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Catherine Chague

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**GEOCHEMISTRY AND ORGANIC PETROLOGY OF BOREAL AND
SUBARCTIC PEATS IN CANADA**

by

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Department of Earth Sciences

**Submitted in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy**

**Faculty of Graduate Studies
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ABSTRACT

Five peat-forming environments were investigated for their organic petrological, mineralogical and geochemical characteristics. Wetlands studied included a salt marsh (Nova Scotia) and four peatlands: a freshwater domed bog (Nova Scotia), a fen (Alberta) and two peat plateau bogs (Northwest Territories). These diverse localities provided the opportunity to assess the influence of natural and anthropogenic factors on peat geochemistry in different depositional environments. Core samples were analyzed using the following methods: organic petrology (maceral analysis and reflectance measurements), low and high temperature ashing, x-ray diffraction, INAA and sulfur analysis, ICP-MS, radiocarbon and cesium dating.

Changes in maceral composition generally correlate with shifts in reflectance, and are useful indicators of the degree of degradation and oxidation in various depositional environments. A downcore decrease of fluorescing and red reflecting huminite macerals shows an increase in the degree of degradation, while an abundance of pyrofusinite in certain intervals is indicative of periods of drought and fire activity. In the salt marsh, oxyfusinite and algae are common.

Br, Cl, I and Se exhibit a strong affinity with the organic fraction and are consequently enriched in peat. Distribution of elements associated with the inorganic fraction on the other hand, can generally be explained in terms of mineral matter distribution.

Peat acts as a sink for air- and waterborne elements. Main factors affecting elemental concentration and distribution are geology of the substratum, proximity to the marine environment, elemental affinity, permafrost, redox changes in the zone of water table fluctuation, tephra incorporation, botanical composition, plant bioaccumulation, degree of degradation of peat, and anthropogenic activity. In particular, a substantial enrichment immediately above the permafrost boundary reflects the influence of permafrost on the mobilization of elements.

Framboidal and anhedral pyrite crystals occurring in association with organic matter are observed in both brackish and freshwater peat-forming systems.

A model was developed in the domed bog, showing that pH, botanical, mineralogical and geochemical composition of peat are related and dependent on the trophic conditions. Furthermore, this model can be useful to help understand characteristics of coal deposits.

RESUME

On a étudié les caractéristiques organiques pétrologiques, minéralogiques et géochimiques de cinq milieux de dépôt de tourbe. Les marécages étudiés furent un marais salant (Nouvelle-Ecosse) et quatre tourbières: une tourbière ombrotrophe bombée d'eau douce (Nouvelle-Ecosse), un fen (Alberta) et deux plateaux à tourbe (Territoires du Nord-Ouest). L'étude de diverses localités permet d'évaluer l'influence de facteurs naturels et anthropogéniques sur la géochimie de la tourbe dans différents milieux de dépôt. Les échantillons de carottes furent analysés par les méthodes suivantes: pétrologie organique (analyse de macéraux et mesures de réflectance), combustion à basse et haute température, diffraction de rayons X, AIAN et analyse de la teneur en soufre, SM-PIHF, datation au radiocarbone et au césium.

Les variations dans la composition en macéraux correspondent généralement aux changements de réflectance, et sont des indices du degré de décomposition et d'oxydation dans les différents milieu de dépôt. Les macéraux du groupe de l'huminite montrant une fluorescence et une réflexion rouge diminuent vers le bas, ce qui indique une augmentation du degré de décomposition. Quant à elle, l'abondance de pyrofusinite dans certains intervalles indique des périodes de sécheresse et d'incendie dans les tourbières. Dans le marais salant, l'oxyfusinite et les algues sont courantes.

Les éléments Br, Cl, I et Se ont une forte affinité pour la fraction organique et sont par conséquent enrichis dans la tourbe. Par contre, les éléments associés avec la partie inorganique suivent généralement la distribution de la teneur en matière minérale.

La tourbe constitue un piège pour les éléments transportés par l'air et l'eau. Les principaux facteurs affectant la concentration et la distribution des éléments sont la géologie du substratum, la proximité de la mer, l'affinité des éléments avec la fraction organique ou la fraction minérale, le pergélisol, les changements de potentiel d'oxydo-réduction dans la zone de fluctuation du niveau d'eau, l'incorporation de téphra, la composition botanique, l'accumulation par les plantes, le degré de décomposition de la tourbe, et l'activité anthropogénique. Un enrichissement prononcé juste au-dessus de la limite du pergélisol indique l'influence de ce dernier sur la mobilité des éléments.

Des cristaux de pyrite framboïdaux et xénomorphes ont été observés en association avec la matière organique, à la fois dans des marais d'eau douce et d'eau saumâtre.

Un modèle a été développé dans la tourbière bombée, qui montre la relation entre le pH et la composition botanique, minérale et géochimique de la tourbe, ainsi que l'influence des conditions trophiques. De plus, ce modèle peut aider à comprendre les caractéristiques de la houille.

à *Grand-Mère*
et
à *Nicolas Hodowaniec*

ESPOIR

Quand je regarde en arrière
Je ne veux me souvenir
Que des jours pleins de lumière
Où rayonnait l'avenir

Je ne veux revoir les roses
Qu'au début de leur printemps
Quand les fleurs à peine écloses
Semblaient défier le temps

Qu'importe si par la suite
Leurs pétales sont flétris
Et si nous voyons trop vite
Tomber au sol leurs débris

C'est la loi de la nature
Tout se fane tout vieillit
Homme ou fleur la créature
Sa tâche faite périt

Mais si ma chair est mortelle
Mon âme sait bien qu'un jour
Elle renaîtra plus belle
Grâce à l'éternel amour

Claude Sabert

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CHAPTER ONE

INTRODUCTION

1.1 OBJECTIVES

The purpose of this study is to interpret the influence of natural and anthropogenic factors on the geochemistry of peat. This will help determine the role of peat as a sink for airborne and water-borne elements. An assessment of the significance of wetlands and peat to global climate change will also be made.

The five study sites are located in Nova Scotia, Alberta and the Northwest Territories (Figure 1.1). These have been chosen to allow a comparison of different depositional environments and to study the effects of anthropogenic pollution on selected sites. They include a freshwater bog (Nova Scotia), a salt marsh adjacent to a highway (Nova Scotia), a fen close to a coal mine and coal power plant (Alberta) and two peat plateau bogs differently affected by permafrost (Northwest Territories).

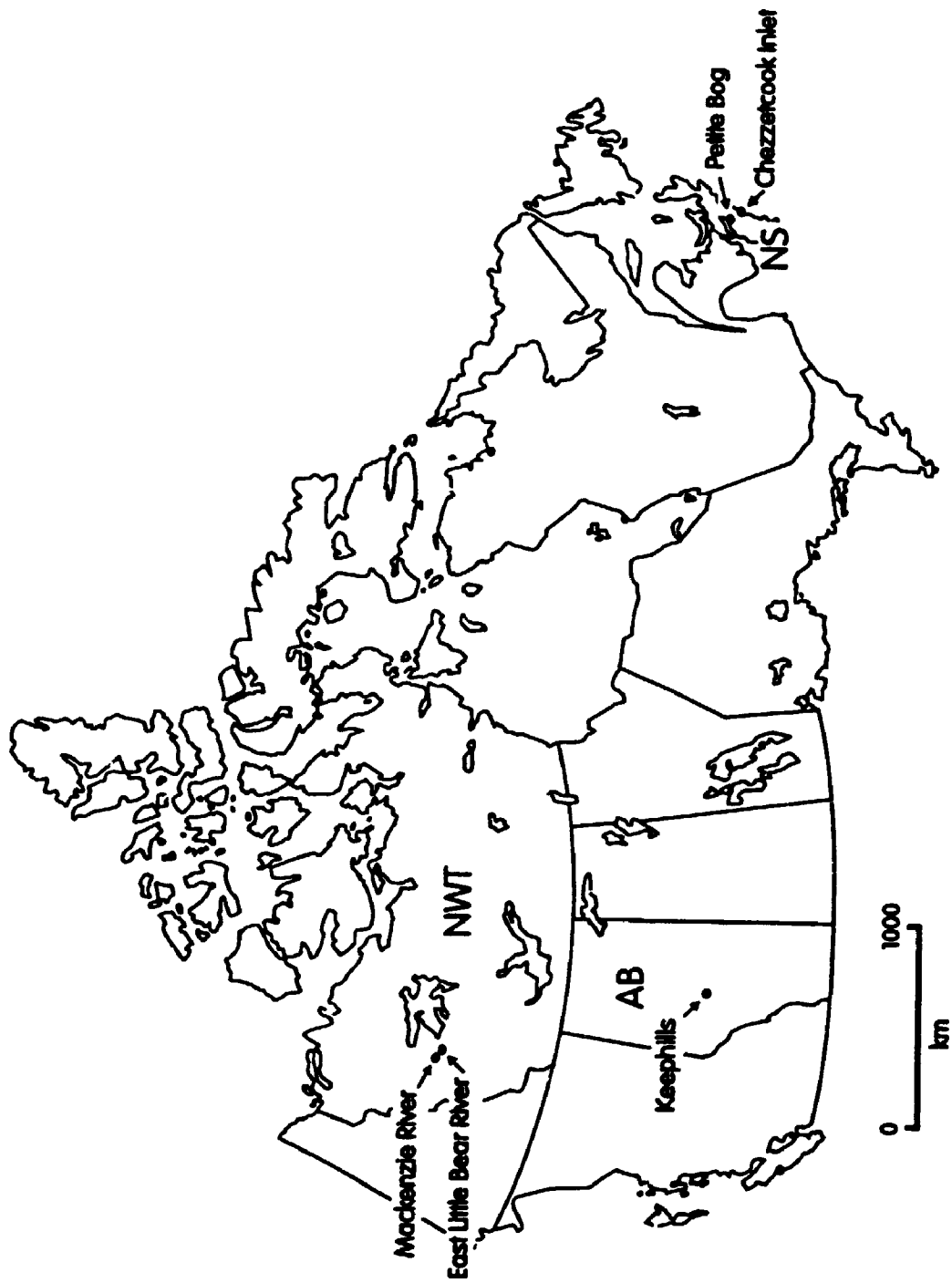
In this research, organic petrological methods and geochemical analyses were used as an innovative approach to assess the geochemical characteristics of the peat. Organic petrology provides valuable information about the degree of degradation of the peat, on the depositional environment, and the history of peat formation (Stach *et al.*, 1982).

Geochemical studies of peat have largely been restricted to bogs (e.g. Pakarinen *et al.*, 1980; Kalcher *et al.*, 1983; Pakarinen and Gorham, 1983; Day *et al.*, 1987; Shotyk, 1987a; Shotyk *et al.*, 1990, 1992). Areas situated in permafrost regions

Figure 1.1

Location of study sites

Petite Bog and Chezzetcook Inlet are located in Nova Scotia (NS), Keephills Fen in Alberta (AB), Mackenzie River deposit and East Little Bear River deposit in the Northwest Territories (NWT).



have usually been avoided, although more than half of Canadian peatlands occur in this zone (Zoltai, 1980). Similarly, as far as the author is aware, no geochemical research has been carried out on salt marshes in Atlantic Canada.

Peat is a precursor of coal (Stach *et al.*, 1982), and the increasing industrial use of this product in recent years (Ruel *et al.*, 1973; Coupal, 1982; Belanger *et al.*, 1988; Spedding, 1988), necessitates a greater understanding of its geochemical characteristics. There is also an urgent need for understanding the role of wetlands and peat in the process of global climate change, and to determine the effect of global warming on such ecosystems.

1.2 DEFINITION AND CLASSIFICATION

Peat is defined as the partially decomposed organic residues which have accumulated under anaerobic and waterlogged conditions (Heinselman, 1963; Clymo, 1983). However, there is still no consensus about the definition of peat with reference to its inorganic content. In soil science, peat is defined as an organic material with a carbon content greater than 17% (Canada Soil Survey Committee, 1978). In the peat fuel industry, the maximum inorganic content of peat is 40% (Monenco Ontario Ltd., 1981), while Andrejko *et al.* (1983) call peat an organic material with an inorganic content not greater than 25% on a dry weight basis. This thesis adopts the limit proposed by Andrejko *et al.* (1983) for the definition of peat. However, organic material with a mineral content greater than 25%, is defined as peaty muck, silty and clayey muck, depending on the inorganic content (see Appendix I). Different peats can also be distinguished by botanical composition and the type of peatlands in which they occur,

their names indicating the most common plant material from which they are composed (Tarnocai, 1984). Peat types encountered in this study are *Sphagnum* peat, brown moss peat, *Carex* or sedge peat, woody sedge peat, woody brown moss peat, amorphous peat, peaty, silty and clayey muck. Descriptions are given in Appendix I.

The sites where peat material occurs are called wetlands and/or peatlands (Zoltai *et al.*, 1973). Wetlands are waterlogged environments, characterized by hydrophytic vegetation and various biological activity adapted to wet conditions. They are divided into organic wetlands or peatlands, and mineral wetlands. The former are unbalanced systems in which the rate of accumulation of organic matter exceeds that of decomposition, and that are characterized by a minimum thickness of peat of 40 cm. The latter are mineral waterlogged soil areas, producing little or no peat, although they can be associated with hydrophytic vegetation (Zoltai *et al.*, 1973; Tarnocai, 1980).

According to the Canadian Wetland Classification system, wetlands are divided in five classes: bog, fen, marsh, swamp and shallow open water, which are further subdivided in 70 forms (Zoltai, 1988). Classes of wetlands described in this study are fen, salt marsh and bog (a domed bog and two peat plateau bogs). Detailed definitions of each wetland class and form studied are given in Appendix I.

1.3 METHODOLOGY

A brief overview of the methods used is given below. Where appropriate, detailed descriptions are referred to in Appendix II. Peat stratigraphy is described using field and microscopic (reflected white light and blue light excitation) observations. Mineralogical and elemental composition were determined, and selected samples were

submitted for radiocarbon dating and cesium isotope analyses. The degree of maturation and/or degradation of the peat material, and difference in depositional environment, were determined using organic petrological methods. Correlation was attempted between geochemical, mineralogical and petrological data, to explain elemental enrichment or depletion, and the possible association of the elements with the organic and/or the inorganic fraction of peat.

1.4 APPLICATIONS

Commercially, peat has been used mainly for horticultural purposes. But more recently, peat is increasingly considered as an alternative energy resource, although the potential use of peat as a fuel is tempered by a growing concern for the quality of the environment, particularly in Sweden and Finland (e.g. Maartmann, 1984; Björner, 1985; Ehdwall *et al.*, 1985; Pohjola and Häsänen, 1985). The commercial importance of peat studies is finally achieving recognition as being essential for understanding the geochemistry of coal, which has direct marketing consideration. Peat, as a raw material and as a fuel, has many potential uses, but it is important to understand the processes that govern its geochemistry in order to make the best use of it.

Environmentally, wetlands are amongst the most valuable ecosystems on Earth. For example, they serve as flood mitigation zones, habitats for rare and endangered flora and fauna, natural filters for sediments and nutrients, sinks for trace elements, and as carbon sinks (Bramryd, 1979; 1980; Mitsch and Gosselink, 1986; Williams, 1990). In the latter role they prevent the release of carbon into the atmosphere, mainly in the form of CO₂ and CH₄, which are some of the main contributors to the

greenhouse effect. Wetlands are threatened with alteration and destruction by both drainage and as a consequence of global warming (Armentano and Menges, 1986). Studies of their geochemistry are essential in order to be able to predict the potential impact of their loss and alteration on the environment.

The following sections describe the industrial uses of peat and peatlands, and their usefulness for environmental applications. Finally the role of wetlands in the assessment of global climate change is addressed.

1.4.1 Industrial uses

Industrial uses of peat are numerous, for example; as a heat source, a growing medium in horticulture, a depolluting agent, a construction and insulating material, and as raw material for the production of activated carbon and other products by pyrolysis (Ruel *et al.*, 1973; Coupal, 1982; Belanger *et al.*, 1988; Spedding, 1988). Furthermore, peat is becoming increasingly useful for medicinal purposes, in the treatment of ophthalmic diseases, gastric ulcers, and rheumatism (Belanger *et al.*, 1988).

Highly humified peat has long been used as a fuel, particularly in Ireland, Finland, Sweden and Russia, and studies on this subject abound in the literature (e.g. Kalmari and Leino, 1980; Komonen and Ekman, 1980; Maher, 1980; Suoninen, 1980; Lang, 1984; Oravainen and Asplund, 1984; Salo *et al.*, 1984; Seppänen *et al.*, 1984; Phelan, 1988). In the last decade, a resurgence of interest in the use of peat for fuel as an alternative energy source in Canada has led to numerous studies (e.g. Campion *et al.*, 1980; Chamberland *et al.*, 1980; Ismail *et al.*, 1980; Guliov and Korpijaakko, 1984; Rowe, 1985). To qualify as fuel peat, peat must have a high level of humification, a high

density and a low mineral matter content (Belanger *et al.*, 1988). Fuel peat can be fired in furnaces for heating or in boilers to generate steam for driving turbines and produce electricity; or it can be processed into different products such as synthetic natural gas, or methanol (Tarnocai, 1985). Due to its low sulfur content, peat as an energy source is a minimal contributor to acid rain in comparison to coal. However, there is some concern about the emissions from combustion of peat. Surveys were carried out at various peat-fired heating plants in Finland (e.g. Pohjola and Häsänen, 1985; Vesterinen and Huotari, 1985; Vesterinen *et al.*, 1988) and Sweden (Björner, 1985; Carlson, 1985), and electrostatic precipitators proved adequate for reducing the emission of harmful elements (Maartmann, 1984).

In Canada, peat is almost exclusively harvested for horticultural purposes. Slightly decomposed peat moss is used as a growing medium, as a soil conditioner and for soil mixes, peat pots, grow bags and grow boards (Belanger *et al.*, 1988). Light fibrous peat moss has a high water holding capacity, high cation exchange capacity, high buffering capacity, and its addition to mineral soils increase their chemical and physical parameters (Belanger *et al.*, 1988).

Peat has been intensively studied for its adsorption properties and ionic characteristics, and identified as having a great potential as a filtering and adsorption agent. The efficiency of the use of peat moss for removing contaminants, such as heavy metals (e.g. Lalancette and Coupal, 1972; Coupal and Lalancette, 1976; Gosset *et al.*, 1986; Borowiec, 1988), pesticides (Cloutier *et al.*, 1985), and oil (Viraraghavan and Mathavan, 1988) from waste waters has been demonstrated.

The value of peatlands for agricultural purposes has long been recognized, and unfortunately agricultural reclamation is the main cause of decline of wetlands in Canada. They have been drained and/or filled in order to make them suitable for growing forage crops, vegetables and cranberries (Tarnocai, 1985; Rubec *et al.*, 1988). The commercial harvest of forest supported by wetlands within the Boreal Forest Zone threatens these ecosystems (Zoltai *et al.*, 1988b).

1.4.2 Environmental applications

Besides being inexpensive and available in large quantities, peat possesses unique properties, as a mechanical, biological and chemical filter, that make it a very effective medium for the treatment of various wastes presenting environmental problems (Belanger *et al.*, 1988). A review of the use of peat in cattle, chicken and fish farms, in fox and mink nurseries, in water purification plants, in compost process, and in combating oil spills is given by Nyrönen and Selin (1985). Its role as a depolluting agent (see Section 1.4.1) is probably one of the most significant for the protection of the environment. It has practical applications for the use of peatlands and mineral wetlands *in situ* as a barrier to the spread of nutrients to groundwater (Loxham and Burghardt, 1983), and as an alternative to sewage treatment plants (Toth, 1980; Nichols, 1981; Borowiec, 1988; Williams, 1990).

Bogs are ombrotrophic ecosystems that receive their water and nutrient input, including heavy metals, solely from atmospheric deposition. Peat material is independent of the influence of groundwater, and therefore it appears that the content of heavy metals in the peat indicates the relative amount of heavy metals present in

atmospheric deposition at the time of peat formation (Martin and Coughtrey, 1982). Thus, ombrotrophic peatlands can be used for monitoring atmospheric deposition near a point source, such as a smelter or a coal-fired plant, or for determining regional differences (Pakarinen and Tolonen, 1977; Glooschenko and Capobianco, 1978; Glooschenko *et al.*, 1986). Successive peat layers can be dated using different methods, such as palynology, ^{14}C -, ^{210}Pb - or ^{137}Cs -analysis, allowing the possible reconstruction of an historical record of heavy metal deposition (Lee and Tallis, 1973; Livett *et al.*, 1979; Schell *et al.*, 1986; Schell, 1987).

1.4.3 Climate change

Increased combustion of fuel and human activity on terrestrial ecosystems have caused an increase of the CO_2 content in the atmosphere, which is one of the main anthropogenic contributors to the greenhouse effect (World Resources Institute, 1992). In terms of global carbon balance, it is essential to consider the net accumulation of organic matter in certain ecosystems, such as wetlands (Bramryd, 1979; 1980). Wetlands represent major accumulations of stored organic carbon, especially in the form of peat. Tarnocai (1988) estimated the total amount of carbon stored in Canadian wetlands to be 1.84×10^{11} tonnes, based on a total weight of 3.35×10^{11} tonnes of peat (Tarnocai, 1984), and an average carbon content of 50%. Significant amounts of CO_2 , CH_4 , H_2S and N_2O , (which are, except for H_2S , important infrared-absorbing trace gases and thus contribute to the greenhouse effect), are processed by wetlands (Armentano and Menges, 1986). A 3-year study, the Northern Wetlands Study (NOWES), was conducted in the Hudson Bay Lowland, to assess the significance of northern wetlands as sources or sinks

for biogenic gases, such as methane and carbon dioxide, from or into the atmosphere. Based on this survey, it has been shown that the contribution of northern wetlands to total methane emissions to the atmosphere is about 3 to 4% of all sources (Glooschenko *et al.*, 1991). Furthermore, this study shows that the Hudson Bay Lowland may act as a CO₂ sink.

Various studies appear to reveal a shift from carbon sinks to carbon sources, as a response to global warming (Billings *et al.*, 1982; 1983; Billings, 1987; Oechel *et al.*, 1993). A study by Billings *et al.* (1982) on cores from the wet coastal arctic tundra, shows that with a slight increase of temperature, the tundra ecosystem would become a net CO₂ source instead of a sink. Lowering the water table by 5 cm would have the same effect, added to a possible loss of postulated insulating effect of peat on soil temperature, thus leading to a lowering of the permafrost table (Billings *et al.*, 1983). The direct effect is an acceleration of the rate of organic matter decomposition (CO₂ source), which then prevails over photosynthesis (CO₂ sink). Oechel *et al.* (1993) present data indicating that the tundra on the North Slope of Alaska has become a net carbon source in the time period coinciding with recent warming in the Arctic, thus suggesting that global warming has affected the carbon flux from the Arctic tundra ecosystem, as postulated by Billings *et al.* (1982) and others.

These results show the possible impact that global warming could have on wetlands as sources or sinks for CO₂. It is not certain yet if global warming will cause an increase of methane production by the wetlands. However, the role of wetlands in the global carbon balance has been invariably altered, thus contributing further to global warming. The effect of drainage on wetlands is well documented; it results in peat

shrinkage and a shift from peat accumulation to peat oxidation, thus releasing CO₂ into the atmosphere, and heavy metals and nutrients into the environment (Armentano and Menges, 1986). This represents an example at a small scale of what may happen at a larger scale as a consequence of global warming. Therefore, it appears essential to understand the geochemistry of peat in order to be able to predict the impact of the alteration of wetlands on the environment due to global climate change.

1.5 PREVIOUS STUDIES

It is estimated that approximately 14% of the land surface of Canada is covered by wetlands (National Wetlands Working Group, 1986), of which more than half are perennially frozen and occur in remote areas (Zoltai, 1980). This largely explains the scarcity of data and surveys for these zones. Nevertheless, a compilation of data on the Canadian wetlands has been published by the National Wetlands Working Group (1988), which provides an invaluable reference source on the botanical, chemical and physical characteristics, and ecology and values of wetlands across the country.

Organic petrological studies of peat are rare when compared with the abundance of references on the organic petrology of coal. However, the peats of many coal formations were deposited in subtropical and tropical latitudes, and the studies of recent peat deposits in warm climatic zones, such as Florida (Cohen, 1968; Cohen and Spackman, 1977; 1980), Georgia (Cohen, 1974), and South Carolina (Staub and Cohen, 1978; 1979), Sarawak, Malaysia (Esterle *et al.*, 1989), and Indonesia (Moore and Hilbert, 1992) were shown to be important for understanding the origin of macerals and lithotypes of coals. These comparative investigations yield valuable information about the peat-

forming environment and the origin of coal. Temperate peats from the Fraser River delta, British Columbia, were investigated by Styan (1981) and Styan and Bustin (1983), who described the petrographic fabric and the composition of different peat types, at different stages of decomposition, in order to obtain information about the ultimate formation of macerals.

Cohen *et al.* (1987) give a review of the most important data provided by the studies of modern peat deposits, which may help to predict the characteristics of coal. The peatification process and the chemical and physical changes occurring at this early stage of coalification are described in Stach *et al.* (1982). Furthermore, the latter provide a classification and thorough description of macerals at the peat stage. Their research represents one of the best references for the organic petrographer. The work of Esterle *et al.* (1989; 1991) is of special interest, since they use reflected light instead of transmitted light for the study of peat, like the author, as opposed to most workers (e.g. Cohen and Spackman, 1972; 1980; Cohen, 1983; Styan and Bustin, 1983). Cohen *et al.* (1987) provide random reflectance values measured on different types of huminite material.

Peat deposits have also proven to be useful in geochemical exploration and they can be used to monitor growth and changes in atmospheric pollution. Since peat is a precursor of coal, all information about the geochemistry of peat is relevant to the study and use of coal. In particular, geochemistry provides evidence of the trophic status of ancient coal beds, one of the most elusive yet important aspects of their origin.

To date, the best historical review of the literature on peat, peatlands and geochemistry of peat has been written by Shotyk (1988). The reader is referred to this paper for a detailed review on these subjects.

Since bogs are ombrotrophic peatlands that receive their nutrients and inorganic constituents solely through atmospheric deposition, their usefulness as tools to record the atmospheric deposition of anthropogenic contaminants has been recognized (e.g. Glooschenko and Capobianco, 1978; Martin and Coughtrey, 1982; Percy, 1983; Taylor and Crowder, 1983; Glooschenko, 1986; Glooschenko *et al.*, 1986). The elemental composition of minerotrophic peats instead is largely dependent upon the chemistry of the underlying or surrounding bedrock. Since peats are able to concentrate heavy metals, the study of the geochemistry of minerotrophic peats has a direct application for geochemical exploration (e.g. Armands, 1967; Salmi, 1967; Boyle, 1977; Coker and DiLabio, 1979; Shotyk, 1987b).

Casagrande and Erchull (1976; 1977) studied the trace metal distribution in minerotrophic Okefenokee peats to help understanding how metals became incorporated into coal. The distribution and movement of elements in Scandinavian ombrotrophic bogs were investigated by Damman (1978), who gave conclusive information about the mobility of elements in a peat profile as related to the water level and its fluctuation. Dissanayake (1984; 1987) studied the geochemistry of peat in Sri Lanka and showed the strong association of metals with the clay particles within the peat. Schell *et al.* (1986) and Schell (1987) dated ombrotrophic *Sphagnum* peat with ^{210}Pb and ^{137}Cs in order to reconstruct the history of the atmospheric chemical deposition for the last 200 years. Raymond *et al.* (1987) described lateral and vertical variations in

chemical, botanical and mineralogical composition within a swamp-bog complex in Maine and developed a depositional model for this complex, based on these variations. Dominik and Stanley (1993) demonstrated the potential usefulness of boron, beryllium and sulfur as indicators of salinity and climate for peats of the Nile delta, Egypt; and in addition they related the elemental composition to the grain size. Various selected kinds of peat in the United States were investigated for their elemental and mineralogical composition in order to determine the relationship between the inorganic content of peat and the depositional and ecological setting (Cameron *et al.*, 1989; Raymond *et al.*, 1990).

Geochemical studies of Canadian peats are far more seldom. Peats of the Fraser River Delta, British Columbia, were intensively studied for their sulfur and minor element composition (Bustin *et al.*, 1985; Bustin and Lowe, 1987). Nicholson (1989) used chemical data to reconstruct the development of a mire complex in Alberta. Finally, Shotyk (1987a; 1988) and Shotyk *et al.* (1990; 1992) investigated numerous peat bogs in Ontario, New Brunswick and Nova Scotia and conducted a detailed study of the geochemistry of peats and peat waters. The distribution and behavior of major and trace elements in peat profiles were interpreted in relation with the mineral and botanic composition of the peat, atmospheric deposition, plant bioaccumulation and leaching (Shotyk, 1987a; Shotyk *et al.*, 1990). The relative depletion or enrichment of selected elements in the peat profile was shown and the mode of association of these elements was discussed (Shotyk, 1987a; 1988). The pore water geochemistry was investigated and the behavior of selected elements was explained in terms of the influence of pH and redox potential in the peatland environment, and summarized in a hypothetical *Sphagnum* bog profile (Shotyk, 1987a; Shotyk *et al.*, 1992).

Previous studies of the salt marsh in the West Head of Chezzetcook Inlet, Nova Scotia, involved the description of the stratigraphy and oceanographic characteristics of the site and the distribution of foraminiferal populations. A reconstruction of the changes in Holocene sea levels was subsequently developed (Scott, 1977a; 1977b; 1980; Scott and Medioli, 1978; 1980a; 1980b; 1982). Thomas and Varekamp (1991) and Varekamp *et al.* (1992) combined the study of foraminiferal assemblages and geochemical characteristics of a coastal salt marsh in Connecticut to demonstrate the punctuated rise in relative sea level in the Holocene. Furthermore, the pollution history of mudflat and marsh sediments in Connecticut was reconstructed using trace element geochemistry and ^{210}Pb analysis (Varekamp, 1991).

Much interest has been given to the study of mineral matter in peat and a compilation of papers on this subject is to be found in Raymond and Andrejko (1983). It is essential to understand the mode of occurrence, form and distribution of mineral matter in peat, considering the economical value of peat as a raw material or as a fuel, and furthermore in order to evaluate mineral matter in coal deposits. The origin and form of sulfur in peat is the subject of many studies, since sulfur in coal is a major consideration in coal marketing, and the abundance and different forms of sulfur are indicators of the depositional environment (e.g. Casagrande *et al.*, 1977; 1980; Altschuler *et al.*, 1983; Cohen *et al.*, 1983; Davies and Raymond, 1983; Berner, 1984; Given and Miller, 1985; Lowe and Bustin, 1985; Bustin and Lowe, 1987; Casagrande, 1987; Dominik and Stanley, 1993).

1.6 PEATIFICATION PROCESS

Waterlogged and oxygen-poor conditions are essential for the conversion of plant and animal debris to peat, since the accumulation of biomass in normal soil forming environments leads to the formation of humus (Gore, 1983; Anderson and Broughm, 1988). The resulting peat type depends on the type of original organic matter and on the amount and character of mineral matter which becomes incorporated in the decomposing organic material (Lüttig, 1986). Above all, it depends on the trophic status of the mire, i.e. the degree to which it is influenced by groundwater (Moore, 1987).

Peat diagenesis or peatification encompasses the physical, microbial and chemical changes that occur in the early stages of coal formation, termed also coalification (Teichmüller and Teichmüller, 1982). Peatification is a biochemical process, controlled mainly by the original plant material, facies, water and ion supply, degree of alkalinity and redox conditions (Teichmüller, 1982). It is divided into a humification and a gelification stage, described briefly in the following; for further details, the reader is referred to Teichmüller (1982). The former stage, which is the most important process during peatification, can be described as a slowly progressing oxidation which is particularly active at the peat surface and immediately below in the peatigenic layer. It results in the transformation of cellulose and lignin in the peat into humic substances. The reactions during the gelification process appear to be of a physico-colloidal nature, leading to the formation of soft, gelified humic tissues. Gelified tissues can be distinguished from ungelified tissues, using organic petrological methods (see Appendix II).

The physical changes during peatification include a decrease of porosity, linked with an increase of density and a reduction of the total water content, increase of the degree of decomposition, change of color towards dark brown and black, and increase of the calorific value (Teichmüller and Teichmüller, 1982; Lüttig, 1986). The easily hydrolyzable substances of plants, such as cellulose, hemicellulose, pectins and proteins are readily decomposed by bacteria and fungi, and lost partially as gaseous (carbon dioxide, methane, ammonia) byproducts and water, while the remaining material is transformed into humic substances. Lignin material is more resistant to bacterial and fungal attack and remains better preserved in peat; however, with increasing peatification, it is also converted into humic compounds. Lipids such as wax, resins, tannins, spores and pollens are virtually not affected by peatification (Naucke, 1976; Teichmüller, 1982). The decomposition of hydrophilic functional groups, particularly hydroxyl groups (-OH), but also carboxyl (-COOH), methoxyl (-OCH₃), carbonyl (> C = O) groups and ring oxygen, result in a decrease of oxygen and increase in carbon content (Naucke, 1976; Teichmüller and Teichmüller, 1982). The changes in carbon, oxygen, hydrogen, nitrogen and sulfur content of peat at different stages of decomposition are given in Naucke (1976).

The formation of humic compounds during peatification is essential since they are natural cation exchangers (Gamble *et al.*, 1983; Rashid, 1985) and are therefore responsible for the capacity of peat to concentrate and exchange metals (Coupal and Lalancette, 1976; Gosset *et al.*, 1986). Numerous studies demonstrate the ability of humic substances to absorb, exchange or complex various metal cations using their carboxyl, phenolic and hydroxyl functional groups (e.g. Wolf *et al.*, 1977; Takamatsu and Yoshida,

1978; Bloom and McBride, 1979; Clymo, 1983; Kadlec and Keoleian, 1986). Chelation is the most important bounding process, followed by surface adsorption and exchange reactions (Rashid, 1985). These reactions influence the solubility, precipitation, mobility, migration, redistribution and accumulation of metal cations, and are responsible for the elemental concentration in peat (Rashid, 1985).

CHAPTER TWO

STUDY AREAS

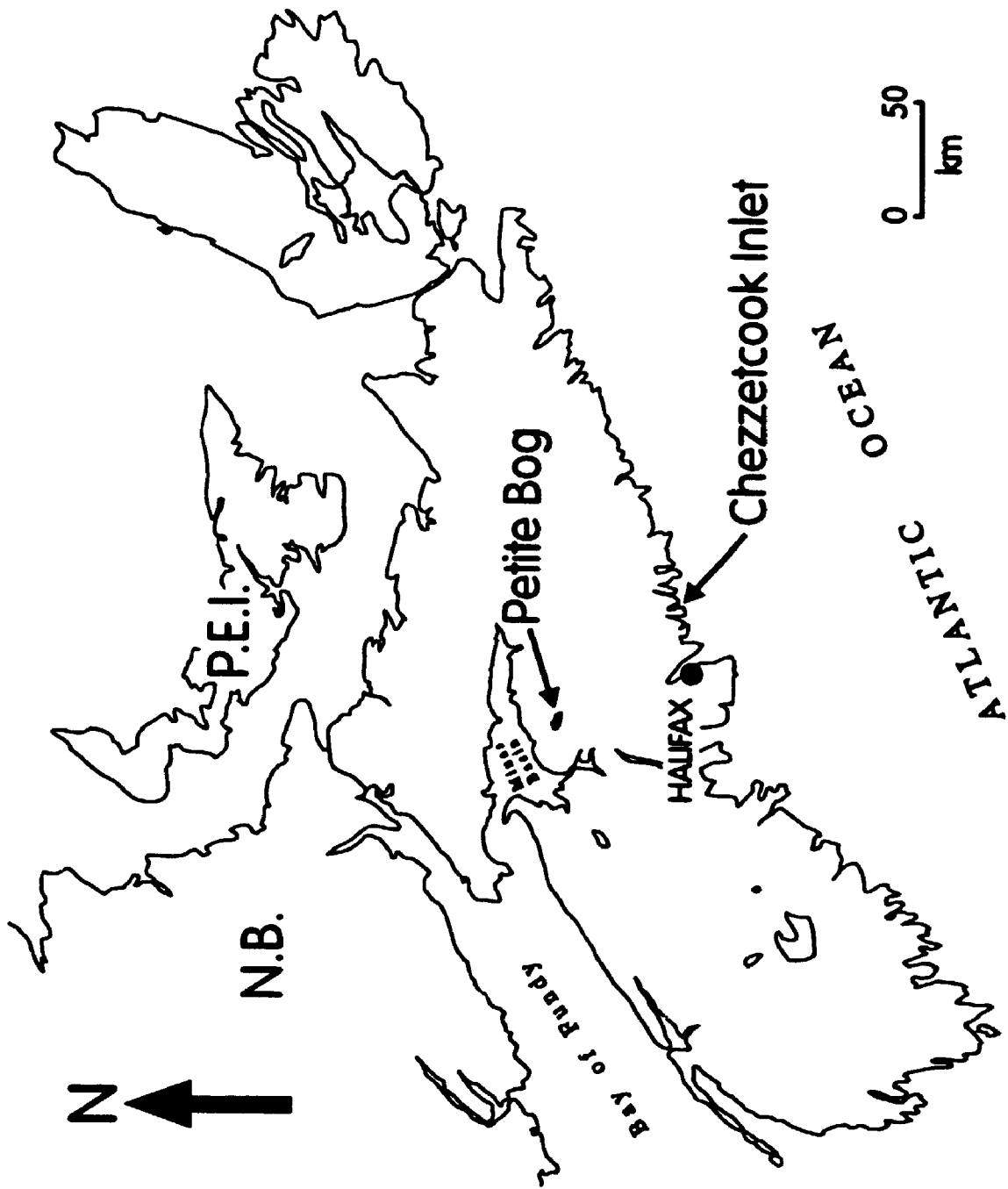
2.1 INTRODUCTION

Five peat-forming environments were selected for this study and represent some of the typical wetland forms encountered in Canada. Wetland regionalization is observed in Canada, generally along a north-south temperature gradient and an east-west precipitation gradient (Zoltai, 1980). Wetlands can be divided into arctic, subarctic, boreal, prairie, temperate, oceanic and mountain types. In each region, physiography and climate-related processes result in the development and establishment of specific kinds of wetland forms (Zoltai, 1980; 1988). In the following sections, the five wetland study areas are described.

2.2 NOVA SCOTIA

Nova Scotia is situated mainly in the Atlantic Boreal Wetland Region, which is characterized by a maritime climate, with cold winters and cool summers (Zoltai, 1980). This wetland region is divided into subregions, based on local variations in climate, topography, elevation, geology and proximity to the coast (Wells and Hirvonen, 1988). The two wetlands investigated are located in the Acadian Atlantic Boreal Wetland Subregion (domed bog, Hants County) and in the Coastal Atlantic Boreal Wetland Subregion (salt marsh, Halifax County), and are characteristic of these areas (Wells and Hirvonen, 1988); (Figure 2.1).

Figure 2.1 **Location map of study areas in Nova Scotia**



2.2.1 Petite Bog, Hants County

Petite Bog is situated approximately 20 km NE of Windsor and 5 km N of the community of Stanley (45°09'N; 63°56'W); (Kennetcook Map 11 E/4, Hants County, Nova Scotia, Scale 1:50,000, 1982). It is the second largest peat deposit in Hants County, with an area of 342 ha. The bog was inventoried and studied in 1982 and 1983, and is referred to as H21-7 (Anderson and Broughm, 1988). The region is characterized by a typical maritime climate with a frost free period of 100-130 days from May to early September and precipitation averaging 350 mm per year, with summer rainfall between 50 and 180 mm (Anderson and Broughm, 1988).

