-grained fraction samples, Fish Scale Zone. Position of Fish Scale Zone is indicated on the resistivity log.
Figure 61. Modified Van Krevelen diagram for fine-grained fraction samples, Zone C. Position of Zone C is indicated on the resistivity log.
Figure 62. Modified Van Krevelen diagram for fine-grained fraction samples, Zone D. Position of Zone D is indicated on the resistivity log.
Figure 63. Modified Van Krevelen diagram for fine-grained fraction samples, Zone E. Position of Zone E is indicated on the resistivity log.
Figure 64. Modified Van Krevelen diagram for fine-grained fraction samples, Second White Speckled Shale. Position of Second White Speckled Shale is indicated on the resistivity log.
TOC and HI are positively correlated, although there are only weak relationships for the samples from the Second White Speckled Shale. The data are plotted on Figures 65 through 70. In an attempt to account for effects of thermal maturation, the equations and $r^2$ values for the multiple regression of HI on TOC and Tmax are also shown on the graphs.

5.2.2.2 Stratigraphic Variations

Stratigraphic patterns of TOC content are remarkably consistent between wells. The stratigraphic profiles of TOC, HI and OI from a typical well is shown in Figure 71. TOC increases upsection from the contact between the Viking Formation and Zone A, then increases relatively sharply into the Fish Scale Zone. This transition into the Fish Scale Zone is less apparent in profiles from wells with only drill cuttings samples which tend to average the TOC profiles somewhat. In cored wells (e.g. 14-32-31-2W5M, Figure 72), the abruptness of the transition is more obvious.

TOC decreases above the Fish Scale Zone and subsequently increases upwards to what is in many wells its highest value, in Zone C immediately below the contact with Zone D. TOC then decreases upwards through Zone D, and is low and relatively constant in Zone E. It increases abruptly into the Second White Speckled Shale (again, the transition being more evident in cores wells than in those with only
Figure 65. TOC vs. Hydrogen Index, Zone A.
Figure 66. TOC vs. Hydrogen Index, Fish Scale Zone.
Figure 67. TOC vs. Hydrogen Index, Zone C.
Figure 68. TOC vs. Hydrogen Index, Zone D.
Figure 69. TOC vs. Hydrogen Index, Zone E.
HI = 3796 + 52.4TOC - 8.34Tmax

r squared = 0.60

Figure 70. TOC vs. Hydrogen Index, Second White Speckled Shale.
Figure 71. Geochemical profile, well 16-9-37-5W5M.
Figure 72. Geochemical profile through Zone A and the Fish Scale Zone, well 14-32-31-2W5M.
drill cuttings). TOC decreases above the Second White Speckled Shale.

Table 3 shows the average TOC, HI and OI values for each stratigraphic level and TOC histograms for each zone are presented as Figures 73 through 78. The highest average TOC (2.72%) lies within Zone C, largely on the strength of the high values at the top of the zone. Zone D (2.54%), the Second White Speckled Shale (2.35%) and the Fish Scale Zone (2.36%) also record high average TOC values, with the lowest organic carbon contents being in Zones E (1.92%) and A (1.61%).

5.2.2.3 Lateral Variations

In order to examine lateral variations in organic character, maps were prepared for each zone showing the distribution of TOC, HI and OI (Figures 79 to 96). The mapped values are the mean values at each well location. Maps of Tmax values are presented in the section concerning thermal maturity (Section 6).

For all zones, HI decreases to the west. Oxygen Indices do not show any obvious pattern for any zone.

TOC in Zone A generally decreases to the west and northwest, although the highest value is in the central part of the study interval at 14-7-36-5W5M. A general westward TOC decrease is also evident for the Fish Scale Zone, Zone C, Zone D and Zone E. The TOC distribution within the Second
<table>
<thead>
<tr>
<th>Zone</th>
<th>TOC</th>
<th>HI</th>
<th>OI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Second White Specks</td>
<td>2.36</td>
<td>240</td>
<td>11</td>
</tr>
<tr>
<td>Zone E</td>
<td>1.92</td>
<td>183</td>
<td>11</td>
</tr>
<tr>
<td>Zone D</td>
<td>2.54</td>
<td>209</td>
<td>10</td>
</tr>
<tr>
<td>Zone C</td>
<td>2.72</td>
<td>243</td>
<td>10</td>
</tr>
<tr>
<td>Fish Scale Zone</td>
<td>2.36</td>
<td>226</td>
<td>13</td>
</tr>
<tr>
<td>Zone A</td>
<td>1.62</td>
<td>152</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3. Average values of pyrolysis parameters.
Figure 73. Distribution of TOC values, Zone A.
Figure 74. Distribution of TOC values, Fish Scale Zone.
Figure 75. Distribution of TOC values, Zone C.
Figure 76. Distribution of TOC values, Zone D.
Figure 77. Distribution of TOC values, Zone E.
Figure 78. Distribution of TOC values, Second White Speckled Shale.
Zone A

Figure 79. TOC map, Zone A.
Figure 80. Hydrogen Index map, Zone A.
Zone A

Oxygen Index

25 kilometres
C.I. = 5 mg CO₂ / g org. C

Figure 81. Oxygen Index map, Zone A.
Figure 82. TOC map, Fish Scale Zone.
Figure 83. Hydrogen Index map, Fish Scale Zone.
Figure 84. Oxygen Index map, Fish Scale Zone.

Oxygen Index

25 kilometres
C.I. = 5 mg CO₂ / g org. C
Figure 85. TOC map, Zone C.
Figure 86. Hydrogen Index map, Zone C.

Hydrogen Index map, Zone C

C.I. = 50 mg HC / g org. C

25 kilometres
Figure 87. Oxygen Index map, Zone C.

Oxygen Index

25 kilometres

C.I. = 5 mg CO₂ / g org. C
Figure 88. TOC map, Zone D.
Figure 89. Hydrogen Index map, Zone D.
Figure 90. Oxygen Index map, Zone D.
Figure 91. TOC map, Zone E.
Figure 92. Hydrogen Index map, Zone E.

Hydrogen Index

25 kilometres

C.I. = 50 mg HC / g org. C
Figure 93. Oxygen Index map, Zone E.
Figure 94. TOC map, Second White Speckled Shale.
Figure 95. Hydrogen Index map, Second White Speckled Shale.
Second White Speckled Shale

Oxygen Index 25 kilometres
C.I. = 5 mg CO₂ / g org. C

Figure 96. Oxygen Index map, Second White Speckled Shale.
White Speckled Shale does not exhibit any particular pattern.

5.3 Stable Carbon Isotope Data

5.3.1 Introduction

The ratios of stable isotopes of carbon $^{13}$C and $^{12}$C, are commonly used to characterize recent and ancient sedimentary organic matter, especially with regard to the relative contributions of marine and terrestrial fractions to the total organic matter. Modern land plants are in general depleted in $^{13}$C as compared to marine phytoplankton and studies of modern sediments show an increase in the $^{13}$C of organic matter away from sources of terrestrial input (e.g., Hedges and Parker, 1976; Gearing et al., 1977).

Large scale stratigraphic variations in the stable carbon isotope ratios of Cretaceous strata have been documented. A large positive (heavy) excursion bracketing the Cenomanian-Turonian stage boundary and co-incident with an 'Oceanic Anoxic Event' has been documented from many localities and is believed to have been a global event (Schlanger and Jenkyns, 1976; Schlanger et al., 1987). The cause is generally ascribed to the burial of large amounts of organic matter, which is isotopically light, leaving a carbon pool for further biological activity enriched in the heavier isotope. The Second White Speckled Shale is co-incident with the isotope anomaly, and provides an
opportunity to compare the organic matter deposited during the anomaly with that deposited in the underlying beds.

5.3.2 Results

The data from the Second White Speckled Shale are examined separately from that pertaining to the rest of the study interval due to the influence of the Cenomanian-Turonian isotope anomaly, the magnitude of which in the organic matter examined in this study is about 1.5 °/oo. The anomalously heavy values associated with samples from the Second White Speckled Shale can be seen in the stratigraphic plot of $^{13}$C data from one location in the central part of the study area (Figure 97).

The $^{13}$C values of organic matter from the study interval (exclusive of data from the Second White Speckled Shale) range between about -27 and -25 °/oo. Values of about -26 to -24 °/oo characterize the Second White Speckled Shale.

Within the dataset from Zones A to E there is a fair negative correlation between TOC and $^{13}$C; the organic matter in richer samples is isotopically lighter than in leaner ones (Figure 98). The data from Zone E actually appear to follow a positive TOC - $^{13}$C relationship, however the sampled TOC range is small and a negative relationship might possibly be established with more data. The Fish Scale Zone data, although falling within the pattern of scatter
Figure 97. $\delta^{13}C$ and TOC profile, well 16-9-37-5W5M.
Figure 98. TOC vs. $\delta^{13}$C, Zones A through E.
for the entire data set do not themselves exhibit any correlation between $\delta^{13}C$ and TOC.

Hydrogen Index and $\delta^{13}C$ are only weakly correlated (Figure 99). Given the correlation between TOC and Hydrogen Index along with the $\delta^{13}C$-TOC relationship, the weak $\delta^{13}C$-HI correlation is difficult to explain, but might be an artifact of the relatively small sample size.

The data from the three most thoroughly sampled sections, in wells 6-15-28-2W5M, 16-9-37-5W5M, and 7-19-45-6W5M (in the southern, central and northern portions of the study area) were examined on a well-by-well basis. Good negative correlations between $\delta^{13}C$ and TOC are exhibited by the data from all three locations (Figure 100). The correlation line for the data from 6-15-28-2W5M differs from those corresponding to the other two sections in having a steeper slope and a more negative intercept on the $\delta^{13}C$ axis. However the isotopically heavy points from the 6-15-28-2W5M data set which influence the regression are all from Zone A, which is represented by only one point in the data from 16-9-37-5W5M and none at all from 7-19-45-6W5M. By removing the 6-15-28-2W5M Zone A points from the analysis it can be seen that all three datasets exhibit very similar TOC - $\delta^{13}C$ correlations over the rest of the study interval (Figure 101).

Analysis of samples from the Second White Speckled Shale show only a weak TOC-$\delta^{13}C$ relationship (Figure 102), the sense of which is positive, opposite to that shown by
Figure 99. Hydrogen Index vs. $\delta^{13}$C, Zones A through E.
Figure 100. TOC vs. $\delta^{13}$C, Zones A through E, from the three most thoroughly-sampled wells.
Figure 101. TOC vs. $\delta^{13}$C, Zones A through E, from the three most thoroughly-sampled wells. Zone A samples from well 6-15-28-2W5M excluded.
Figure 102. TOC vs. δ¹³C, Second White Speckled Shale.
the data from the underlying zones. The $\delta^{13}C$ - HI relationship is also positive, and stronger than the $\delta^{13}C$ - TOC correlation (Figure 103). This difference between the strength of the correlations between $\delta^{13}C$ and TOC on the one hand and HI on the other is, as with the data from Zones A to E, difficult to explain but possibly a consequence of the small sample size.

Analyses of small numbers of bioturbated samples from Zone A and the Second White Speckled Shale do not reveal any differences in isotopic signature between bioturbated and laminated samples (Figure 104).

Plots of isotope ratios obtained from coarser versus finer grained rocks show no differences (Figures 105 to 107). However, comparisons between data from siltstones and immediately adjacent mudstones (less than 1 cm stratigraphic separation) from the Fish Scale Zone and the Second White Speckled Shale show the organic matter in the siltstones to be isotopically lighter in all samples (Figure 108).

5.4 Discussion

All the data indicate a largely marine character for the organic matter, with only a minor terrestrially-derived component.

The organic petrography supports a largely marine autochthonous origin for the kerogen. High TOC and HI samples are characterized by abundant fluorescing groundmass, lamalginite and brown-fluorescing bituminite.
Figure 103. Hydrogen Index vs. $\delta^{13}$C, Second White Speckled Shale.
Figure 104. TOC vs. δ¹³C, bioturbated vs. laminated samples.
Figure 105. TOC vs. $\delta^{13}$C, siltstone samples vs. samples of mudstone / argillaceous siltstone, Zone A.
Figure 106. TOC vs. δ¹³C, siltstone, sandstone and mudstone / argillaceous siltstone, Fish Scale Zone.
Figure 107. TOC vs. $\delta^{13}$C, siltstone, limestone and mudstone / argillaceous siltstone, Second White Speckled Shale.
Figure 108. $\delta^{13}C$ contrast between siltstone samples and immediately adjacent samples of mudstone or argillaceous siltstone.
The decrease in both the abundance of these components and their fluorescence intensity with increasing thermal maturation suggests they are the most important oil-generating constituents. Brown-fluorescing bituminite appears to be the most reactive, completely absent in strata deposited under more oxygenated conditions. Lamalginate and fluorescing groundmass are both of probable algal origin (Largeau et al., 1990; Derenne et al., 1991). The origin of the brown-fluorescing bituminite is less certain. The large number of liptodetrinite inclusions in most samples may suggest that the material is fecal. However the oriented nature of the inclusions (parallel to bedding) and the observation that the bituminite grades to fluorescing groundmass argue against a fecal origin. More likely, the bituminite may represent larger fragments of laminated algal material which trapped liptodetrinite on a sticky surface. A third possibility is that the inclusions were functional parts of the bituminite’s precursor organism, however the lack of inclusions in some examples of bituminite does not support this interpretation.

Recognizable algal forms, tasmanitids and leiospheres, are only secondary components. Their survival when much other material was apparently altered to fluorescing groundmass suggests they are relatively resistant components. Because of this resistance to alteration, and their relatively small contribution to the total kerogen, they are probably not major oil-producing components.
Liptodetrinite is apparently most resistant to degradation amongst the fluorescing kerogen types. It is the dominant material in lean (low TOC and HI) samples, where more reactive material has presumably been destroyed. Zone A, deposited in the most oxygenated setting of any of the studied strata, is dominated by liptodetrinite. This material is also the most common fluorescing kerogen in the lean samples of Zone E.

Disintegration of any fluorescing kerogen type could produce liptodetrinite (Ward, 1984 p.85) which would presumably represent the most resistant portions of the parent organic matter.

The predominance of liptodetrinite in lean, low HI samples suggests it is not an important hydrocarbon-producing element. Powell and Boreham (1991), studying terrestrial settings, noted that samples of coal and source rocks rich in liptodetrinite (and sporinite) give lower yields of normal hydrocarbons than samples richer in other liptinite macerals.

Organic matter of terrestrial origin is rare. Although relatively more abundant in leaner samples due to the lack of much marine kerogen and possibly also to increases in terrestrial input, terrestrially-derived material is nonetheless uncommon. Oxygen Index values (discussed below) are low for samples spanning the entire range of TOC values encountered, indicating low vitrinite content. It therefore appears that the study area was sufficiently far from any
sources of terrestrial kerogen input that the autochthonous marine influence was dominant.

The non-fluorescent ovoid bodies recognized in several samples appear to be the same as those referred to as bituminite III by Stasiuk and Goodarzi (1988). These have been shown to be 'white specks', fecal pellets composed largely of calcite. Doubtless some organic matter is present in material of fecal origin, however these bodies are probably unimportant in terms of source rock potential.

The presence of green-fluorescing oil is consistent with Tmax values (discussed in Section 6) indicative of 'oil window' levels of thermal maturation. The presence of oil within Inoceramus shell prisms is most significant. In zones, such as the Second White Speckled Shale, with abundant Inoceramus debris, it is conceivable that large volumes of oil could reside within the bioclastic carbonate grains. If much of the generated oil remains within the source rock, expulsion efficiency may have been low and the possibility exists that under appropriate conditions, such as reservoir enhancement by fracturing, these Inoceramus-rich zones could be oil reservoirs.

The distribution of organic matter types is not related to stratigraphic level, but rather to organic richness. Kerogen assemblages are similar in samples with similar TOC values from different zones. The types of organic matter available for incorporation into the sediments are therefore believed to have been similar throughout deposition of the
rocks in the study interval. The observed variations in most cases do not seem to be due to dilution by mineral matter. Leaner samples do not simply contain a diluted version of the kerogen assemblage found in richer samples, but are dominated by more resistant macerals, in particular liptodetrinite. Variations in the composition of the primary producers could explain the kerogen differences. However, because samples with similar kerogen constituents can be found at all stratigraphic levels this hypothesis would require somewhat periodic oscillations in phytoplankton composition which would be difficult to explain. Variations in the magnitude of primary productivity could be used to explain the variations in organic content. In low productivity settings the limited amount of labile organic debris might be more completely metabolized by bacteria than in higher productivity settings in which there could be excess organic matter. Destruction of organic matter could also occur while settling through a deep water column. More complete destruction of labile material, unrelated to primary productivity variations, could also result from very low sedimentation rates allowing for longer exposure of the organic matter at or near the sediment-water interface. Higher sedimentation rates generally correspond to greater degrees of preservation of organic matter regardless of depositional oxygen concentrations (Curtis, 1987; Betts and Holland, 1991).
One stratigraphically-restricted organic matter type does occur, however. In the Fish Scale Zone large, tabular bodies of presumed algal origin are present which do not occur anywhere else in the section. Their significance is unclear.

Geographic variations in kerogen type consist of westerly decreases in the content of more labile kerogen (fluorescing groundmass, brown-fluorescing bituminite and lamalginite). These variations are very probably the result of higher levels of thermal maturation.

The pyrolysis data also support a marine origin for most of the kerogen, as the vast majority of the samples plot within the Type I/II field of a modified van Krevelen diagram. A discussion of the stratigraphic variations in TOC are included in the discussion of the depositional model (Section 9).

The decrease in HI concomitant with the increase in Tmax to the west and the fact that, on modified Van Krevelen diagrams variation between samples occurs along the Type curves and not across fields, suggests the organic matter type does not vary significantly either throughout the area or stratigraphically. Terrestrial (vitrinite) input was low.

Lateral variations in TOC are relatively minimal. Much of the westward decrease in TOC for all zones is explained by TOC loss due to increased levels of thermal maturation.

The stable carbon isotope data of the organic matter also suggest a marine origin. Given the petrographic and
pyrolysis evidence that higher TOC values characterize samples containing larger amounts of marine-derived organic matter, the negative correlation between isotope ratios and TOC for Zones A through E suggests marine organic matter is isotopically lighter than terrestrial material, the opposite of the modern situation. This reversal of isotopic character is well-documented for Cretaceous rocks. The most commonly accepted hypothesis of this phenomenon is that under the higher partial pressures of CO2 believed to have prevailed during Cretaceous time, phytoplankton fractionate carbon isotopes differently than at present, resulting in lighter marine organic matter. Terrestrial material was not similarly affected (Popp et al., 1989). Although still somewhat controversial, the hypothesis that isotopically light organic matter indicates high paleo-concentrations of CO2 has much support. It is certainly consistent with evidence of a warm Cretaceous climate.

The TOC - δ13C correlation is very weak for the data from the Second White Speckled Shale, deposited during the Cenomanian-Turonian isotope anomaly. The negative sign of the correlation relationship may suggest a change in the isotope fractionation behavior of phytoplankton as a result of a lowering of atmospheric CO2 concentrations.

The interpretation of the paired siltstone - mudstone sample data from the Fish Scale Zone presents some difficulties. In the Second White Speckled Shale, organic matter in siltstones is isotopically lighter than that in
mudstones. Siltstones contain less organic carbon and presumably more terrestrial organic matter that do mudstones. The positive TOC - \( \delta^{13}C \) relationship exhibited by all the Second White Speckled Shale samples suggests organic matter in leaner samples (siltstones) should be lighter, consistent with the observations. However, in the Fish Scale Zone, isotopically lighter organic matter should characterize richer (mudstone) samples, if the negative TOC - \( \delta^{13}C \) relationship shown in Figure 98 is accepted. One possible explanation is that the Fish Scale Zone may, like the Second White Speckled Shale, represent an episode of lowered atmospheric levels of CO\(_2\). It should be noted in this regard that the TOC and \( \delta^{13}C \) values for this interval examined on its own show little correlation (as is the case for the Second White Speckled Shale) and this may indicate a change in phytoplankton isotope fractionation.

From a study of the Campanian Lea Park Formation of Saskatchewan, Whittaker and Kyser (1990) determined that terrestrial organic matter in that interval is characterized by a \( \delta^{13}C \) value of about -24 \(^{0}/oo\). Marine organic matter has a stable carbon isotope ratio of about -32 \(^{0}/oo\). These values would suggest that the organic matter examined in the present study, with carbon isotope ratios in the range of about -25\(^{0}/oo\) to -27\(^{0}/oo\), is largely of terrestrial origin. Such a conclusion is in conflict with the pyrolysis and petrographic data, all of which points toward a mainly marine origin for the organic matter. The differences
between the results of this study and that of Whittaker and Kyser (1990) may suggest some temporal variation in isotope ratios.

The Cenomanian-Turonian isotope anomaly is addressed in a separate discussion of a depositional model for the rocks of the study interval.

6. Thermal Maturity

6.1 Introduction

It is a fundamental premise of the organic theory of petroleum origin that as organic matter in rocks is subjected to increasing temperatures over time, a fraction of the organic matter is converted to fluid hydrocarbons. The timing, rate and extent of this conversion depend largely on the organic matter type and on the time-temperature history of the sediments containing the kerogen (Tissot and Welte, 1984).