Bedrock consists of a succession of gently folded grey sandstones and red shales of continental origin, referred to as the Scotch Village Formation, which is part of the Pictou Group of early Pennsylvanian age (Stevenson, 1959; Keppie, 1979). This sequence unconformably overlies the early Carboniferous Windsor Group, which consists of red siltstone, gypsum, anhydrite and limestone (Boehner, 1986). A small karst area with a salt spring occurs 3 km west of the southwestern edge of Petite Bog (Stevenson, 1959; Boehner, 1986). This salt deposit, known as the Stanley occurrence, is of low economic value, and little is known about its lateral extent, structural configuration and salt quality (Boehner, 1986). However, the occurrence of salt brines in the vicinity of the bog may be a source of elements, such as Cl, Br, Na, K, and SO₄ in groundwaters seeping through the minerotrophic part of the Petite Bog mire complex. Surficial geology is dominated by late Wisconsinan Lawrencetown Tills derived from red to grey-brown sandstones and siltstones, which are present in the form of sandy-clayey loams (Cann *et al.*, 1954; Stea and Fowler, 1981; Anderson and Broughm, 1988; Stea *et al.*, 1992).

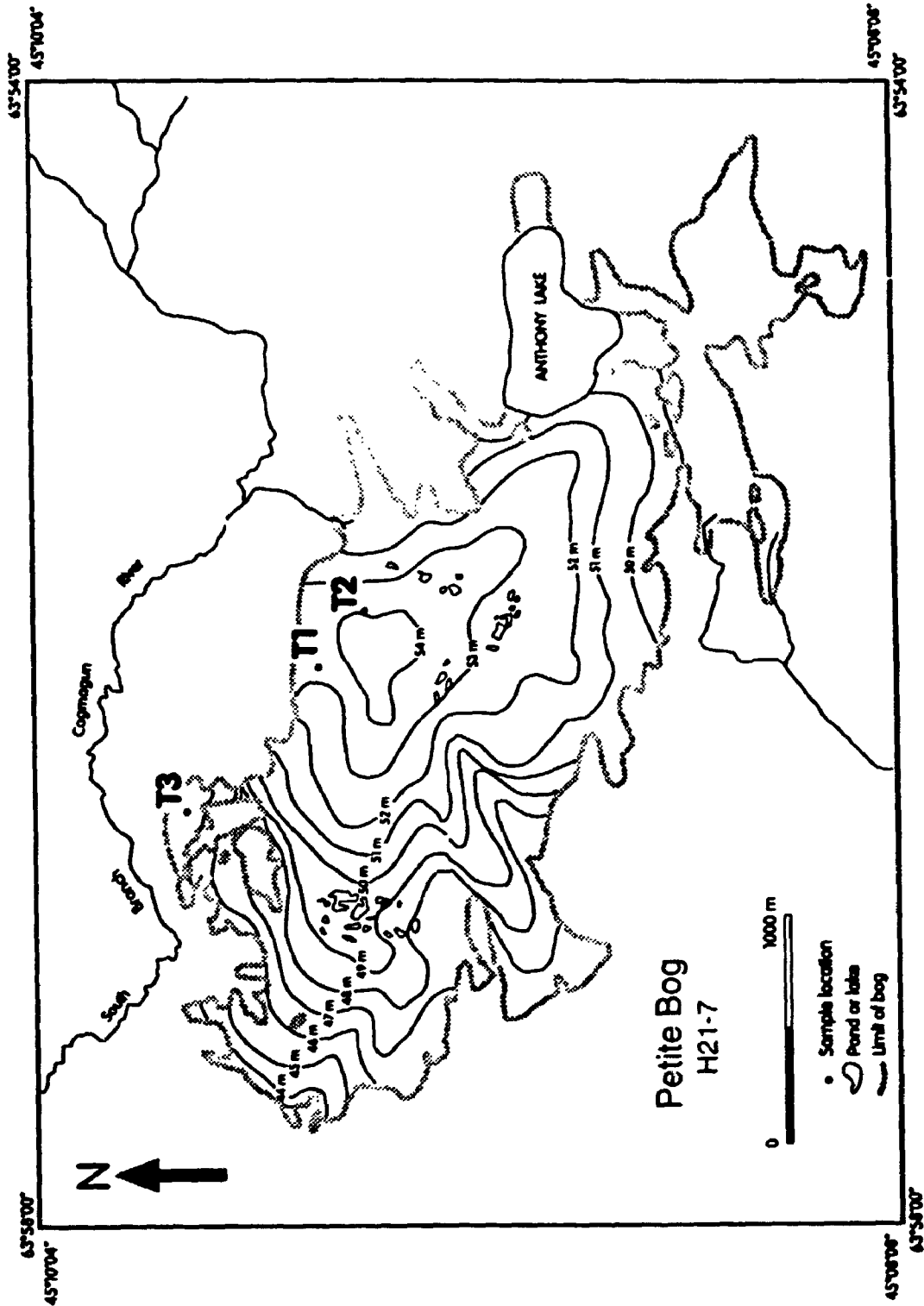
As with many other peat deposits in the County, the bog is believed to have developed as a result of the infilling of a lake or basin formed in till (kettle hole) following deglaciation at the end of the Late Wisconsinan about 10,000 years ago (Anderson and Broughm, 1988; Wells and Hirvonen, 1988; Stea *et al.*, 1992). Low oxygen concentration and low microbial activity in this anaerobic environment allow slow accumulation of undecomposed organic matter, which gradually builds above the water table and becomes independent of nutrient-rich seepage waters. As a consequence, minerotrophic plant species such as sedges and reeds, are gradually replaced by oligotrophic mosses, such as *Sphagnum* species, which obtain their nutrient needs solely through precipitation. Decreasing groundwater influence is related to lower microbial activity and oxygen deficiency; thus peat accumulation prevails over peat decomposition, contributing to the formation of a dome (Moore and Bellamy, 1974; Anderson and Broughm, 1988). However, peat accumulation is also controlled by climate, in particular the seasonality of precipitation and temperature (Calder and Gibling, 1994; Lottes and Ziegler, 1994).

Petite Bog is an asymmetrical domed bog with a maximum peat depth of 8.30 m and a maximum elevation of 54.30 m asl (metres above sea level); (Figure 2.2). Poorly humified surficial layers average 3.40 m in depth, while humified layers average 1.80 m in thickness. The total volume of peat has been estimated at 17.76 Mm³, or 2.86 million tonnes (Anderson and Broughm, 1988).

Most of the bog surface is covered by trees, commonly black spruce (*Picea mariana*) which are usually stunted to shrub height, and low ericaceous shrubs. *Sphagnum* mosses are the dominant bog plants, while the pitcher plant *Sarracenia*

Figure 2.2

Elevation map with sample locations, Petite Bog, Nova Scotia
Elevation in m asl (1 m contour interval).
(modified after Department of Mines and Energy, Province of
Nova Scotia, 1982)



purpurea is common, and orchids and iris occur in places (Plate 2.1a). Graminoid cover replaces *Sphagnum* moss near the margin of the bog, in the so-called lagg (Plate 2.1b).

Three cores were taken, which provide a good illustration of the progressive development of the domed bog; the minerotrophic stage (or fen stage) in bog evolution (core T3, in the lagg zone of the bog), the ombrotrophic stage (core T1, near the north margin of the bog), and dome development (core T2, at the edge of the dome); (Figure 2.2).

2.2.2 Salt marsh, Chezzetcook Inlet, Halifax County

Chezzetcook Inlet is located about 45 km ENE of Halifax, on the east shore of Nova Scotia (West Chezzetcook Map 11 D/11, Halifax County, Nova Scotia, Scale 1:50,000, 1991). Most of the mature marsh areas occur in the upper estuary, which is divided into West and East Heads. The area investigated (44°42'N; 63°15'W) is situated in the West Head (Figure 2.3), and is mostly middle marsh with steep-sided channels (Scott and Medioli, 1980a). Salinity in the upper estuary shows seasonal variations; in spring it is lowest, due to freshwater runoff (down to a few ‰), and in mid-summer, it reaches its maximum value (up to 20‰); (Scott and Medioli, 1980a).

Bedrock geology of the immediate area is dominated by quartzites, gneiss, greywackes and minor slates of the Goldenville Formation, Early Ordovician age, which is part of the Meguma Group (McBride, 1978). Surface geology consists mainly of Quartzite Till, a stony till derived from local sources. Numerous drumlins occur south of the Head of Chezzetcook Inlet and are largely composed of Lawrencetown Till (Stea and Fowler, 1979).

Plate 2.1

Vegetation in Petite Bog and in the salt marsh, Chezzetcook Inlet, Nova Scotia

- a - Treed margin (near core location T1), Petite Bog, Nova Scotia. In foreground, stunted trees and *Sphagnum* moss, typical of bog vegetation.
- b - Graminoid cover in lagg zone (near core location T3), Petite Bog, Nova Scotia.
- c - Salt marsh vegetation (near core location CH1a), West Head of Chezzetcook Inlet, Nova Scotia.

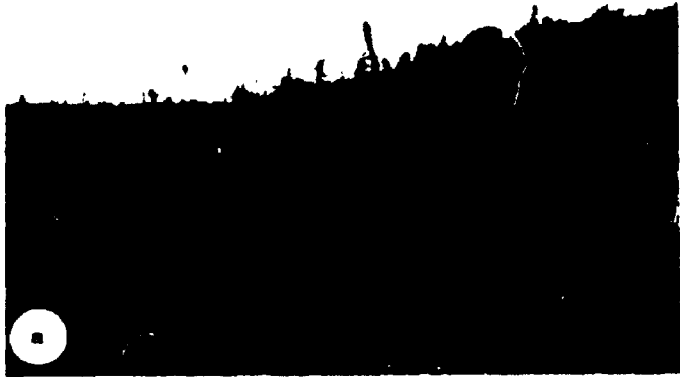
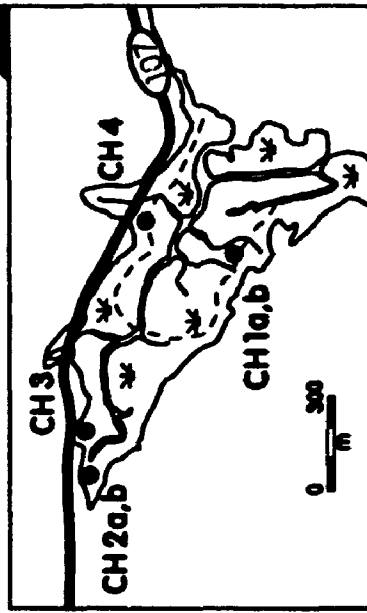
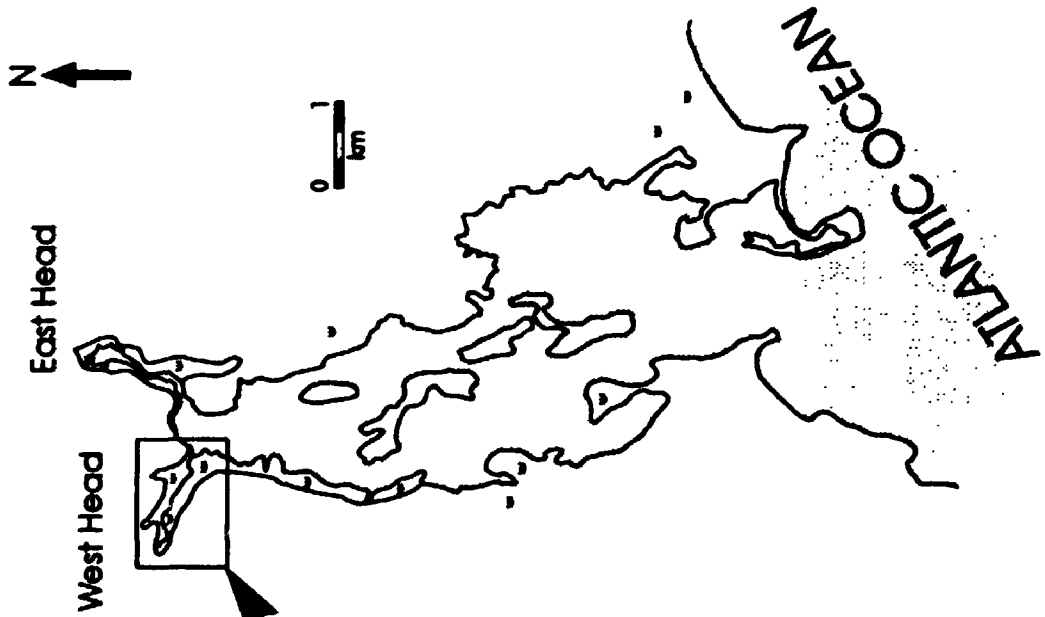


Figure 2.3

**Map of Chezzetcook Inlet and enlarged map of the West Head
with sample locations, Nova Scotia
(modified after Scott, 1980)**



Chezetcook Inlet

- Sample location
- * Marsh
- Road
- - - Mudflat extent

Chezzetcook salt marsh started forming as a result of sea-level rise approximately 6000 years ago, and is linked with the submergence of the Nova Scotia coast (Scott, 1980). A drill core in the West Head of the estuary shows the presence of freshwater peat, overlain by a gradational salt marsh sequence, which grades sharply into 10 m thick intertidal mudflats (see also Section 3.2.1.2); (Scott, 1977b, 1980). A shift back to extensive marsh formation 200 years ago in the West Head of Chezzetcook Inlet is believed to be associated with settlement by European immigrants (i.e. silting as a consequence of forest denudation); (Scott, 1980). Further development of salt marshes toward the mouth of the estuary since 1950 may be attributed to an increased sediment supply directly related to road construction at that time (Scott, 1980). A new road (Highway 107) was recently constructed across the northern portion of the salt marsh, and this may result in an increased sedimentation rate and anthropogenic pollution.

Marsh vegetation consists primarily of *Spartina patens*, which is typical of middle marsh (Plate 2.1c), underlain by *Spartina alterniflora* (Scott and Medioli, 1980a). Eel grass (*Zostera*) beds form on mudflats below sea level, and play a significant role in the formation of the salt marsh by trapping sediment, so that some surfaces rise faster than sea level, thereby enhancing the salt marsh colonization (Scott and Medioli, 1980a).

Two cores were taken, one representing the whole salt marsh sequence overlying the mudflat in the middle marsh (CH1a), the other representing the shallower marsh sequence overlying sedge peat in the high marsh (CH2a) located at the tip of West Head. In addition, surface cores (to a maximum depth of 0.20 m) were taken at locations

CH1b, CH2b, CH3 and CH4, in order to study the impact of heavy metal pollution caused by recent highway construction. Samples were taken at variable distances from the road (Figure 2.3).

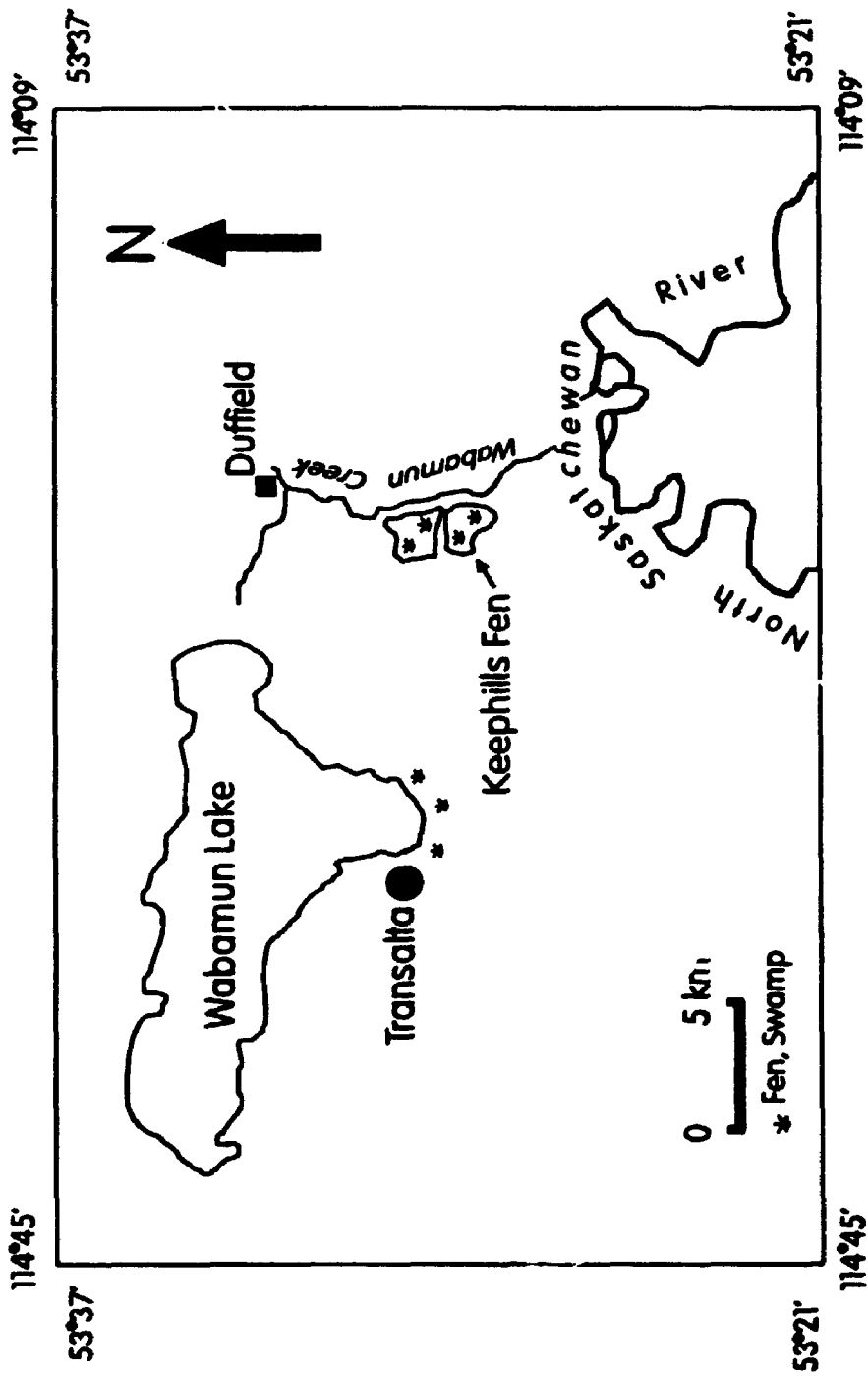
2.3 ALBERTA

2.3.1 Keephills Fen

The fen is located approximately 70 km W of Edmonton, and 10 km E of the Highvale Coal Mine and Transalta Power Station (53°28'N; 114°23'W); (Figure 2.4). It is situated in the boreal wetland region, characterized by a typical continental climate, with low annual precipitations and extremes in temperature (Zoltai *et al.*, 1988b). Mean July temperature average 10 to 17°C, while January temperatures average -15 to -25°C (Vitt and Andrus, 1977). According to 30-year mean meteorological data from the Glenevis station (approximately 30 km N of the fen), the study area has a growing season of 190 days, precipitation during this time reaches 389 mm, with total precipitation ranges between 500 and 600 mm (a total of 76 precipitation days); and annual mean temperatures average 2°C (Gignac and Vitt, 1990).

The 100 ha small fen is situated in the Interior Plains of Alberta, at an elevation of approximately 720 m asl. Bedrock geology is dominated by the Upper Maastrichtian Scollard Member, which is the younger formation in the Edmonton Group. It contains the thick Ardley Coal beds associated with a progradational sequence of clastic sediments (argillaceous sandstone, siltstone, mudstone and shale) deposited in shallow-water basins or lakes (Gibson, 1977; Smith, 1989). The light grey to buff weathered sandstone beds are mainly fine-grained, quartzose, bentonitic and parts can be

Figure 2.4 **Location map of Keephills Fen, Alberta**



very calcareous (Gibson, 1977). Surficial geology at the study area consists of a discontinuous outwash cover, composed of sand and gravel, and glacio-lacustrine deposits (Andriashek *et al.*, 1979; Klassen, 1989). The fen is situated in an area that became free of ice around 12,000 years ago (Prest, 1970; Klassen, 1989). However, numerous radiocarbon data of basal peat in the boreal wetland region show that, most commonly, peat formation was initiated some 2,000 years after the retreat of the Laurentide Ice Sheet (Zoltai *et al.*, 1988b).

Keephills Fen can be classified as a horizontal treed fen, a form of dry fen (Zoltai *et al.*, 1988b). Vegetation consists of black spruce (*Picea mariana*), tamarack (*Larix laricina*), swamp birch (*Betula pumila*), willow (*Salix wulfox*), and shrubs such as Labrador tea (*Ledum groenlandicum*), crowberry, bog cranberry, lichens, sedges (*Carex aquatilis*), bryophytes (*Sphagnum* moss, *Pleurozium schreberi*, *Tomenthypnum nitens*, and *Polytricum*), and mushrooms (Turchenek, pers. comm., 1991); (Plate 2.2a). *Tomenthypnum nitens* is characteristic of calcareous rich fens in the boreal forest region of North America and is very common in Alberta (Vitt and Hamilton, 1975; Slack *et al.*, 1980). *Sphagnum* mosses are rare, due to the prevalence of minerotrophic conditions.

A single core taken in the north part of the fen, consists of a 2.90 m thick peat sequence underlain by marl.

2.4 NORTHWEST TERRITORIES

The study areas are situated in the Low Subarctic Wetland Region, a region characterized by very cold winters and short, warm summers (Zoltai *et al.*, 1988a). Mean annual temperature is -6.6°C, with a mean daily July temperature of 15.3°C and a mean

Plate 2.2

Vegetation in Keephills Fen, Alberta and East Little Bear River Deposit and Mackenzie River Deposit, Northwest Territories

- a - Keephills Fen, Alberta. See text for description.
- b - East Little Bear River Deposit, Northwest Territories. Peat layer is underlain by silt sediments.
- c - Mackenzie River Deposit, Northwest Territories.



daily January temperature of -29.6°C . Precipitation averages 330 mm per year, while approximately 160 mm fall as snow (Atmospheric Environment Service, 1982). At Norman Wells, the number of days per year with frost reaches 239 (Burns, 1973). Permafrost is widespread in the subarctic region. The sites studied lie in the northern part of the "discontinuous widespread permafrost zone" (Brown, 1970), in which some unfrozen areas occur in a mainly frozen landscape.

Distinctive wetland forms are produced as a result of excess water and a severe climate. The main characteristic is their elevation above the water table of the lowlands, due to the effect of permafrost (Brown, 1970). A description of the most common subarctic wetland forms is to be found in Zoltai *et al.* (1988a). Wetland forms studied here are peat plateau bogs, which are perennially frozen ombrotrophic peatlands elevated approximately one meter above the water table of the surrounding wetlands (Zoltai and Tarnocai, 1975). The dry layer of exposed peat elevated above the water level insulates the underlying frozen mass from summer thawing, thereby initiating perennially frozen conditions (Brown, 1970). These elevated surfaces are exposed to winter winds which remove or reduce the insulating snow cover, resulting in greater permafrost penetration. Peat accumulation over the years is accompanied by an increase of permafrost thickness, thus leading to the formation of plateaux (Brown, 1970).

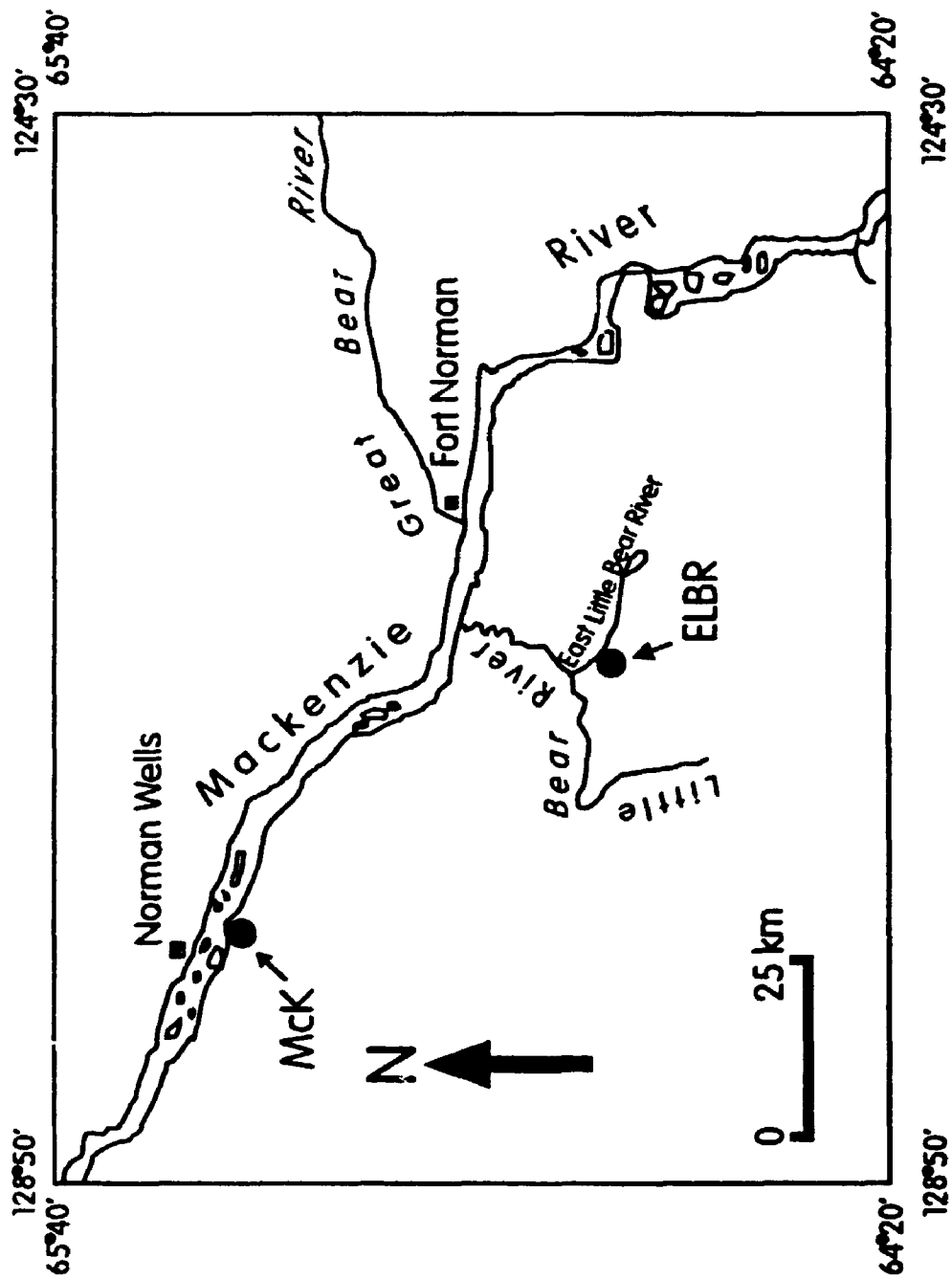
The two peat plateau bogs investigated are located on the left bank of the East Little Bear River, 25 km SSW of Fort Norman and on the left bank of the Mackenzie River, opposite Norman Wells, respectively (Figure 2.5).

Figure 2.5

Location map of study areas in the Northwest Territories

McK = Mackenzie River deposit

ELBR = East Little Bear deposit



2.4.1 East Little Bear River deposit

The peat deposit (64°43'N; 125°53'W) occurs within the Mackenzie Plain, which borders the NW part of the Mackenzie Mountains (Bostock, 1970), and is located in the Mackenzie Plain Synclinorium (Aitken and Cook, 1974). Bedrock geology consists of the East Fork Formation, of Campanian-Maastrichtian age, which conformably overlies the Little Bear Formation, constituting the core of the Mackenzie Plain Synclinorium (Yorath and Cook, 1981). The East Fork Formation consists of black, plastic shale, fine to medium grained sandstone, and locally interbedded mudstone (Yorath and Cook, 1981). Surficial sediments are essentially the silts, sands, and gravels characteristic of an alluvial floodplain, while the riverbank consists of colluvium (Hanley and Hughes, 1973). The peat deposit is located toward the upper part of the riverbank at an elevation of 150 m asl and its thickness varies between 1.20 and 1.60 m (Plate 2.2b).

Vegetation consists of small black spruce (*Picea mariana*), Labrador tea (*Ledum groenlandicum*), small tamarack trees (*Larix laricina*), and the ground layer is dominated by lichen, *Sphagnum* moss, graminoids and mushrooms.

Two sites were sampled at this deposit. At the river bank edge, where no permafrost occurs, a core of 1.80 m length was sampled. Within the peat plateau (at a distance of 10 m), another core of 1.30 m length was taken, in which permafrost was at 0.68 m depth. Sampling took place at the end of August, and therefore it can be assumed that the thickness of the measured unfrozen layer represents a good approximation of the maximum thickness of the active layer (Zoltai and Tarnocai, 1975).

2.4.2 Mackenzie River deposit

This peat deposit (65°12'N; 126°43'W) is located in the Mackenzie Plain. Bedrock geology consists of fine-grained sandstones and mudstones of the Trevor Formation, Late Albian to Turonian age (Yorath and Cook, 1981). Surficial deposits are glacio-lacustrine sediments dominated by fine-grained sand and silt, with a local veneer of eolian silt or sand (Hanley and Hughes, 1973). Peat occurs toward the upper part of the river bank, similar to the East Little Bear River deposit, at an elevation of 100 m asl (Plate 2.2c).

Smith (1992) postulates the existence of Glacial Lake Mackenzie, which extended over 800 km, between Fort Good Hope and Fort Simpson (N.W.T.), and formed as a result of a limestone barrier near Fort Good Hope and the glacial depression of the basin. Based on paleogeographic reconstruction of the proglacial lake (Fig. 9 - Smith, 1992), the peat deposit probably formed only after the lake retreated, around 10,290 years BP (Smith, 1992).

Vegetation cover consists of black spruce (*Picea mariana*), alder (*Alnus rugosa*), Labrador tea (*Ledum groenlandicum*), tamarack (*Larix laricina*), bearberry (*Arctostaphylos spp.*), *Sphagnum* moss and lichen.

A single core was taken within the peat plateau. Permafrost table was encountered at 0.17 m depth and underneath, ice lenses occurred in the mainly woody amorphous peat.

CHAPTER THREE

RESULTS

3.1 INTRODUCTION

In this chapter, peat stratigraphy is described, based on field and microscopic observations, and mineralogy is reported. Concentrations and distribution of selected major and trace elements are given versus ash content for each peat profile studied. In this study, ash content is defined as the percentage of inorganic matter remaining after combustion at high temperature. Interpretation of the results is presented in Chapter Four.

3.2 PEAT STRATIGRAPHY - ORGANIC PETROLOGY/MINERALOGY

3.2.1 Nova Scotia

3.2.1.1 **Petite Bog**

Three cores, T1, T2, and T3, were taken in Petite Bog (Figure 2.2). They are described separately, and a reconstruction of general peat stratigraphy through the bog is given in Chapter Four (Section 4.2.1.1). Field observations (peat type and degree of humification) were provided by Sandy Anderson and Wayne Broughm.

3.2.1.1.1 Core T1

The 3.00 m long core consisted of a 2.80 m thick peat sequence underlain by a fine layer of ooze overlying silty, bottom sediments. Sedge peat is the dominant

constituent of the basal peat zone (2.30-2.80 m), indicating minerotrophic conditions in the early stages of lake infilling. With decreasing depth, sedge peat is gradually replaced by *Sphagnum* peat. The upper section of the core (0 to 1.40 m depth) is composed of *Sphagnum* peat. Shrub fragments comprise up to 10% of the peat component in the lower part of the core (Figure 3.1, Table 3.1). Charcoal pieces were found at 2.25 and 2.65 m depth, respectively (Figure 3.1).

There is an increase of ash content, degree of humification (H), and *Carex* component with depth (Figure 3.1, Table 3.1). Ash content is below 1% in the ombrotrophic, poorly humified (H = 3) upper section of the core (0 to 1.65 m depth), and does not exceed 9% in the transitional, mesotrophic zone (composed of *Carex* and *Sphagnum* peat); (1.65 to 2.30 m depth); (maximum H = 6). However, it reaches up to 53% in the basal section of the core (2.60-2.70 m); (H = 7). The two intervals with higher ash content in the transitional and basal zone correspond with those containing charcoal. Ooze contains 27% organic material, while the organic content of silty bottom sediments is only 12% (Table 3.1).

pH measurements carried out in the field indicate acidic conditions in the bog. pH values increase from 3.6 at the surface to 4.8 at the interface between the peat sequence and ooze (Figure 3.1, Table 3.1).

The inorganic fraction of the bottom sediment low temperature ash (LTA) consists mainly of quartz (85%). Minor quantities of kaolinite, chlorite, mica and feldspars (plagioclase and K-feldspars) are present. Ooze mineralogy (unashed sample) is dominated by quartz with a significant proportion of mica, and only a few percent of

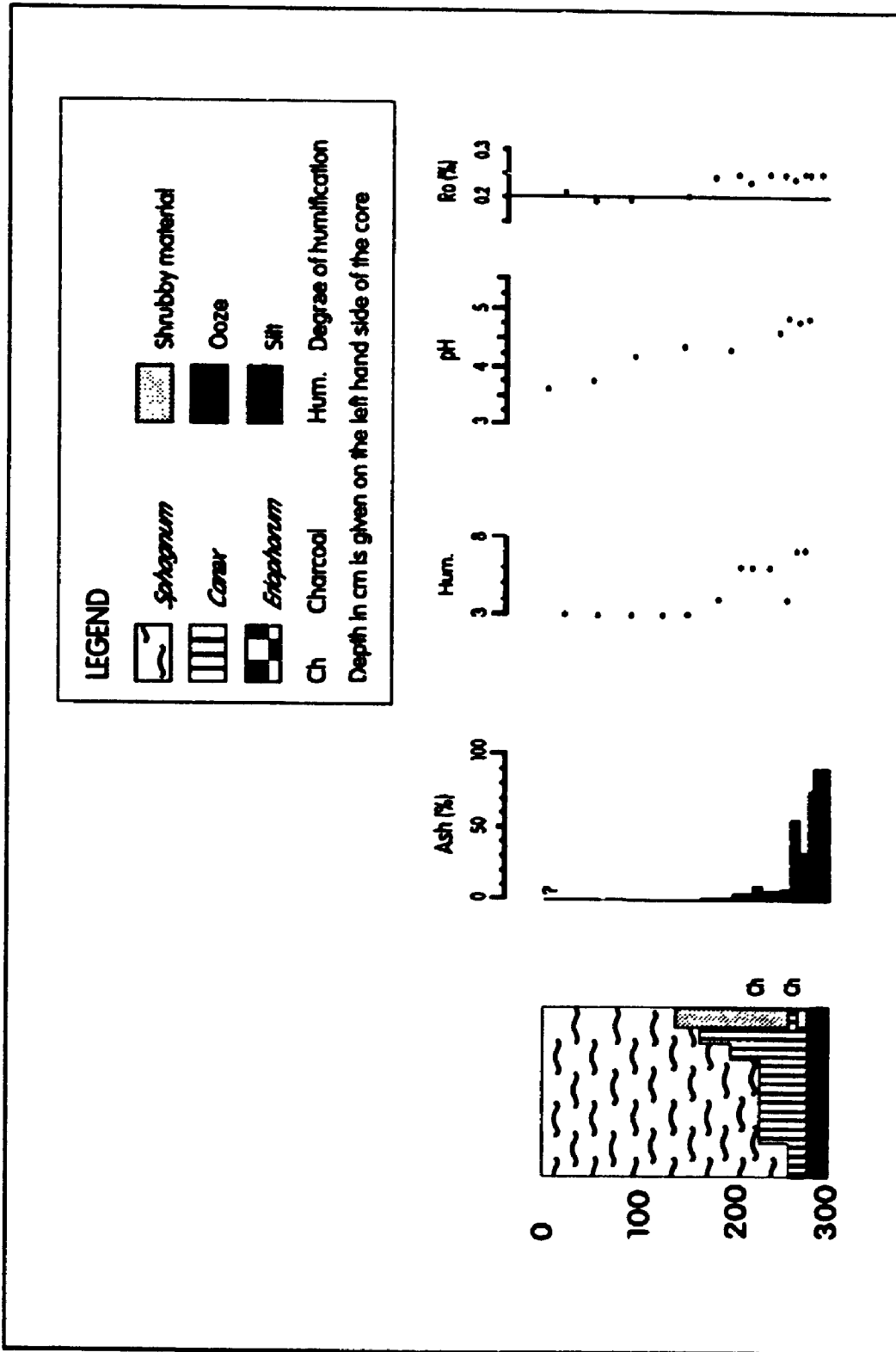


Figure 3.1 Peat type, ash content, degree of humification, pH and random reflectance (Ro%) of core T1, Petite Bog, Nova Scotia.

Depth (cm)	Peat type	Degree of humification	Ash (%)	pH	Ro (%)
0				3.6	
10-35	S0	3	0.9	n.a.	0.21 - 0.13'
35-70	S0	3	0.4	3.8	0.19
70-100	S0	3	0.3	n.a.	0.19 - 0.10'
100-140	S0	3	0.3	4.2	n.a.
140-165	S9N1	3	0.5	4.3	0.20 - 0.10'
165-200	S8C1N1	4	1.2	n.a.	0.24
200-220	S7C2N1	6	4.2	4.2	0.25
220-230	S7C2N1	6	9.1	n.a.	0.23 - 0.12'
230-250	C7S2N1	6	6.1	n.a.	0.25
250-260	C9N1	4	7.6	4.5	0.25
260-270	C0	7	53.4	4.8	0.24
270-280	C9N1	7	31.3	4.7	0.25 - 0.17'
280-285	ooze	-	72.7	4.8	0.25
285-300	silt	-	88.2	-	0.25

Peat type is determined as percent of peat constituents using recognizable features of original plants. 1 → 9 = 10% → 90%, 0 = 100%; S = *Sphagnum*, C = *Carex*, N = shrubby material.

The degree of humification is divided into 10 parts, according to the modified von Post Humification Scale (see Appendix III).

Random reflectance (Ro%) was determined on phlobaphinite, unless otherwise noted ' = textinite.
n.a. = not available

Table 3.1 Peat type, degree of humification, ash content, pH and random reflectance (Ro%) of core T1, Petite Bog, Nova Scotia.

clay minerals. The inorganic fraction of peat comprises mainly quartz and mica, with minor feldspar and clay minerals (Table 3.2).

Three types of peat were distinguished in this core: *Sphagnum*, *Sphagnum-Carex* and *Carex*.

First, the *Sphagnum* peat was fibrous and consisted almost exclusively of *Sphagnum* leaves and stems. In the surface layer no macerals (*sensu stricto*) were observed, probably due to the immaturity of peaty material. Cellulose-rich fibrous material was brown in reflected white light (did not display any reflectivity) and exhibited green to yellow fluorescence under blue light excitation (Plate 3.1a). Further down the profile, peat material was characterized by the abundance of well preserved textinite A, displaying red internal reflection and weak reflectivity in reflected white light (Plate 3.2a). Microspores and pollen grains were common. Phlobaphinite, characteristic of rootlets and wood fragments, was rare. A downward shift from red textinite A toward gray textinite B (Plate 3.2b) is observed.

Second, in the *Sphagnum-Carex* peat, textinite B was dominant over textinite A, probably as a result of advancing humification. Fusinite (pyro- and oxyfusinite) was common in this type of peat, reflecting a higher degree of oxidation as opposed to solely *Sphagnum* peat. At 2.25 m depth, large pieces of pyrofusinite were observed (Plate 3.1b, 3.1c). These were characterized by very high reflectivity and a yellow tint, usually due to the high degree of charring. Field observations revealed the presence of charcoal at this depth.