Levels of thermal maturity can be measured in a number of ways. In this study the principal maturation parameter used is the Tmax measurement derived from Rock Eval pyrolysis. This value, the temperature of maximum pyrolysate generation during the S2 phase, increases with increasing maturity. Although Tmax can be influenced by a number of factors other than maturity, such as sample size (Peters, 1986), it is a relatively reliable indicator of thermal
maturity, especially for Type II kerogen (Espitalie, 1986). The main phase of liquid oil generation (the 'oil window') generally occurs at Tmax values between 435°C and 465°C or 470°C (Espitalie et al., 1977; Peters, 1986). Tmax values were obtained for all samples in the study.

Perhaps the most commonly used measure of thermal maturity is vitrinite reflectance, generally performed with oil immersion objectives and designated Ro (reflectance in oil). Ro increases with maturation. Mean vitrinite reflectance values from ten samples from Zone A were measured, and the relation between Tmax and Ro examined. Zone A was selected because of the possibility that the lowermost interval in the transgressive sequence might contain the largest amounts of terrestrial organic matter although further petrographic work did not show this to be true. The relatively lean nature of the interval, however, does avoid the potential for suppression of vitrinite reflectance possible in alginate-rich rocks (Price and Barker, 1985).

In order to examine the possible relationships between thermal maturity on one hand and TOC, Hydrogen Index and Oxygen Index on the other, correlations were made between these values on a zone by zone basis. Maps were prepared to illustrate lateral variations in maturation within each interval.
6.2 Results

Figure 109 shows the strong correlation between vitrinite reflectance and Tmax. Note that the Tmax values used are the average values for the zone in each sampled well. Because Tmax can vary several degrees between adjacent samples the average value for the zone is used. For the samples examined in this study the oil window bounding Tmax values of 435°C and 465°C correspond to Ro values of 0.59% and 1.21%, respectively.

In the following discussion of the relationship between TOC and thermal maturity expressed as Tmax, a linear relationship is assumed. The actual relationship between the fraction of organic matter converted to petroleum and thermal maturation is unfortunately not linear (Espitalie et al., 1985). However the portion of the transformation ratio curve between Tmax values of about 430°C and 510°C is approximately linear. The distribution of average Tmax values in this study is shown in Figure 110. The majority of the values fall within the linear portion of the curve, so the use of linear regression in the following analysis is justified. The linear form of the relationship also facilitates multiple linear regression in the evaluation of the other influences in TOC, discussed later in this thesis.

TOC decreases with Tmax for all zones except Zone E and the Second White Speckled Shale (Figures 111 to 116), however the correlations are weak. Stronger negative
Figure 109. Relationship between Tmax and vitrinite reflectance.
Figure 110: Distribution of Tmax values in all samples of fine-grained fraction.
Figure 111. Tmax vs. TOC, Zone A
Figure 112. Tmax vs. TOC, Fish Scale Zone.
Figure 113. Tmax vs. TOC, Zone C.
Figure 114. Tmax vs. TOC, Zone D.
Figure 115. Tmax vs. TOC, Zone E.
Figure 116. Tmax vs. TOC, Second White Speckled Shale.
correlations exist between Hydrogen Index and Tmax for all zones (Figures 117 to 122). Oxygen Index is uncorrelated to Tmax (Figures 123 to 128).

Given the relatively good correlations between Tmax and Hydrogen Index, it is possible to gain some idea of the average Hydrogen Index value of the organic matter at an immature stage of thermal evolution. This can be done by determining the HI value at the point at which the HI-Tmax regression line crosses the Tmax value corresponding to the onset of oil generation. If the top of the oil window is assumed to occur at a Tmax value of 430°C the corresponding HI values for the six zones are shown in Table 4. The highest 'original' Hydrogen Indices determined in this manner are in the Fish Scale Zone and Zone C. Zone D and the Second White Speckled Shale are characterized by somewhat lower values, and the lowest values are associated with Zones E and A.

Maps of Tmax for each zone are included as Figures 129 to 134. The entire study interval is sufficiently thin that there are no substantial differences between the maps. All show an increase in thermal maturation generally to the west-northwest. The 'iso-Tmax' contours are, somewhat surprisingly, oblique to the northwest trend of the thrust belt. The maps show that maturation levels in the study interval span the entire oil window.
Zone A

$r^2 = 0.56$

Figure 117. $T_{max}$ vs. Hydrogen Index, Zone A.
Figure 118. Tmax vs. Hydrogen Index, Fish Scale Zone.
Figure 119. Tmax vs. Hydrogen Index, Zone C.
Figure 120. Tmax vs. Hydrogen Index, Zone D.
Figure 121. Tmax vs. Hydrogen Index, Zone E.
Figure 122. Tmax vs. Hydrogen Index, Second White Speckled Shale.
Figure 123. Tmax vs. Oxygen Index, Zone A.
Figure 124. Tmax vs. Oxygen Index, Fish Scale Zone.
Figure 125. Tmax vs. Oxygen Index, Zone C.
Figure 126. Tmax vs. Oxygen Index, Zone D.
Figure 127. Tmax vs. Oxygen Index, Zone E.
Figure 128. Tmax vs. Oxygen Index, Second White Speckled Shale.
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<tr>
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<tr>
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<td>309</td>
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<tr>
<td>Zone C</td>
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<td>Zone A</td>
<td>240</td>
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</table>

Table 4. Estimates of pre-maturation Hydrogen Index values, calculated by extrapolating Tmax-HI relationships to a Tmax value of 430°C.
Figure 129. Tmax map, Zone A.
Figure 130. Tmax map, Fish Scale Zone.
Figure 131. Tmax map, Zone C.
Figure 132. Tmax map, Zone D.
Figure 133. Tmax map, Zone E.

Tmax

25 kilometres C.I. = 5°C
Figure 134. Tmax map, Second White Speckled Shale.
7. Evaluation of Possible Controls on Organic Matter Distribution

7.1 Introduction

The results of the previous sections have shown the variation which exists in the distribution of organic matter in the study interval. The effects of post-burial thermal alteration on the organic content of the rocks has been assessed. An attempt is made here to evaluate the influence of some of the possible depositional controls on that distribution as well. Although not an influence, the set of relationships between organic content and major element geochemistry are presented in this section. The clay mineralogy of the strata, sediment grain size, depositional oxygenation conditions and sedimentation rate are all considered. Results are presented for each section, followed by a discussion of all of the topics considered.

7.2 Relationship of Major Element Geochemistry to Organic Content

The data set as a whole shows only a weak ($r^2=0.17$) positive relationship between TOC and calcium content (Figure 135). However when the data is examined on a zone-by-zone basis, more significant relationships emerge for zones C ($r^2=0.75$) and E ($r^2=0.62$). Only these two regression lines are shown on Figure 135. The TOC-calcium relationship
Figure 135. Calcium vs. TOC.
is also evident on the plot of zone-average TOC and calcium content, Figure 136, with an $r^2$ value of 0.49.

There is a weak ($r^2=0.233$) negative correlation between TOC and silicon content (Figure 137), more clearly shown in the plot of zone average values ($r^2=0.64$) (Figure 138). The correlation results mainly from the relationships exhibited by Zone A ($r^2=0.43$), the Fish Scale Zone ($r^2=0.61$) and Zone C ($r^2=0.91$). Only these regression lines are shown on Figure 137. In stratigraphically higher intervals there is little correlation.

In both raw data form and normalized to a calcium-free basis $\text{Al}_2\text{O}_3$ is unrelated to TOC, except for the data from Zone C, which exhibits a fair negative correlation with an $r^2$ value of 0.5 (Figures 139 and 140).

No other relationships to organic carbon were observed in the major element geochemistry data set.

7.3 Clay Mineralogy

7.3.1 Introduction

The common association of organic matter with rocks rich in clay-sized material is well-established (e.g. Bitterli, 1963). The degree of adsorption of organic matter onto clay mineral surfaces could be influenced by clay type, because different mineral species are characterized by significantly different surface properties (Stevenson, 1982). Depositional setting and climate can influence both
Figure 136. Calcium vs. TOC using mean values for each zone.
Figure 137. Silicon vs. TOC.
Figure 138. Silicon vs. TOC, using mean values for each zone.
Figure 139. Aluminum vs. TOC.
Figure 140. $\text{Al}_2\text{O}_3$, vs. TOC, using mean values for each zone.
the clay composition and organic content of sediments (e.g. Pratt, 1984) and the presence of organic matter may also influence diagenetic changes to the clay mineral fraction (Lunkad, 1986). It therefore was considered important to examine the clay mineralogy of the study interval in order to determine if any relationships exist between the composition of the clay fraction and the content of organic matter. Both the clay mineralogy of the rocks and the relationship of the clay mineralogy to the organic content are examined.

7.3.2 Previous Work

Several studies have considered the clay mineralogy of zones wholly or partially correlative to the study interval. Hattin (1971) determined that clay minerals in insoluble residues of samples of the Greenhorn Formation of Kansas consist of smectite, illite, undefined mixed-layer species and kaolinite. Pratt (1984) noted the predominance of mixed-layer illite-smectite clays and discrete illite in the Greenhorn Formation of Colorado. Increases in the amount of illite relative to mixed-layer clays were taken to indicate increased fluvial input to the basin of deposition, and to correlate to wetter climatic periods during which laminated (non-bioturbated) rocks were deposited beneath a salinity-stratified water body.

Macauley et al. (1985) in a study of the Second White Speckled Shale/Favel Formation of Manitoba, Saskatchewan and
eastern Alberta also noted the presence of mixed layer clays, illite and chlorite-kaolinite (undifferentiated). The Boundary Creek Formation of the Northwest Territories contains illite, chlorite and smectite, in that order (Young, 1975). Williams and Bayliss (1988) studied two boreholes in Saskatchewan. They showed the clay minerals in the Westgate, Belle Fourche and Pavel Formations to consist of smectite, illite and kaolinite, although their 'smectite' category also included chlorite, vermiculite and mixed-layer clays.

7.3.3 Results

7.3.3.1 Mineralogy

X-ray diffraction studies of twenty one samples (Table 5) of core material show the presence of two principal clay mineral species in the study interval: illite and kaolinite. Lesser amounts of an ordered mixed layer illite-smectite (IS) clay also occur in most samples. Minor chlorite may also be present in some samples.

Illite is the dominant clay mineral in most samples. It produces a strong peak indicating a basal spacing of about 1 nm (10 Angstroms) in glycolated samples (Figure 141). The peak is generally broad and asymmetric towards lower values of 20 in un-glycolated samples. The peak character results from the presence of a mixed-layer illite-smectite (IS) clay. The IS clay produces a peak sufficiently close to the illite peak that the two peaks are not resolved and the
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Averages By Zone

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Table 5. Clay mineral data from X-ray diffraction and Rock-Eval parameters.

FSZ=Fish Scale Zone; 2WS=Second White Speckled Shale; P.C. Ratio=Peak Contraction Ratio
Untreated

asymmetrical IS + illite peak

~0.7 nm kaolinite peak

Glycolated

~1 nm illite peak

broad, poorly-defined IS peak

Heated to 550°C

~0.7 nm peak destroyed by heating

Well Location: 6-10-37-8W5M  Depth: 2805.9m  Zone A

Figure 141. X-ray diffractograms of a typical sample.
result is a single broad feature. Upon glycolation, however, the IS peak migrates and a sharper illite peak results. Confirmation that the broad nature of the peak was not due to the presence of 'degraded' (K-deficient) illite was obtained by treating several samples with a solution of KCl. No changes in peak character resulted from this treatment (Figure 142).

The presence of a mixed-layer clay with expanding (smectite) layers is indicated by the peak migration discussed above. After glycolation the peak at about 1 nm becomes noticeably sharper in most cases due to the migration of the IS peak from about 1-1.1 nm to 1.2-1.4 nm. This behavior indicates that the IS clay is an ordered variety with relatively few smectite layers and in which single smectite layers are distributed in an illite lattice, no two smectite layers being adjacent (Reynolds and Hower, 1970; Schulz et al., 1980). In disordered IS clays, x-ray diffraction of glycolated samples produces two peaks indicating the basal spacings of the illite and smectite layers (about 1 and 1.7 nm, respectively).

The peak produced by the IS clay in most glycolated samples is sufficiently broad, and of sufficiently low intensity with respect to background to prevent its measurement with confidence. In the few samples in which such measurements were made, the basal spacings of 1.2 to 1.4 nm indicate approximately 65 to 80% illite layers, using the method of Schulz et al. (1980).
Figure 142. Typical sample showing lack of effect of KCl treatment on clay mineral diffraction pattern.
The second most abundant clay mineral in most samples (based on peak heights) is kaolinite, identified on the basis of a peak indicating a basal spacing of about 0.7 nm. This peak is unaffected by glycolation and disappears on heating to 550°C (Figure 141). A small peak at about 1.4 nm in some samples suggests that minor chlorite may be present, but kaolinite predominates. (The 1.4 nm peak survives heating to 550°C, showing that it is not due to the presence of vermiculite.) In order to verify that the 70 nm peak is caused by the presence of kaolinite, several samples were digested in hot (90°C) 6N hydrochloric acid. The survival of the 70 nm peak (Figure 143) confirms that it results from kaolinite because chlorites are destroyed by such acid treatment (Brindley, 1972).

The relative abundances of illite and kaolinite were estimated from the ratios of the peak heights. The IS glycolated peak height was measured in samples where the peak was sufficiently well-defined, although even in these instances confidence is low. An attempt was also made to estimate variations in the amount of IS clay relative to the amount of illite by measuring the contraction of the 1 nm peak (caused by the migration of the IS peak away from the illite peak) before and after glycolation. The width of the peak was measured at half the height between the peak maximum and the background level as measured between the 1 and 70 nm peaks. In a few samples the background readings to the left (lower 2θ) of the 1 nm peak were sufficiently high
Figure 143. Sample diffractograms showing lack of effect of acid treatment on the 0.7 nm peak.
that the peak width had to be measured slightly above half height. The results are expressed as ratios of the 1 nm peak width before and after glycolation, referred to here as the 'peak contraction ratios'. The validity of the peak contraction ratio is not clear, as there is no correlation between this ratio and the ratio of the measured IS to illite peaks (Figure 144). However in the absence of any better way to measure the relative concentration of IS clays, the peak contraction ratio data are presented below.

No systematic variations in clay mineralogy were observed as a function of stratigraphic position. The low values of both illite/kaolinite and mixed-layer clays/kaolinite result from one anomalous point. No lateral variations are apparent either, as differences between samples from the same zone in the same well are generally at least as great as differences between wells (see Table 5).

7.3.3.2 Relationship of Clays to Organic Matter

There are no significant relationships between the illite to kaolinite peak height ratios and any of the Rock-Eval parameters either within the data set as a whole or within subsets separated by stratigraphic interval. Figure 145 shows the lack of correlation between the illite/kaolinite ratio and TOC. There is a strong positive correlation ($r^2 = .81$) between the illite/kaolinite peak height ratios (I/K) and the potassium to aluminum ratios of
Figure 144. Ratio of Mixed Layer IS clay to illite vs. "peak contraction ratio".
Figure 145. Ratio of illite to kaolinite vs. TOC.
the whole rock samples as determined by x-ray fluorescence (Figure 146). If the one anomalous point, which represents a sample with an unusually large amount of kaolinite, is removed from the data set, the correlation is even stronger ($r^2 = .89$). Given this excellent correlation, the K/Al ratios were plotted against TOC in order to evaluate the larger XRF data set. There is no correlation between the K/Al ratio and the source rock parameters provided by the Rock Eval instrument, however (Figure 147).

Variations in the amount of mixed-layer IS clays, as estimated from the peak contraction ratio do not correlate to any Rock-Eval derived parameters for the entire data set, or for individual stratigraphic intervals (Figure 148).

7.4 Grain Size

7.4.1 Introduction

Rocks rich in organic matter, and hydrogen-rich organic matter in particular, are almost invariably fine-grained. The association of organic matter and fine-grained mineral matter has been variously attributed to: 1) adsorption of organic matter onto mineral surfaces (fine-grained rocks and especially those rich in clay minerals have substantially greater surface areas than do coarse-grained rocks); 2) to the hydraulic equivalence of organic matter and clay and silt sized material (Trask, 1939); 3) to the fact that coarse-grained rocks were generally deposited under more
Figure 146. Ratio of Illite to Kaolinite vs. ratio of Potassium to Aluminum.
Figure 147. Potassium to aluminum ratio vs. TOC.
agitated and therefore presumably more oxygenated conditions (DeMaison and Moore, 1980); and to 4) the greater permeability of coarse-grained rocks which would allow greater movement of oxidants into the sediment (Tissot and Welte, 1984; Tyson, 1987).

In order to evaluate the influence of grain size on organic content, two approaches - at two different scales - were undertaken. Firstly, the organic contents of the relatively uncommon and relatively clay-free siltstones, sandstones and limestones were determined and compared to those of the much more abundant finer-grained sediments (mudstone and argillaceous siltstone). Coarse-grained samples include siltstone and sandstone from Zone A and the Fish Scale Zone, along with calcareous siltstones and limestones from the Second White Speckled Shale. There was insufficient volume of coarser-grained material from the other zones to permit analysis. Secondly, an attempt was made to correlate variations of TOC in the fine-grained rocks (rare claystones, more abundant mudstones and argillaceous siltstones) to variations in the grain size of this fraction, with ‘grain size’ actually referring to visual estimates of silt content. Samples were assigned a numeric value on a scale ranging from 1 (claystone) to 13 (slightly argillaceous siltstone) (Table 1). Although clearly subjective the numeric grain size classification was demonstrated to be reproducible by re-estimating the silt
content of a number of random samples several days to weeks after their having been initially described.

7.4.2 Results

7.4.2.1. Comparison of Finer and Coarser-grained Lithologies

A. Kerogen Type

With a few exceptions, the kerogen in siltstone samples from Zone A falls within the same Type I/II field on a modified van Krevelen diagram as that in the mudstone samples from the same zone (Figure 149). The sandstone samples (Figure 150) also fall largely within this field, with a small (but proportionately larger) number of Type III values.

The kerogen in siltstone from the Fish Scale Zone falls within the Type II field, while the sandstone samples contain predominantly Type III kerogen (Figures 151 to 152).

The calcareous siltstones and, to a greater degree, the limestones of the Second White Speckled Shale contain kerogen largely intermediate in composition between Types II and III (Figures 153 to 154).

Coarser-grained samples contain less fluorescing organic matter than finer-grained samples, and somewhat more common vitrinite and semi-fusinite, occurring as larger fragments.
Figure 149. Modified Van Krevelen diagram, siltstone samples, Zone A.
Figure 150. Modified Van Krevelen diagram, sandstone samples, Zone A.
Figure 151. Modified Van Krevelen diagram, siltstone samples, Fish Scale Zone.
Figure 152. Modified Van Krevelen diagram, sandstone samples, Fish Scale Zone.
Figure 153. Modified Van Krevelen diagram, siltstone samples, Second White Speckled Shale.
Figure 154. Modified Van Krevelen diagram, limestone samples, Second White Speckled Shale.
B. Total Organic Carbon

Figures 155 to 157 show the distributions of total organic carbon for the different lithologies sampled in Zone A, the Fish Scale Zone and the Second White Speckled Shale. For all zones there is a progressive decrease of TOC from mudstone through siltstone to sandstone or limestone.

7.4.2.2 Influence of Silt Content of Fine-Grained Lithologies

There is no apparent relationship between average TOC and average grain size of the fine-grained fraction when viewed stratigraphically (Figure 158).

For all zones, plots are presented of grain size (silt content) versus TOC (Figures 159 to 164). Because the grain size data is on an interval, and not a continuous scale, it is not possible to attempt to remove from the TOC distribution the influence of variations in thermal maturity by multiple regression on Tmax and grain size. An attempt is made to make an accommodation for thermal maturation by plotting grain size against the residual values derived from linear regression of TOC on Tmax (Figures 165 to 170).

Oxygen Index, which varies little with thermal maturation, is also plotted against grain size (Figures 171 to 176). These OI-grain size plots were intended to show whether variations in silt content are related to variations in the content of oxygen-rich terrestrial organic matter (vitritnite). On both types of graph, Spearman’s rank
Figure 155. TOC distribution by lithology, Zone A.
Figure 156. TOC distribution by lithology, Fish Scale Zone.
Figure 157. TOC distribution by lithology, Second White Speckled Shale.
Figure 158. Comparison of mean grain size and TOC.
Figure 159. "Grain size" (silt content) vs. TOC, Zone A.
Figure 160. "Grain size" (silt content) vs. TOC, Fish Scale Zone.
Figure 161. "Grain size" (silt content) vs. TOC, Zone C.
Figure 162. "Grain size" (silt content) vs. TOC, Zone D.
Figure 163. "Grain size" (silt content) vs. TOC, Zone E.
Figure 164. "Grain size" (silt content) vs. TOC, Second White Speckled Shale.
Figure 165. "Grain size" (silt content) vs. residual TOC (after TOC-Tmax regression), Zone A.
Figure 166. "Grain size" (silt content) vs. residual TOC (after TOC-Tmax regression), Fish Scale Zone.
Figure 167. "Grain size" (silt content) vs. residual TOC (after TOC-Tmax regression), Zone C.
Figure 168. "Grain size" (silt content) vs. residual TOC (after TOC-Tmax regression), Zone D.
Figure 169. "Grain size" (silt content) vs. residual TOC (after TOC-Tmax regression), Zone E.
Figure 170. "Grain size" (silt content) vs. residual TOC (after TOC-Tmax regression), Second White Speckled Shale.
Figure 171. "Grain size" (silt content) vs. Oxygen Index, Zone A.
Figure 172. "Grain size" (silt content) vs. Oxygen Index, Fish Scale Zone.
Figure 173. "Grain size" (still courtesy) vs. Oxygen Index, Zone C.
Figure 174. "Grain size" (silt content) vs. Oxygen Index, Zone D.
Figure 175. "Grain Size" (solid content) vs. Oxygen Index, Zone E.
Figure 176. "Grain size" (silt content) vs. Oxygen Index, Second White Speckled Shale.