The *Carex* peat differed from the other types of peat because of the lack of fibrous and well preserved material, and the abundance of attrinitic material. This

Depth (cm)	lab	LTA	Q	M	F	K	W	C	B	O
Core T1										
10-35	1	x	76	M	p,f	k	-	-	-	-
100-140	1	x	60	22	tr	k	e	-	-	-
200-220	2	x	51	37	-	c	-	-	-	-
220-230	2	x	65	17	-	k	-	-	-	-
280-285	2	-	70	16	-	s,c	-	-	-	-
285-300	1	x	85	M	p,f	c,k	-	-	-	-
Core T2										
0-10	1	x	82	M	f,p	k	-	-	-	-
50-102	2	x	49	M	-	14k	-	-	28	-
270-300	2	x	49	M	p	-	-	-	42	-
300-350	2	x	45	-	-	-	-	-	49	a
350-360	1	x	23	M	-	tr	-	71	-	-
350-360	2	x	21	M	-	-	-	16	56	-
450-500	2	x	27	M	-	-	13h	-	56	-
575-580	2	x	90	-	-	-	-	-	B	-
700-740	2	x	72	20	-	-	-	-	B	-
740-750	1	x	87	M	f,p	c,k	-	-	-	-
Core T3										
10-20	1	x	63	24	tr	m,k	-	-	-	-
30-50	2	x	46	41	-	c,k	-	-	-	-
60-70	2	x	51	21	-	k	-	-	21	-
70-85	1	x	61	39	-	tr	-	-	-	-
160-170	1	x	74	M	p	12m	-	-	-	-

lab = Laboratory (1 = GSC Calgary, 2 = UWO London)

LTA = low temperature ash (x = LTA, - = unashed sample)

Q = quartz, M = mica, F = feldspars (f = K-feldspars, p = plagioclase), K = clays (c = chlorite, k = kaolinite, m = mixed-layer clays, s = sepiolite), W = calcium oxalate hydrate (e = weddelite, h = howellite), C = calcite, B = bassanite, O = others (a = amphibole)

Where concentrations are greater than 10%, a value is quoted, otherwise minerals are listed in order of concentration, from high to low (e.g. c.k = chlorite is in greater concentration than kaolinite), tr = trace amounts.

Table 3.2 Mineralogy of cores T1, T2 and T3, Petite Bog, Nova Scotia.

Plate 3.1

Color microphotographs of maceral types in peat of Petite Bog, Nova Scotia, 1

All photomicrographs taken in color, oil immersion. a under blue light excitation, b, c and d under reflected white light. The long axis of each photograph is 200 μm .

- a - Poorly degraded cell wall material displaying green fluorescence. Petite Bog, Nova Scotia.
- b - Pyrofusinite. Secondary xylem of angiosperm. Petite Bog, Nova Scotia.
- c - Pyrofusinite. Secondary xylem from undetermined plant material. Petite Bog, Nova Scotia. This type of pyrofusinite was commonly observed in all peatlands studied.
- d - Sclerotinite (fungal bodies) within matrix. Petite Bog, Nova Scotia.

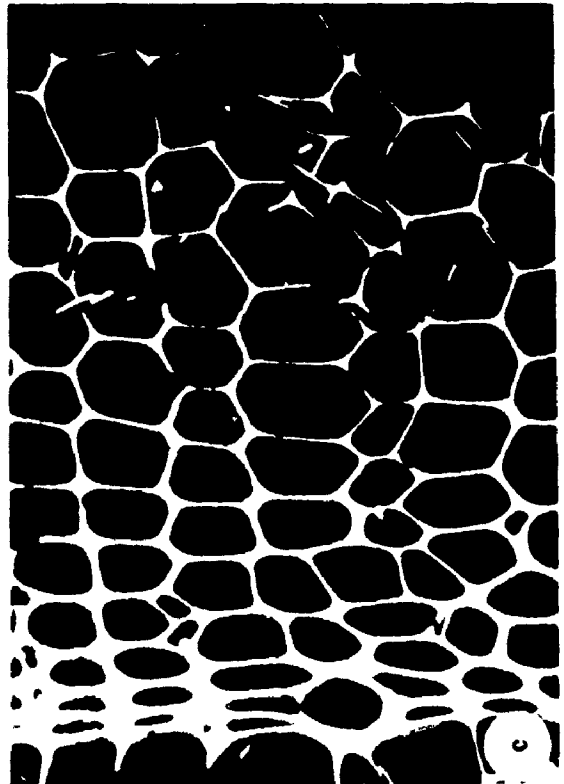
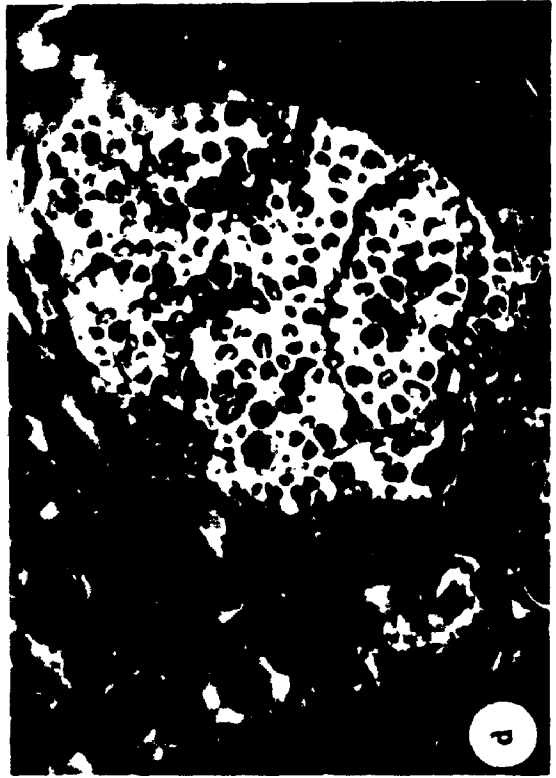
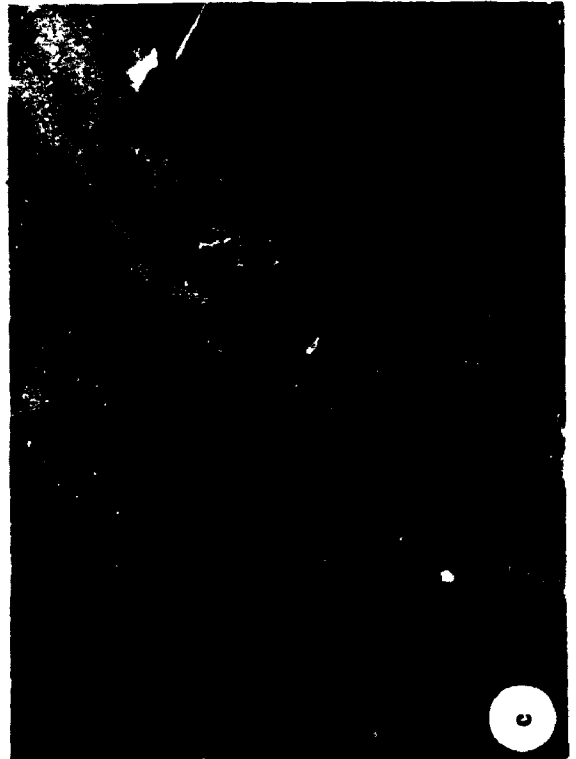
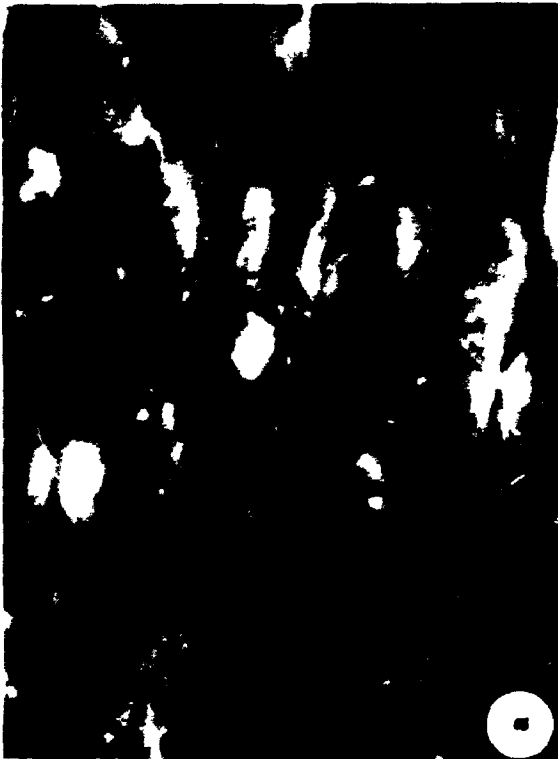


Plate 3.2

Color microphotographs of maceral types in peat of Petite Bog, Nova Scotia, 2

All photomicrographs taken in color, oil immersion. a, b and d under reflected white light, c under blue light excitation.

- a - Red reflecting textinite A. Petite Bog, Nova Scotia. The long axis of the photograph is 140 μm .
- b - Gray reflecting textinite B. Petite Bog, Nova Scotia. The long axis of the photograph is 140 μm .
- c - Cutinite displaying strong yellow fluorescence. Petite Bog, Nova Scotia. The long axis of the photograph is 200 μm .
- d - Same field as (c) but using reflected white light. Note the high relief. The gray background is epoxy resin. Petite Bog, Nova Scotia. The long axis of the photograph is 200 μm .



results from alteration and desegregation of huminitic material, probably enhanced by oxidizing waters flowing through the basal layer of peat in the bog. Furthermore, textinite was replaced by ulminite. Microspores and pollen were abundant, as was cutinite. Fungal remains (sclerotinite) were observed. Mineral matter trapped within the organic material became more abundant with depth. Corpohuminite was also more abundant than in upper layers, showing the higher component of woody material and rootlets. Furthermore, *Carex* are vascular plants, thus having rootlets, while *Sphagnum* are bryophytes, composed solely of leaves and stems. This explains the scarcity of phlobaphinite in *Sphagnum* peat, as opposed to *Carex* peat.

In the ooze and bottom sediments, microscopy reveals the presence of small fragments of ulminite and corpohuminite, as well as some inertinite material and a few spores, imbedded in the inorganic fraction.

Reflectance measurements were carried out mainly on phlobaphinite, to allow comparison through the profile (see Appendix II). They reveal a shift between purely ombrotrophic *Sphagnum* peat, which is either little or not humified ($R_o < 0.2\%$), and minerotrophic peat in the lower section containing *Carex*, which is more degraded. ($R_o > 0.2\%$); (Figure 3.1, Table 3.1). Some reflectance measurements were taken on textinite, for comparison. Although the reflectance values are lower than those taken on phlobaphinite, they show a similar trend, being higher in the basal peat ($R_o = 0.17\%$) than in the surficial peat layer ($R_o = 0.13\%$).

3.2.1.1.2 Core T2

A 7.50 m long core was taken, consisting of a 7.40 m thick peat sequence overlying silty sediments. A similar peat succession to Core T1 was observed. The 0.60 m thick basal peat layer consists mainly of *Carex* peat, while *Sphagnum* peat becomes dominant with decreasing depth. The top 5.20 m of the peat core are composed almost exclusively of *Sphagnum* peat, with a minor component (up to 10%) of shrubby material in places (Figure 3.2, Table 3.3). In the lower section of the core, shrubby material comprises up to 20% of the peat material. At 5.60-5.75 m depth, cotton grass, *Eriophorum*, constitutes 20% of the peat. This overlies an horizon containing charcoal. Small charcoal pieces occur at 5.75, 5.80 and 5.90 m depth, reflecting the occurrence of repeated fires during early peat accumulation in the bog.

Ash content in the strictly ombrotrophic part of the peat sequence (0.10 to 5.20 m depth) does not exceed 1.3% and averages 0.7%. However, the surface layer (0 to 0.10 m depth) is characterized by mineral matter enrichment as compared with the underlying peat. The inorganic fraction increases with depth but does not exceed 5%, except in the basal peat layer immediately above silty bottom sediments, here it reaches 21% (Table 3.3). The 5.20 m thick *Sphagnum* peat sequence composing the dome of the bog is poorly humified ($H = 3$). Conversely, the more minerotrophic section of the peat sequence has a generally higher degree of humification (Table 3.3).

pH measurements were taken in the upper 4 m of the peat sequence. They increase slightly with depth, ranging from 3.7 to 4.3 (Figure 3.2, Table 3.3).

Mineralogy of the bottom sediment LTA consists mainly of quartz (87%), with a minor fraction of mica, feldspars and clay minerals. Quartz is also the dominant

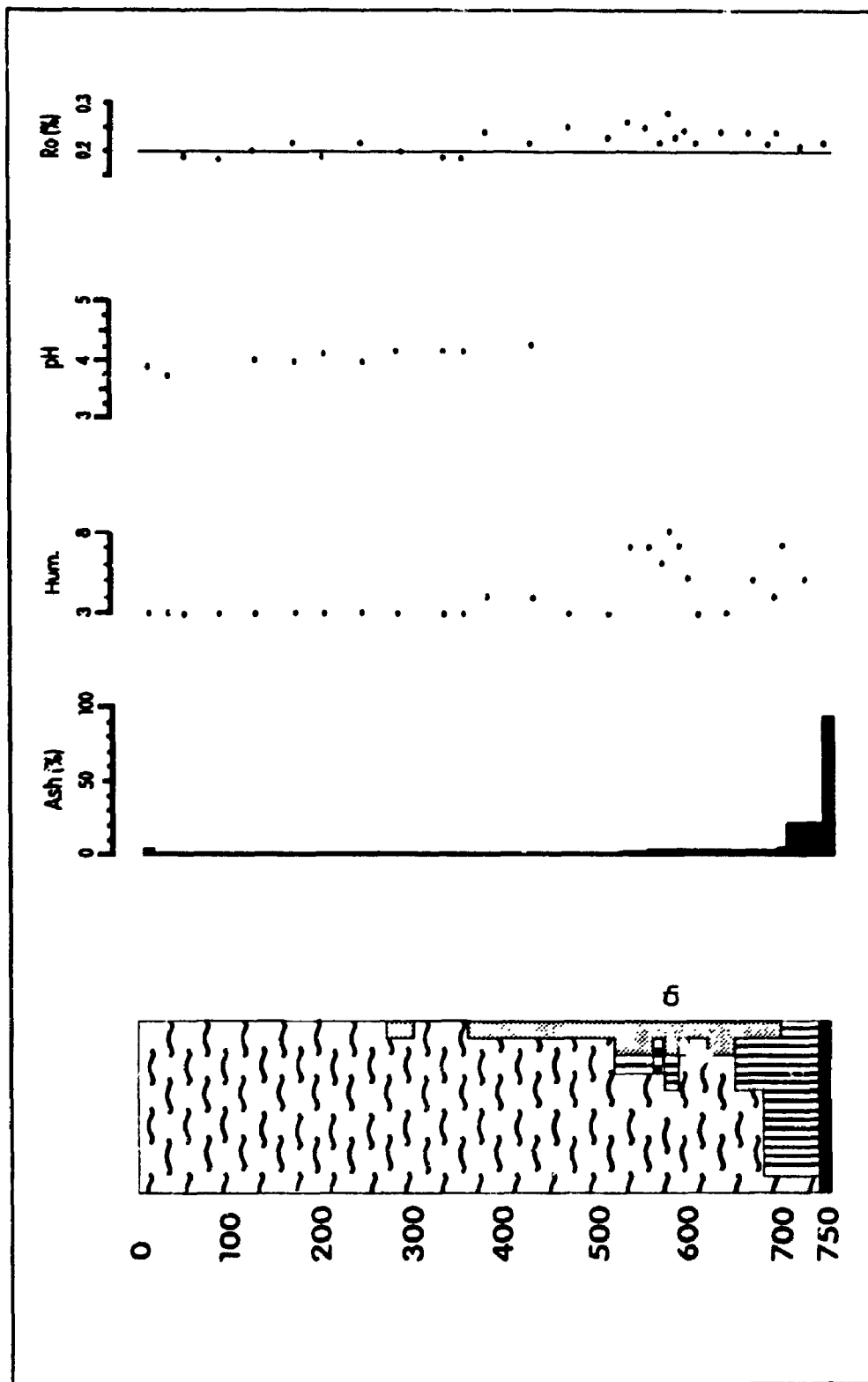


Figure 3.2 Peat type, ash content, degree of humification, pH and random reflectance (Ro%) of core T2, Petite Bog, Nova Scotia. (Legend see Fig. 3.1)

Depth (cm)	Peat type	Degree of humification	Ash (%)	pH	Ro (%)
0-10	S0	3	4.1	3.9	n.a.
10-30	S0	3	0.7	3.7	n.a.
30-50	S0	3	0.8	n.a.	0.19
50-102	S0	3	0.8	4.0	0.18 - 0.15'
102-140	S0	3	0.6	4.0	0.20
140-175	S0	3	0.4	4.1	0.22
175-225	S0	3	0.4	4.0	0.19
225-270	S0	3	0.5	4.2	0.22
270-300	S9N1	3	0.4	4.2	0.20
300-350	S0	3	0.4	4.2	0.19
350-360	S0	3	0.5	n.a.	0.19
360-400	S9N1	4	0.6	4.3	0.24
400-450	S9N1	4	1.3	n.a.	0.22
450-500	S9N1	3	1.3	"	0.25
500-520	S9N1	3	1.0	"	0.23
520-550	S7N2C1	7	1.7	"	0.26 - 0.18'
550-560	S7N2C1	7	2.2	"	0.25
560-575	S7Er2N1	6	2.3	"	0.22
575-580	S6C2N2	8	2.6	"	0.28
580-590	S6C2N2	7	3.7	"	0.23
590-600	S8C1N1	5	2.5	"	0.24
600-620	S9N1	3	2.7	"	0.22
620-650	S8N2	3	2.6	"	0.24
650-680	S6C3N1	5	3.1	"	0.24
680-690	C8S1N1	4	2.5	"	0.22
690-700	C8S1N1	7	4.6	"	0.24
700-740	C9S1	5	21.0	"	0.22
740-750	silt	-	92.1	-	0.22

Peat type is determined as percent of peat constituents using recognizable features of original plants. 1 → 9 = 10% → 90%, 0 = 100%; S = *Sphagnum*, C = *Carex*, E = *Eriophorum*, N = shrubby material. The degree of humification is divided into 10 parts, according to the modified von Post Humification Scale (see Appendix III).

Random reflectance (Ro%) was determined on phlobaphinite, unless otherwise noted ' = textinite.
n.a. = not available

Table 3.3 Peat type, degree of humification, ash content, pH and random reflectance (Ro%) of core T2, Petite Bog, Nova Scotia.

mineral fraction of peat in the overlying peat sequence. Bassanite was abundant in many samples. Mica and clay minerals constitute the other common mineral components. Calcite was observed at 3.50 to 3.60 m depth in duplicate samples (Table 3.2).

As in Core T1, three types of peat were distinguished: *Sphagnum* peat, *Sphagnum-Carex* peat and *Carex* peat.

Surface *Sphagnum* peat (0 to 0.10 m depth) consisted of fibrous material which was brown in reflected white light, and showed fluorescence under blue light excitation. Inertinite material occurred in trace amounts. Further down the core (0.10 to 5.20 m depth), textinite A and B were both observed, but phlobaphinite was minor, due to the scarcity of woody component in *Sphagnum* peat. Fungal remains (sclerotinite) were dispersed in the matrix. Pollen grains and microspores were common, displaying yellow to orange fluorescence. Textinite B became more dominant with increasing depth.

Sphagnum-Carex peat (5.20 to 6.80 m depth) was characterized by the occurrence of *Carex* twigs and rootlets. These were represented by phlobaphinite (and suberinite). Textinite B, which originated from *Sphagnum* leaves and stems, was common. High fluorescing cutinite and pollen grains were also common. Rootlets and some large pieces of sclerotinite were observed (Plate 3.1d). Fusinite and inertodetrinite were more frequent than in the upper section of the peat sequence. Between 5.75 and 5.80 m depth, inertinite material and highly oxidized textinite comprised up to 90% of the peat material. An increase of inorganic matter was observed.

Carex peat (6.80 to 7.40 m depth) contained large quantities of humodetrinite, and phlobaphinite. The proportion of mineral matter was highest in this type of peat.

Bottom sediments contained humodetrinite and fragments of textinite B and ulminite imbedded in an inorganic matrix.

Random reflectance measured on phlobaphinite displayed similar trend than observed in core T1. Ombrotrophic peats in the upper section are poorly humified ($R_o < 0.22\%$). Below a depth of 3.60 m, R_o is higher ($> 0.22\%$), reflecting a higher degree of degradation (Figure 3.2, Table 3.3).

3.2.1.1.3 Core T3

A 1.70 m long core was taken in the lagg zone of the mire complex. The 1.60 m thick peat sequence, composed mainly of *Carex* peat, was underlain by clayey bottom sediments. *Sphagnum* peat dominated over *Carex* peat only in the surface layer (0 to 0.20 m depth); (Figure 3.3, Table 3.4). A rapid decrease of the *Sphagnum* component was observed downcore, reflecting the strongly minerotrophic conditions in this wet part of the mire.

Ash content is relatively high. Figures vary from 2.8 to 30.8%, the highest being in the basal peat layer immediately above the bottom sediments. Ash content between 0.30 and 0.50 m depth reaches almost 18%. Comparison with the other cores indicates that the degree of humification is higher in this part of the bog, and is very similar to the lower section of cores T1 and T2 ($4 < H < 7$); (Table 3.4).

pH values vary between 4.5 at the surface and 5.5 at 0.50 m depth, reaching 5.3 at the base of the peat sequence (Figure 3.3, Table 3.4).

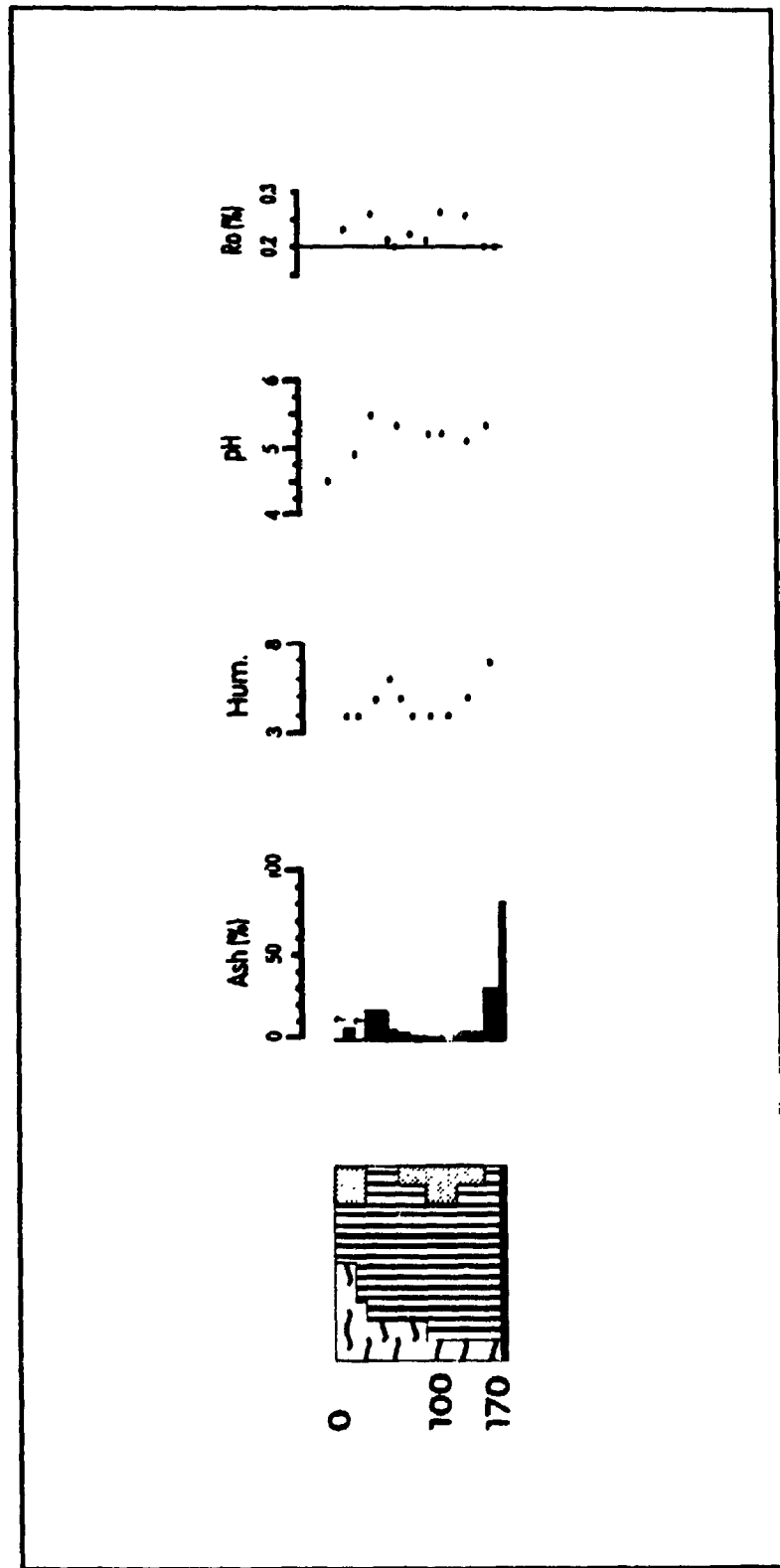


Figure 3.3 Peat type, ash content, degree of humification, pH and random reflectance (Ro%) of core T3, Petite Bog, Nova Scotia. (Legend see Fig. 3.1)

Depth (cm)	Peat type	Degree of humification	Ash (%)	pH	Ro (%)
0				4.5	
10-20	S5C3N2	4	8.9	n.a.	0.23
20-30	C5S3N2	4	n.a.	4.9	n.a.
30-50	C8S2	5	17.6	5.5	0.26
50-60	C8S2	6	6.8	n.a.	0.21
60-70	C7S2N1	5	5.3	5.3	0.20
70-85	C7S2N1	4	3.3	n.a.	0.22
85-100	C7N2S1	4	2.8	5.2	0.21
100-115	C7N2S1	4	3.5	5.2	0.27
115-140	C8S1N1	5	4.8	5.1	0.26
140-160	C9S1	7	30.8	5.3	0.20
160-170	silt	-	80.4	-	0.20

Peat type is determined as percent of peat constituents using recognizable features of original plants. 1 → 9 = 10% → 90%, 0 = 100%; S = *Sphagnum*, C = *Carex*, N = shrubby material.

The degree of humification is divided into 10 parts, according to the modified von Post Humification Scale (see Appendix III).

Random reflectance (Ro%) was determined on phloretininite.

n.a. = not available

Table 3.4 Peat type, degree of humification, ash content, pH and random reflectance (Ro%) of core T3, Petite Bog, Nova Scotia.

Mineralogy of bottom sediment LTA is dominated by quartz (74%), with a significant proportion of mixed-layer clays (12%), mica and plagioclase. Phyllosilicates represent a major component of the inorganic fraction of the peat in the lagg area, although quartz is still the dominant fraction (Table 3.2).

Here, only two types of peat were distinguished: *Sphagnum-Carex* peat and *Carex* peat. The *Sphagnum* component is dominant only in the surface peat layer, and its abundance in the vegetation cover of this area of the bog was observed during field sampling.

Sphagnum-Carex peat in the surface layer is characterized by the dominance of *Sphagnum* leaves and stems, which occurs in the form of textinite A and B. Inertodetrinite is observed, as well as a few pollen grains and spores, and some rootlets.

In the *Carex* peat (0.20 to 1.60 m depth), the inertinite content (pyrofusinite and oxyfusinite) was high in a few intervals. Microspores and pollen grains displayed an orange fluorescence, an indicator of oxidizing conditions in the rheotrophic lagg zone. Phlobaphinite constituted a significant portion of the organic material, while textinite B and ulminite prevailed over textinite A. Cutinite was evident throughout the peat sequence, displaying high relief in reflected white light and bright yellow fluorescence under blue light excitation (Plate 3.2c, 3.2d).

In the bottom sediments, humodetrinite, ulminite fragments, and numerous fragments of pollen grains were observed imbedded in the inorganic matrix.

Reflectance values have no vertical trend, but are similar to those measured in the lower minerotrophic sections of cores T1 and T2 (mean Ro% = 0.23%); (Figure 3.3, Table 3.4).

3.2.1.2 Salt marsh, Chezzetcook Inlet

3.2.1.2.1 Introduction

Scott (1980) reported a vegetation pattern in the West Head of the Chezzetcook Inlet as follows: *Cyperaceae* and *Juncus gerardi*, (which are plants typical of high marsh), underlain by *Spartina patens*, (characteristic for middle marsh), and *Spartina alterniflora*, (a low marsh plant). Bottom sediments consisted of mudflat (Figure 3.4). Two cores (CH1a and CH2a), representing the above sequence, were taken. Due to the high degree of degradation, botanical composition was not identifiable. During coring of both cores CH1a and CH2a (with the MacAulay auger), gas-filled bubbles and a purgent odor, taken to be H₂S, were detected (J. Calder and A. Beaton, pers. comm., 1991). In the following sections, both cores are described, based on organic petrological analysis, and their mineralogy.

3.2.1.2.2 Core CH1a

The 2 m core consisted of amorphous organic material (originating from *Spartina* plant remains); (Scott, 1977b, 1980) in a fine clayey matrix. Ash content averaged 58%, and therefore the organic-rich material is termed clayey muck (Appendix 1). Only the 0.05 m thick basal layer has an inorganic content (ash) smaller than 30% (Figure 3.5, Table 3.5).

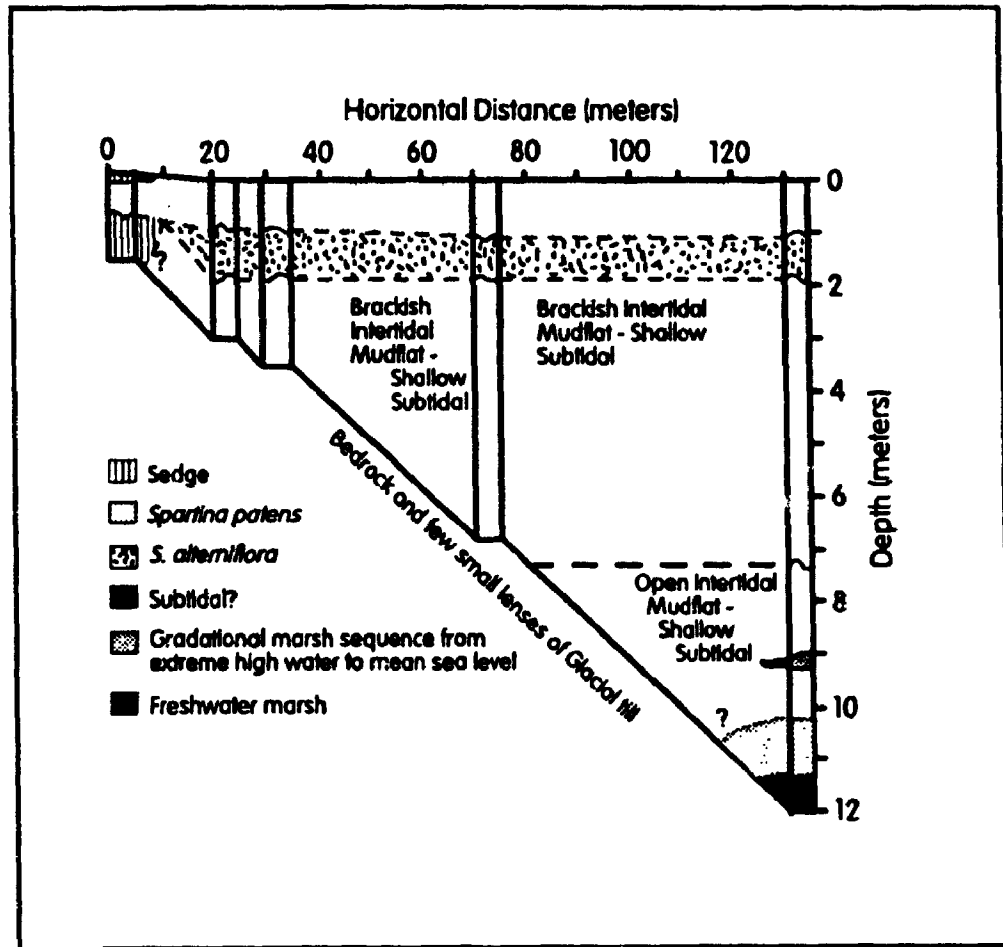


Figure 3.4 Stratigraphy in West Head of Chezzetcook Inlet, Nova Scotia. (Modified after Scott, 1980).

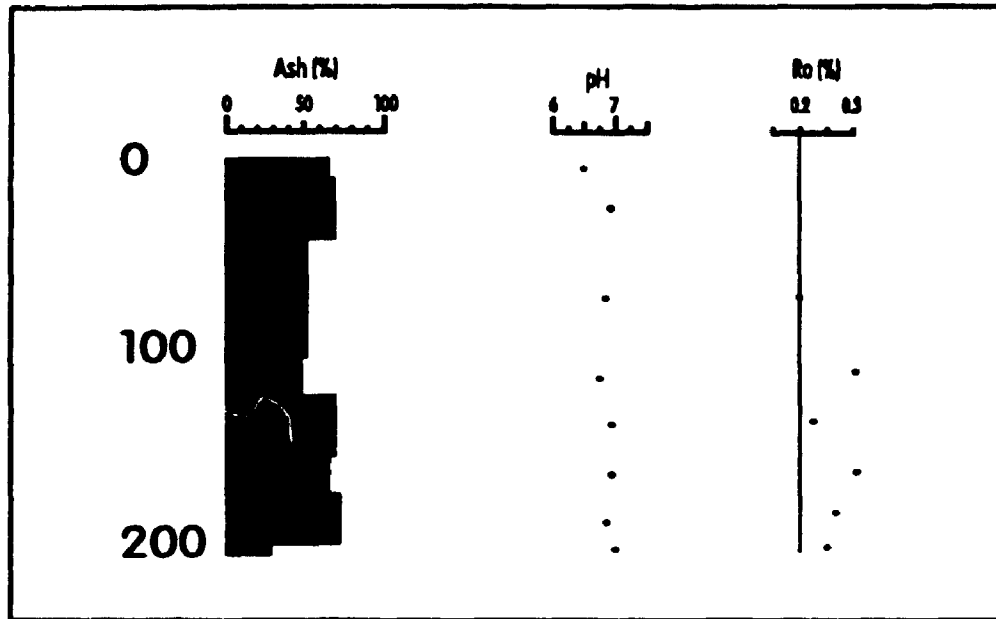


Figure 3.5 Ash content, pH and random reflectance (Ro%) of core CH1a, Chezzetcook Inlet, Nova Scotia.

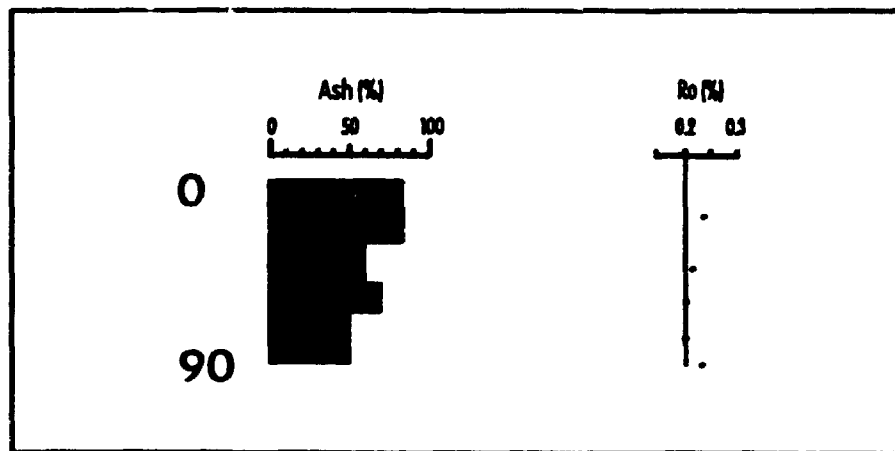


Figure 3.6 Ash content and random reflectance (Ro%) of core CH2a, Chezzetcook Inlet, Nova Scotia.

Depth (cm)	Ash (%)	pH	Ro (%)
Core CH1a			
0-10	65.4	6.5	n.a.
10-40	68.9	6.9	0.26 - 0.16'
40-100	51.0	6.8	0.20
100-120	47.1	6.7	0.24 - 0.18'
120-150	68.1	6.9	0.22
150-170	65.6	6.9	0.25
170-195	71.5	6.8	0.25
195-200	28.0	7.0	0.24
Core CH2a			
0-30	77.2	n.a.	0.24
30-50	56.4	n.a.	0.21
50-65	64.8	n.a.	0.20
65-85	48.2	n.a.	0.20
85-90	48.0	n.a.	0.22

Random reflectance (Ro%) was determined on phlobaphinite, unless otherwise noted ' textinite.
n.a. = not available

Table 3.5 Ash content, pH and random reflectance (Ro%) of cores CH1a and CH2a, Chezzetcook Inlet, Nova Scotia.

Microscopic analysis revealed the presence of oxidized plant material in an inorganic matrix. The upper 0.40 m of the sequence is heavily rooted, resulting in an abundance of phlobaphinite. Macerals of the humotelinite group were represented by ulminite, in which the cell structures were often not recognizable, due to collapse of cell lumens. Humodetrinite was abundant in the core, probably as a result of frequent flooding. Oxyfusinite prevailed over pyrofusinite, which is expected in salt marsh environments, subject to alternate periods of flooding and drought, as opposite to fires (Plate 3.3a, 3.3b). Sclerotinite was rarely observed. Pollen and microspores were not abundant. Highly fluorescent algae, such as *Pediastrum*, *Botryococcus*, and freshwater and brackish Dinoflagellates (L. Stasiuk, pers. comm., 1992), were observed under blue light excitation (Plate 3.3c). Framboidal pyrite was common, and occurred usually in association within the cortex of rootlets (Plate 3.3d). Rare anhedral crystals of pyrite were also observed.

Mineralogy of the muck was dominated by quartz (48-80%), with abundant mica, feldspars and clay minerals. Chlorite was the dominant clay mineral. Halite constituted a significant portion in the surface sample (0 to 0.10 m depth); (unashed raw sample), and pyrite comprised up to 2% of the mineral fraction (Table 3.6).

pH measurements taken before high tide gave values between 6.5 and 7.1 (Figure 3.5, Table 3.5). In comparison, pH of sea water in the vicinity was 8.5.