Second White Specks

rs = -0.13
p = 0.46
correlation coefficient ($r_s$), is shown instead of the more familiar Pearson's correlation coefficient which is not appropriate for use with data on an interval scale.

TOC and grain size are uncorrelated for all zones except the Fish Scale Zone, where a negative correlation is apparent. Residual TOC versus grain size is again essentially uncorrelated with grain size for all zones except the Fish Scale Zone, where a negative correlation is again observed ($r_s=-.36, p=.03$).

A weak positive correlation exists between grain size and oxygen index for the data from Zone D ($r_s=0.31, p=.06$).

Comparison of the maps of grain size distribution and TOC for Zone A show an apparent relationship, with the highest TOC values (in the west-central part of the map area) associated with a rapid change from coarser to finer grained rocks. The grain size distribution pattern suggest the an area of input of coarser-grained material from the west. No relationships between TOC and grain size were noted for any of the other zones.

7.5 Depositional Oxygenation Conditions

7.5.1 Introduction

Low depositional oxygen levels are commonly invoked as a major control on the accumulation of organic-rich rocks (DeMaison and Moore, 1980). Anaerobic bacteria, and in particular sulphate-reducers, are not demonstrably less efficient than aerobes in degrading organic matter (see
review in Pedersen and Calvert, 1990), however most rocks containing abundant hydrogen-rich organic matter are interpreted to have been deposited under oxygen-deficient conditions (Tyson, 1987). The association of potential petroleum source rocks and oxygen-deficient depositional settings has been explained by emphasizing the importance of burrowing macrobenthos in facilitating the diffusion of oxidants into the sediment from the water column (Demaison and Moore, 1980; Tyson, 1987).

Depositional oxygenation conditions can be inferred in a number of ways the most common of which is the extent of bioturbation, with laminated (non-bioturbated) sediments taken to be indicative of oxygen concentrations too low for the survival of burrowing organisms (e.g. Pratt, 1984).

Among chemical indicators of paleo-oxygen concentrations one of the most widely used is the set of relationships between organic carbon, sulphur and iron. Sulphur is fixed as pyrite in sediments by the reaction of detrital iron with hydrogen sulphide produced by anaerobic microbial reduction of aqueous sulphide (Davis et al., 1988). Pyrite can be formed directly or through intermediate steps from amorphous FeS (Davison, 1988). The large volumes of H₂S which may be produced under oxygen-deficient depositional conditions result in the formation of large amounts of pyrite and consequently high sulphur to carbon ratios in the host sediments. A slope of about 0.4 is common on a plot of organic carbon (X) versus sulphur (Y), with a
zero intercept or, in the case of sediment deposited beneath waters containing free \( \text{H}_2\text{S} \), a positive sulphur intercept (Leventhal, 1983).

The pyrite-forming reaction may be limited, however, by the availability of reactive iron. Organic matter with a hydrogen index less than about 1 or 150 also appears to be less easily utilized by sulphate-reducing bacteria than more hydrogen-rich organic matter (Davis et al., 1988; Dean and Arthur, 1989). As a result, pyrite formation may be limited in sediments dominated by hydrogen-poor organic matter. Davis et al. (1988) give examples of limitation of pyrite formation by both reactive iron and organic matter in the Mowry Shale.

The utility of \( S/C \) ratios in discriminating between those sediments deposited in oxygenated and oxygen-deficient conditions has been shown to be questionable by Raiswell et al. (1988), however, who demonstrate the lack of environmental definition provided by this type of data. This is presumably a consequence of the various possible limitations on pyrite formation. Dean and Arthur (1989) note the lack of correlation between sulphur and organic carbon in iron-limited systems. Raiswell et al. (1988) suggest a better measure of depositional oxygenation conditions is provided by the degree to which reactive iron is incorporated into pyrite. This 'Degree of Pyritization' (DOP) parameter is defined as the ratio of pyritic iron to pyritic iron plus reactive iron (soluble in hot hydrochloric
acid). It has an added advantage in that it is independent of the degree of thermal maturation, which S/C ratios are not, due to the decrease of TOC which results from increasing thermal maturation.

In this study, total iron, reactive iron, total sulphur and total organic carbon were determined for 53 samples, selected to represent a range of pyrolysis-derived TOC and HI values throughout all the units of the study interval. Pyritic sulphur was not determined directly. However there is a strong correlation between total iron and total sulphur falling close to the line representing the stochiometric composition of pyrite (Figure 177), implying that most of the sulphur is associated with iron as pyrite. A similar conclusion was arrived at by Dean and Arthur (1989) studying Cretaceous organic-rich shales from the American portion of the interior Seaway. In addition, pyrite was observed to be a common constituent of the rocks in the study interval, and no sulphates or other sulphur-bearing minerals were noted. The small number of points of Figure 177 falling above the line representing the composition of pyrite represent samples with excess sulphur, the significance of which is not clear. Under the assumption that all sulphur is in pyrite, the amount of pyritic iron in each sample was determined based on the sulphur content and the stochiometric formula for pyrite. As the DOP determined in this way may not be exactly equivalent to the DOP calculated
Figure 177. Iron vs. sulphur.

- Second White Specks
  - Zone E: □
  - Zone D: ●
  - Zone C: *
- Fish Scale Zone: ■
  - Zone A: △

Stochiometric Composition of Pyrite
from chemically-determined pyritic iron, the degree of pyritization used in this study is referred to as DOP*.

7.5.2 Results

By far the largest part of the study interval can be characterized as laminated. There are two main exceptions. In the lowermost portion of Zone A bioturbation is moderately common, particular in sandier and siltier intervals. Bioturbated bioclastic limestone beds occur in the Second White Speckled Shale. In addition, throughout the study interval, rare small horizontal burrows occur, associated with laminae of siltstone or calcareous siltstone. The burrows generally occur beneath the coarse laminae (which are themselves not bioturbated) and are filled with the same relatively coarse-grained material.

The ratios of sulphur to carbon are shown in Figure 178. All samples from Zone A and several from the Fish Scale Zone plot along the 'normal marine' line with a S/C ratio of about 0.4. The remainder of the data points fall along a parallel line with an intercept on the sulphur axis of 2%.

The DOP* data are plotted stratigraphically in Figure 179, along with the environmental designations of Raiswell et al. (1988). Zone A is characterized by relatively low DOP* values, indicative of aerobic to restricted conditions. DOP* values from the Fish Scale Zone span the entire range from those indicative of aerobic conditions to those suggesting inhospitable conditions. The strata above the Fish Scale
Figure 178. TOC vs. sulphur showing "normal marine" ratio of 0.4.

Most data points fall along a parallel line with an intercept on the sulphur axis of about 2%.

Selected Zones:
- Second White Specks
- Zone E
- Zone D
- Zone C
- Fish Scale Zone
- Zone A

"Normal Marine":
S/C = 0.4
Figure 179. Stratigraphic distribution of DOP* values. "Aerobic", "restricted" and "inhospitable" environmental designations from Raiswell et al. (1988).
Zone all lie within the field suggestive of inhospitable conditions, with the exception of a few samples from Zone E which fall into the 'restricted' field.

The relationship of DOP* and TOC is shown as Figure 180. Samples characterized by low DOP* values (largely from Zone A) contain low levels of organic carbon, while high DOP* samples cover a wide TOC range. A good TOC-DOP* correlation exists for samples with DOP* values in excess of about 0.7. The average DOP* and TOC values for each zone are plotted on Figure 181. The data from all zones except Zone A show a good positive correlation between DOP* and TOC. This is not an effect of variations in thermal maturation, as can be seen from the relatively small range of average Tmax values plotted on the graph. The Tmax of Zone A is higher than those associated with the other zones, but at lower maturities and therefore lower TOC values it would nonetheless plot in a different TOC-DOP* field than the other data.

7.6 Sedimentation Rate

7.6.1 Introduction

The positive relationship between sedimentation rate and organic carbon content of sediments deposited under normal (oxygenated) conditions is well-known (Muller and Suess, 1979). The increased preservation of organic matter under conditions of high sedimentation rate is attributed to
Figure 180. DOP* vs. TOC.
Figure 181. DOP* vs. TOC using mean values for each zone. Mean Tmax values are also shown. Zone A data excluded from regression.
more rapid burial to depths below the sediment-water interface at which microbial activity is low. Betts and Holland (1991) demonstrate a good positive correlation between sedimentation rate and burial efficiency of organic carbon regardless of oxygen levels, however they did not distinguish between hydrogen-rich and hydrogen-poor (more resistant) organic matter.

The relationship between sedimentation rate and organic matter preservation in oxygen-deficient depositional settings is less clear. Muller and Suess (1979) speculated that the positive relationship might hold, although with higher organic contents than under more oxygenated conditions. This was the result determined by Johnson-Ibach (1982) who examined relationships between sedimentation rate and organic content in sediments of several lithologies, including black shales (presumed to be the products of deposition under oxygen-deficient conditions). TOC was found to increase with sedimentation rate up to a critical value, above which the effects of dilution by mineral matter caused a progressive TOC decrease. At a given sedimentation rate, black shales were found to have higher organic carbon content that the other lithologies examined, and the critical sedimentation rate above which dilution becomes the dominant influence is also highest for the black shale lithology. This is consistent with the assertion of Curtis (1987) that prolonged exposure at the sediment surface would
increase the destruction of organic matter, regardless of the oxygen concentration of the bottom water.

These findings are, however, at odds with the view that organic rich rocks are often the consequence of very low sedimentation rates; in sequence stratigraphic terminology, that they represent condensed sections. The Second White Speckled Shale and the Fish Scale Zone have been described as condensed sections (Allan and Creaney, 1988; Cant, 1989). Another example is provided by Nixon (1973) who noted that the highest organic carbon contents in the Mowry Shale occur where the zone is thinnest, and therefore where the sedimentation rate was lowest. Davis et al. (1988) however noted that the thinner, more basinal deposits of the Mowry Shale were also the least bioturbated, suggesting that depositional oxygen concentrations may also have had an influence on preservation of organic matter.

In order to assess the influence of sedimentation rate on the strata of the Colorado Group, available published data concerning sedimentation rates of these rocks were reviewed. Relationships between TOC and lateral thickness variations of each stratigraphic unit were also examined, because such variations reflect lateral variations of sedimentation rate.

7.6.2 Results

The Second White Speckled Shale is stratigraphically coincident with a worldwide anomaly in the stable carbon
isotope composition of organic matter, as discussed previously. The duration of this anomaly has been estimated by various workers to have been between 300,000 and 1,000,000 years (Arthur and Premoli-Silva, 1982; Pratt and Threlkeld, 1984; Arthur et al., 1987; Hart and Leary, 1991). In the eastern Canadian plains, sedimentation rates based on radiometric ages of volcanic ash beds for the interval encompassing the Favel Formation (Second White Speckled Shale equivalent), the Morden Shale and the Boyne Formation have been estimated at 19.8 to 36.6 m/Ma (Williams and Baadsgaard, 1975). From these rates and the thickness of the Favel Formation the duration of Favel deposition can be estimated at 0.8 to 1.5 Ma. Within the study area, the thickness of the Second White Speckled Shale ranges from 5 and 31 metres, with a mean value of 14 metres. With deposition probably having occurred over 0.3 to 1 Ma, these thickness values give compacted sedimentation rates between 5 and 103 metres per million years, with an average of about 20 metres per million years (assuming a duration of the event of 700,000 years). The remainder of the section, from the top of the Viking Formation to the base of the Second White Speckled Shale, spans the latest Albian to the end of the Cenomanian, a period of approximately 8 Ma using the time scale of Harland et al. (1989). With thicknesses between 92 and 158 metres, implied sedimentation rates are between 11.5 and 19.75 metres per million years, within the
range of values calculated for the Second White Speckled Shale.

Plots of thickness versus TOC for each zone are shown as Figures 182 to 187. However, in order to establish any relationships between thickness and TOC, it is necessary to account for the variations in TOC caused by thermal maturation. Multiple regression analysis of TOC on Tmax and thickness was therefore performed. The results are shown in Table 6. An improvement in the TOC-Tmax correlation by the addition of the thickness variable is indicated by a reduction of the standard deviation about the regression surface.

The Zone A, Fish Scale Zone and Zone E samples show positive relationships between TOC and thickness after accounting for thermal maturity. A negative correlation characterizes the TOC-thickness data from Zone D. TOC and thickness are unrelated in Zone C and the Second White Speckled Shale.

7.7. Discussion

The positive correlations between TOC and calcium content for zones C and E suggest that some of the variation in organic content in these zones is related to variations in primary productivity, if it is assumed that the calcium is largely in biogenic calcite associated with calcareous plankton. The weak negative correlations between TOC and silicon content in Zone A, the Fish Scale Zone and Zone C
Figure 182. Thickness vs. TOC, Zone A.

TOC (%) vs. Thickness (metres)

r squared = 0.16
Figure 183. Thickness vs. TOC, Fish Scale Zone.
Figure 184. Thickness vs. TOC, Zone C.

TOC (%) vs. Thickness (metres) for Zone C.

$r^2 = 0.26$
Figure 185. Thickness vs. TOC, Zone D.

Zone D

r squared = 0.13
Figure 186. Thickness vs. TOC, Zone E.

Zone E

$\text{r squared} = 0.08$
Figure 187. Thickness vs. TOC, Second White Speckled Shale.

Second White Specks

$\text{r squared } = 0.01$
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<th>Zone</th>
<th>Correlation</th>
<th>r-squared</th>
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<th>p value of regression</th>
<th>p value of thickness term</th>
<th>Thickness coefficient</th>
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Table 5. Statistical parameters from regression of TOC on 1) Tmax, 2) thickness, and 3) Tmax and thickness together.
may suggest that increased coarse-grained material, assumed to be mainly quartz, is associated with lower organic contents. The general lack of correlation between TOC and aluminum, probably residing for the most part in clay minerals, supports the absence of clay-organic matter relationships as discussed below.

The lack of correlation of clay mineralogy with organic matter content has two possible explanations. No correlation may ever have existed, as in the black shales of the Atlantic basin described by Chamley and Robert (1982). However if any relationships did exist they may have been obscured by diagenetic alteration of the clays.

The absence of discrete smectite and the relative unimportance of IS clays is in contrast to correlative units described in the literature (Hattin, 1971; Young, 1975; Pratt, 1984; Macauley et al., 1985; Williams and Bayliss, 1988) and in conflict with the evidence of volcanic activity (ash beds). The formation of much of the illite and the ordered IS clays probably resulted from transformation of smectite and disordered IS clay, as described by Hower et al. (1976). The ‘illitization’ reactions are complex and not yet completely understood (e.g. Lanson and Champion, 1991), however they have been successfully modelled as a single first order reaction by Dutta (1986), using a frequency factor of $0.4 \times 10^5$ yr$^{-1}$ and activation energy of 80.8 kJ/mol. Using a very simple thermal model run on the BasinMod software of Platte River Associates it can be seen (Figure
that the transformation to illite occurs in upper oil window conditions, which are present in the study area. The simple model assumes a 3500 metre thick section, subsiding continuously from 95 Ma to the present, under a geothermal gradient of 2.5°C/100m. These parameters are not meant to accurately represent those in the study interval; the purpose of the model is simply to illustrate that the percentages of illite recognized in IS clays in this study are generally consistent with the measured levels of thermal maturation. Burtner and Warner (1986) in a study of the Mowry Shale of the western interior of the United States came to similar conclusions. The only IS clay present in Mowry samples with Tmax values greater than 437°C (early oil window) is an ordered IS species.

The presence of both discrete illite and IS clays may suggests that at least some of the illite is not of diagenetic origin. However the relationships between IS clays and illite are complex; Lanson and Champion (1991) have recognized the co-evolution of both species. The amount of original illite in the present study is difficult to determine.

Many reports relate the transformation of smectite to smectite-poor mixed layer clays and illite to burial depth rather than to any independent measure of thermal maturation such as vitrinite reflectance. The 'illitization' occurs in various localities at burial depths between 2000 m and 6000 m (Hower et al., 1976; Pearson and Small, 1988; Chamley,
Figure 188. BasinMod thermal model showing conversion of smectite to illite along with maturity as vitrinite reflectance.
1989 and references therein). Extrapolating from the work of Nurkowski (1984) concerning original burial depths, at least 1800 metres of overburden have been removed from the study area. Given current burial depths in excess of 1000 metres, maximum burial has been sufficient to place the rocks of the study interval at depths where the smectite to illite transition occurs.

Given the lack of any correlations between organic content and clay mineralogy it appears the latter exerted no influence on the former, although diagenetic alteration has made it impossible to be certain.

Grain size does exert some influence on organic content. The coarser grained lithologies are lean with respect to organic matter and what they do contain is relatively hydrogen-poor. The presumably higher permeability of these coarser zones allowed diffusion of oxidants into the sediment and consequent microbial degradation. In addition, marine kerogen may have been preferentially deposited with the finer-grained equivalents of these laminae.

Correlations between visually-estimated silt content and TOC, residual TOC and OI are weak. However the Fish Scale Zone data illustrate the expected relationships, with higher silt contents corresponding to lower TOC and higher OI, suggesting that silt and terrestrial organic matter were co-deposited and possibly that organic content was diluted by mineral matter.
The data from Zone D show a good positive correlation between OI and grain size. The interpretation is the same as for the Fish Scale Zone data. For both intervals, the data are suggestive of relatively high levels of terrestrial input, both organic and mineral, relative to the other zones which show no relationships between TOC or OI on one hand and grain size on the other.

Overall low sedimentation rates are likely to have characterized the entire study interval, allowing water body stratification and resulting oxygen-deficient bottom conditions to have developed (Wignall, 1990). However, variations in sedimentation rate within the study interval cannot be shown to be major influences on TOC, especially with regard to Zone C and the Second White Speckled Shale, the data from which show no correlation between TOC and thickness. However in Zone A, the Fish Scale Zone and Zone E there are positive relationships between TOC and thickness suggesting a 'normal' situation with preservation increasing with more rapid burial. The data from Zone D, with some decrease in TOC with increasing thickness (sedimentation rate), suggest dilution by mineral matter during this regressive episode.

The lack of any thickness-TOC relationships in the Second White Speckled Shale is evidence of how organic deposition, when this zone was laid down, was relatively unaffected by local factors and was subject to external
control, although possibly a higher sedimentation rate than for Zone E may have aided preservation.

Both S/C ratios and DOP* data indicate 'normal marine' conditions during deposition of Zone A, and a transition to oxygen-deficient conditions during Fish Scale Zone deposition. Oxygen deficient conditions, probably with H₂S-bearing bottom waters as shown by the carbon-sulphur plot (Figure 178) and the DOP* data (Figure 179), persisted throughout the deposition of the remainder of the strata in the study interval, although some low DOP* values in Zone E and the presence of bioturbated limestones in the Second White Speckled Shale indicate episodic oxygenation of bottom waters.

Depositional oxygen conditions had a significant influence on TOC. This is shown by the relatively low organic content of Zone A, deposited in the most oxygenated environment of any of the study interval zones. However, low oxygen concentrations alone are clearly insufficient to facilitate high TOC development, as shown by the low TOC values of Zone E. Although DOP* data from Zone E does include a few low values indicative of episodic oxygenation, the overall depositional setting was oxygen-deficient.

In summary, each of depositional oxygen conditions, grain size and sedimentation rate influence TOC, but generally in complex ways. Clay mineralogy has no effect. Correlations between the organic parameters and various influences vary in significance, however no single factor is
obviously most important. Other factors must be involved in controlling lateral TOC variations. The distribution of organic matter may be irregular as a consequence of current transport of organic matter and non-uniform deposition against bottom topography. A predictive model incorporating such factors would be extremely difficult to construct.
8. Gamma Ray Spectroscopy

8.1 Introduction

Many organic-rich mudrocks are characterized by high levels of natural radioactivity and are often informally referred to as 'hot shales'. Correlations between uranium content and organic richness have been noted by numerous workers (e.g. Leckie et al., 1990). The addition of authigenic uranium to sediments from sea water is facilitated by the presence of organic matter and by reducing conditions (Kochenov et al., 1977) and high levels of uranium occur in many organic-rich rocks deposited under oxygen-deficient conditions (Myers and Wignall, 1987). Diagenetic process can also result in uranium precipitation. The rocks of the study interval show substantial variation in radioactivity as observed on downhole geophysical well logs. In order to examine possible relationships between organic content and radioactivity 31 core samples from 3 wells were analysed by gamma ray spectrometer at the Pacific Geoscience Centre (PGC). In addition, measured TOC values were compared with spectral gamma ray data for the 4 wells for which both downhole spectral gamma ray logs and Rock-Eval data were available.

8.2 Results

Stratigraphic plots of gamma ray spectroscopy data for samples from the two most thoroughly sampled wells are shown
as Figures 189 and 190. Relatively high uranium concentrations characterize the Fish Scale Zone, Zone C and Zone D, while much lower levels occur in Zones A and E, and the Second White Speckled Shale.