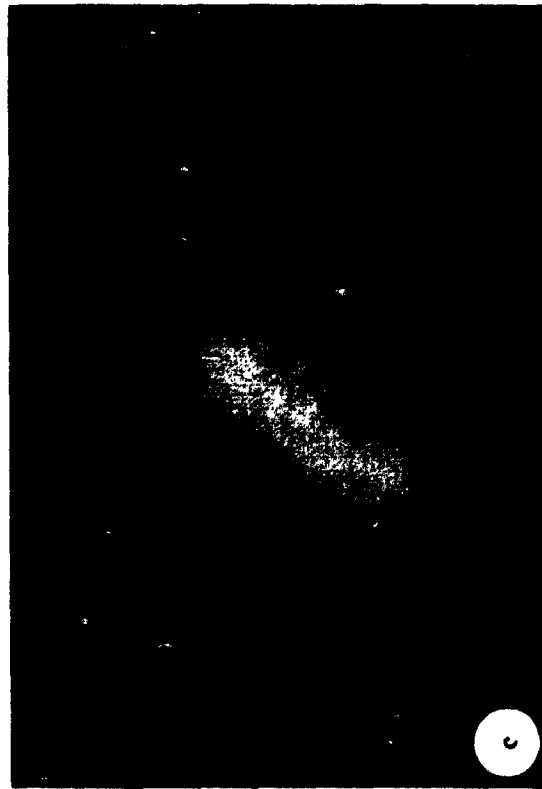
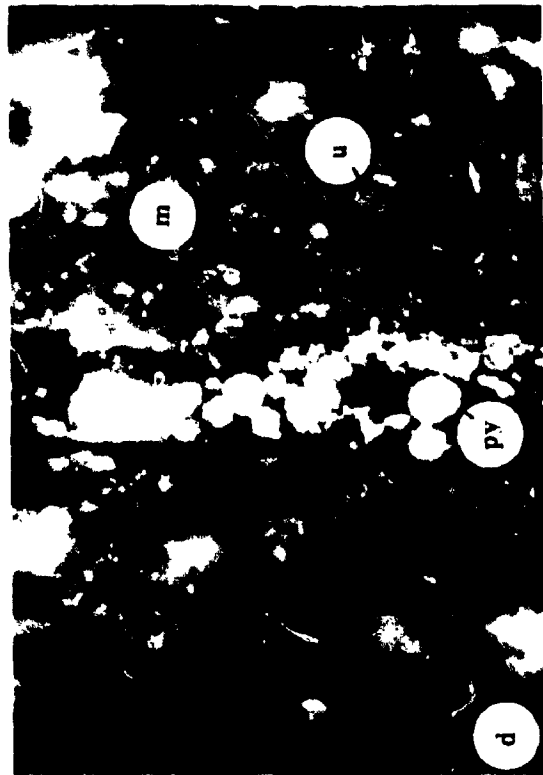
Random reflectance values (measured on phlobaphinite) do not show any increasing or decreasing trend with depth, but average 0.22% (Figure 3.5, Table 3.5).

Plate 3.3

Color microphotographs of maceral types in the salt marsh, Chezzetcook Inlet, Nova Scotia

All photomicrographs taken in color, oil immersion. a, b and d under reflected white light, c under blue light excitation.

- a - Oxyfusinite. Oxidized undetermined plant material. Salt marsh, Chezzetcook Inlet, Nova Scotia. The long axis of the photograph is 200 μm .
- b - Oxyfusinite. Oxidized undetermined plant material. Salt marsh, Chezzetcook Inlet, Nova Scotia. The long axis of the photograph is 200 μm .
- c - Algae (probably *Botryococcus*) displaying yellow fluorescence. Salt marsh, Chezzetcook Inlet, Nova Scotia. The long axis of the photograph is 150 μm .
- d - Framboidal pyrite (py) occurring within plant cortex. (u = ulminite, m = mineral matter). Salt marsh, Chezzetcook Inlet, Nova Scotia. The long axis of the photograph is 200 μm .



Depth (cm)	lab	LTA	Q	M	F	K	H	Py	O
Core CH1a									
0-10	2	-	60	M	p	c,m	16	Py	-
10-40	1	x	79	M	p	c,m	-	Py	-
100-120	2		59	15	p	c,m	-	Py	-
170-195	1	x	74	M	p,f	c,k	-	Py	a
195-200	2	x	48	20	p	c	H	Py	-
Core CH2a									
0-30	1	x	77	M	p,f	c,k,m	-	Py	-
50-65	2	-	75	M	p	c	H	-	-
85-90	1	-	69	M	p,f	c,m	-	Py	-

lab = Laboratory (1 = GSC Calgary, 2 = UWO London)

LTA = low temperature ash (x = LTA, - = unashed sample)

Q = quartz, M = mica, F = feldspars (f = K-feldspars, p = plagioclase), K = clays (c = chlorite, k = kaolinite, m = mixed-layer clays), H = halite, Py = pyrite, O = others (a = amphibole).

Where concentrations are greater than 10%, a value is quoted, otherwise minerals are listed in order of concentration, from high to low (e.g. c,k = chlorite is in greater concentration than kaolinite).

Table 3.6 Mineralogy of cores CH1a and CH2a, Chezzetcook Inlet, Nova Scotia.

3.2.1.2.3 Core CH2a

A 0.90 m core was taken beyond the mudflats at the Head of the estuary, and consisted mainly of remains of *Spartina patens*. Surface vegetation is dominated by rough marsh plants (Scott, pers. comm., 1993). Ash content varied between 48 and 77% (Figure 3.6, Table 3.5) and averaged 59%.

The huminitic material in core CH2a consisted mainly of ulminite and humodetrinite, which were highly oxidized in places. As in core CH1a, yellow fluorescing algae were observed. Orange fluorescing pollen grains and microspores were disseminated in the inorganic matrix. Some root material (phlobaphinite and suberinite), which did not appear to be extensively oxidized, was found in places. Pyrite framboids were common, appearing to have formed in rootlets, as suggested above (Section 3.2.1.2.2).

Mineralogy of the muck was dominated by quartz (70-77%), feldspars, mica and clay minerals, with minor amounts of pyrite (Table 3.6).

Reflectance measurements indicated a high degree of oxidation, but no trend was noticeable across the profile. Random reflectance values averaged 0.21% (Figure 3.6, Table 3.5).

3.2.2 Alberta

3.2.2.1 Keephills Fen

A 3.45 m core consisted of a 2.90 m peat sequence underlain by marl. Except in the surface layer (0 to 0.05 m depth), which was dominated by *Sphagnum* peat, the entire peat sequence was composed mainly of brown moss (*Tomenthypnum nitens*,

Aulacomnium palustre, *Dicranum scoparium Hedw.*) peat (Turchenek, pers. comm., 1992), with a minor sedge fraction in the 0.50 m top section. Shrubby material ranged between 5 and 50% of the organic material, with an average of 10% in the entire core (Figure 3.7, Table 3.7). Charcoal fragments were observed in the upper 0.50 m. In the basal peat layer overlying marl sediments, a thin peat layer (2.80 to 2.90 m depth) overlain by a very thin lens of marl, could be distinguished by a green color as opposed to the dark brown color of the overlying humified brown moss.

pH measurements at the surface and at 0.30 m depth yield pH values of 5.5 and 6.0 respectively, typical for transitional or moderate-rich fens.

Ash content in the peat sequence varied between 4% (surface layer) and 27% (Figure 3.7, Table 3.7), and averaged 15%. The underlying marl had a high organic content (over 50%), with small gastropod shells imbedded in the sediment.

Bottom sediments (LTA) consisted almost entirely of calcite (99%), with 1% gypsum. Carbonate calculated as CaCO_3 accounted for between 50 and 65% of the total dry solids of the sediment. Mineralogy of the brown moss-peat sequence was dominated by calcite, while gypsum, bassanite, weddelite, and dolomite were present in small amounts. In the upper section of the core, quartz became more important in the inorganic fraction. At 0.20-0.30 m depth, quartz was the dominant mineral, with a significant percentage of plagioclase and bassanite, and minor amounts of K-feldspars and calcite. Quartz predominance is accentuated in the surface layer (0 to 0.05 m depth), where this mineral constitutes about 60% of the inorganic fraction, with a significant portion of bassanite, and minor amounts of feldspars and whewellite (Table 3.8).

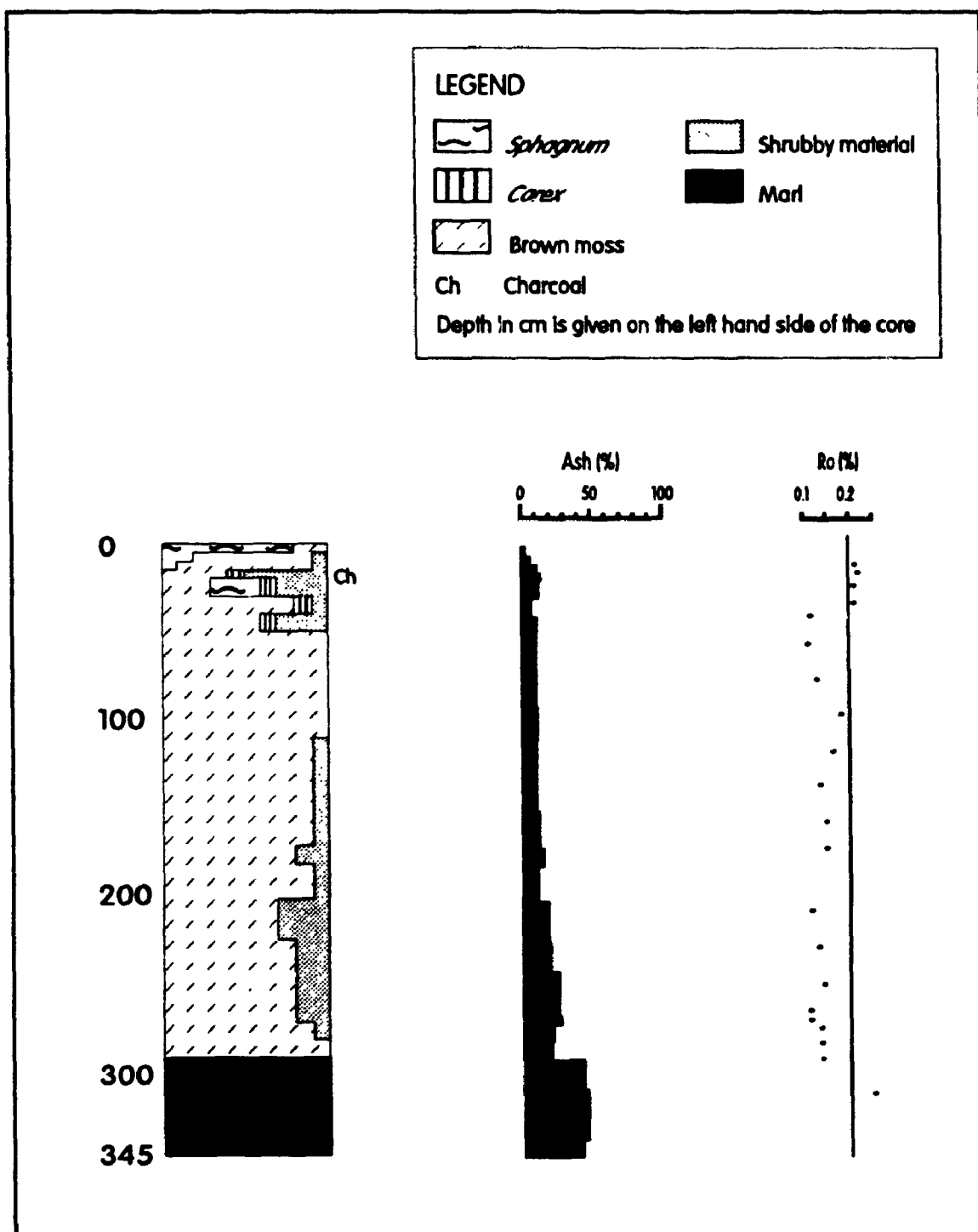


Figure 3.7 Peat type, ash content and random reflectance (Ro%) of Keepphills Fen, Alberta.

Depth (cm)	Peat type	Ash (%)	Ro (%)
0-5	S8B2	4.2	n.a. - 0.13'
5-10	B7S2N1	8.2	0.11'
10-15	B7S1C1N1	11.3	0.21 - 0.15'
15-20	N5B4C1	15.4	0.22 - 0.12'
20-30	B3S3N3C1	13.9	0.21
30-40	B8C1N1	9.4	0.21
40-50	B6N3C1	12.1	0.12
50-70	B0	11.0	0.11
70-96	B0	11.0*	0.13
90-110	B0	11.9	0.18 - 0.13'
110-130	B9N1	10.9	0.16
130-150	B9N1	10.9*	0.13
150-171	B9N1	14.5	0.15
171-181	B8N2	16.5	0.15
181-200	B9N1	11.0	n.a.
200-224	B7N3	19.9	0.12
224-240	B8N2	20.6	0.13
240-264	B8N2	27.1	0.14
264-270	B8N2	27.2	0.11
270-274	B9N1	22.3	0.11
274-280	B9N1	22.3*	0.13
280-290	B0	21.1	0.13
290-300	marl	44.1	0.13
300-306	marl	44.1*	n.a.
306-322	marl	47.4	0.25
322-335	marl	47.4*	n.a.
335-345	marl	42.6	n.a.

Peat type is determined as percent of peat constituents using recognizable features of original plants. 1 → 9 - 10% → 90%, 0 = 100%; B = brown moss, S = *Sphagnum*, C = *Carex*, N = shrubby material.

* = samples homogenized for ash content determination and INAA incorporating unit immediately above. Therefore both have same ash content.

Random reflectance (Ro%) was determined on phlobaphinite, unless otherwise noted ' = textinite.

n.a. - not available

Table 3.7 Peat type, ash content and random reflectance (Ro%) of Keephills Fen, Alberta.

Depth (cm)	lab	LTA	Q	M	F	K	W	C	B	O
0-5	2	x	59	M	p	k	h	-	10	d
15-20	1	x	54	-	tr	-	e	38	-	g
20-30	2	x	39	-	29p,f	-	-	C	18	-
150-171	1	x	11	-	-	-	e	71	-	g,d
171-181	2	x	Q	-	-	-	-	90	8	-
240-264	2	x	Q	-	-	-	h	86	B	-
280-290	2	x	tr	-	-	-	-	92	B	-
306-322	1	x	-	-	-	-	-	100	-	-
335-345	1	x	-	-	-	-	-	99	-	g

lab = Laboratory (1 = GSC Calgary, 2 = UWO London)

LTA = low temperature ash (x = LTA)

Q = quartz, M = mica, F = feldspars (f = K-feldspars, p = plagioclase), K = clays (k = kaolinite), W = calcium oxalate hydrate (e = weddellite, h = whewellite), C = calcite, B = bassanite, O = others (d = dolomite, g = gypsum)

Where concentrations are greater than 10%, a value is quoted, otherwise minerals are listed in order of concentration, from high to low. (e.g. g,d = gypsum is in greater concentration than dolomite), tr = trace amounts.

Table 3.8 Mineralogy, Keephills Fen, Alberta.

Three types of peat were distinguished: *Sphagnum*-brown moss peat, woody brown moss-*Carex-Sphagnum* peat and brown moss peat.

Sphagnum-brown moss peat formed the surface layer (0 to 0.05 m depth) of the fen. *Sphagnum* leaves and stems dominated, most commonly in the form of non humified fibrous material, which was brown in reflected white light and fluoresced as a yellow color under blue light excitation. Textinite A was observed, displaying red internal reflection, while gray textinite B was more scarce. Few pollen grains were found.

An underlying woody brown moss-*Carex-Sphagnum* peat sequence (0.05 to 0.50 m depth) contained higher humified peaty material. The proportion of textinite B increased, although red textinite was still abundant. Pollen grains and microspores displayed a green yellow fluorescence. Inertinite material occurred frequently as pyrofusinite and inertodetrinite, and more seldom as oxyfusinite. Scarce fungal remains (sclerotinite) were disseminated in the matrix. Woody fragments, probably rootlets, were evident. Much mineral matter was observed.

In brown moss peat (0.50 to 2.90 m depth), brown moss leaves and stems were dominant over roots. Transitions from red textinite to gray textinite were observed (Plate 3.4a). Sclerotinite was found in some intervals in minor amounts, and few inertinite fragments occurred. Under blue light excitation, cutinite, microspores and pollen grains were observed. Most common were disaccate, vesiculate pollen grains, which appear to be *Picea* pollen grains (Plate 3.4b). Rare pyrite framboids were observed. Probe analysis also revealed the presence of tiny anhedral pyrite (Plate 3.5c). A 10 cm thick layer (2.80 to 2.90 m depth), characterized by a green color and lack of decomposition

Plate 3.4

Color microphotographs of maceral types in peat of Keephills Fen, Alberta

All photomicrographs taken in color, oil immersion. a, and c under reflected white light, b under blue light excitation. The long axis of each photograph is 200 μm .

- a - Transition from red reflecting (textinite A) to gray reflecting (textinite B) plant material. Keephills Fen, Alberta.
- b - Disaccate pollen grain. Keephills Fen, Alberta.
- c - Cell fillings (probably corpohuminite) within the underlying marl. Keephills Fen, Alberta.

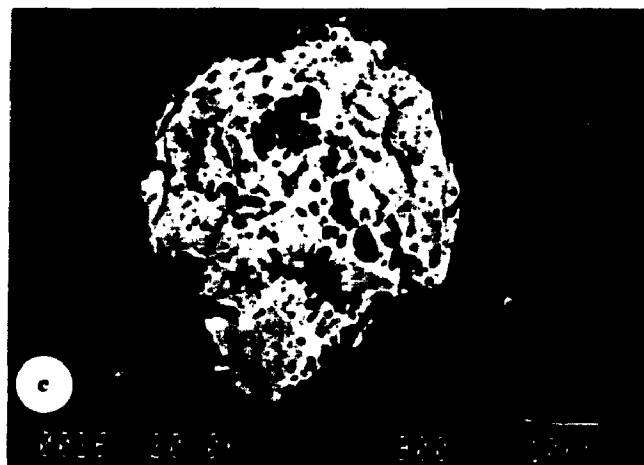
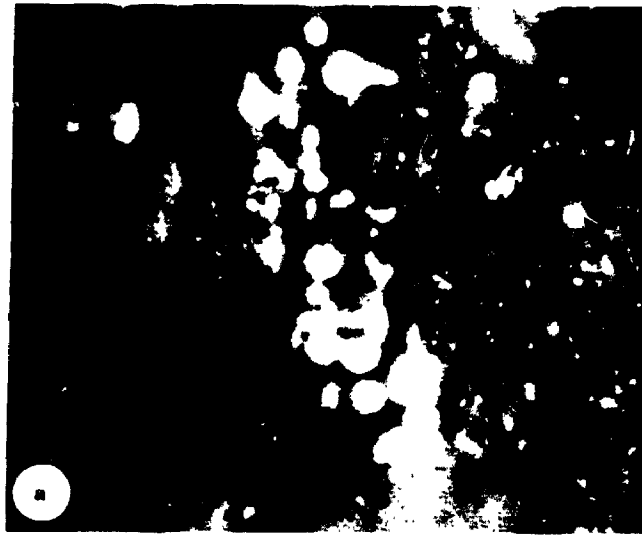


Plate 3.5

Color microphotographs and SEM photomicrograph of pyrite, Keephills Fen, Alberta

Photomicrographs a and b taken in color, oil immersion. a under reflected white light, b under blue light excitation.

- a - Framboidal pyrite occurring within marl underlying the peat sequence. (m = mineral matter). Keephills Fen, Alberta. The long axis of the photograph is 190 μm .
- b - Same field as (a) but under blue light excitation. Framboids occur within plant cortex. Keephills Fen, Alberta. The long axis of the photograph is 190 μm .
- c - SEM photomicrograph of anhedral pyrite occurring within the peat sequence. Keephills Fen, Alberta.



in the field, exhibited abundant poorly-humified cell wall material, displaying red internal reflection but no reflectivity in reflected white light (textinite A).

Pyrofusinite was abundant in the marl underlying the peat sequence. Cell fillings (probably corpohuminite?) were observed (Plate 3.4c). The fine matrix consisted of mineral matter, and humodetrinite. Pyrite framboids were observed and appear to have formed in association with rootlets, as seen under blue light excitation (Plate 3.5a, 3.5b).

Reflectance measurements were taken on huminite and phlobaphinite and values range between 0.10% and 0.22% in the peat sequence (Figure 3.7, Table 3.7).

3.2.3 Northwest Territories

3.2.3.1 East Little Bear River deposit

Two cores were taken, core 1 at the edge of the river bank and core 2, within the peat plateau bog. Peat stratigraphy of both cores is described in the following sections.

3.2.3.1.1 Core 1

A 1.80 m core consisted of a 1.40 m peat sequence underlain by silty bottom sediments. Except for the surface layer, which was composed mainly of *Sphagnum* peat, brown moss and *Carex* dominated peat composition, with a minor shrubby component (Figure 3.8, Table 3.9).

In the peat sequence, ash content was highest (34%) in the surface layer (0 to 0.10 m depth). Below, the inorganic fraction varied between 4.6% and 26%, averaging 9.5%. Underlying silty sediments contain less than 15% organic matter.

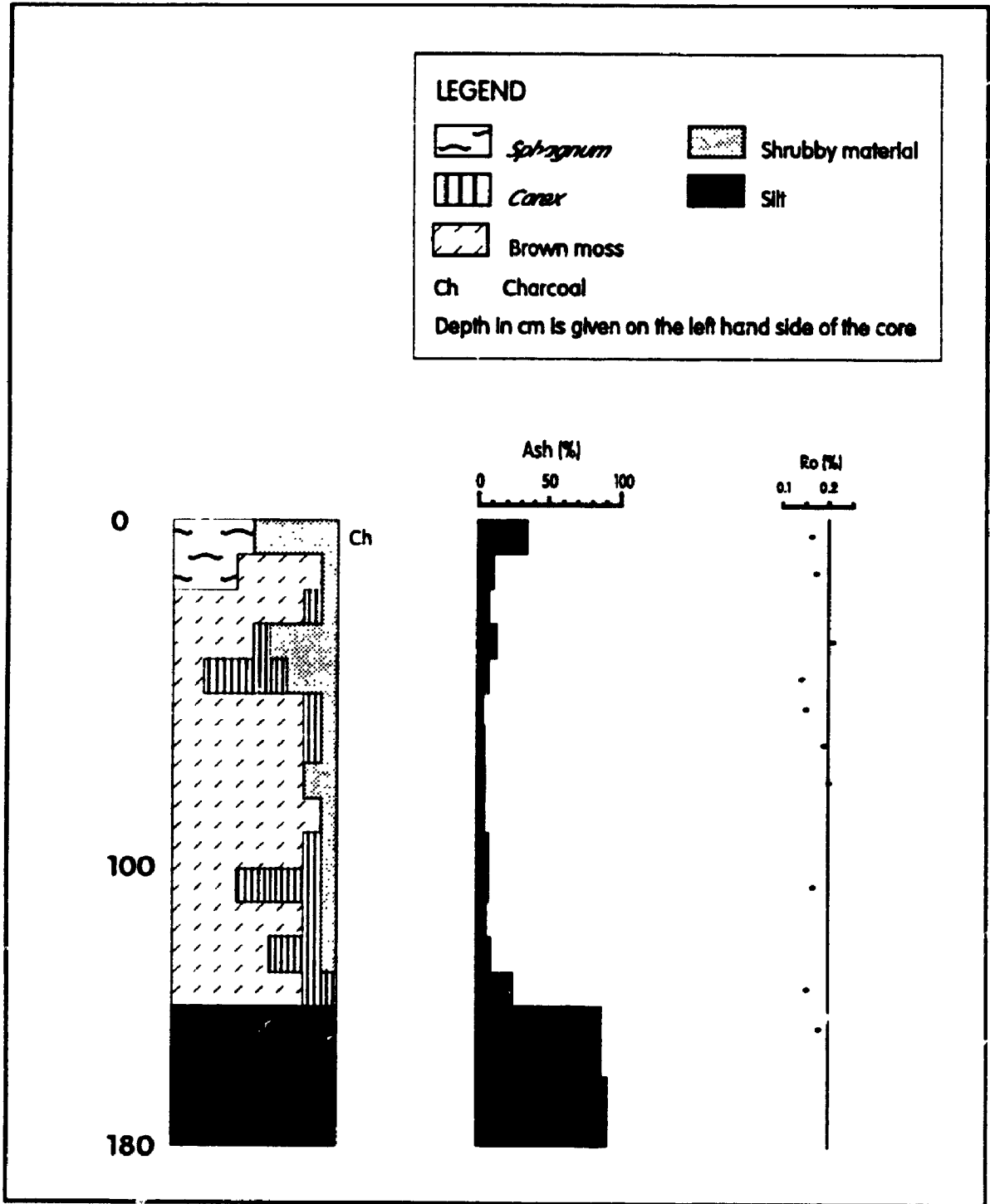


Figure 3.8 Peat type, ash content and random reflectance (Ro%) of core 1, East Little Bear River Deposit, Northwest Territories.

Depth (cm)	Peat type	Ash (%)	Ro (%)	Depth (cm)	Peat type	Ash (%)	Ro (%)
Core 1				Core 2			
0-10	S5N5	34.4	0.16	0-10	S8C1N1	26.0	0.20
10-20	B5S4N1	11.2	0.17	10-20	B5S4C1	9.8	n.a.
20-30	B8C1N1	8.1	n.a.	20-30	C6B2N2	12.9	0.19
30-40	B5N4C1	13.2	0.21	30-40	C7N3	15.3	0.19
40-50	C5N3B2	8.3	0.14	40-50	B4C4N2	10.8	0.18
50-60	B8C1N1	4.6	0.15	50-60	B9N1	5.1	n.a.
60-70	B8C1N1	5.6	0.19	60-68	B9N1	4.9	0.16
70-80	B8N2	6.2	0.20	68-70	B9N1	3.0	0.20
80-90	B9N1	5.5	n.a.	70-80	B0	4.8	n.a.
90-100	B8C1N1	8.0	n.a.	80-90	B7C2N1	5.6	0.16
100-110	C5B4N1	8.5	0.17	90-95	B7C2N1	9.5	0.18
110-120	B8C1N1	7.7	n.a.	95-100	B8C1N1	5.9	0.20
120-130	B6C3N1	10.1	n.a.	100-105	B7C2N1	10.4	0.21
130-140	B8C2	25.9	0.15	105-110	C7B2N1	11.6	0.18
150-160	silt	86.7	0.18	110-115	C9N1	11.4	0.20
170-180	silt	91.9	n.a.	115-120	B7C2N1	20.8	0.23
				120-125	silt	62.4	0.22
				125-130	silt	88.1	0.26

Peat type is determined as percent of peat constituents using recognizable features of original plants 1 → 9 = 10% → 90%, 0 = 100%; B = brown moss, S = *Sphagnum*, C = *Carex*, N = shrubby material.

Random reflectance (Ro%) was determined on phlobaphinite.

n.a. = not available

Table 3.9 Peat type, ash content and random reflectance (Ro%) of cores 1 and 2, East Little Bear River Deposit, Northwest Territories.

(Figure 3.8, Table 3.9). Charcoal fragments were abundant in the upper section of this core. Peat was not frozen at the time of sampling (carried out at the end of the summer). Thus, although it is probable that peat is frozen in the winter, permafrost did not affect peat at the core location.

Mineralogy of the bottom sediments was dominated by quartz (79%), with a minor fraction composed of plagioclase, clay minerals and dolomite. In the lower part of the core, the inorganic fraction consisted mainly of quartz, with a minor fraction of bassanite and mica. In the middle of the peat profile, the mineralogy comprised quartz and bassanite. In the upper layers, quartz represented close to 90% of the mineral fraction, with only minor amounts of mica (Table 3.10).

Two types of peat were distinguished: woody *Sphagnum*-sedge peat in the surface layer and woody brown moss-sedge peat underneath.

In the surface layer (0 to 0.10 m depth), frequent pyrofusinite fragments and phlobaphinite were observed in a fine matrix composed of mineral matter. Rootlets were frequent (Plate 3.6a, 3.6b) Pollen grains displayed an orange fluorescence.

In the woody brown moss-sedge peat sequence, huminite material was dominated by phlobaphinite, with a significant portion of textinite A and B. Inertinite fragments were scarce. Sclerotinite was rare. Pollen grains and microspores were common, displaying yellow and orange fluorescence, while cutinite was scarce. A long (600 μm) fragment of humified material, possibly a needle tip (?), was observed in the lower section of the peat sequence (Plate 3.6c).

Depth (cm)	lab	LTA	Q	M	F	K	W	C	B	O
Core 1										
0-10	2	x	88	M	p	k	-	-	-	-
10-20	2	x	93	M	p	-	-	-	-	-
100-110	2	x	47	-	p,f	c	-	-	40	-
130-140	2	x	80	M	p	-	-	-	B	-
210-220	1	x	79	M	p	m,c	-	C	-	d,r
Core 2										
0-10	1	x	83	M	p,f	k,m	-	-	-	-
50-68	2	x	63	-	p,f	-	h	-	11	-
70-80	1	x	38	-	p,f	tr	-	49	-	si,g
90-95	2	x	63	-	p,f	-	10h	-	12	-
125-130	1	x	80	M	p,f	m,c,k	-	C	-	d

lab = Laboratory (1 = GSC Calgary, 2 = UWO London)

LTA = low temperature ash (x = LTA)

Q = quartz, M = mica, F = feldspars (f = K-feldspars, p = plagioclase), K = clays (c = chlorite, k = kaolinite, m = mixed-layer clays), W = calcium oxalate hydrate (h = whewellite), C = calcite, B = bassanite, O = others (d = dolomite, r = romarchite, si = amorphous silicate)

Where concentrations are greater than 10%, a value is quoted, otherwise minerals are listed in order of concentration, from high to low (e.g. m,c = mixed-layer clays are in greater concentration than chlorite), tr = trace amounts.

Table 3.10 Mineralogy of cores 1 and 2, East Little Bear River Deposit, Northwest Territories.

Plate 3.6

Color microphotographs of maceral types in peat of East Little Bear River Deposit and Mackenzie River Deposit, Northwest Territories

All photomicrographs taken in color, oil immersion. a, c, d and e under reflected white light, b under blue light excitation.

- a - Cross section of an undetermined stem/root. Note gray reflecting cell filling. East Little Bear River Deposit, Northwest Territories. The horizontal axis of the photograph is 140 μm .
- b - Same field as (a) but under blue light excitation. (s = suberinite). East Little Bear River Deposit, Northwest Territories. The horizontal axis of the photograph is 140 μm .
- c - Gray reflecting elongated plant material (pine needle ?). East Little Bear River Deposit, Northwest Territories.
- d - Ulminite (u) and sclerotinite (sc) disseminated in inorganic matrix. Mackenzie River Deposit, Northwest Territories. The horizontal axis of the photograph is 140 μm .
- e - Fragment of cork cells. Mackenzie River Deposit, Northwest Territories. The horizontal axis of the photograph is 140 μm .



Bottom sediments contained a few fragments of inertinite disseminated in the inorganic matrix. Cutinite and microspores were observed, displaying a yellow fluorescence.

Reflectance measurements were carried out on phlobaphinite, due to scarcity of textinite material suitable for analysis. Random reflectance values vary between 0.14 and 0.21% (Figure 3.8, Table 3.9).

3.2.3.1.2 Core 2

The 1.30 m core consisted of a 1.20 m peat sequence underlain by silty sediments. Brown moss and *Carex* were the dominant peat components, except in the surface layer, where *Sphagnum* was prevalent. Woody material was also present in minor amounts (Figure 3.9, Table 3.9). Charcoal pieces occurred at the surface, as well as at 0.25 m and 0.35 m depth (Figure 3.9).

Like core 1, the surface layer contained a high percentage of mineral matter (26%), while ash content in the remaining peat sequence varied between 3% and 21%, averaging 9.5% (Figure 3.9, Table 3.9). Permafrost was found at 0.68 m depth. Basal peat (1.15 to 1.20 m depth), which overlaid the silty bottom sediments, was unfrozen at the time of sampling (carried out at the end of the summer).

Mineralogy of the bottom sediments was similar to that observed in core 1, with quartz as the dominant fraction. The inorganic fraction of the overlying peat sequence (LTA) consisted mainly of quartz and bassanite, or calcite, with a significant proportion of feldspars (Table 3.10).

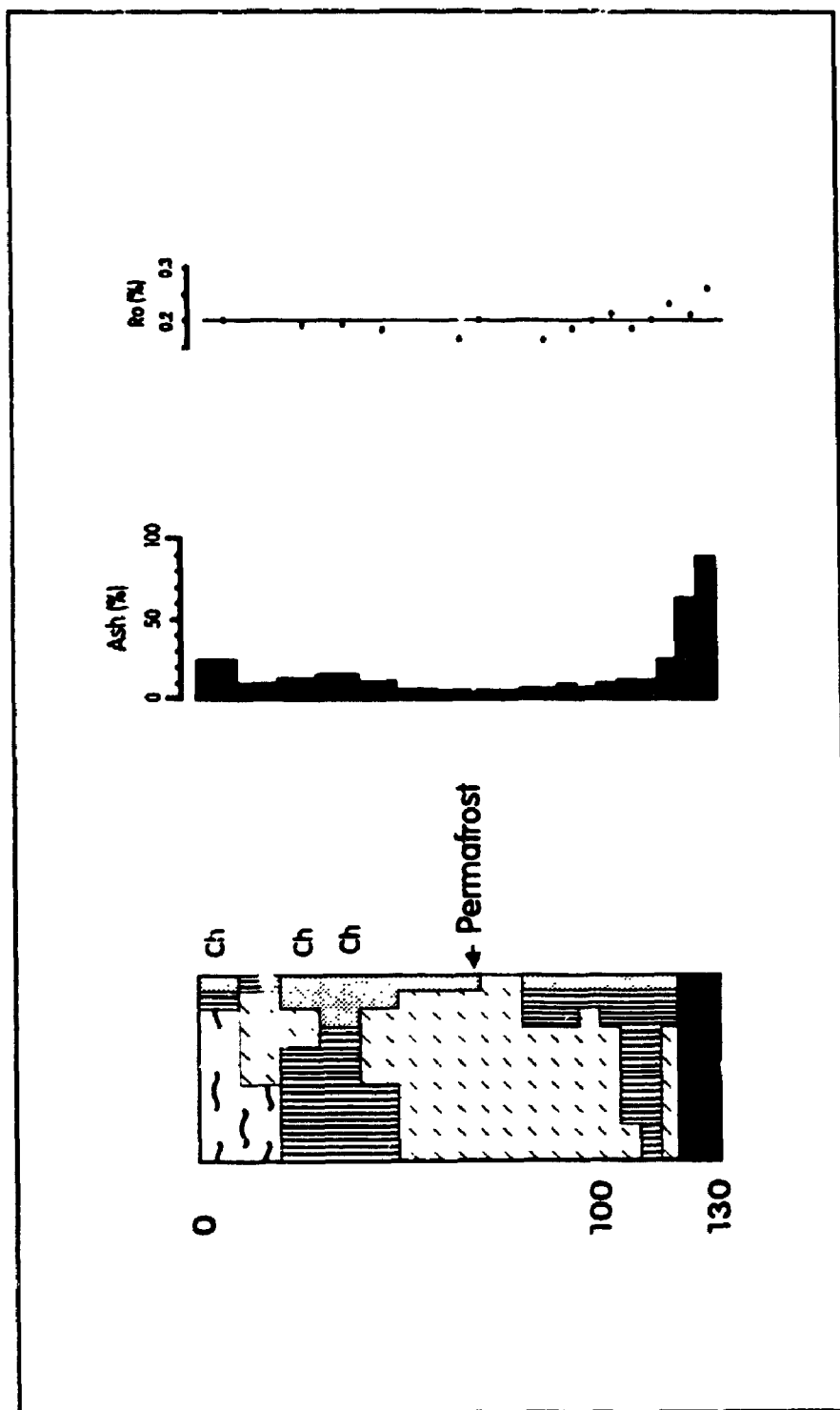


Figure 3.9 Peat type, ash content and random reflectance (Ro%) of core 2, East Little Bear River Deposit, Northwest Territories. (Legend see Fig. 3.8)

As in core 1, two peat types could be distinguished: woody *Sphagnum*-sedge peat in the surface layer and woody brown moss-sedge peat underneath. However, the *Carex* component is dominant in some intervals (Figure 3.9, Table 3.9).

In the woody *Sphagnum*-sedge peat (0 to 0.10 m depth), textinite B was dominant over textinite A. Pyrofusinite and inertodetrinite were common. Humodetrinite was observed as well. Rootlets were present, embedded in a fine inorganic matrix. Pollen grains and cutinite were common.

In the underlying layer (0.10 to 0.20 m depth), brown fibres and red textinite prevailed over gray textinite B. Pollen grains and microspores were common. At 0.25 m depth, pyrofusinite, oxyfusinite and inertodetrinite were abundant, and large pieces of ulminite were observed. In the remaining peat sequence, woody fragments and rootlets were frequent, thus phlobaphinite comprised a large component of the huminite material. Cell wall material composed of gray textinite B was observed, and prevailed over red textinite A.

A few inertodetrinite and ulminite fragments were disseminated in the fine inorganic matrix of the bottom sediments.

Reflectance measurements give similar values to those observed in core 1, with most R_o values below 0.2% (Figure 3.9, Table 3.9).

3.2.3.2 Mackenzie River deposit

A 2.80 m core consisting of woody organic material was taken. Except in the surface layer (active layer), where *Sphagnum* was dominant, plant material was not identifiable. It is therefore termed amorphous peat material. There was also a significant

woody fraction (Figure 3.10, Table 3.11). Permafrost occurred at 0.17 m depth. Ash content varied between 24 and 71% (Figure 3.10, Table 3.11), and therefore the organic material can not be called peat, but rather peaty and silty muck. Ice lenses between a few mm and 2 cm thickness were found in the organic material during sampling.

Mineralogy was dominated by quartz, with a significant fraction composed of feldspars and mica, and minor amounts of calcite and clay minerals (Table 3.12).

Microscopic analysis gave evidence of the abundance of mineral matter, as dispersed macerals were commonly observed within the inorganic matrix (Plate 3.6d). Phlobaphinite constituted the dominant huminite material, due to the abundance of woody material (Plate 3.6e). However, red textinite A and gray textinite B were observed, disseminated in the fine inorganic matrix. Few pollen grains and microspores occurred, commonly displaying a yellow fluorescing color. Large pieces of inertinite material (oxyfusinite and pyrofusinite), as well as charred and oxidized cell wall material were evident at several depths. However, the material was very heterogeneous, since low humified leaf material, still displaying light greenish fluorescence, occurred at the same depth intervals.

Reflectance measurements on phlobaphinite gave values between 0.18% and 0.24% for R_o (Figure 3.10, Table 3.11).