Correlations of TOC with uranium, thorium and potassium, along with uranium/thorium ratio, were attempted. The most significant relationships are positive correlations between TOC and U/Th and TOC and U. Figures 191 and 192 display the data from the samples analysed at the PGC; the data derived from downhole logs is shown on Figures 193 and 194. Multiple regression with Tmax to account for thermal maturation effects does not improve the correlations. Potassium is only very weakly (and inversely) correlated to TOC; thorium and TOC are unrelated.

Plots of uranium against DOP* for the 12 samples for which this type of data is available show low U levels in low DOP* samples, and a strong correlation between DOP* and U for the higher DOP* samples (Figure 195). There is also, however, a similar relationship between U and TOC.

8.3 Discussion

The positive correlation between TOC and uranium supports the widely-made observation of the association of organic matter and uranium. The relationship between TOC and U in this study suggests that the U is somehow adsorbed onto or incorporated into the organic matter, that both organic matter preservation and uranium precipitation are enhanced
Figure 189. Profile of uranium, thorium and potassium data, well 14-32-31-2W5M.
Figure 190. Profile of uranium, thorium and potassium data, well 7-19-45-6W5M.
Figure 191. TOC vs. uranium content. Uranium data from analysis of core samples.

Uranium (ppm) vs. TOC (%)

Second White Specks
Zone E
Zone D
Zone C
Fish Scale Zone
Zone A

$r squared = 0.59$
Figure 192. TOC vs. uranium/thorium ratio. Uranium and thorium data from analysis of core samples.
Figure 193. TOC vs. uranium content. Uranium data from spectral gamma ray logs.

- Zone E: □
- Zone D: △
- Zone C: ○
- Fish Scale Zone: *
- Zone A: ■

$r$ squared = 0.32
Figure 194. TOC vs. uranium/thorium ratio. Uranium and thorium data from spectral gamma ray logs.
Figure 195. DOP* vs. uranium content.

Zone A data excluded from regression.

$\text{Uranium (ppm)}$

$\text{DOP*}$

Second White Specks
- Zone E
- Zone D
- Zone C

Fish Scale Zone
- Zone A

$\text{r squared} = 0.44$

not included in regression
by a common factor, probably an oxygen-poor depositional environment, as suggested by Myers and Wignall (1987), or that diagenetic uranium precipitation was favoured by the presence of organic matter. Because low TOC and uranium values occur in some deposits of oxygen-poor conditions (notably Zone E) it seems that organic matter is a required element for uranium precipitation and that reducing conditions alone are insufficient. The lack of much uranium in the oxic deposits of Zone A probably resulted from the oxidizing setting in addition to the lack of organic matter due to aerobic degradation.
9. Depositional Model

The rocks of the study interval represent the deposits of an overall transgressive section punctuated by several episodes of regression evidenced by grain size changes and related to sea level fall or to tectonic uplift of the western sediment provenance (Figure 196).

Zone A

The unconformable nature of the top of the Viking has been documented (Boreen and Walker, 1991). The presence of bioturbated and sandy to conglomeratic layers only in the lowermost portion of Zone A, overlain by largely laminated mudstones and argillaceous siltstones suggests a relatively rapid initial transgression. The presence of graded siltstone layers in Zone A in the 14-31-45-15W5M well in the western part of the study area and finer, more uniformly laminated sediments to the east suggests a western sediment source. A western provenance is also indicated by the grain size map of the fine-grained fraction. The upsection decrease in the vertical spacing of the graded units is consistent with their becoming more distal with transgression. The lamination in the eastern part of the study area, defined by thin silt laminae, is interpreted to be the distal equivalent of the graded lamination present in the extreme west. The principal depositional mechanism was probably from relatively low density turbid flows generated
Relative Sea Level

Transgression \[\Rightarrow\] Regression

Second White Specks
Zone E
Zone D
Zone C
Fish Scale Zone
Zone A

(no scale)

Figure 196. Relative sea level chart for the study interval.
by seismicity (note the presence of volcanic ash beds in the section as well as clastic dykes ascribed by Leckie and Potocki (1988) to a possible seismic origin) or, perhaps more likely, by storm events, which flowed basinward (to the east). Davis and Byers (1989) refer to similar centimetre scale graded siltstone and mudstone intervals in the Mowry Shale of Wyoming as either fine-grained turbidites or distal storm deposits, although they acknowledge the distinction between the two may be artificial as turbidites could have a storm origin.

The laminated (unbioturbated) nature of most of the section points to relatively low oxygen conditions. However DOP\* data, discussed in Section 7.5, suggest this section was deposited under more oxygenated conditions than the overlying beds. A dysaerobic environment is likely. A relatively stagnant water body is envisaged, for most of Zone A time unconnected to the Gulfian Sea and with circulation hampered by constriction at the northern end of the Seaway (Williams and Stelck, 1976).

Organic matter was largely autochthonous but may have been redeposited within the basin by storm-generated turbid flows. An unusual concentration of small algal bodies in the 6-15-28-2W5M well in the southwestern part of the study area may represent community influenced by relatively nearshore conditions where the zone is thinnest. Much organic matter was oxidized in the water column and in the sediment. Higher sedimentation rates towards the basin depocentre in the east
aided preservation of organic material. Sedimentation rates were generally high enough to allow survival of sufficient organic matter into the zone of methanogenesis to result in the formation of siderite beds. However, in absolute terms sedimentation rates were probably relatively low as much sediment may have been trapped in estuarine complexes formed in former incised valleys during the transgression (Wignall, 1990). With continuing increase in relative sea level, deposition (throughout the rest of the study interval) would not have kept pace with subsidence allowing deepening and therefore stratification to form in the water column.

The isopach map of Zone A shows the basin to have thickened to the east. The study area therefore lay to the west of the basin axis during Zone A time.

Fish Scale Zone

The Fish Scale Zone is interpreted to represent a regression. The increase in sand content as compared to the underlying zone and the abundant sedimentary structures indicative of high energy are most easily explained by regression. McNeil (1984) also considered the Fish Scale Zone to be a regressive deposit. The depositional mechanism of the sandstone layers is not entirely clear, however they appear to be event deposits, probably associated with storms. Putnam and Oliver (1983) have previously referred to the sands as tempestites, and Eriksen and Slingerland (1990) have produced computer simulations of the Colorado Group Sea
which indicate the basin was strongly influenced by storms. The grain size distribution map indicates a probable western source for the sediment. During a regression associated with a sea level fall, coarse sediment which had been trapped in estuaries during Zone A time would have been redeposited in more basinal locations. These hypothesized estuarine deposits may have been the source of the sand in the Fish Scale Zone. In addition, the isopach map of the Fish Scale Zone shows a relatively low relief basin, without the pronounced eastward thickening exhibited by Zone A. This suggests a westward tilting of the basin, probably accompanied by uplift of the western highlands. The uplift to the west would have provided increased coarse sediment supply to the basin.

The Fish Scale Zone has been interpreted as a transgressive deposit (McNeil and Caldwell, 1981), the result of a stillstand (Stott, 1984) and a condensed section (Allan and Creaney, 1988) deposited after a transgression in relatively deep water and sediment-starved conditions. However, Caldwell (1984) argued on micropaleontological grounds that there is no unusual condensation. Without very detailed stratigraphic data it is impossible to positively determine if the section is condensed. However the basal contact provides useful information. The pulsed nature of the contact suggests relatively short-duration episodes of transgression and regression. It is assumed that transgressive intervals would have been deposited more
slowly than regressive ones. It seems highly likely that the laminated argillaceous beds are the more slowly-deposited (more condensed) transgressive episodes, and that the sandy intervals (typical Fish Scale Zone lithology) are the result of more rapid deposition in shallower water. The presence of contorted lamination also suggests relatively high sedimentation rates, with deformation caused by rapid loading. However it is also possible the convolute bedding could have been a consequence of earthquakes, the cause cited by Leckie and Potocki (1988) for the development of sandstone dykes in Zone A.

The abundance of fish scales does not necessarily suggest a condensed section. The DOP* data show the Fish Scale Zone to have been deposited during the initial development of 'hostile bottom' conditions (terminology of Raiswell et al., 1988) when free hydrogen sulphide may have been present in the lower portion of the water column. The agitation of the water column evident from the sedimentary structures in the coarser beds would have caused some H₂S to be introduced into the upper waters near the interface between the water masses, resulting in mass fish mortality and addition of large volumes of fish debris to the sediment. Some oxygen was probably introduced into the bottom waters by storm mixing but would have been consumed rapidly by the decay of the organic debris.

The reason for the onset of anoxia is not entirely clear. However regression and tectonic movement may have
temporarily further restricted the basin to the north (note the narrow northern opening of the seaway shown on Figure 3), hindering circulation and facilitating development of an oxygen-deficient bottom water layer. In addition the influx of clastic material associated with sea level fall and/or tectonic uplift of the source area may have been accompanied by nutrients derived from soils. A temporary increase in primary productivity could have resulted, the detritus from which would have intensified the oxygen-deficient bottom layer. Storm-mixing of the water column and resulting mass mortality in surface waters would have added yet more organic material, rapidly consuming any oxygen introduced by the mixing and possibly further intensifying the oxygen-deficient layer. The small horizontal burrows found throughout the study interval and to a small extent within the Fish Scale Zone probably were produced by organisms introduced into the oxygen-deficient setting by storm action. Their burrows are confined to thin zones underlying coarse laminae, probably also the result of storms. The organisms could be characterized as the 'doomed pioneers' of Follmi and Grimm (1990), introduced into a hostile environment in which their survival time was very limited.

The possibility also exists that the Fish Scale Zone was influenced by global environmental factors. The apparent lack of correlation between TOC and $\delta^{13}C$ for the Fish Scale Zone samples suggests some changes in the isotopic fractionation behavior of phytoplankton may have occurred.
Such changes could have arisen as a consequence of lowered levels of atmospheric CO$_2$ associated with the burial of large amounts of organic matter in marine sediments. This would be analogous to the conditions hypothesized to have existed during the Cenomanian-Turonian 'Oceanic Anoxic Event'.

In the oxygen-deficient setting of the Fish Scale Zone preservation of organic matter was improved. Organic matter was largely autochthonous, and primary productivity, although difficult to quantify, may have been high as a consequence of an influx of nutrients, as discussed above. The preservation of organic matter was relatively insensitive to the minor variations in sedimentation rate (the interval thickness does not vary much), although some minor dilution effects may have had an influence.

Zone C

Zone C represents a return to transgressive conditions. It is composed mainly of laminated mudstone suggestive of quiet water deposition. The first significant occurrences of white specks, and calcareous siltstone occur in this zone. Although the Gulfian and Boreal seas had joined by the time of Fish Scale Zone deposition, the increased volume of carbonate components in Zone C may suggest a significant northward incursion of warm Gulfian waters. Caldwell (1984) also considers an upsection increase in carbonate in the Colorado Group strata to have resulted from the invasion of
warmer waters from the south. The grain size distribution map shows an increase in grain size to the north-northwest. This pattern suggests the initiation of basin-parallel currents, not active during deposition of the underlying zones, which transported sediment to the south-southeast. However, the currents would probably have been episodic and storm-related (Ericksen and Slingerland, 1990).

Zone C thickens towards the disturbed belt to the west (Figure 21). This general pattern, the result of westward tilting of the basin due to tectonic loading to the west, also characterizes overlying zones.

A stable oxygen-deficient bottom water layer was in place by this time, probably increasing in area with the ongoing transgression, as in the 'expanding puddle' model of Wignall (1990). The upsection increase in organic carbon content through Zone C may reflect increased productivity (there is a positive correlation between TOC and calcium content, presumably from biogenic calcite present as nanofossil debris, and organic matter is predominantly autochthonous marine material), although the reason for a productivity increase is not clear. Continued transgression would have permitted the development of a thickening, oxygen-deficient water layer which may have contributed to increased organic preservation. Any currents present in the basin may have been confined to the upper portion of the water column.
Zone D

Even higher carbonate contents characterize Zone D than Zone C, suggestive of a further incursion of warm waters. The slightly higher siltstone content of Zone D, as compared to both underlying and overlying zones, along with the apparent lithostratigraphic correlation to the regressive Dunvegan Formation suggests a slight regressive episode. As a consequence of the overall transgression and the westward tilting of the basin, the study area in Zone D time was much farther from the western shoreline and in deeper water than was the Fish Scale Zone. The regression of Zone D therefore added less coarse clastic material than that associated with the Fish Scale Zone, and did not result in the development of high-energy sedimentary structures. The sediment source was to the northwest, but quite distant from the study area. The cause of the upsection TOC decrease is not clear. Lateral variations in sedimentation rate do not provide any support for the suggestion that stratigraphic variations in sedimentation rate would influence the TOC. The Zone is quite homogeneous and does not show any physical evidence of stratigraphic changes in depositional conditions. Upward deepening could be a cause of an associated decrease in TOC if increased degradation of organic matter occurred while settling through a thicker water column. However the interpretation of the zone as a regressive deposit implies water depths no greater than during deposition of Zone C, in which organic contents are high. Variations in primary
productivity may therefore be the cause of the upsection TOC decrease, although the reasons for such variations are not obvious.

Organic matter is predominantly of marine origin. Although terrestrial organic matter is not common the positive correlation between TOC and silt content suggests some vitrinite precursors were transported and deposited along with coarser-grained mineral matter.

Zone E

The deposits of Zone E consist of relatively monotonous, finely laminated mudstones suggestive of quiet water deposition in a distal setting. The transgressive cycle is interpreted to have been at or near maximum transgression during deposition of these beds. On a calcium-free basis, Zone E has the lowest silicon content of all the zones. This is interpreted as indicating low quartz content. Such a composition is consistent with deposition at or near maximum transgression, in a distal setting. The lack of any obvious pattern in grain size is also suggestive of a deposition a substantial distance from shore, far from the influence of coastal sediment sources.

Slow sedimentation rates associated with the deep water setting resulted in extensive degradation of organic matter at the sediment-water interface. Evidence of episodic, although weak, oxygenation from the DOP* data also suggests some dissipation of the oxygen-deficient water layer and
consequent increased degradation of organic matter while settling. The reason for the weakening of the anoxic layer is not clear, however in the deeper-water isolated setting, primary productivity may have been lower than during deposition of the underlying zones. At or near maximum transgression there may have been connections with the Pacific Ocean to the west as suggested by Lang and McGugan (1988) and current pattern in the basin may have changed, disrupting the water column stratification.

Second White Speckled Shale

The Second White Speckled Shale also represents deposits of a relatively deep water setting. The silt content, the lowest of any of the zones (Figure 158) of the fine-grained fraction suggests maximum transgression. However the presence of calcareous siltstones in greater volume than in Zone E suggests either a slight regression, an increase in current activity, or uplift of the provenance area to the west or northwest. The evidence of some higher energy structures, not found in Zone E, along with the increase in coarser-grained material support a minor regression.

Organic contents of the Second White Speckled Shale are substantially higher than those of Zone E, despite similar episodes of oxygenation evident from the presence of intensely bioturbated inoceramite limestone beds. A more
detailed discussion of the deposition of the Second White Speckled Shale is presented in the following section.
10. Discussion of the Cenomanian-Turonian 'Anoxic Event'

The Second White Speckled Shale lies at the Cenomanian-Turonian stage boundary, at which level a major 'Oceanic Anoxic Event' has been interpreted from many locations (OAE 2 of Schlanger and Jenkyns, 1976). The data presented in this study allows several observations to be made concerning these beds in the context of the entire study interval.

The Cenomanian-Turonian event and its attendant isotope anomaly are generally explained as a result of high surface productivity and consequent expansion of the oxygen-minimum zone in a transgressive setting with a warm climate and little oxygen-rich bottom water (Schlanger and Jenkyns, 1976). The expanded $O_2$ minimum zone led to increased preservation of organic matter, the burial of large amounts of isotopically light biogenic carbon (Scholle and Arthur, 1980) and to a sequence of extinction events (Jarvis et al., 1988). The oceanic carbon pool was consequently enriched in $^{13}C$, leading to the heavy isotope anomaly. The possibility has also been suggested, however, that the anomaly may be the result of high input of isotopically heavy terrestrial organic matter (Jeans et al., 1991).

The hypothesized high surface productivity has been explained as a result of the great Late Cenomanian transgression (Schlanger et al., 1987). As a result of the high sea level, broad shallow shelves were formed over large areas. Large volumes of warm saline water were formed by
evaporation. These dense warm waters sank and caused upwelling by displacing deep, nutrient-rich waters upwards. Productivity increased in surface waters as a result of the upwelling.

In the current study, the data suggest the Second White Speckled Shale, essentially coincident with the Cenomanian-Turonian isotope anomaly, was deposited either at or slightly after maximum transgression. Episodic oxygenation of bottom waters and some high-energy conditions are evident from the bioturbated and rippled inoceramite limestone beds. Periodic oxygenation may also have occurred during Zone E time, as shown by the DOP* data. The preservation of large amounts of organic matter in the Second White Speckled Shale therefore occurred despite conditions (possibly including a thick oxygenated water column) which probably aided in the destruction of organic matter during deposition of Zone E. The increased sedimentation rate would have improved organic matter preservation in the Second White Speckled Shale as opposed to Zone E, but this is unlikely to have been a global condition.

The concentrations of inoceramids, if not a result of reduced clastic input, suggest a proliferation of the bivalves. Inoceramids were probably benthic and may have harboured chemosynthetic symbiont bacteria (MacLeod and Hoppe, 1992), permitting them to live in hostile, oxygen deficient environments. However the bioturbated nature of some of the thicker inoceramite limestone beds suggest they
proliferated under an oxygenated setting as well. A proliferation of inoceramids may also represent an increase in their food supply due to an increase in the flux of sedimenting organic matter the sea floor, possibly as a consequence of higher productivity of surface waters, possibly together with an episode of higher oxygen levels in bottom waters. Under more oxygen-deficient conditions, or conditions of lower surface water productivity, Inoceramus populations returned to background levels and larger amount of organic carbon were preserved, both as a consequence of less degradation and less consumption by the macrobenthos. The reason for the hypothesized productivity increase is not entirely clear, but was almost certainly of global extent. Increased upwelling due to production of warm saline waters on widespread shallow shelves and consequent changes to oceanic circulation are not inconsistent with the data presented in this study. Sedimentary structures within the Second White Speckled Shale are indicative of increased energy, probably current related (as compared to Zone E) and may reflect upwelling conditions.

The alternation between limestone and mudstone may have resulted from climatic oscillations between arid and humid conditions, as explained by Pratt (1984) for the Cenomanian-Turonian Greenhorn Formation of Colorado. Muds were deposited during humid periods when freshwater influx produced a salinity stratified sea, and presumably introduced more clastics. More oxygenation resulted during
drier periods when no fresh water cap was present and mixing of the water column could occur.

As noted above, the presence of some higher-energy structures in the Second White Speckled Shale does suggest the possibility of disruption of the water column stratification and possibly upwelling. However stratification was re-established frequently as shown by the laminated mudstones with high DOP* values. The higher energy deposits are restricted to the limestones, consistent with their having been deposited during more arid climatic periods in an unstratified sea.

The Cenomanian-Turonian isotope anomaly coincident with deposition of the Second White Speckled Shale is a worldwide phenomenon and not easily explained by local conditions. However nothing in this study contradicts the generally held concept. There is no evidence of the possibility suggested by Jeans et al. (1991) that the isotope anomaly resulted from an influx of terrestrial organic matter.

Jeans et al. (1991) note the Cenomanian-Turonian isotope anomaly occurs at the beginning of a global atmospheric cooling trend. This suggests a major transfer of carbon from atmospheric CO₂ to marine sediments due to the burial of large amounts of sedimentary organic matter. The reduction in CO₂ levels during Second White Speckled Shale deposition appears, on the basis of the positive TOC-δ¹³C correlation, to have changed the degree to which marine phytoplankton fractionate carbon isotopes, as compared to
the underlying zones. Marine organic matter deposited during the duration of the isotope anomaly would then have been isotopically heavier than that deposited in the underlying beds. This increase in the $^{13}$C content of the organic matter would have added to the magnitude of the isotope anomaly.
11. Commercial Implications

The strata described in this study are important petroleum source rocks and have generated the oil, and probably at least some of the gas, reservoired in the Viking Formation (Allan and Creaney, 1987). Their potential commercial significance extends beyond their source rock capacity, however. It is a significant result of this study that much of the oil generated from the kerogen of the Second White Speckled Shale may never have been expelled. The interval appears to lack conventional reservoirs. The coarser-grained interbeds, both calcareous siltstone and bioclastic limestone, are generally thin and cemented by calcite. However the porosity and permeability could both be improved by natural fracturing and possible accompanying solution of cement. Fractured shale reservoirs of this type could constitute attractive targets for horizontal drilling.

To the north of the study area, an increase in coarse clastic material from the Dunvegan delta complex could provide sufficient reservoir to constitute a conventional drilling target as well. Such reservoirs would be in a very favourable stratigraphic position, immediately overlying the richest potential source beds in the study interval (Zone C) and possibly lying within the oil window.

Sandstone of the Fish Scale Zone is an oil reservoir (locally called the Barons sandstone) in the Barons oil field of southern Alberta (Townships 11 and 12, Range
22W4M) (Alberta Society of Petroleum Geologists, 1960; Putnam and Oliver, 1983). The oil-bearing sandstones are, in contrast to the non-hydrocarbon bearing rocks, free of calcite cement (Putnam and Oliver, 1983). This suggests the possibility of conventional reservoirs in areas where early-formed traps were protected from cementation by the presence of oil. The reservoirs sandstones are quite thin, however, and their distribution is difficult to predict. The grain size distribution map of the zone (Figure 18) could provide a starting point for exploration, however.
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