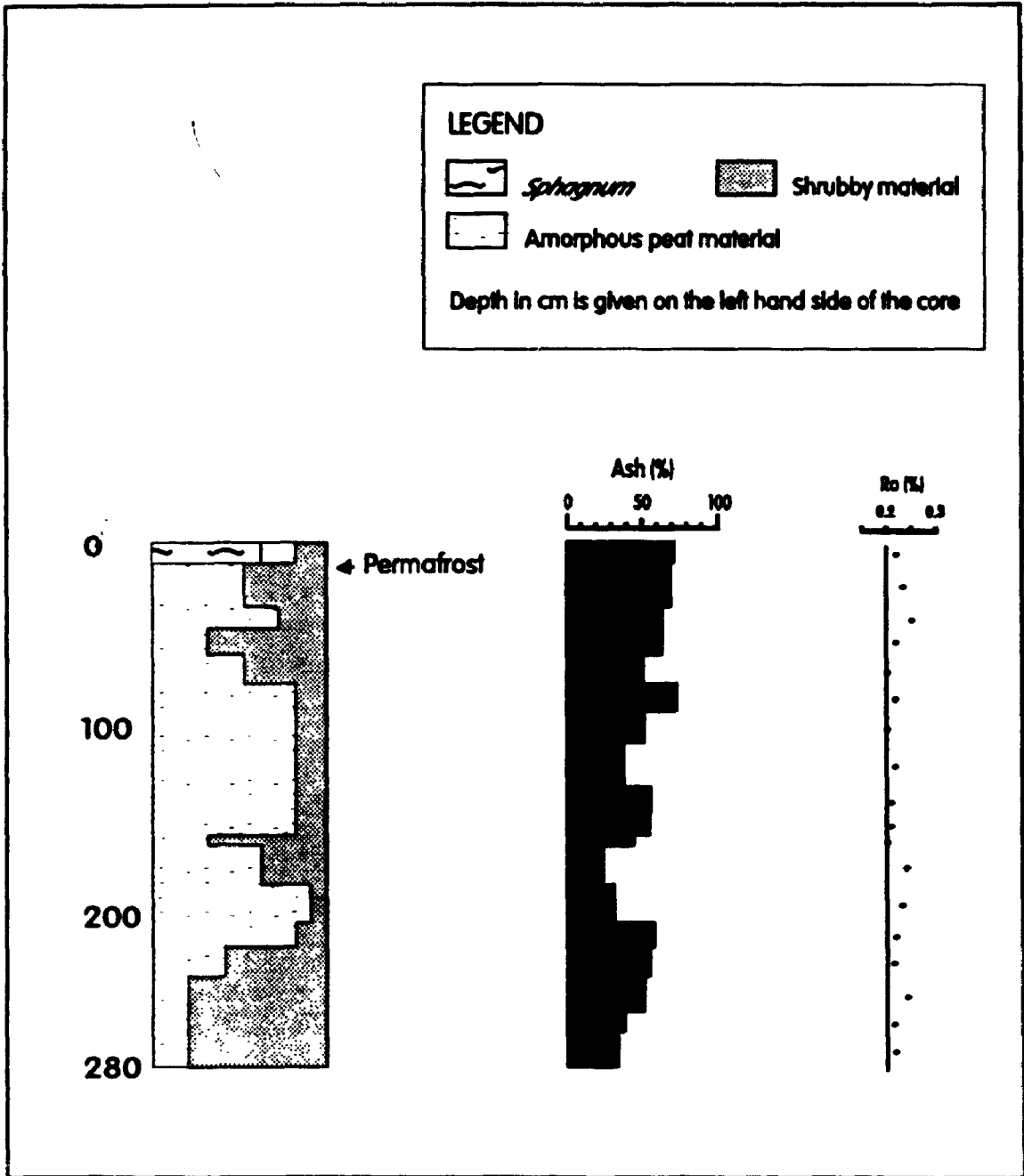


Figure 3.10 Peat type, ash content and random reflectance (Ro%) of Mackenzie River Deposit, Northwest Territories.

Depth (cm)	Peat type	Ash (%)	Ro (%)
0-10	S6A2N2	71.0	0.22
10-33	A5N5	69.6	0.23
33-45	A7N3	63.3	0.25
45-59	N7A3	63.3	0.22
59-75	A5N5	50.1	0.20
75-90	A8N2	73.3	0.22
90-107	A8N2	50.3	0.20
107-131	A8N2	38.2	0.22
131-144	A8N2	57.2	0.21
144-157	A8N2	56.1	0.21
157-162	N7A3	45.2	0.20
162-183	A6N4	24.3	0.24
183-203	A9N1	34.3	0.23
203-216	A8N2	58.4	0.22
216-232	N6A4	55.8	0.21
232-250	N8A2	52.2	0.24
250-262	N8N2	39.0	0.22
262-280	N8A2	31.5	0.22

Peat type is determined as percent of peat constituents using recognizable features of original plants. 1 → 9 = 10% → 90%, 0 = 100%; A = amorphous peat material, S = *Sphagnum*, N = shrubby/woody material.

Random reflectance was determined on phlobaphenite.

Table 3.11 Peat type, ash content and random reflectance (Ro%) of Mackenzie River Deposit, Northwest Territories.

Depth (cm)	lab	LTA	Q	M	F	K	C	O
0-10	1	x	80	M	p,f	c	C	a,g
45-59	2	-	69	M	p,f	-	-	-
121-131	1	x	90	tr	p,f	c,k	C	-
162-183	2	x	91	M	p	c	-	-
241-250	1	x	73	M	p,f	c,k	C	d
250-279	2	x	85	M	p	c	-	-

lab = Laboratory (1 = GSC Calgary, 2 = UWO London)

LTA = low temperature ash (x = LTA, - = unashed sample)

Q = quartz, M = mica, F = feldspars (f = K-feldspars, p = plagioclase), K = clays (c = chlorite, k = kaolinite), C = calcite, O = others (a = amphibole, d = dolomite, g = gypsum).

Where concentrations are greater than 10%, a value is quoted, otherwise minerals are listed in order of concentration, from high to low (e.g. c,k = chlorite is in greater concentration than kaolinite), tr = trace amounts.

Table 3.12 Mineralogy, Mackenzie River Deposit, Northwest Territories.

3.3 GEOCHEMISTRY

3.3.1 Nova Scotia

3.3.1.1 **Petite Bog**

Vertical and lateral distribution of major and trace elements, based on the three cores T1, T2 and T3, is reported versus the ash content of the peat sequence. Data are shown in Appendix IV (Tables 1, 2 and 3). Basal *Carex* peats in cores T1 and T3 have ash content higher than 25%, and are therefore termed peaty, silty and clayey muck. However, these intervals are included in the following, since botanically they are peat and represent parts of the mire evolution.

3.3.1.1.1 Major elements

3.3.1.1.1.1 Al

There is a strong positive correlation between aluminum and ash distribution in all cores (Figure 3.11). Averaged over the three cores, mean Al concentration is about 0.8% for an average ash content of 5.5% ($n = 48$ peat samples). Al levels range from 0.05% to 8.40% in core T1, the highest value being found in the basal peat layer having 53% ash. Al concentrations range from 0.05 to 1.5%, and from 0.5% to 5.7% in cores T2 and T3, respectively. Surface enrichments of Al and ash in core T2 appear to be proportional.

3.3.1.1.1.2 Na and K

In cores T1 and T3, sodium distribution appears to follow the ash content. In core T2 on the other hand, Na levels decrease slightly downcore. Na concentrations

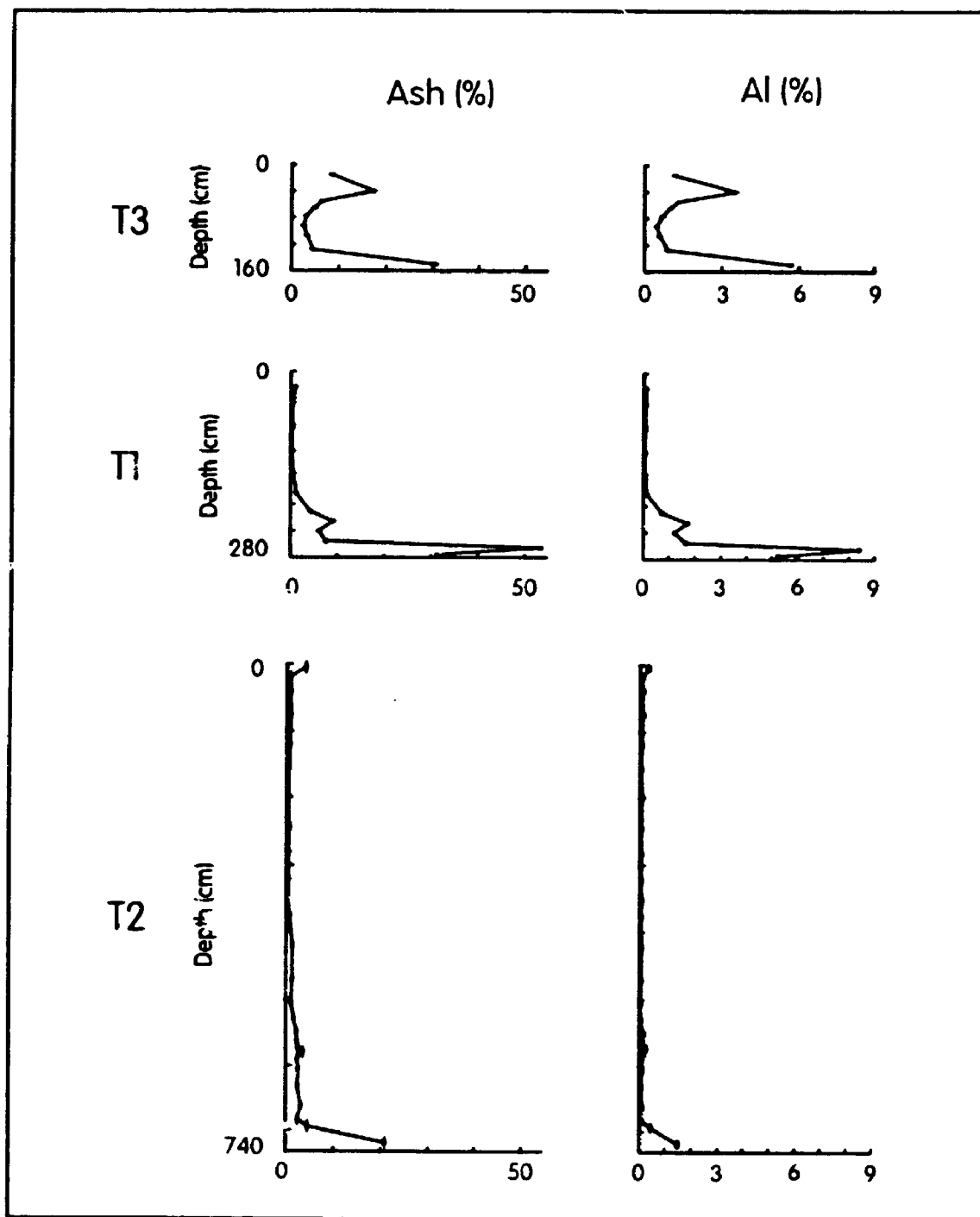


Figure 3.11 Ash and Al distribution in cores T1, T2 and T3, Petite Bog, Nova Scotia.

range from 137 to 1760 ppm in core T1, 145 and 1760 ppm in core T2, and 119 to 1020 ppm in core T3 (Figure 3.12). Mean Na content is 320 ppm in the bog.

Potassium concentration is below detection limit in core T2, except in the surface sample (0.11% K) and in the basal peat layers (0.09 and 0.27% K). In core T1, potassium is present in measurable amounts below a depth of 2.00 m, in peat with an ash content greater than 4%. Potassium concentration in core T3 is detected only in the top 0.60 m and in basal peat below 1.15 m (Figure 3.12).

3.3.1.1.1.3 Mg and Ca

Magnesium, like Al, appears to be associated with the inorganic fraction of peat. Its concentration increases with increasing ash content. Mg concentrations range from 35 to 2700 ppm in core T1, 60 to 179 ppm in core T2, and 195 to 1810 ppm in core T3 (Figure 3.13).

The calcium distribution pattern differs from that of Mg and Al. There appears to be no direct relationship between ash content and Ca concentration. However, Ca levels are low in the upper sections of each core and increase downcore. Ca concentrations range from 0.03 to 0.11% in core T1 and 0.21 to 0.38% in core T3. In core T2, Ca levels are below 0.2% in the top 4 m, increasing downcore to 1.17% in the basal peat (Figure 3.13).

3.3.1.1.1.4 S

Total sulfur concentrations range from nil to 0.4% in the bog, being highest in the lagg zone (core T3). However, S does not appear to closely follow ash distribution.

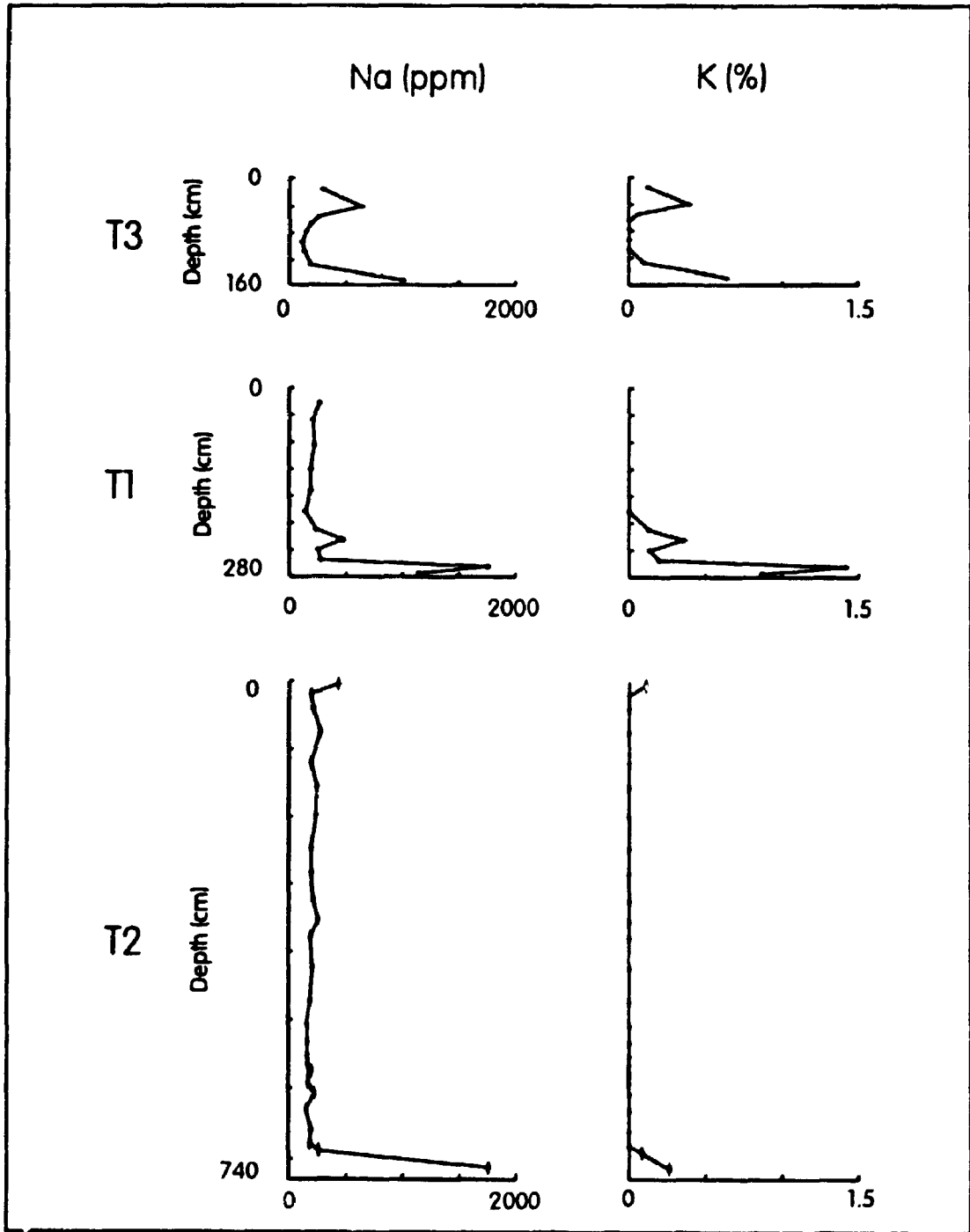


Figure 3.12 Na and K distribution in cores T1, T2 and T3, Petite Bog, Nova Scotia.

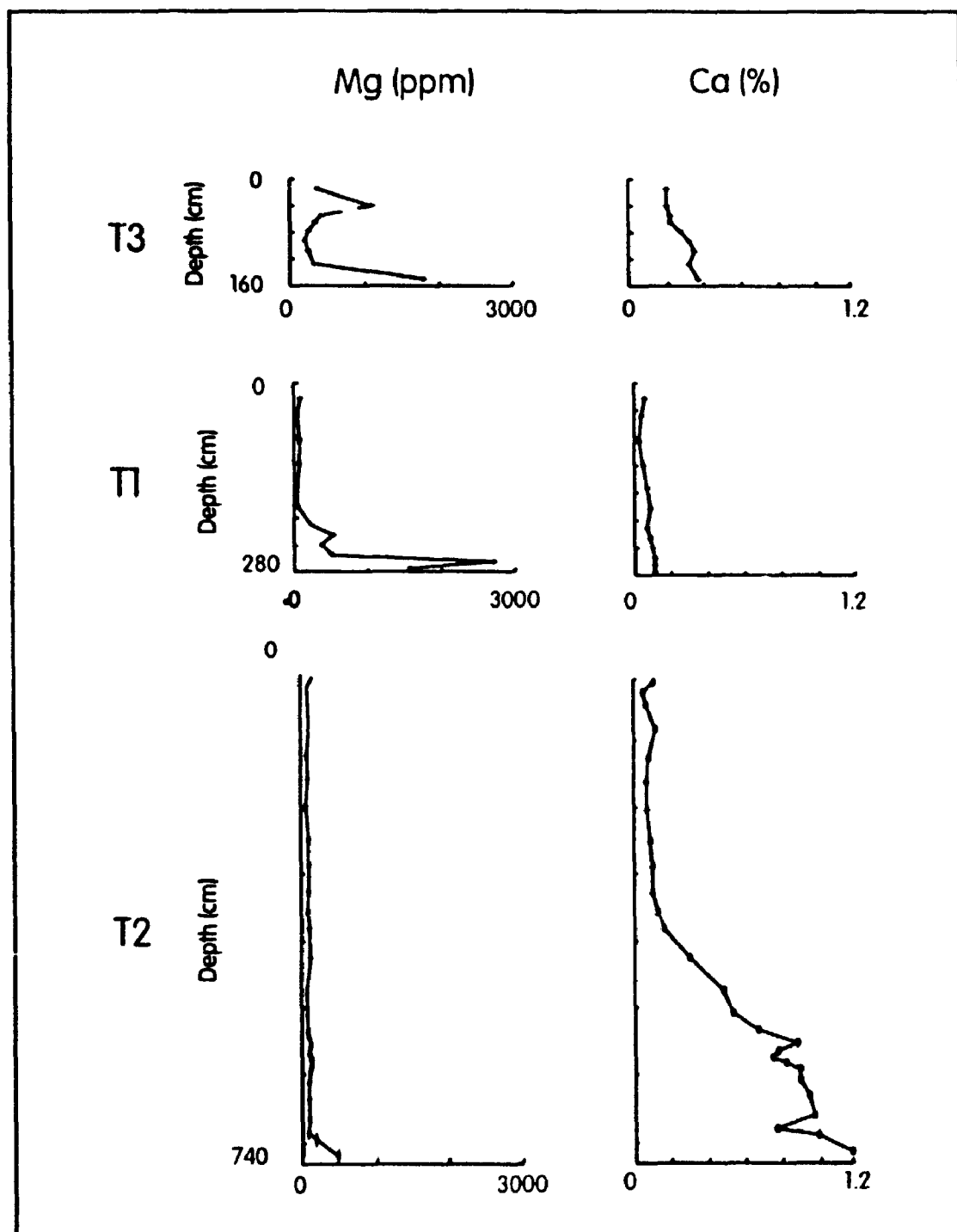


Figure 3.13 Mg and Ca distribution in cores T1, T2 and T3, Petite Bog, Nova Scotia.

Mean S is 0.10% in core T2, 0.13% in core T1 and 0.29% in core T3 (Figure 3.14).

Sulfur concentrations range from 0.05% to 0.27% in the bottom sediments.

3.3.1.1.2 Trace elements

3.3.1.1.2.1 Cr

Chromium appears to be associated with the inorganic fraction. Mean concentration in the bog is 13 ppm for an average ash content of 5.5%. Cr content ranges from 2 to 142 ppm in core T1, nil to 34 ppm in core T2, and 5 to 74 ppm in core T3 (Figure 3.15). A small peak occurs at a depth of 5.75-5.80 m (16 ppm Cr), in the interval rich in charcoal (see Section 3.2.1.1.2, Figure 3.2). In the bottom sediments, Cr levels vary from 65 to 133 ppm.

3.3.1.1.2.2 Br, Cl and I

Bromine, chlorine and iodine do not appear to follow ash distribution in the peat sequence. Furthermore, lowest concentrations are found in the silty sediments underlying peat (nil to 5 ppm Br, 61 to 100 ppm Cl and nil to 1.7 ppm I). Br and I show similar vertical distribution in all cores. In core T1, Br, Cl and I average 31 ppm, 495 ppm and 9 ppm, respectively. In core T2, mean Br, Cl and I contents are 25 ppm, 589 ppm and 9 ppm, respectively. In core T3, Br, Cl and I average 35 ppm, 450 ppm and 13 ppm, respectively. A peak in concentration for all three elements is observed at a depth of 2.00-2.20 m in core T1, 2.70-3.00 m in core T2, and 0.60-0.70 m in core T3 (Figure 3.16).

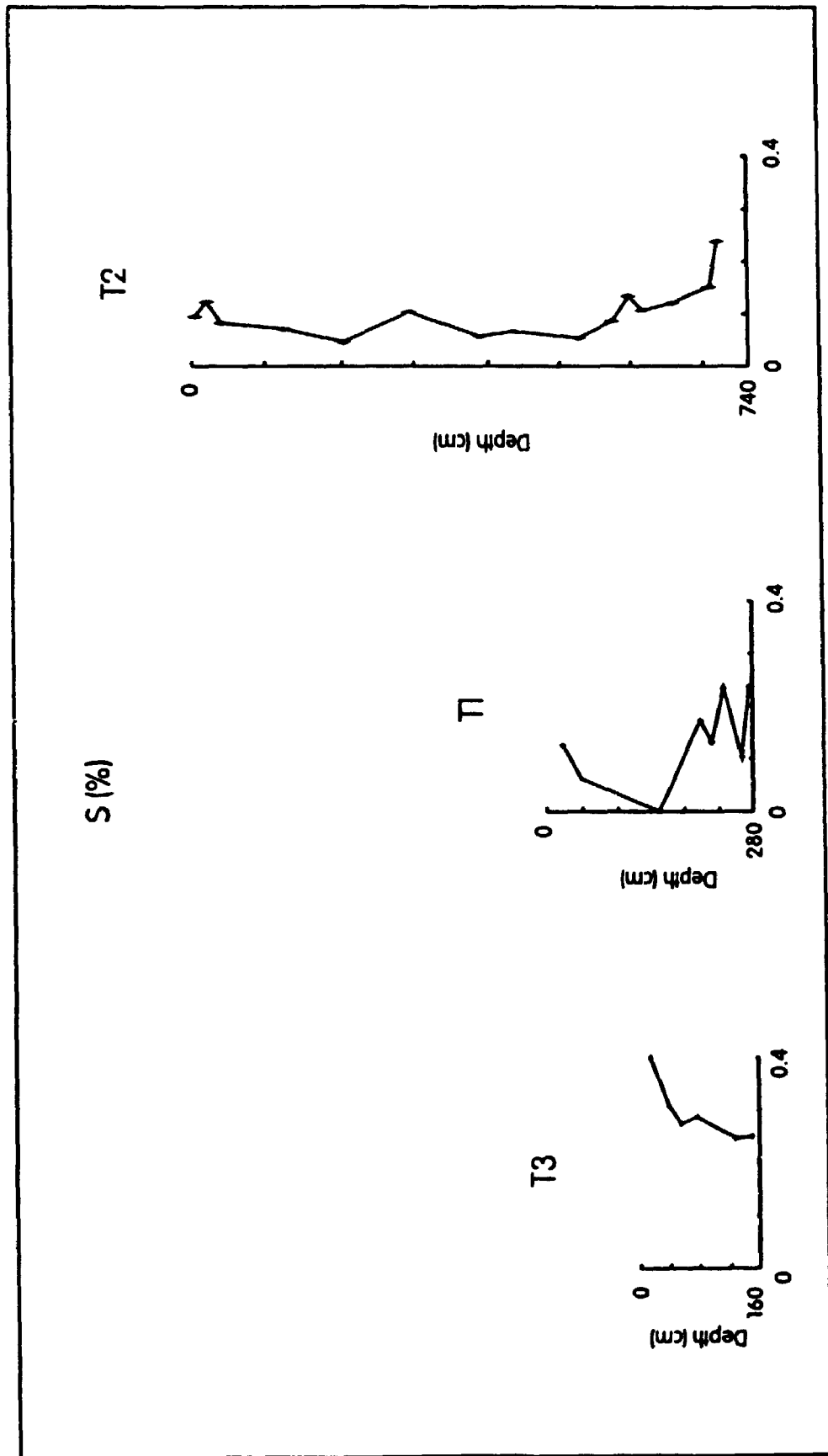


Figure 3.14 S distribution in cores T1, T2 and T3, Petite Bog, Nova Scotia.

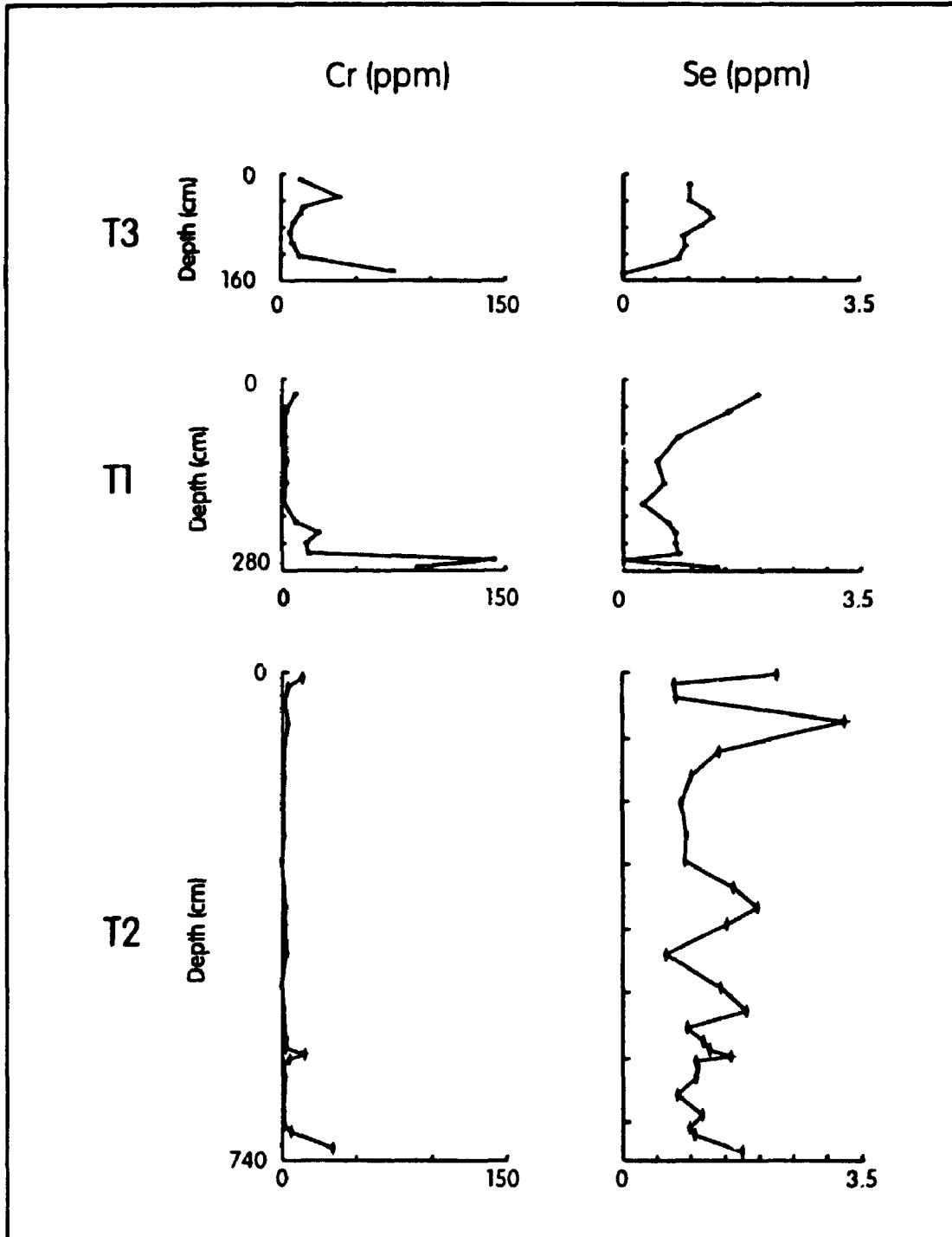


Figure 3.15 Cr and Se distribution in cores T1, T2 and T3, Petite Bog, Nova Scotia.

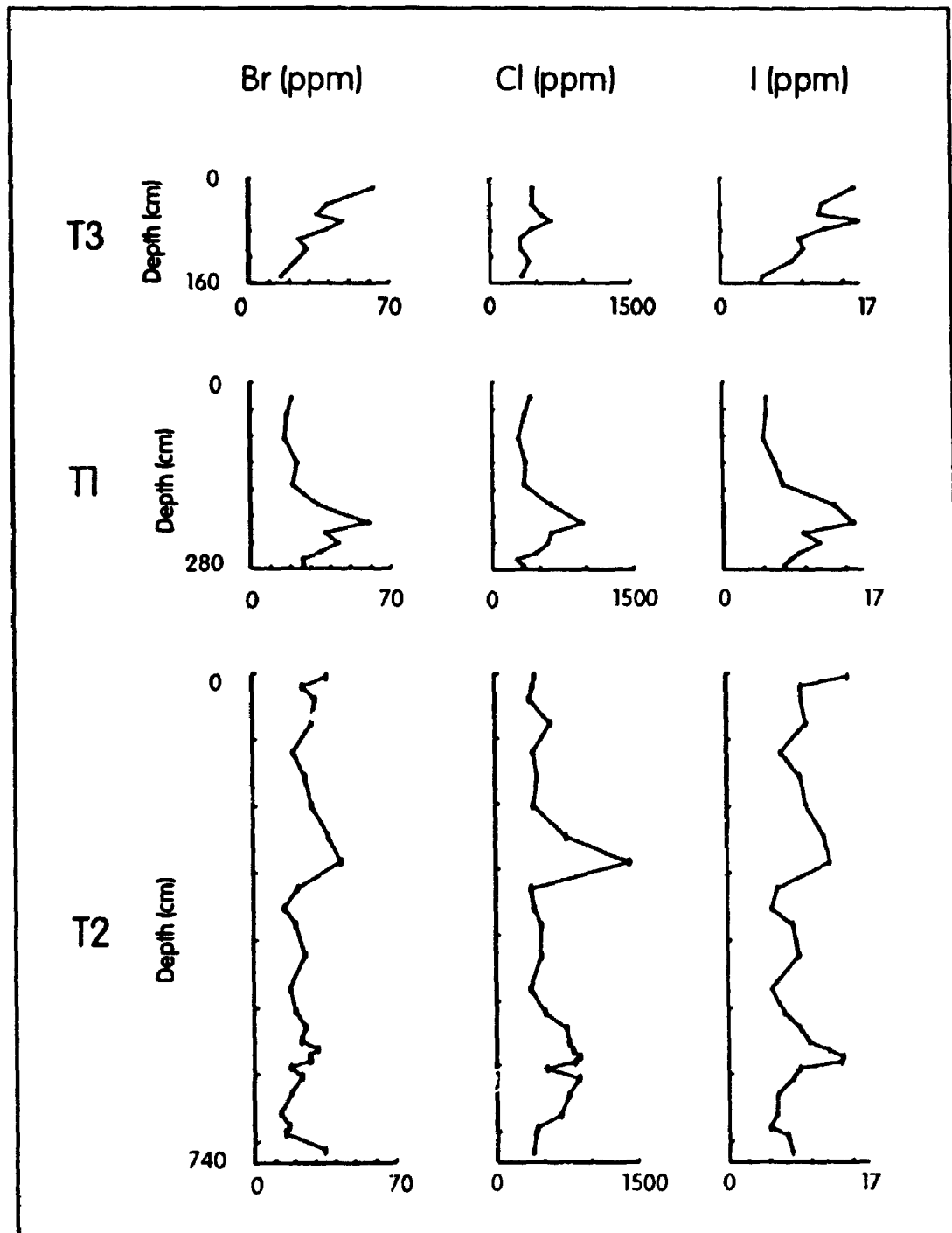


Figure 3.16 Br, Cl and I distribution in cores T1, T2 and T3, Petite Bog, Nova Scotia.

3.3.1.1.2.3 Fe and Mn

Iron content is lowest in core T2 (149 to 10890 ppm). Furthermore, it is particularly low in the ombrotrophic section of the peat sequence. Fe concentration is below 520 ppm in the top 4 m of the peat sequence which is characterized by a mean ash content lower than 1%. Surficial enrichments (in core T2) of Fe and ash appear to coincide. Similar distribution is observed in core T1, with the lowest levels in the ombrotrophic section. Fe levels range from 366 to 13480 ppm in core T1, and 4320 to 12620 ppm in core T3. Highest Fe concentrations in both these cores are found in the basal peats (Figure 3.17).

Manganese concentrations vary from 3 to 226 ppm in core T2, 14 to 136 ppm in core T1, and 115 to 316 ppm in core T3. Mn levels are below 10 ppm in the upper section of core T2 (0.10 to 2.70 m). However, there is a substantial enrichment at the surface (50 ppm). A peak in concentration is also observed near the surface (0.10-0.20 m depth) in core T3. Mn levels are lower in the ombrotrophic section of core T1 and increase with depth (Figure 3.17).

3.3.1.1.2.4 Se

Selenium distribution pattern differs in each core, although higher concentrations are generally observed in the ombrotrophic sections of the cores. Se levels range from nil to 2 ppm in core T1, 0.8 to 3.2 ppm in core T2, and nil to 1.3 ppm in core T3 (Figure 3.15). No Se was detected in the bottom sediments.

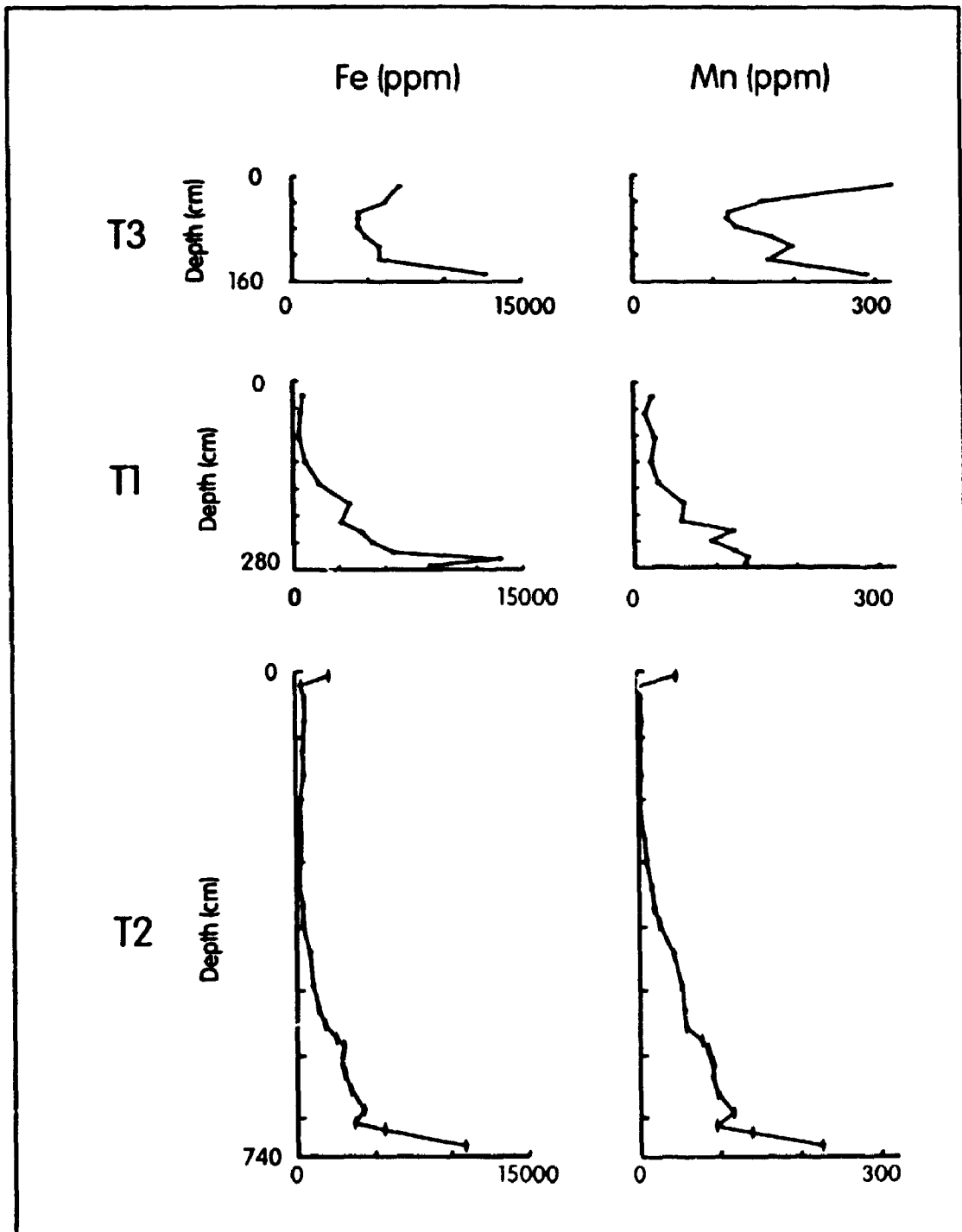


Figure 3.17 Fe and Mn distribution in cores T1, T2 and T3, Petite Bog, Nova Scotia.

3.3.1.2 Salt marsh, Chezzetcook Inlet

Major and trace elements distributions are reported for both cores CH1a and CH2a, situated in the middle marsh and high marsh, respectively. Secondly, variations in ash content and trace element concentrations of surface samples taken at four sites CH1b, CH2b, CH3 and CH4, are presented. Data are shown in Appendix IV (Tables 4, 5, 6, 7, 8 and 9).

3.3.1.2.1 Cores CH1a and CH2a

3.3.1.2.1.1 Major elements

3.3.1.2.1.1.1 *Al and Si*

Aluminum distribution pattern approximates that of the ash content. Mean Al content is 5.9% in core CH1a and 4.8% in core CH2a (Figure 3.18). Silicon concentration is high in both cores, averaging 19.8% in core CH1a and 16.7% in core CH2a (Figure 3.18).

3.3.1.2.1.1.2 *Na and K*

In core CH1a, sodium concentration decreases abruptly from 3.4% at the surface to 0.9% at 0.70 m depth. The decrease continues downcore from 0.70 m at a more subdued rate. In core CH2a, Na concentration has a higher average than CH1a (2.0% Na as opposed to 1.3% in core CH1a) but shows little variation in the profile (Figure 3.18).

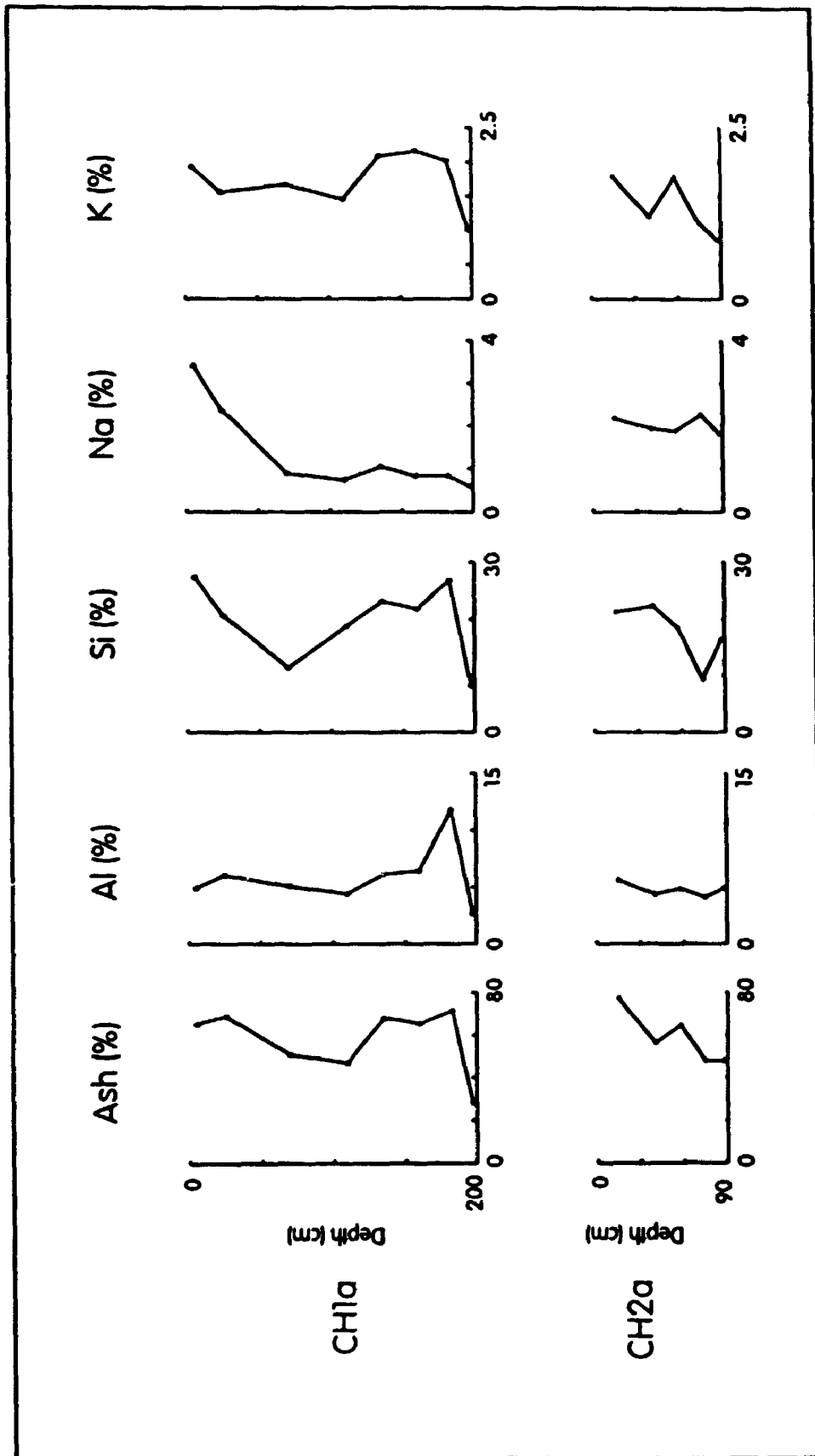


Figure 3.18 Ash, Al, Si, Na and K distribution in cores CH1a and CH2a, Chezzetcook Inlet, Nova Scotia

The potassium distribution pattern correlates with the inorganic fraction. Concentrations are lowest in the basal sedge peat of core CH1a (1.0%), where the ash content is as low as 28%. Concentrations average 1.7% in core CH1a and 1.35% in core CH2a (Figure 3.18).

3.3.1.2.1.1.3 *Mg and Ca*

Magnesium concentration is slightly higher in core CH1a than in core CH2a (mean values: 2367 ppm and 2034 ppm, respectively), and appears to be associated with the inorganic fraction (Figure 3.19).

Calcium distribution in both cores suggests that this element is partly associated with the organic matter and partly with the inorganic fraction. Mean Ca content is 0.7% in core CH1a and 0.65% in core CH2a (Figure 3.19).

3.3.1.2.1.1.4 *S*

Total sulfur content varies between 1.0% and 2.0% in core CH2a, with an average of 1.5%. In core CH1a, it averages 2.3%, ranging from 1.5% at the surface to 4.6% at 1.15 m (Figure 3.19).

3.3.1.2.1.2 Trace elements

3.3.1.2.1.2.1 *Cr, Ni and Ba*

Chromium distribution patterns in both cores are similar. Concentrations are highest in the surface sample, over two times as much as that found underneath. Furthermore, surface Cr content in core CH1a is almost twice that of core CH2a

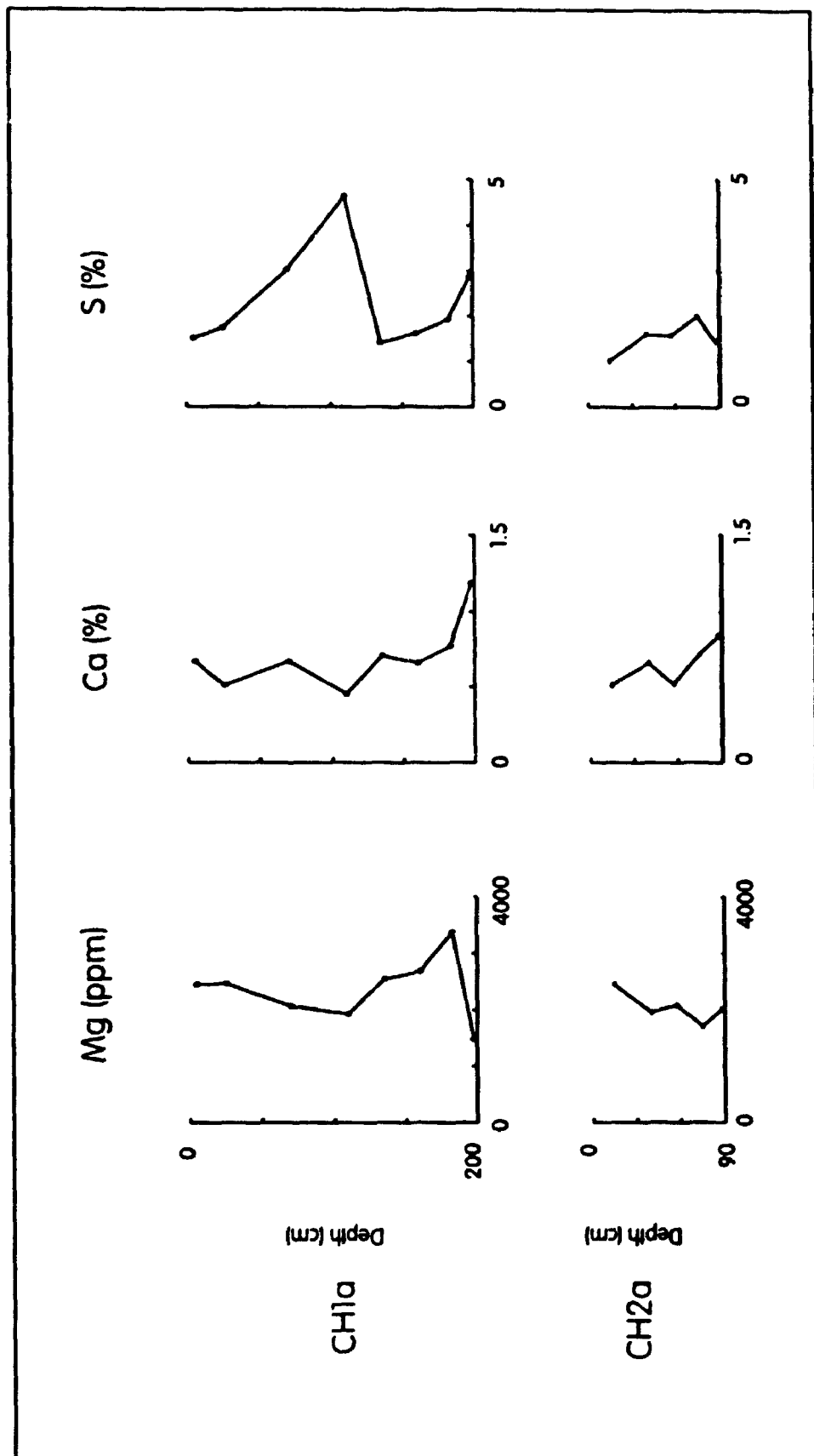


Figure 3.19 Mg, Ca and S distribution in cores CH1a and CH2a, Chezzetcook Inlet, Nova Scotia.

(280 ppm and 149 ppm, respectively). Ni and Cr distributions are similar. Maximum Ni concentrations are found in the surface samples of both cores, with 87 ppm in core CH1a and 51 ppm in core CH2a. In addition, there is a small peak in concentration at 1.15 m depth (41 ppm Ni); (Figure 3.20).

Maximum barium concentrations occur in the surface samples of both cores, (610 ppm in core CH1a and 520 ppm in core CH2a), with means of 387 ppm and 302 ppm, respectively. Ba distribution correlates with fluctuations in both Ni and Cr in both cores, suggesting an association between these elements (Figure 3.20).

3.3.1.2.1.2.2 *Br, Cl and I*

Bromine behavior differs in both cores. In core CH1a, its distribution pattern suggests an association with organic matter, while in core CH2a, Br concentration appears to increase with increasing ash content. Mean Br content is 340 ppm in core CH1a and 169 ppm in core CH2a (Figure 3.21).

Highest chlorine concentration is found in the surface sample of core CH1a, where it reaches a level of 48500 ppm. This decreases rapidly to 5280 ppm at 0.70 m depth, and fluctuates downcore between 5280 ppm and 870 ppm. In core CH2a, highest Cl content occurs at 0.75 m depth (25400 ppm). Cl does not display a distinct pattern, suggesting association with both the organic and inorganic fractions (Figure 3.21).

Iodine concentration is also highest in the surface sample of core CH1a (58 ppm), averaging 49 ppm overall and showing little downcore variation. In core

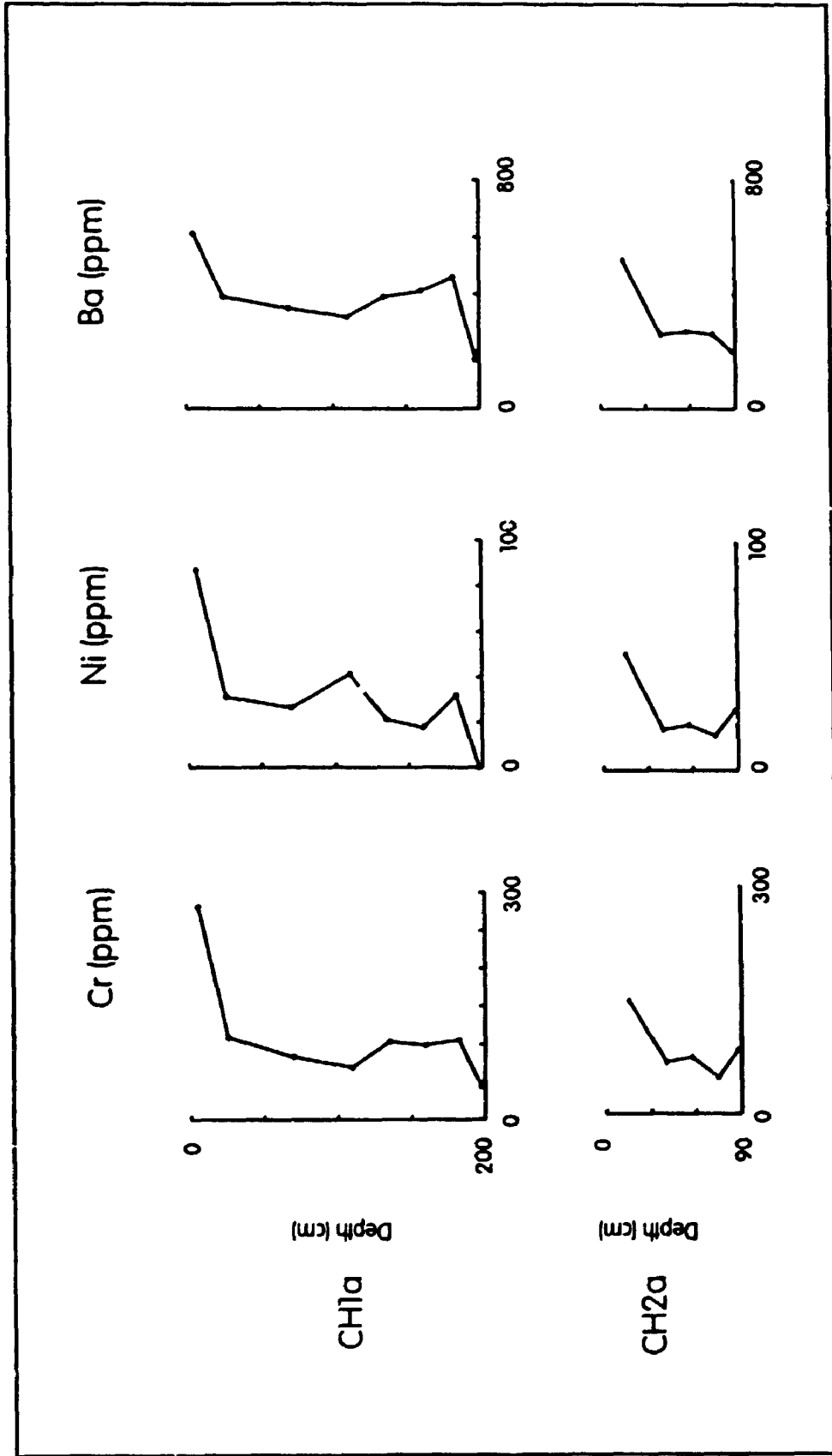


Figure 3.20 Cr, Ni and Ba distribution in cores CH1a and CH2a, Chezzetcook Inlet, Nova Scotia.

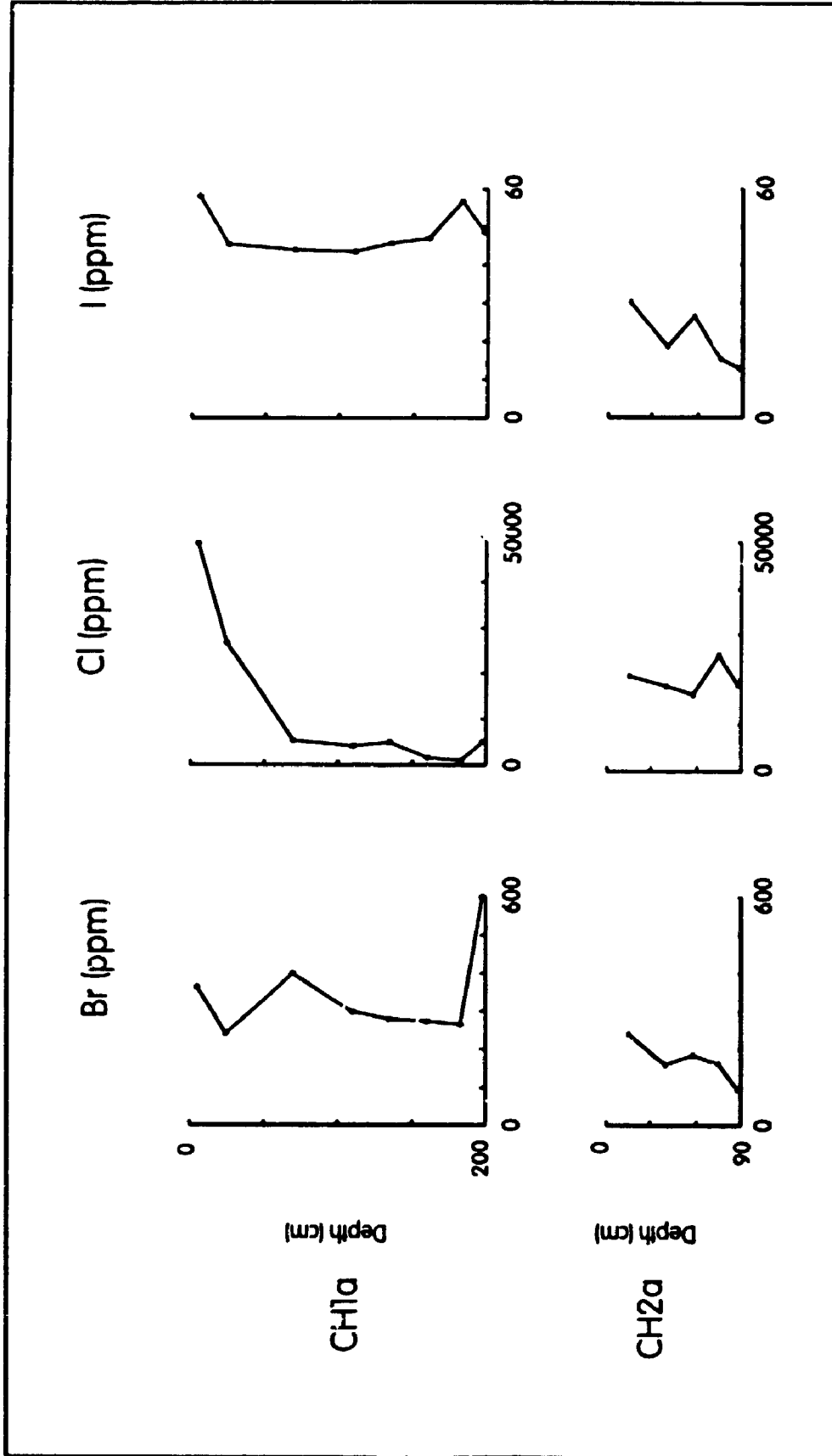


Figure 3.21 Br, Cl and I distribution in cores CH1a and CH2a, Chezzetcook Inlet, Nova Scotia.

CH2a, I content varies between 13 ppm in the bottom and 30 ppm in the top samples (mean of 21 ppm). Fluctuations in the concentration of I are similar to those of Br in core CH2a (Figure 3.21).

3.3.1.2.1.2.3 *Fe*

Mean iron content is 3.4% in core CH1a. A peak concentration of 4.9% was recorded at 1.15 m. In core CH2a, Fe averages 1.9%, ranging from 0.7% to 2.9% (Figure 3.22).

3.3.1.2.1.2.4 *As, Co and Mo*

In core CH1a, arsenic level attains a maximum of 26 ppm at 1.15 m. This also appears to correlate with maximum concentrations in Fe (4.9%), Co (18 ppm), Mo (47 ppm) and S (4.6%); (Figures 3.19 and 3.22). Mean As, Co and Mo in core CH1a are 11 ppm, 14 ppm and 12 ppm, respectively. In core CH2a, they are lower. As and Co average 6 ppm and 8 ppm, respectively, while Mo is mostly below detection limit (<1 ppm); (Figure 3.22).

3.3.1.2.2 Cores CH1b, CH2b, CH3 and CH4

3.3.1.2.2.1 Ash content

Ash content increases with depth in all cores. Except in the uppermost sample of core CH1b, which consisted mainly of *Juncus* stems and roots and is characterized by a high organic content (only 22.6% ash), ash content ranges from 42% to 72% (Figure 3.23).

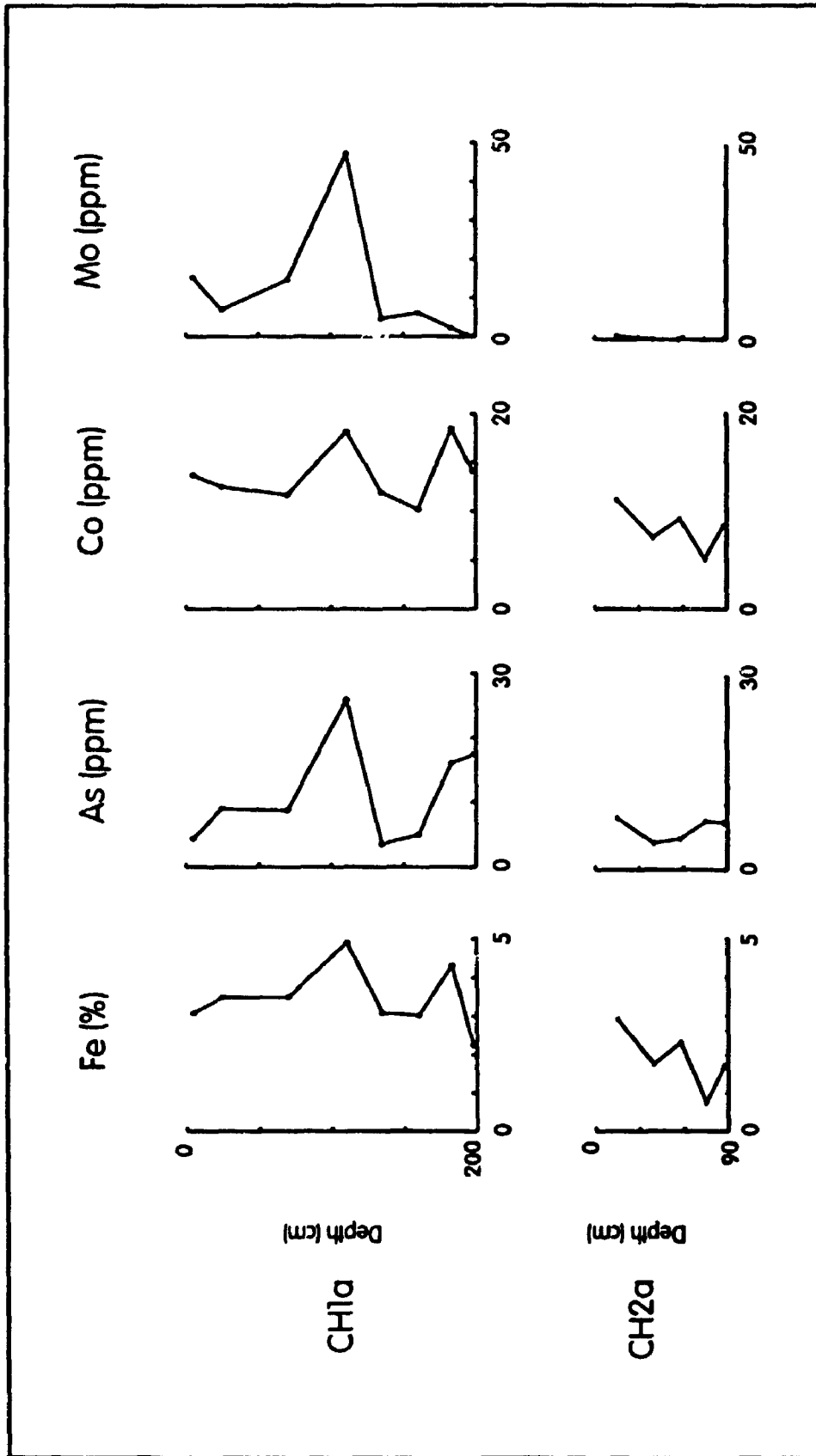


Figure 3.22 Fe, As, Co and Mo distribution in cores CH1a and CH2a, Chezzetcook Inlet, Nova Scotia.

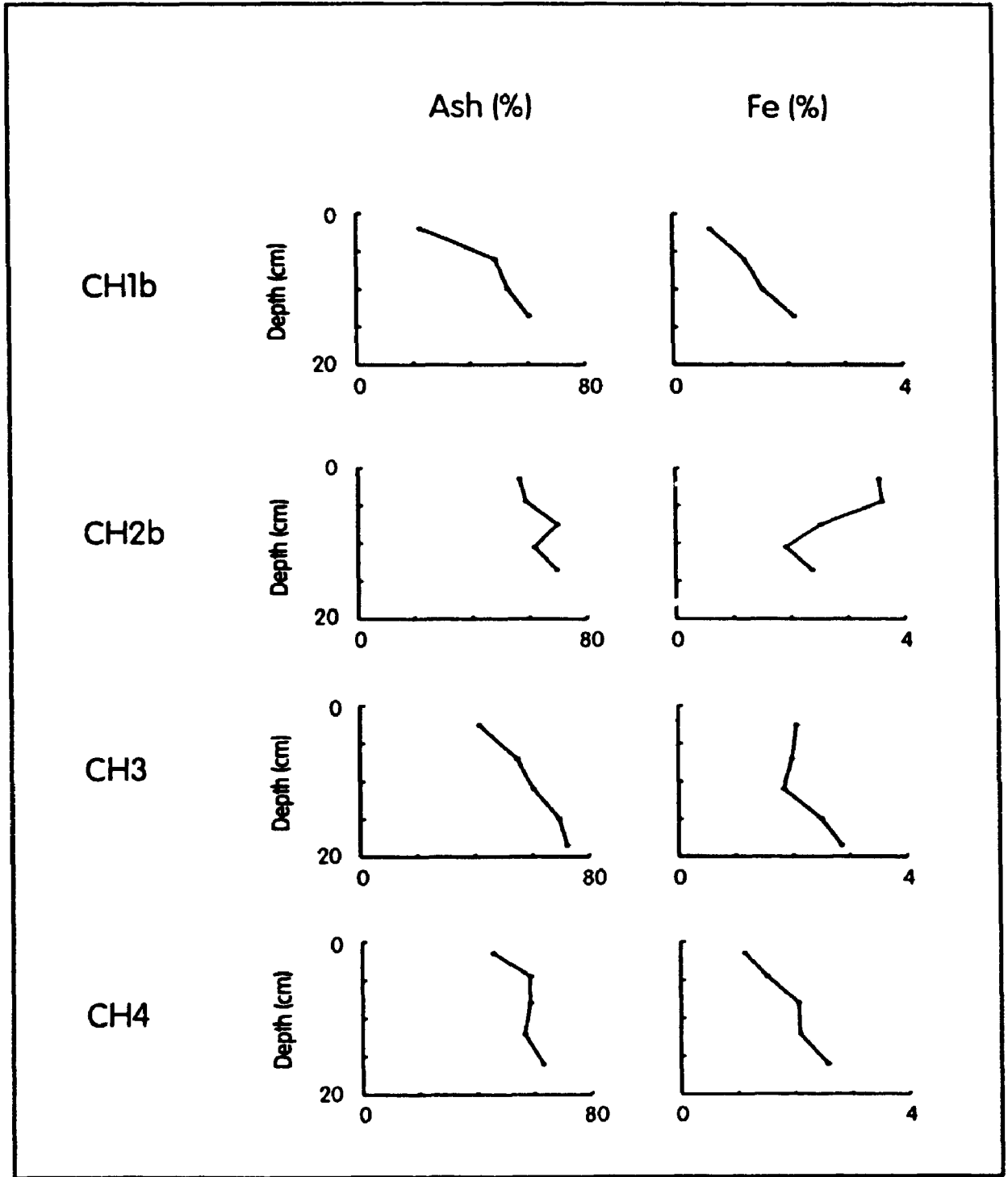


Figure 3.23 Ash and Fe distribution in cores CH1b, CH2b, CH3 and CH4, Chezzetcook Inlet, Nova Scotia.

3.3.1.2.2.2 Trace elements

3.3.1.2.2.2.1 *Cr and Ni*

Chromium content increases with depth in all cores. There appears to be a strong positive correlation between Cr and ash content. Lowest Cr concentration occurs at the surface of core CH1b (13 ppm Cr, 23% ash), while the highest value is measured at a depth of 18.5 cm in core CH3 (60 ppm Cr, 72% ash); (Figure 3.24).

In core CH1b and CH4 (middle marsh), nickel concentration shows little variation with depth, ranging from 12 to 27 ppm, and 17 and 28 ppm respectively. Ni content is slightly higher in core CH3 (23 to 46 ppm Ni). Core CH2b is characterized by surface enrichment of Ni (62 ppm), although there is no similar increase in ash content (Figure 3.24).

3.3.1.2.2.2.2 *Fe*

Iron concentration is lowest in cores CH1b and CH4 (mean Fe content 1.40% and 1.70%, respectively) and highest in cores CH3 and CH2b (mean Fe content 2.24% and 2.75%, respectively). Surface enrichment is observed in core CH2b (3.6% Fe); (Figure 3.23).

3.3.1.2.2.2.3 *Co and Mo*

Small increases in cobalt concentration with depth are recorded in cores CH1b, CH3 and CH4 (3 to 8 ppm, 7 to 11 ppm, 5 to 10 ppm, respectively). However, there is a substantial enrichment in near-surface samples of core CH2b (Figure 3.25).

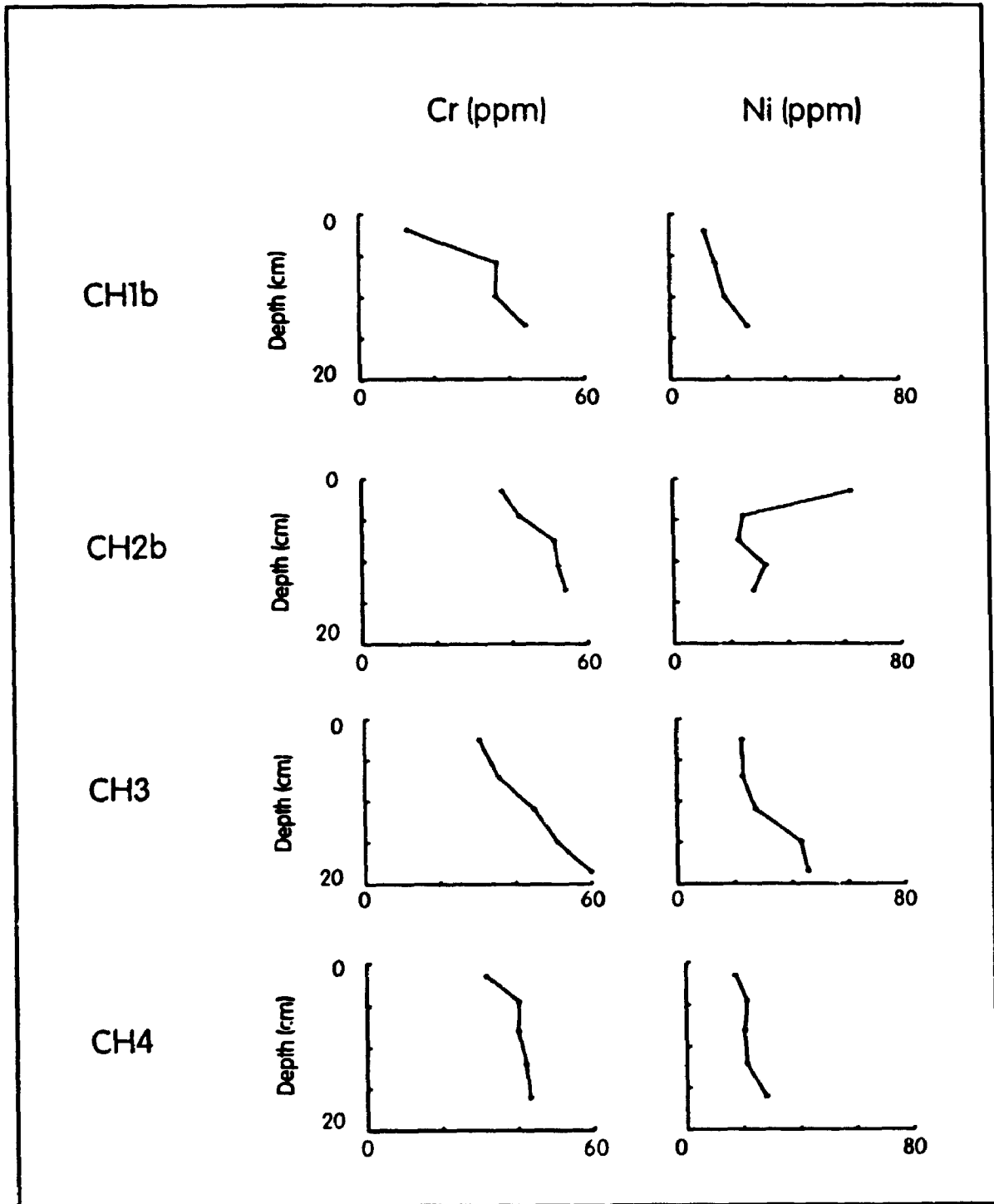


Figure 3.24 Cr and Ni distribution in cores CH1b, CH2b, CH3 and CH4, Chezzetcook Inlet, Nova Scotia.

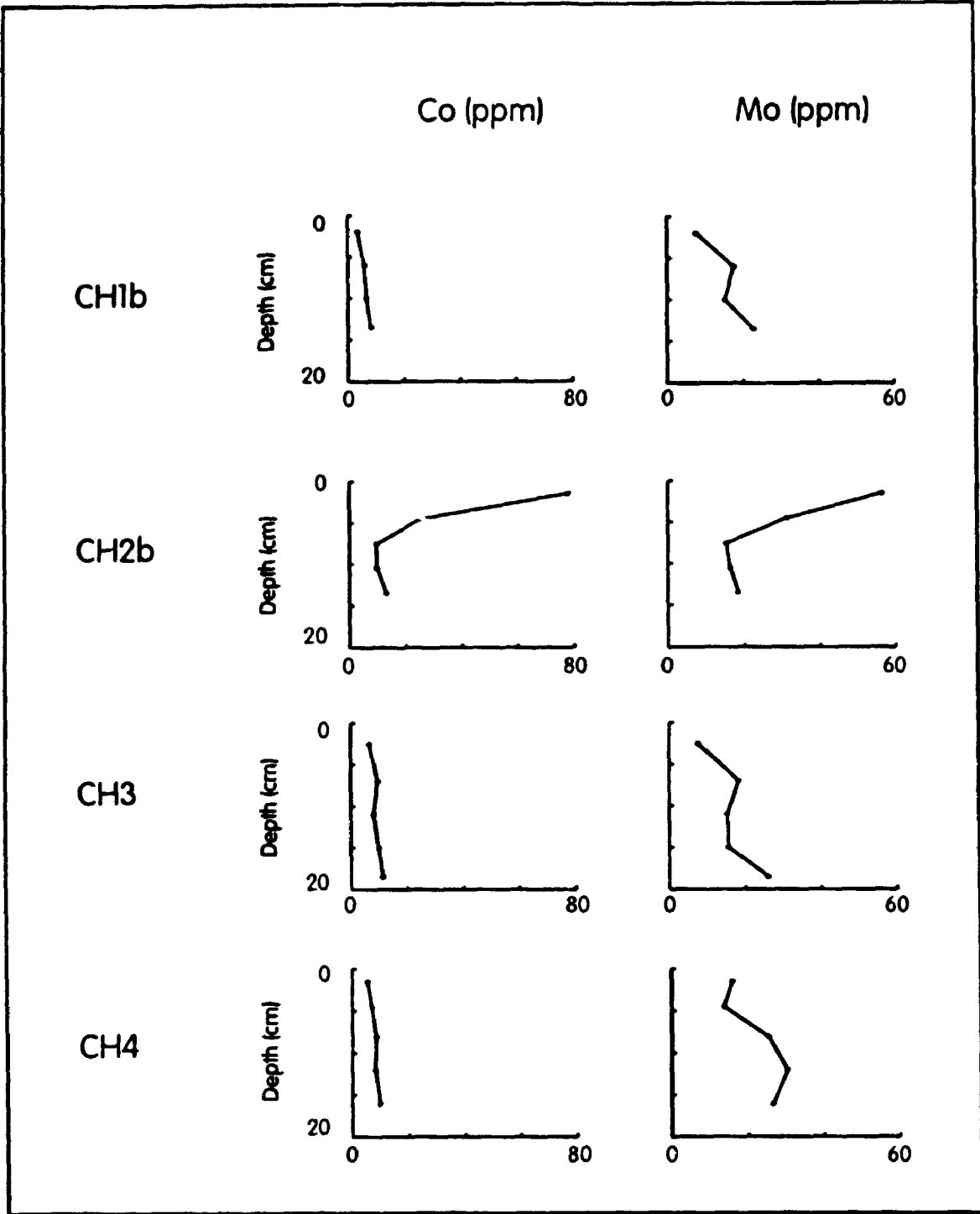


Figure 3.25 Co and Mo distribution in cores CH1b, CH2b, CH3 and CH4, Chezzetcook Inlet, Nova Scotia.

Molybdenum concentration increases with depth in cores CH1b, CH3 and CH4 (8 to 23 ppm, 8 to 26 ppm, 14 to 30 ppm, respectively). However, in core CH2b, Mo shows considerable enrichment near the surface (56 ppm Mo); (Figure 3.25).

3.3.1.2.2.2.4 *As*

Arsenic behavior differs in every core, suggesting various sources and association for this element. Concentrations of As range from 7 to 15 ppm in core CH1b, 14 to 57 ppm in core CH2b, 24 to 47 ppm in core CH3, and 11 to 73 ppm in core CH4 (Figure 3.26).

3.3.1.2.2.2.5 *Br*

Bromine content is high, except near the surface in core CH4, where Br concentration drops to 4 ppm. In all other samples, Br concentrations range from 307 to 910 ppm (Figure 3.26).

3.3.2 **Alberta**

3.3.2.1 **Keephills Fen**

Data are shown in Appendix IV (Table 10).

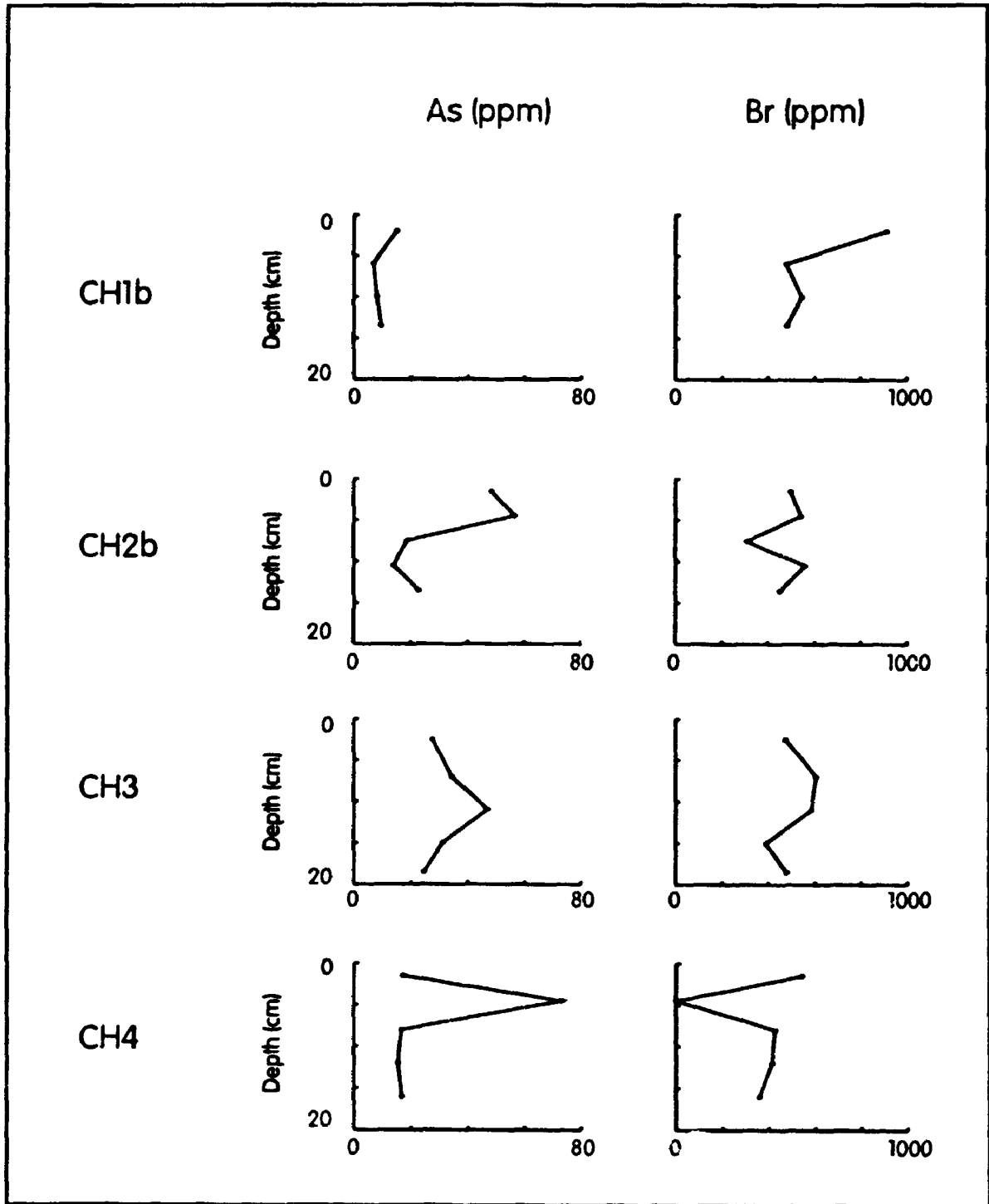


Figure 3.26 As and Br distribution in cores CH1b, CH2b, CH3 and CH4, Chezzetcook Inlet, Nova Scotia.

3.3.2.1.1 Major elements

3.3.2.1.1.1 Al and Si

Aluminum distribution has two peaks, one between 0.05 and 0.20 m (0.5 to 0.6% Al) and one at 2.50 m depth (0.9% Al). In the remainder of the profile, Al content is below 0.25% (Figure 3.27). Al is lowest in the marl (average 0.048%).

Silicon concentration is below detection limit in all samples, except between 0.10 and 0.20 m (2.3 and 3.8% Si) and at 2.50 m depth (4.5% Si); (Figure 3.27).

3.3.2.1.1.2 Na and K

Sodium concentrations peak at 2.50 m (3640 ppm Na), and between 0.05 and 0.20 m (up to 1050 ppm Na). The concentrations compare with generally low Na background levels below 700 ppm Na on average (Figure 3.27). Potassium was not detected, except in the upper profile, where it has a concentration of 0.23% (0 to 0.05 m depth) and 0.17% (0.05 to 0.10 m depth).

3.3.2.1.1.3 Ca and Mg

Calcium concentration is lowest at the surface (0.43% Ca) and increases downward to 5.9% Ca at 0.25 m depth. Further downcore, it increases slowly with depth, following ash distribution (Figure 3.28). In the marl, Ca averages 31.6%.

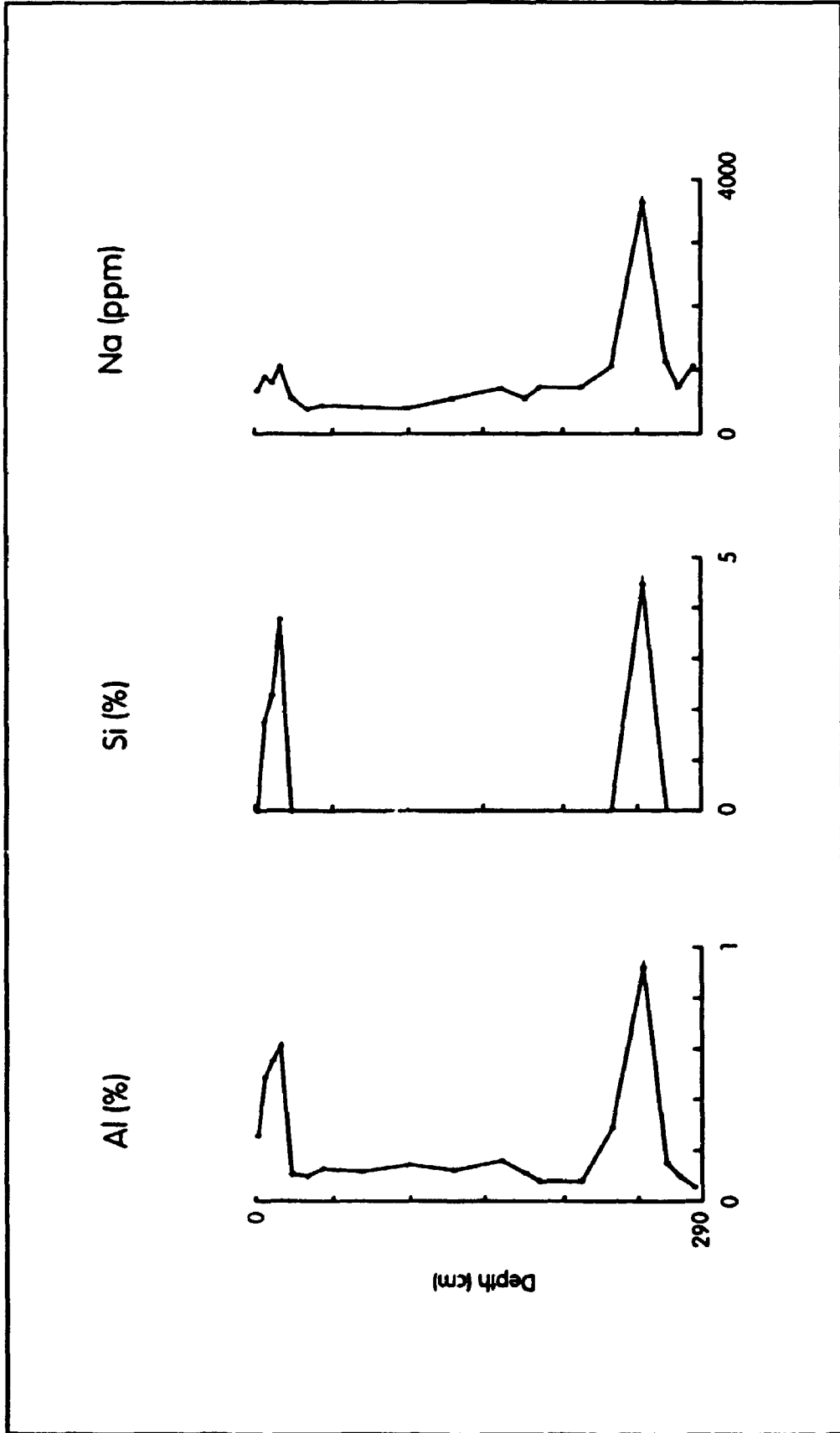


Figure 3.27 Al, Si and Na distribution in Keephills Fen, Alberta.

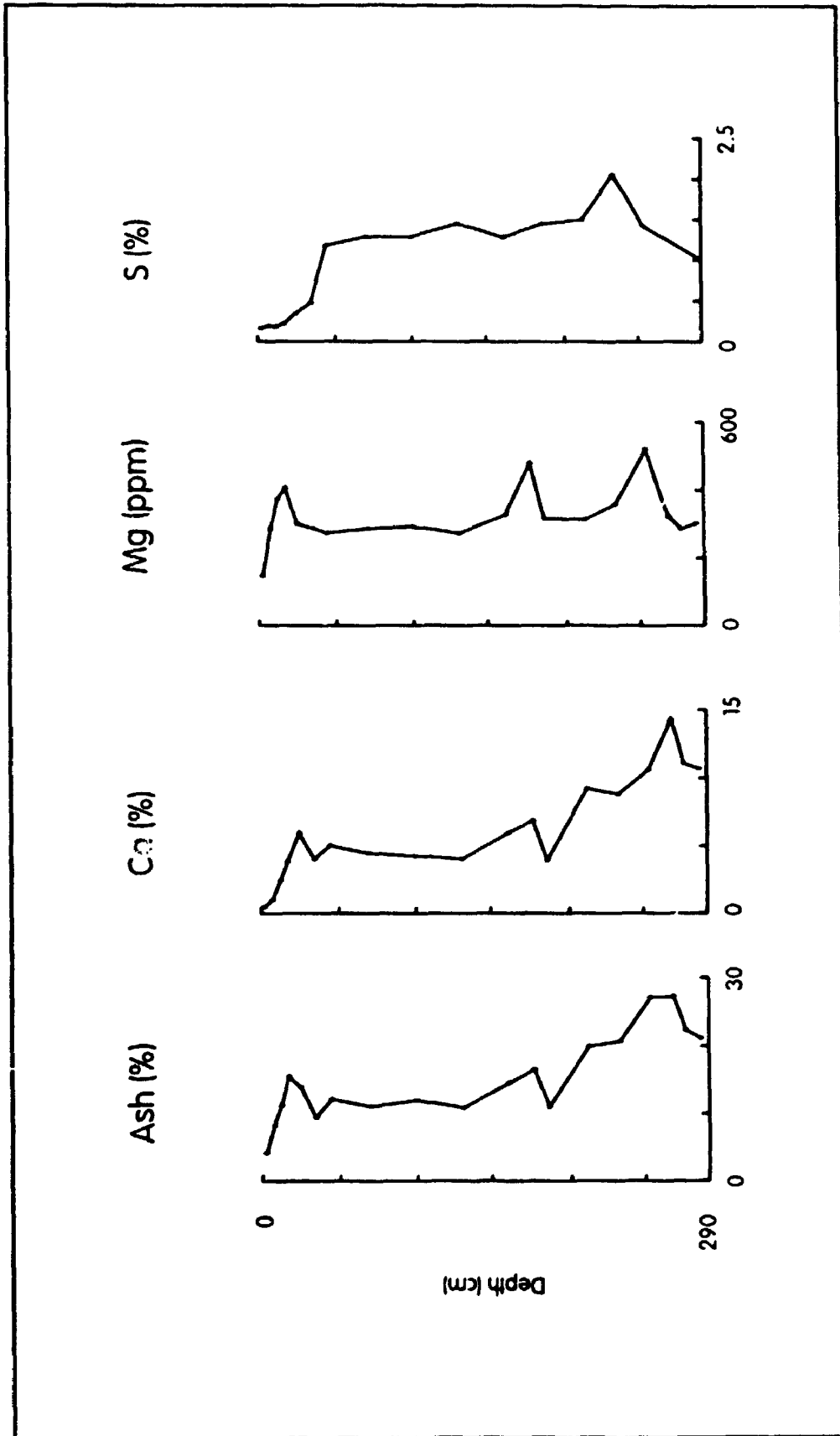


Figure 3.28 Ash, Ca, Mg and S distribution in Keephills Fen, Alberta.

Similar to calcium, magnesium concentration is lowest at the surface (147 ppm). However, there are three peaks in concentration, at 0.10 to 0.20 m depth (404 ppm Mg), at 1.70-1.80 m depth (477 ppm Mg) and at 2.50 m depth (519 ppm); (Figure 3.28). In the marl sediments, Mg levels reach 504 ppm.

3.3.2.1.1.4 S

Total sulfur content increases rapidly from 0.16% at the surface to 1.2% at 0.45 m. Below, it increases slowly with depth to 2% at 2.30 m depth (Figure 3.28). In the marl, S concentration is 0.9% immediately below the peat sequence (2.90 m) and 1.8% at 3.40 m. Over the whole section, total sulfur content averages 1%.

3.3.2.1.2 Trace elements

3.3.2.1.2.1 Cr, V and Ba

Chromium and vanadium contents increase rapidly from the surface to 0.20 m depth, where they reach maximum concentrations (9.9 ppm and 8.4 ppm, respectively). Below, their concentrations decrease but show some variation in the peat profile, with a small peak at 2.50 m depth (4.4 ppm Cr and 3.7 ppm V); (Figure 3.29).

The barium distribution pattern appears to be more random, although there is a maximum concentration at 0.20-0.30 m (130 ppm Ba); (Figure 3.29). Concentration in the marl is variable, ranging from 38 to 134 ppm Ba.

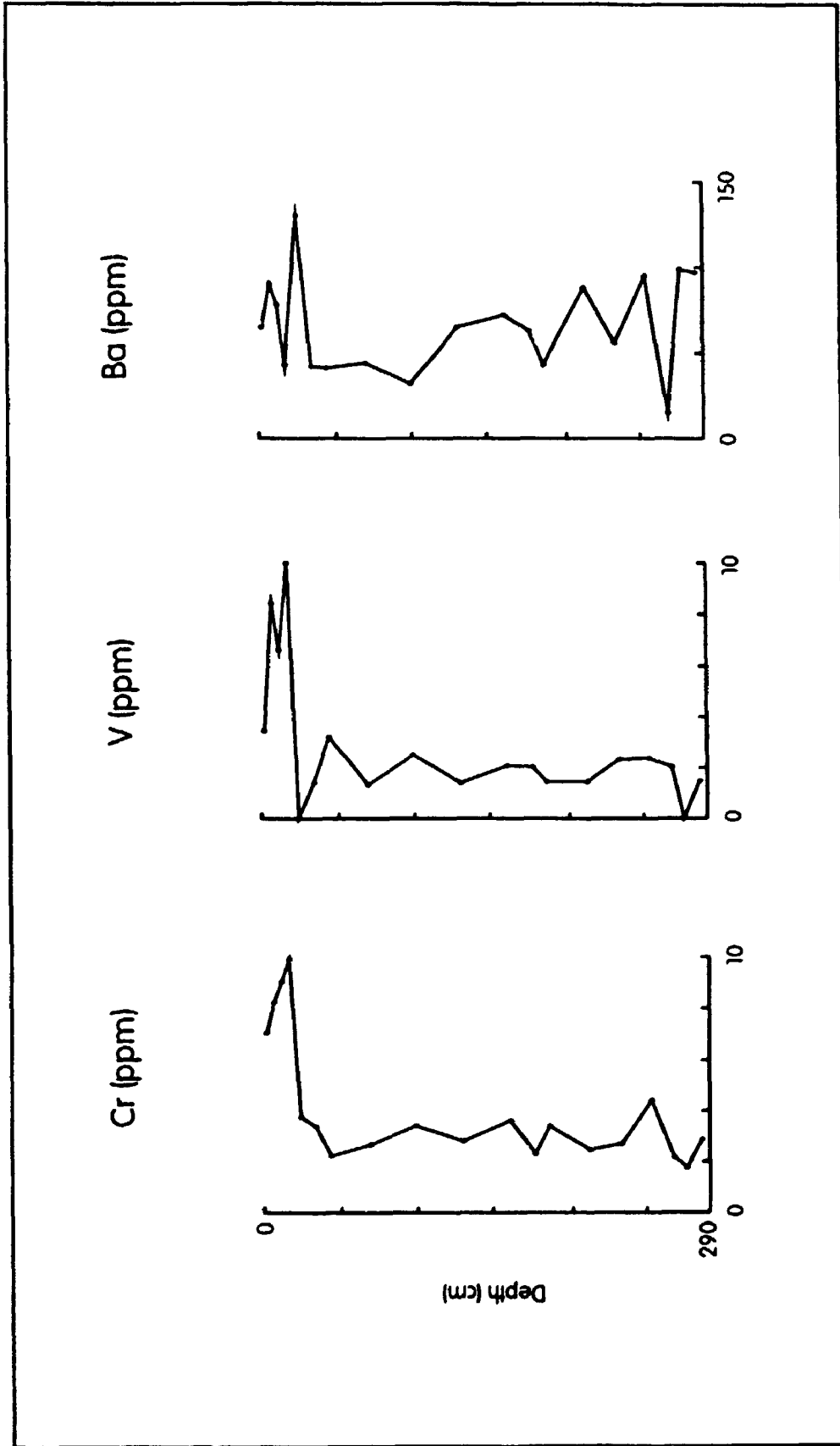


Figure 3.29 Cr, V and Ba distribution in Keephills Fen, Alberta.

3.3.2.1.2.2 Br, Cl and I

Bromine content increases sharply from the surface (close to 5 ppm) to 0.35 m (53 ppm). Below this, Br levels decrease with depth, while ash content increases. Fluctuations in iodine content are similar. I concentration peaks at 0.25 m (25 ppm I), and then decreases with depth (Figure 3.30).

Chlorine concentration is highest at the surface (to a maximum of 228 ppm) and then generally decreases with depth. However there are two small peaks at 1.70 m and 2.50 m (Figure 3.30).

3.3.2.1.2.3 Fe, Mn and Ti

Iron concentration does not exceed 0.1% in most of the samples. However, there is a sharp increase near the surface (0.05 to 0.20 m depth, up to 0.27% Fe) and another sharp increase at 2.50 m (0.24% Fe); (Figure 3.31). In the marl, Fe increases from 0.02% immediately below the peat sequence to 0.56% about 0.40 m further down.

Manganese level is enriched at a depth of 0.10-0.30 m (2820 ppm). Below, Mn content ranges from 58 to 970 ppm (Figure 3.31). In the marl, Mn levels vary between 502 and 1070 ppm.

Titanium distribution is similar to that of Fe. There are two peaks, one near the surface (up to 300 ppm Ti) and one at a depth of 2.50-2.60 m (up to 200 ppm). In the remaining peat samples, Ti levels are below 90 ppm (Figure 3.31).

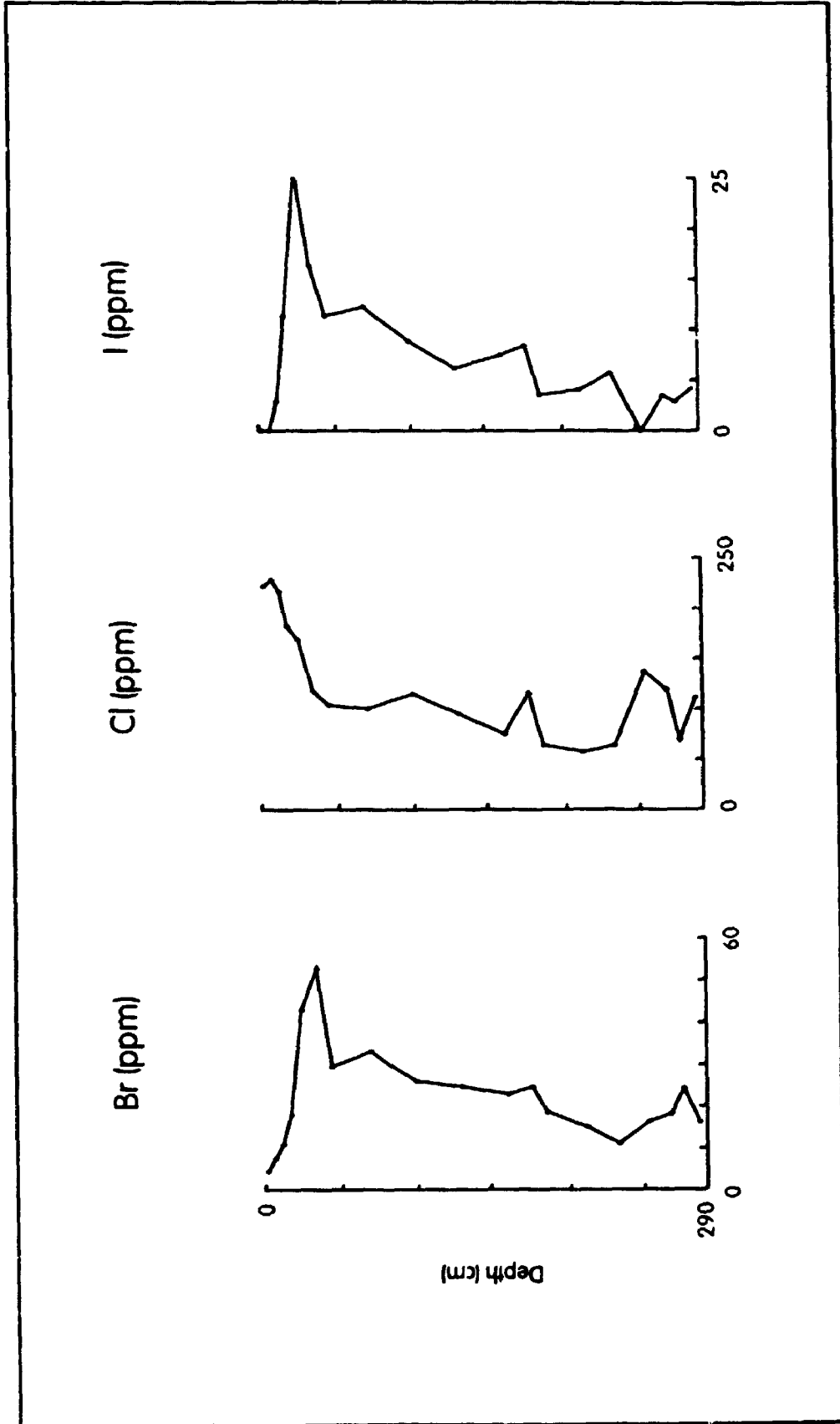


Figure 3.30 Br, Cl and I distribution in Keephills Fer., Alberta.

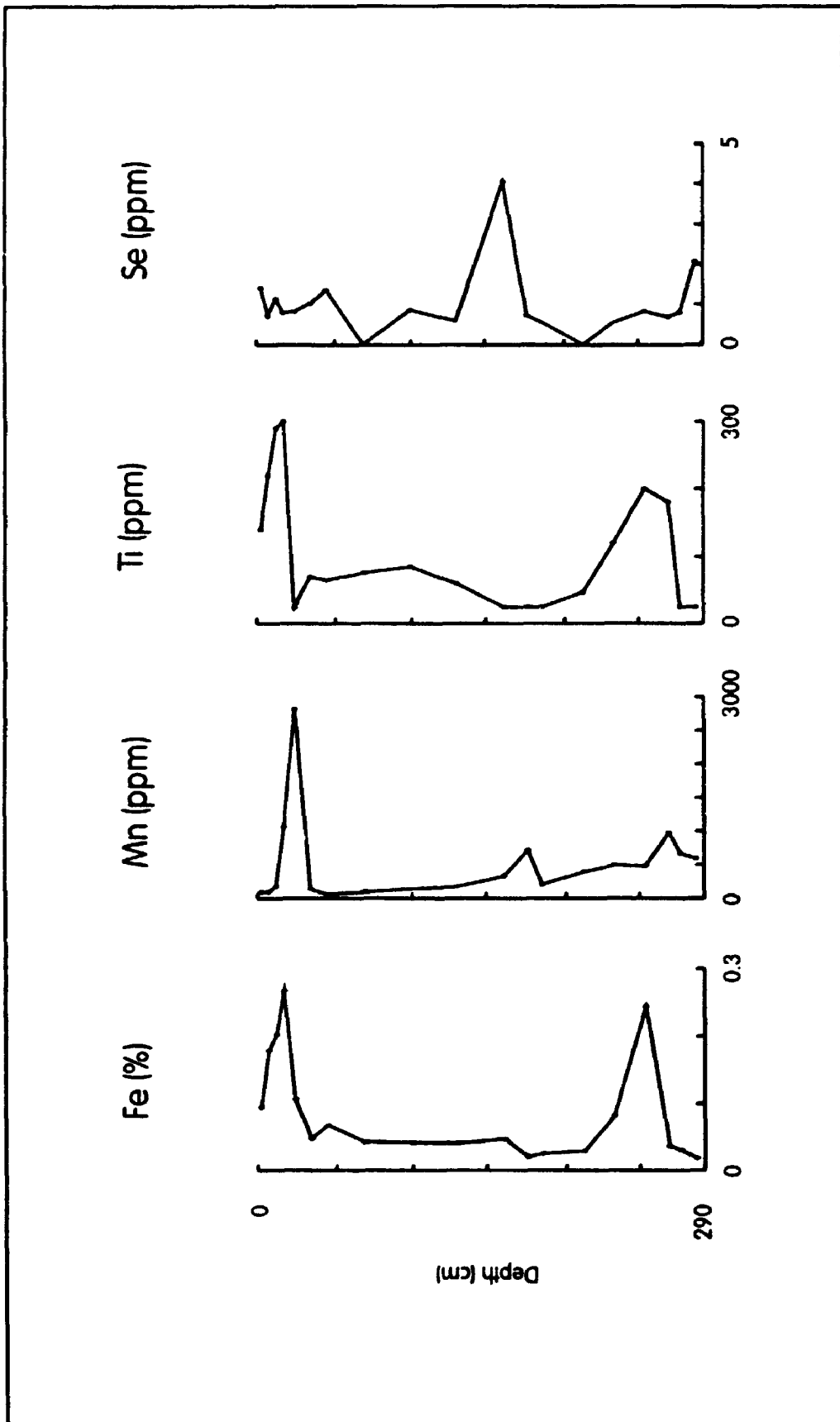


Figure 3.31 Fe, Mn, Ti and Se distribution in Keephills Fen, Alberta.

3.3.2.1.2.4 Se

The selenium distribution pattern has two peaks at 1.60 m (4 ppm Se) and 2.85 m, in the layer immediately above the marl (2 ppm Se); (Figure 3.31).

3.3.3 Northwest Territories

3.3.3.1 **East Little Bear River deposit**

Data are shown in Appendix IV (Tables 11 and 12).

3.3.3.1.1 Core 1

3.3.3.1.1.1 Major elements

3.3.3.1.1.1.1 *Al and Si*

Aluminum and silicon exhibit similar distributions, which correlate approximately with fluctuations in the ash content. High concentrations in the surface layer appear to parallel the surficial enrichment of inorganic content. Al concentration ranges between 2.5% at the surface (34.4% ash) and 0.11% at 0.85 m (5.5% ash). Silicon content is highest in the surface sample (11.3%), while it is below detection limit in all samples with an ash content under 10% (Figure 3.32). Al and Si concentrations in the mineral substrate average 6.8% and 32.5%, respectively.

3.3.3.1.1.1.2 *Na and K*

Sodium and potassium concentrations appear to correlate with ash content. Maximum concentrations in the peat sequence occur at the surface (0.18% Na, 0.61% K), and decrease with depth similar to ash content. Concentrations of K are below detection

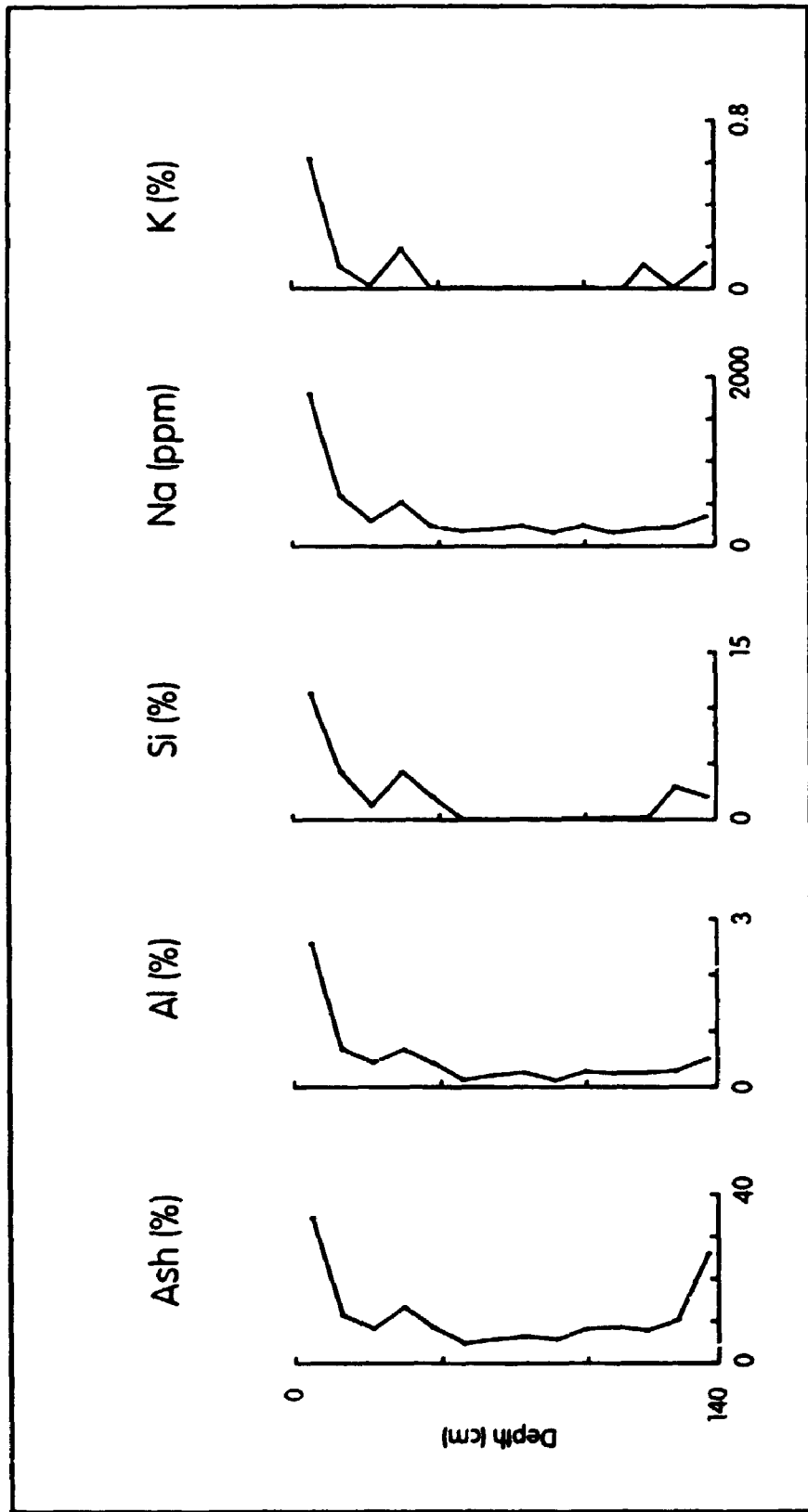


Figure 3.32 Ash, Al, Si, Na and K distribution in core 1, East Little Bear River Deposit, Northwest Territories

limit in all samples with ash content lower than 10% (Figure 3.32). In the mineral substrate, Na and K average 0.53% and 1.8%, respectively.

3.3.3.1.1.1.3 *Mg and Ca*

Magnesium content reaches its maximum at the surface of the peat sequence (896 ppm) and is lowest at 1.15 m (118 ppm); (Figure 3.33). Mg appears to be associated with the inorganic fraction. It averages 2575 ppm in the mineral substrate.

Calcium concentration on the other hand is lowest at the surface (0.44%), while it ranges between 1.2% and 2.3% in the peat sequence below (average ash content = 8.1%); (Figure 3.33). Ca content decreases in the basal peat to 0.69% but increases downcore in the mineral substrate, where it averages 2.1%.

3.3.3.1.1.1.4 *S*

Total sulfur content is below 0.2% from the surface to 0.75 m, ranging from 0.12% to 0.19% in this interval. From there to the bottom of the peat deposit, it increases from 0.18% at 0.75 m to 1.47% at 1.35 m in the basal peat layer (Figure 3.33). Sulfur concentration is lowest (< 0.15%) in the mineral substrate.

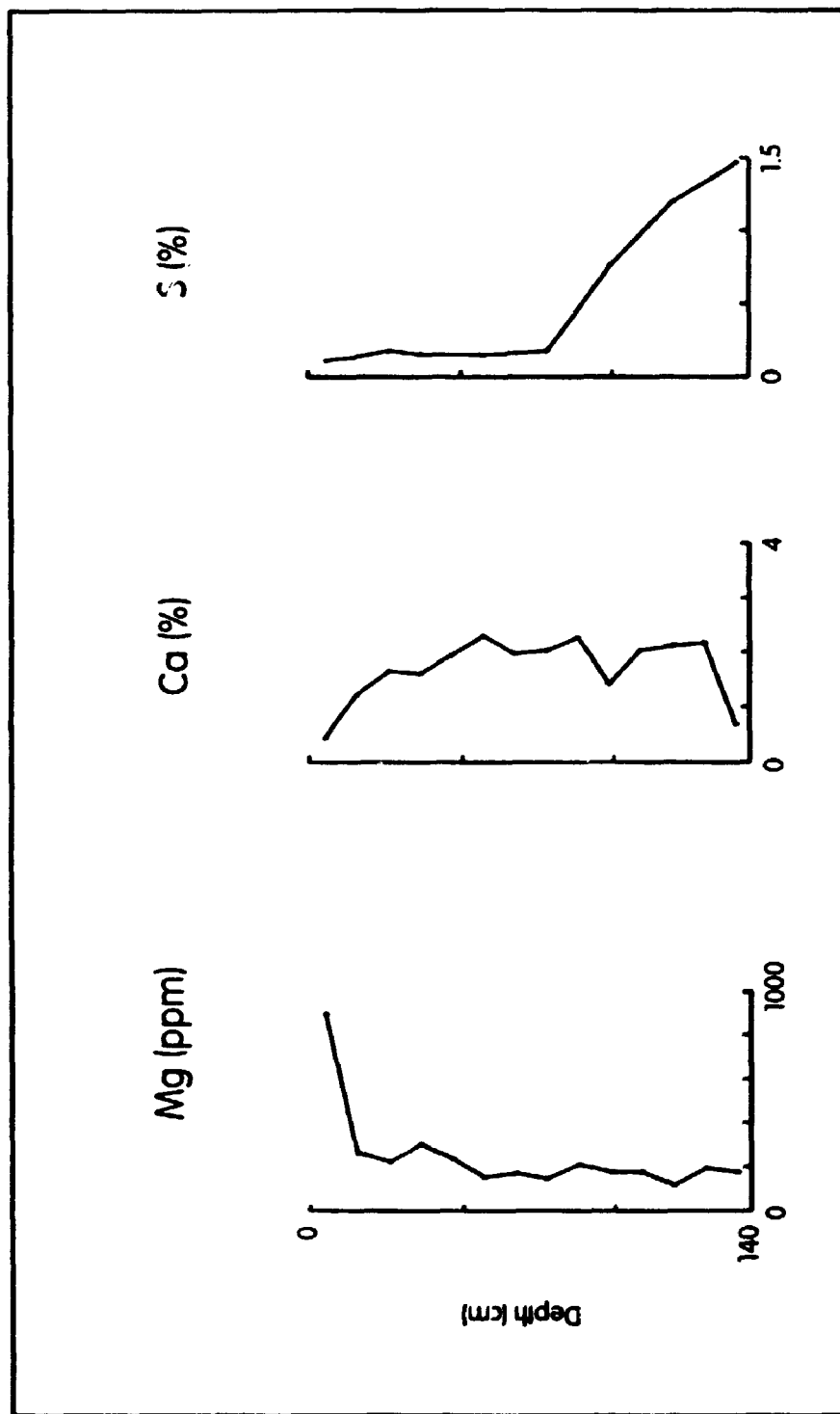


Figure 3.33 Mg, Ca and S distribution in core 1, East Little Bear River Deposit, Northwest Territories.

3.3.3.1.1.2 Trace elements

3.3.3.1.1.2.1 *Cr and Ba*

The chromium distribution pattern reveals a strong affinity with the inorganic fraction. At the surface, Cr content is highest (37 ppm), falling to a minimum at 0.55 m (2 ppm Cr, 4.5% ash); (Figure 3.34). In the mineral substrate, Cr concentration averages 100 ppm.

Barium appears to be associated with the inorganic fraction, as its concentration is maximum at the surface (650 ppm) and lowest in samples with ash content below 10% (Figure 3.34). Ba content averages 1447 ppm in the mineral substrate.

3.3.3.1.1.2.2 *Br, Cl and I*

Highest iodine and chlorine concentrations are found at 0.15 m (7 ppm I and 216 ppm Cl); these decrease downward reaching a minimum value in the interval overlying the mineral substrate (1 ppm I and 32 ppm Cl). Large fluctuations in Cl content in the peat sequence are observed but appear to be random (Figure 3.35). In the mineral substrate, Cl level decreases downward and no Cl was detected below 1.95 m. Iodine is below detection limit in the mineral substrate.

Bromine concentration is highest at 1.05 m (24 ppm Br) and lowest in the basal peat layer (5 ppm). No bromine was detected in the mineral substrate. Like Cl and I, Br content increases from the surface to 0.15 m and then decreases downward. However, Br concentration increases slightly with depth from 0.55 m (Figure 3.35).

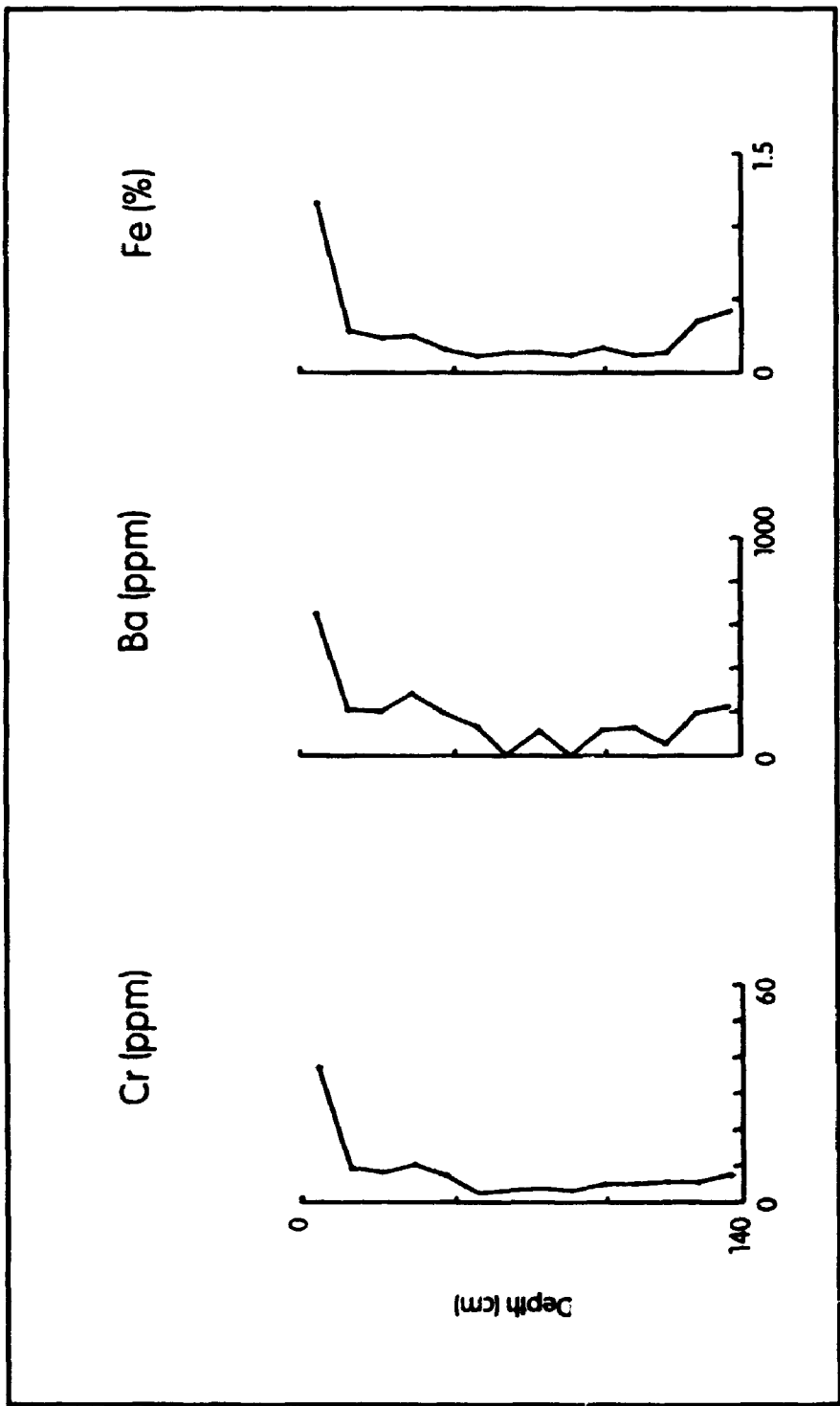


Figure 3.34 Cr, Ba and Fe distribution in core 1, East Little Bear River Deposit, Northwest Territories.

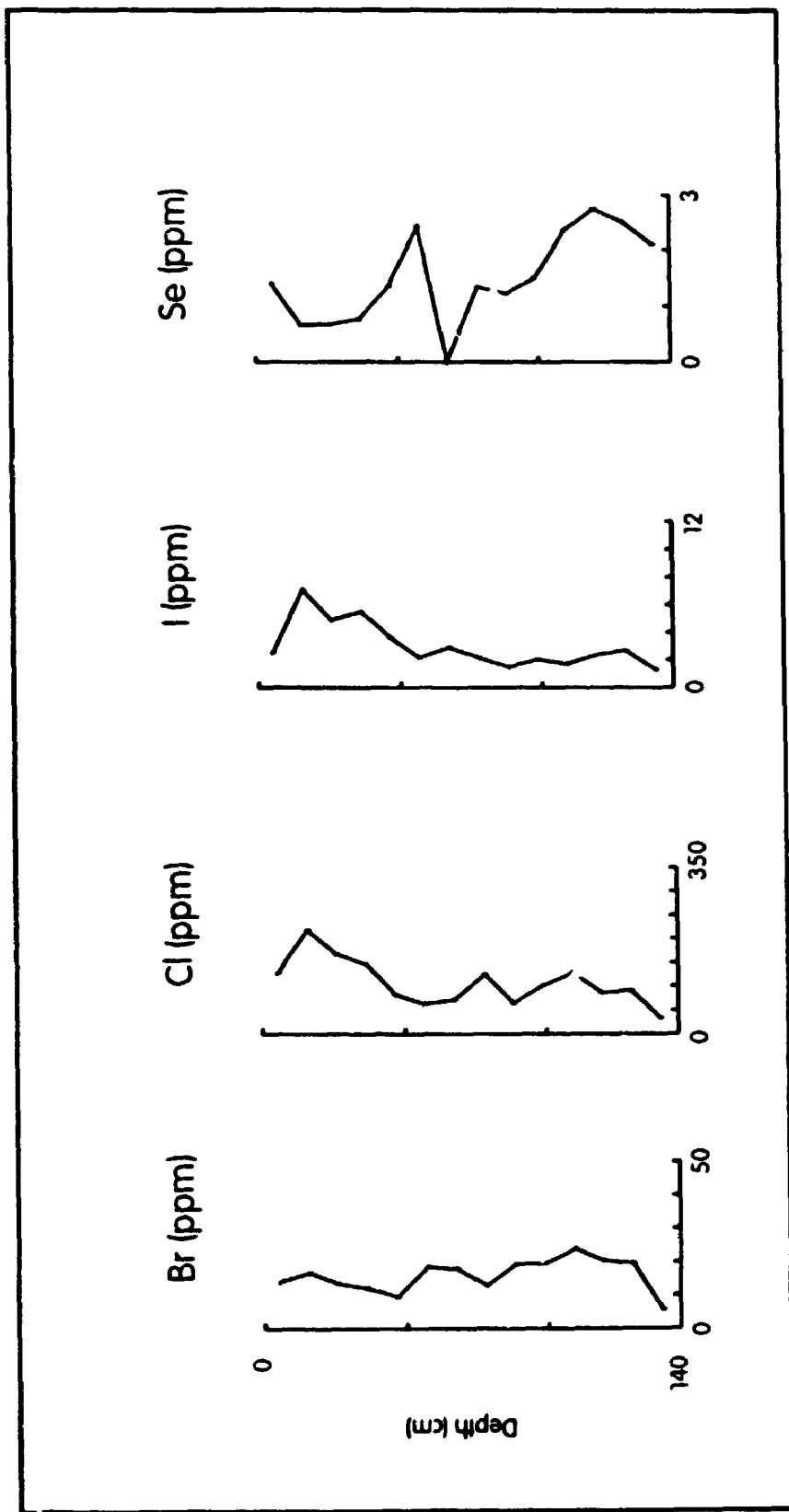


Figure 3.35 Br, Cl, I and Se distribution in core 1, East Little Bear River Deposit, Northwest Territories.

3.3.3.1.1.2.3 *Fe*

Iron content is highest at the surface (1.2%) and decreases rapidly, in conjunction with a decrease in ash content. The lowest value is measured at 0.55 m (0.11% Fe, 4.6% ash); (Figure 3.34). In the mineral substrate, Fe averages 2.7%.

3.3.3.1.1.2.4 *Se*

The selenium distribution pattern suggests association with both the inorganic and organic fraction in this peat profile. Se concentration decreases with ash content from the surface to 0.15 m, where it is just above the detection limit (Figure 3.35). It attains a maximum concentration in the mineral substrate at 1.55 m (5 ppm), but decreases below detection limit in the other samples of mineral substrate.

3.3.3.1.2 Core 2

In this core, permafrost was found at 0.68 m depth. Chemical analyses reveal that the majority of elements studied are enriched immediately above the permafrost boundary, while their concentration drops below detection limit in the first perennially frozen peat layer. Ash content is highest at the surface (26%), and fluctuates between 3% and 15% in the peat sequence, except in the basal layer, where it reaches 21%. Immediately above the permafrost boundary, ash content equals 5%, and is only slightly lower in the underlying perennially frozen layer (3%); (Figure 3.36).

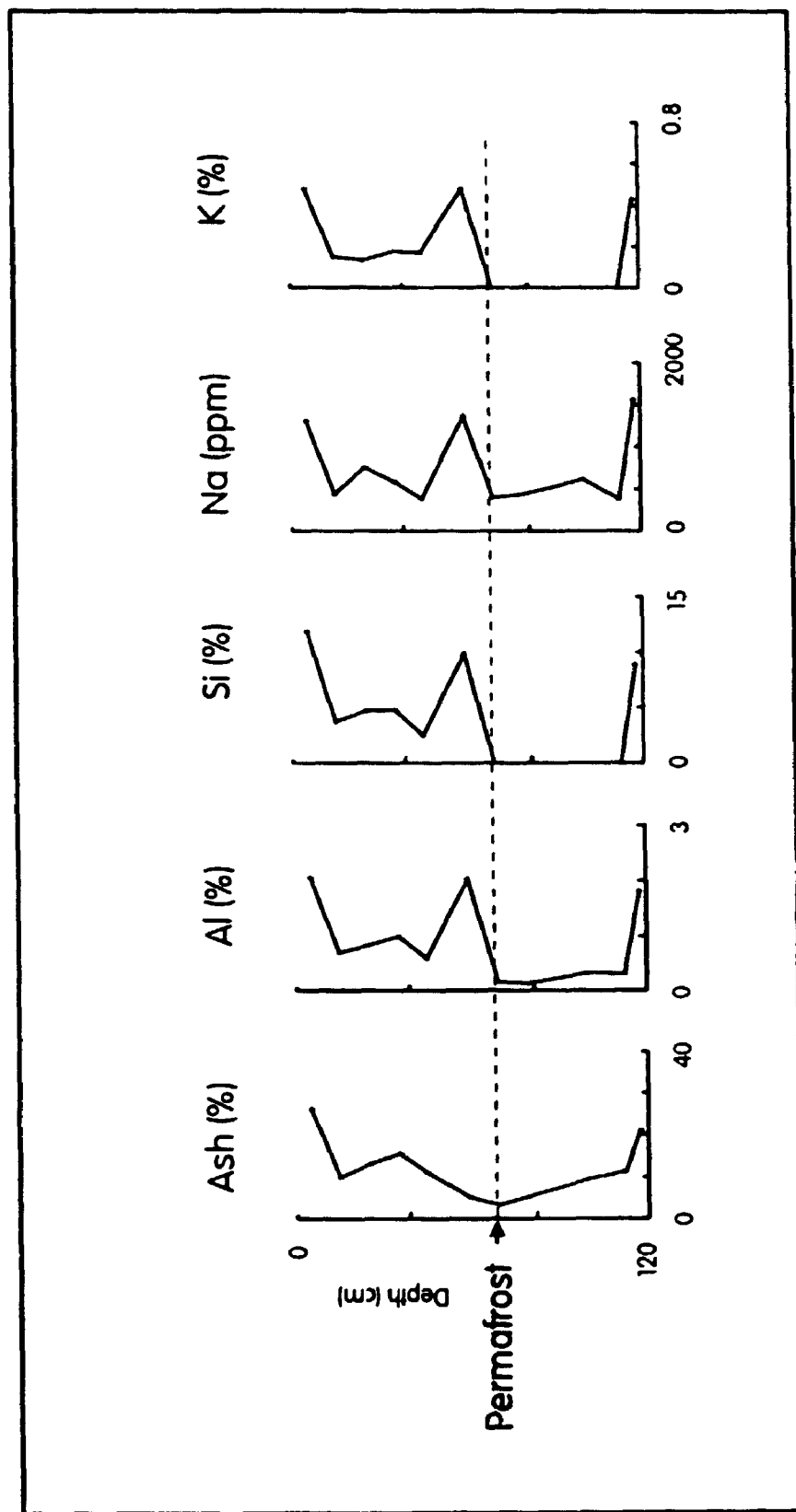


Figure 3.36 Ash, Al, Si, Na and K distribution in core 2, East Little Bear River Deposit, Northwest Territories.

3.3.3.1.2.1 Major elements

3.3.3.1.2.1.1 *Al and Si*

Aluminum content appears to follow ash distribution in the peat profile, except in the layer immediately above the permafrost boundary (2% Al, 5% ash). Surface enrichments of Al and ash on the other hand appear to be proportional (2% Al, 26% ash); (Figure 3.36). Al averages 5.8% in the mineral substrate.

Silicon concentration shows similar enrichment above the permafrost boundary (9.8% Si), while it is not detectable below, except in the basal layer and mineral substrate. Surface enrichment (11.9% Si) appears to coincide with ash enrichment (Figure 3.36). Mean Si content in the mineral substrate is 29.3%.

3.3.3.1.2.1.2 *Na and K*

Sodium and potassium show enrichment at the surface (0.13% Na and 0.48% K), probably associated with the increase in ash content, and immediately above the permafrost boundary (0.14% Na and 0.48% K). No potassium was detected below the permafrost boundary in the peat (<25% ash), while Na content averages 0.05% in this section (Figure 3.36). In the mineral substrate, Na and K levels are 0.48% and 0.14%, respectively.

3.3.3.1.2.1.3 *Mg and Ca*

Magnesium distribution closely follows the ash distribution in the peat profile, except immediately above the permafrost boundary, where Mg shows enrichment

(710 ppm Mg). Surface enrichment (641 ppm Mg) appears to coincide with ash enrichment (Figure 3.37). In the mineral substrate, Mg levels are 1870 ppm.

A slight but steady increase in calcium concentration downcore (from 0.4% to 3% Ca) is disrupted by a marked enrichment immediately above the permafrost boundary (3.8% Ca); (Figure 3.37). Ca levels average 2.4%.

3.3.3.1.2.1.4 S

The total sulfur distribution pattern differs from those of the previously described major elements. S concentration increases steadily from the surface (0.12% S) to 0.45 m (0.32% S). There is a slight decline above the permafrost boundary, but then concentrations increase downward in the peat sequence to reach 1% in the basal layer (Figure 3.37). In the mineral substrate, total sulfur is low (0.13% S).

3.3.3.1.2.2 Trace elements

3.3.3.1.2.2.1 *Cr and Ba*

Chromium and barium distribution patterns are similar, showing decrease downward from the surface (from a maximum of 45 ppm Cr and 570 ppm Ba), closely related to the ash distribution, and displaying an enrichment immediately above the permafrost boundary (58 ppm Cr, 1000 ppm Ba); (Figure 3.38). In the mineral substrate, Cr and Ba levels are 95 ppm and 1210 ppm, respectively.

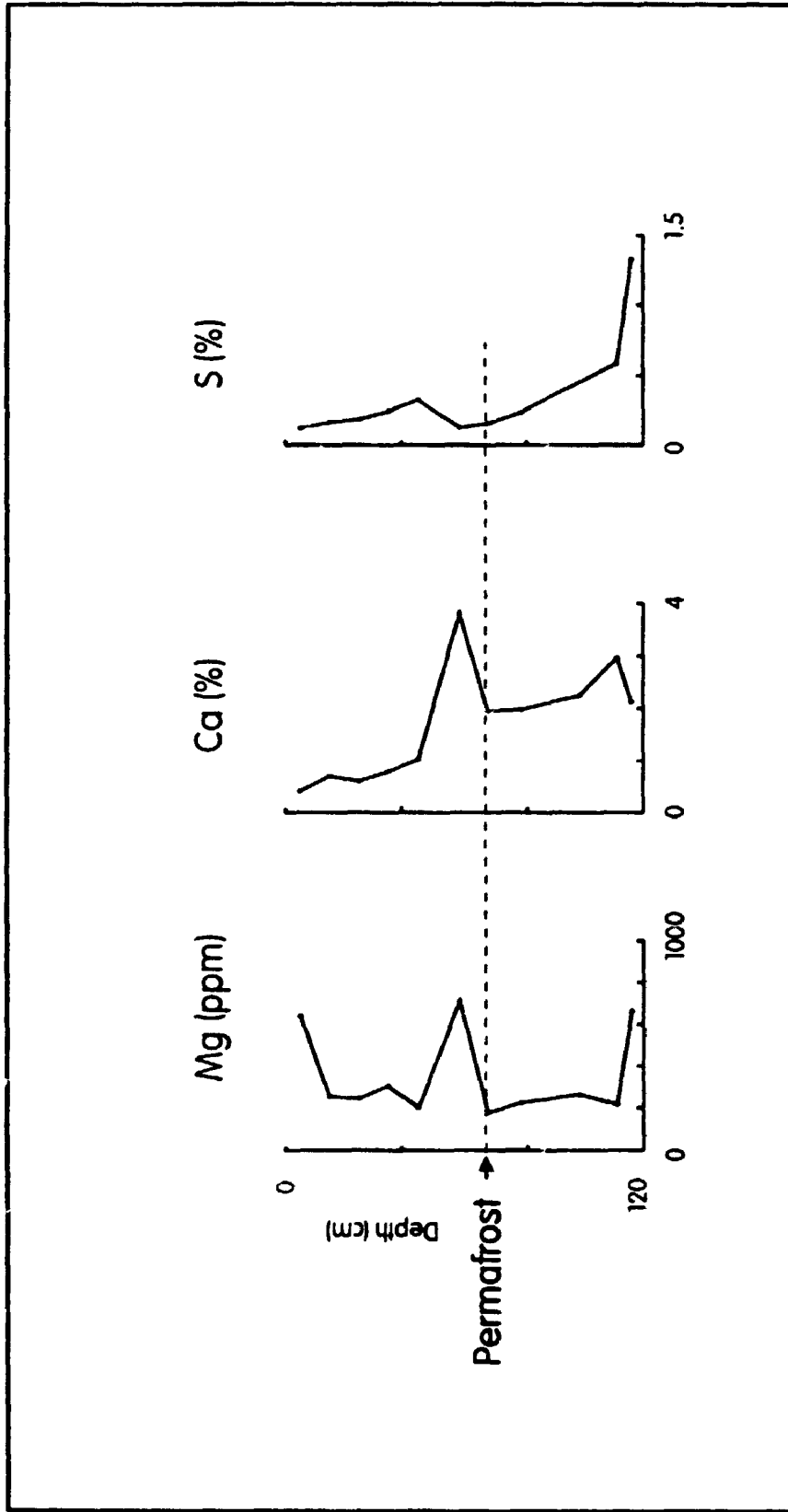


Figure 3.37 Mg, Ca and S distribution in core 2, East Little Bear River Deposit, Northwest Territories.

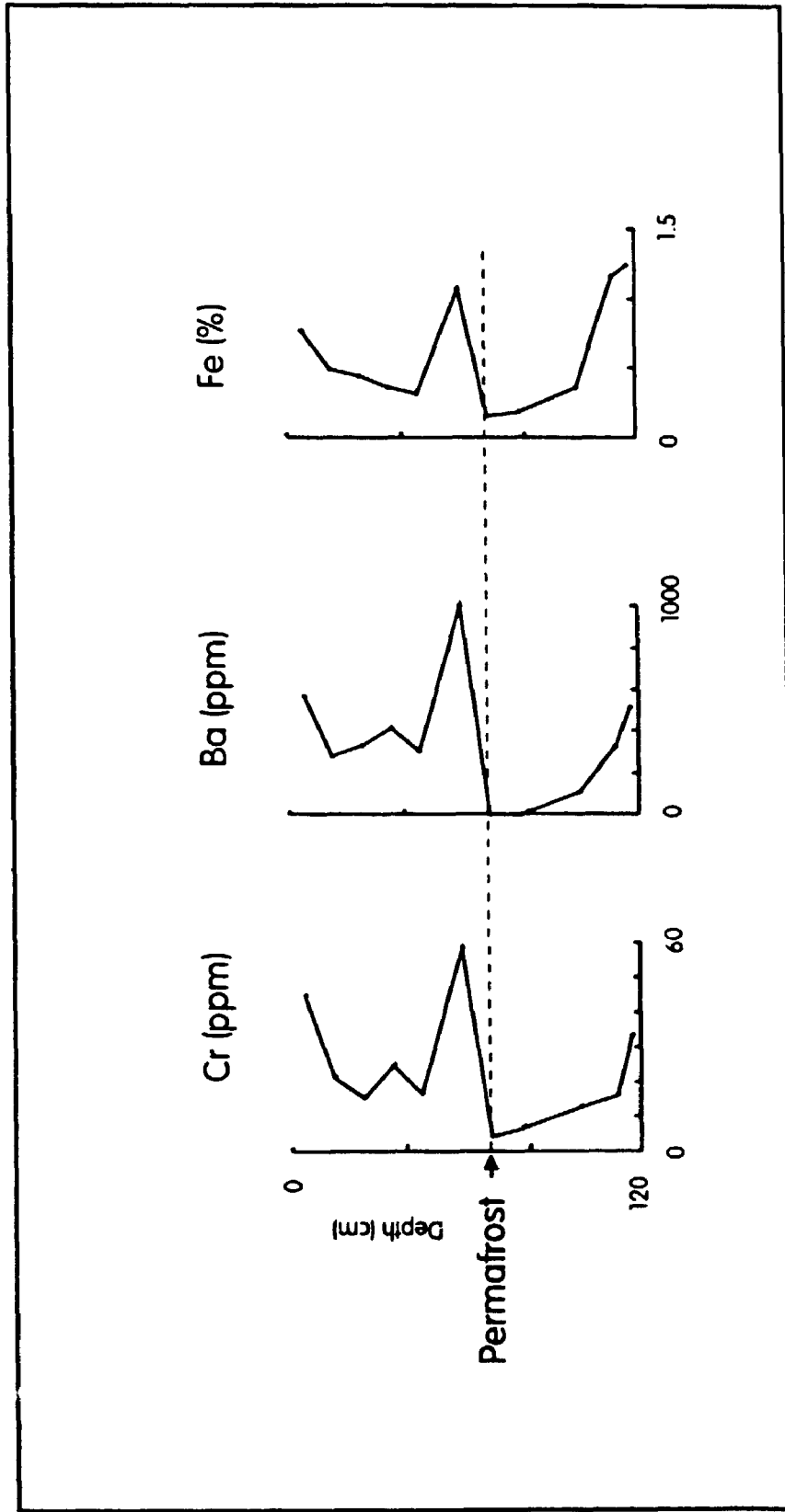


Figure 3.38 Cr, Ba and Fe distribution in core 2, East Little Bear River Deposit, Northwest Territories.

3.3.3.1.2.2.2 *Br, Cl and I*

The distribution pattern of these three halogens is similar to the other elements, in that they display a strong enrichment immediately above the permafrost boundary (44 ppm Br, 336 ppm Cl, 11 ppm I). In the remaining peat sequence, Br concentration is almost constant, ranging from 9 to 16 ppm, while Cl and I contents are more variable (Figure 3.39). In the mineral substrate, Br and I are not detected, and Cl content was about 66 ppm.

3.3.3.1.2.2.3 *Fe*

A steady decrease in iron content downward in the peat profile (from a maximum level of 0.8%) is interrupted by a marked increase immediately above the permafrost boundary (1.1% Fe). Fe content declines to 0.15% in the perennially frozen layer but then increases slightly with depth. However, it displays enrichment in the basal peat layers (1.23% Fe); (Figure 3.38). Fe level reaches a maximum in the mineral substrate (2.7% Fe).

3.3.3.1.2.2.4 *Se*

Selenium content is below detection limit in the upper section of the profile and displays an apparently random distribution pattern in relation to ash content. However, Se displays a significant enrichment immediately above the permafrost boundary (2.6 ppm Se), followed by a drop in concentration in the layers underneath (Figure 3.39). In the mineral substrate, Se levels average 1.2 ppm.

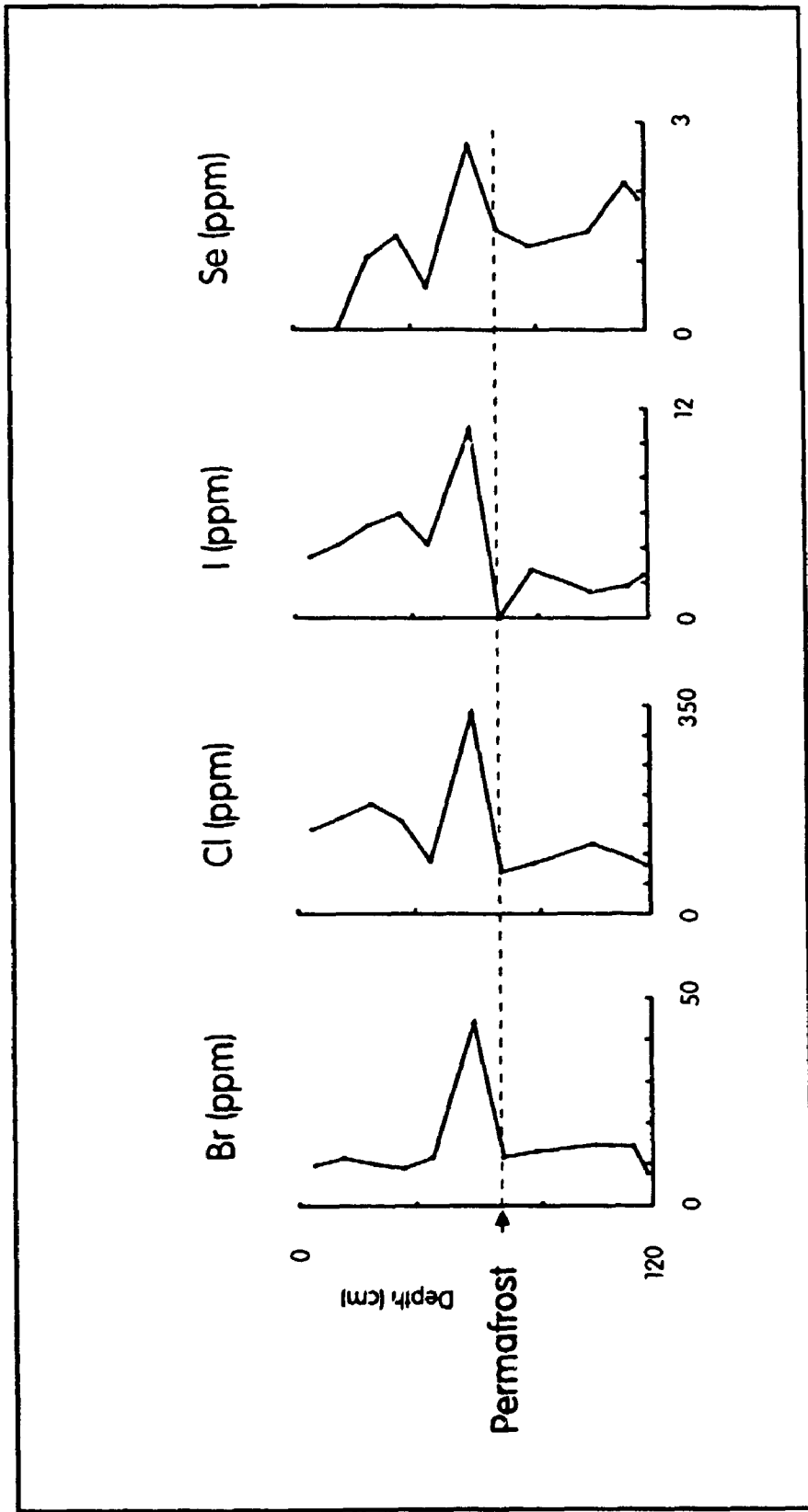


Figure 3.39 Br, Cl, I and Se distribution in core 2, East Little Bear River Deposit, Northwest Territories.

3.3.3.2 Mackenzie River deposit

Ash content ranges between 24.3% (1.70 m depth) and 73.3% (0.80 m depth), with an average of 53.5% (Figure 3.40). Therefore all organic material in this core, except at one interval, is termed peaty and silty muck, not peat. Data are shown in Appendix IV (Table 13).

3.3.3.2.1 Major elements

3.3.3.2.1.1 Al and Si

Aluminum and silicon distribution patterns appear to follow the ash distribution. Si content ranges from 12.3% to 26.8%. Al concentration on the other hand varies from 2.2% to 3.8% (Figure 3.40).

3.3.3.2.1.2 K and Na

Potassium concentration ranges from 0.5% to 1.1%. Sodium content is highest at the surface (5750 ppm) and lowest at 1.70 m. Both elements appear to show affinity with the inorganic fraction (Figure 3.41).

3.3.3.2.1.3 Mg and Ca

Magnesium concentration is highest at the surface (1840 ppm) and lowest at 1.70 m (1023 ppm). Mg appears to have a strong affinity with the inorganic fraction (Figure 3.41). Maximum calcium concentration is observed at 0.80 m (4.6%), in conjunction with the increase of ash content at this depth. Mean Ca content is 3.1%. However, fluctuations in Ca content throughout the profile do not show a definite

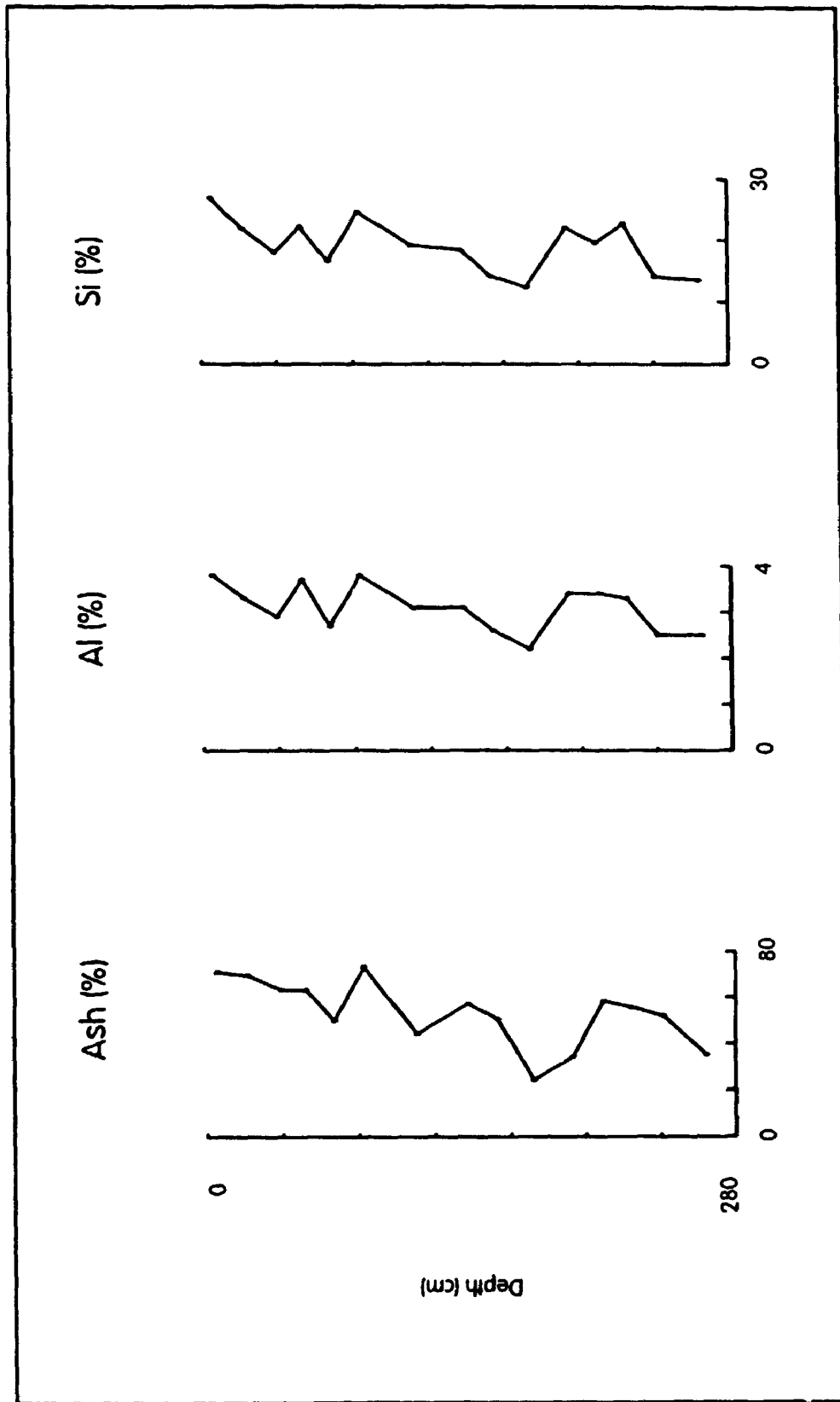


Figure 3.40 Ash, Al and Si distribution in Mackenzie River Deposit, Northwest Territories.

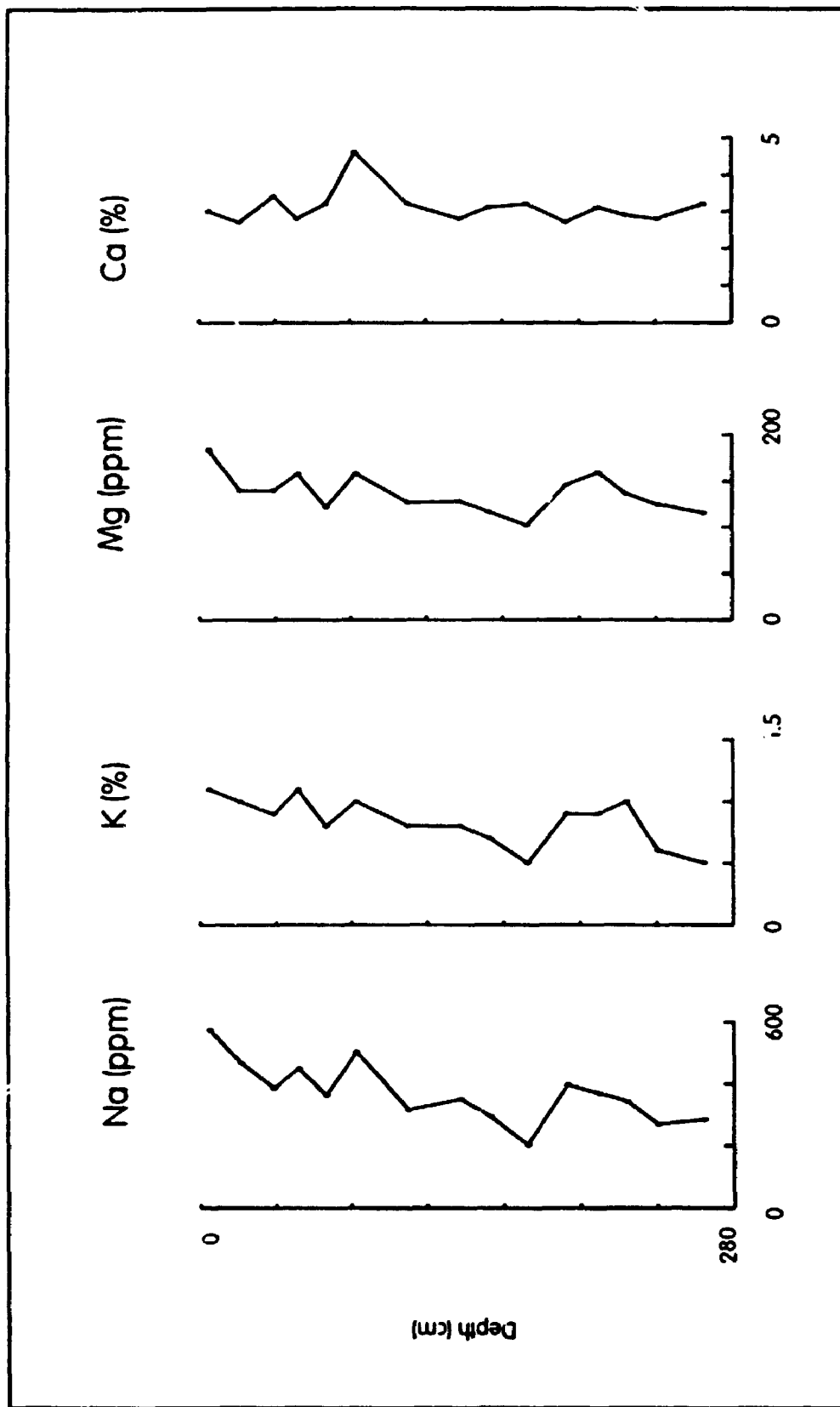


Figure 3.41 Na, K, Mg and Ca distribution in Mackenzie River Deposit, Northwest Territories.

relationship with ash distribution, suggesting association of this element with both the organic and inorganic fraction (Figure 3.41).

3.3.3.2.1.4 S

Only three data were obtained for this profile, and it can only be concluded that total sulfur is in low concentration in the core (mean S: 0.1%); (see Table 13, Appendix IV).

3.3.3.2.2 Trace elements

3.3.3.2.2.1 Ba

Barium display similar distribution patterns to those of Al, Mg, Si, Na, K and Mg, with maximum concentrations at 0.80 m. Ba content ranges from 530 to 850 ppm (Figure 3.42).

3.3.3.2.2.2 Br, Cl and I

The distribution pattern of chlorine suggests affinity of this element with organic matter. Cl concentration is usually higher where ash content is lower, and ranges from 48 to 83 ppm. Bromine content ranges from 7 ppm to 18 ppm (Figure 3.42), while I concentrations are very low and mostly below the detection limit.

3.3.3.2.2.3 Fe

Iron appears to be mainly associated with the inorganic fraction, and its concentration varies between 1.1% and 1.9% (Figure 3.42).

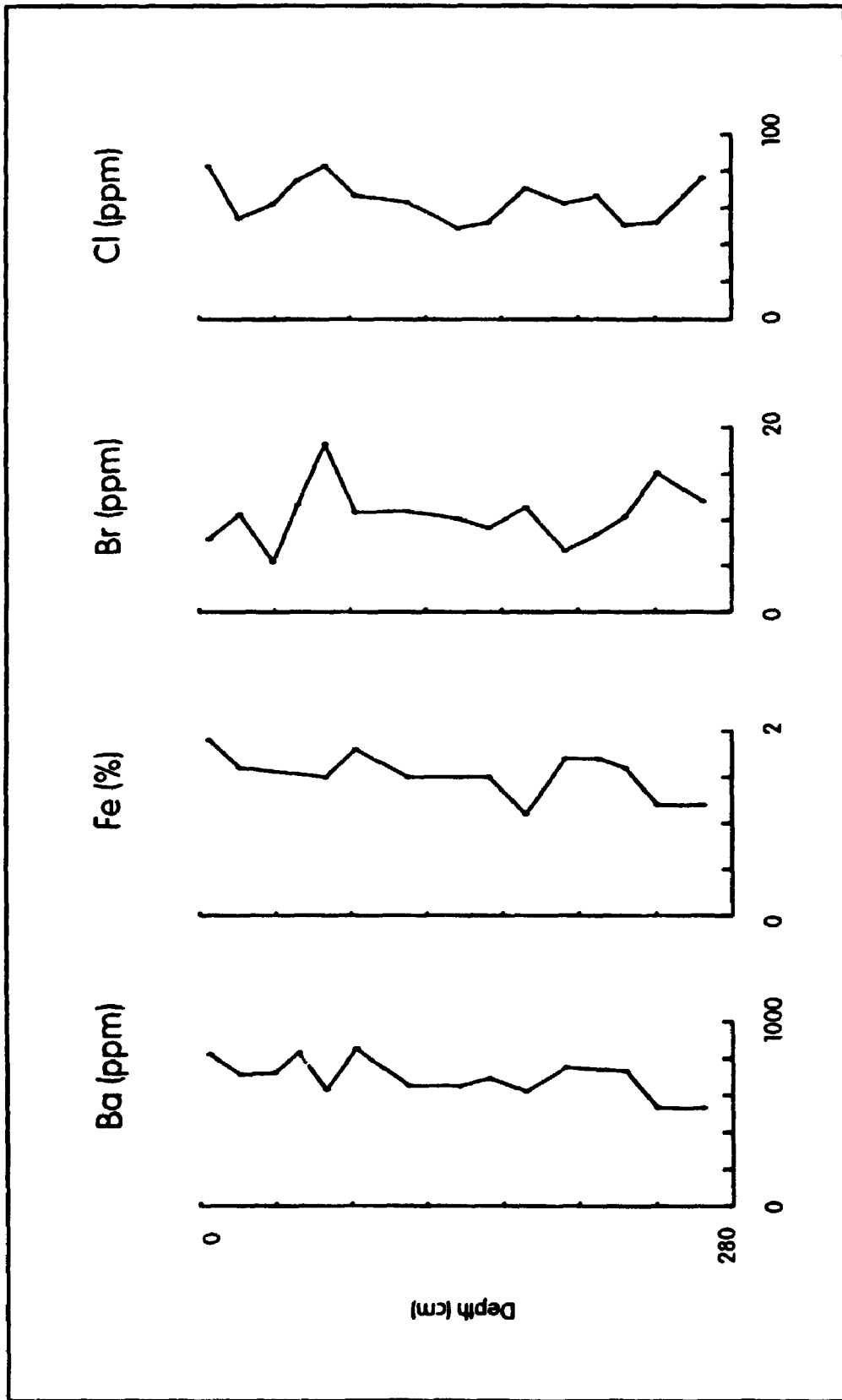


Figure 3.42 Ba, Fe, Br and Cl distribution in Mackenzie River Deposit, Northwest Territories.

CHAPTER FOUR

INTERPRETATION OF SITE SPECIFIC RESULTS

4.1 INTRODUCTION

Changes in depositional environment within each wetland studied are presented, based on observations reported in Chapter Three. Maceral composition and reflectance measurements provide information about the degree of degradation of the peat, relative to the type and depth of peat. However, reflectance measurements can not be used as a maturity indicator, due to scarcity of material suitable for analysis. Similarly, in this study, reflectance readings are only valid for intra-, not inter-site comparison.

Abundance and distribution of mineral matter is discussed, and occurrence and formation of pyrite in freshwater and brackish environments is addressed.

Geochemical variations are interpreted as related to depositional environment (e.g. lithology, trophic status, botanical composition), elemental affinity with the inorganic or organic fraction, and the influence of natural (e.g. peat fires, sea spray, tephra, permafrost) and anthropogenic factors.

4.2 NOVA SCOTIA

4.2.1 **Petite Bog**

4.2.1.1 **Reconstruction of general peat stratigraphy**

Variations in botanical composition, degree of humification and pH values in the three cores suggest that they are representative of different stages of a fen to bog sequence, ending with the formation of a dome (Figure 4.1).

In core T3, situated in the lagg area, almost the complete sequence was dominated by *Carex* peat. It exhibited high ash content and moderately high pH. Furthermore, peat is in an advanced degree of humification, as determined in the field and reinforced by reflectance measurements. A similar minerotrophic peat sequence dominated by *Carex* peat, although thinner, was found at the bottom of cores T1 and T2, overlying the bottom sediments. A relatively high pH is maintained, because acids released by organic matter decomposition are partly neutralized by the mineral bases contained in seeping groundwater (Shotyk, 1988). Upcore, *Carex* peat is progressively replaced by oligotrophic *Sphagnum* species, as observed in cores T1 and T2, and in the surface layer of core T3. This shift to ombrotrophic conditions is correlated with a decrease in ash content, degree of humification and pH (Figure 4.1; Tables 3.1, 3.3 and 3.4). As peat accumulates, it becomes more independent of the influence of groundwater rich in mineral bases, resulting in a decrease in pH and nutrient supply. This has a direct effect on the vegetation, as plants characteristic of minerotrophic conditions are unable to grow in an acidic and nutrient-poor environment and are replaced by oligotrophic species, such as *Sphagnum*. The strictly ombrotrophic peat sequence composed almost exclusively of *Sphagnum* is 1.65 m thick in core T1 (near the margin of the bog), while

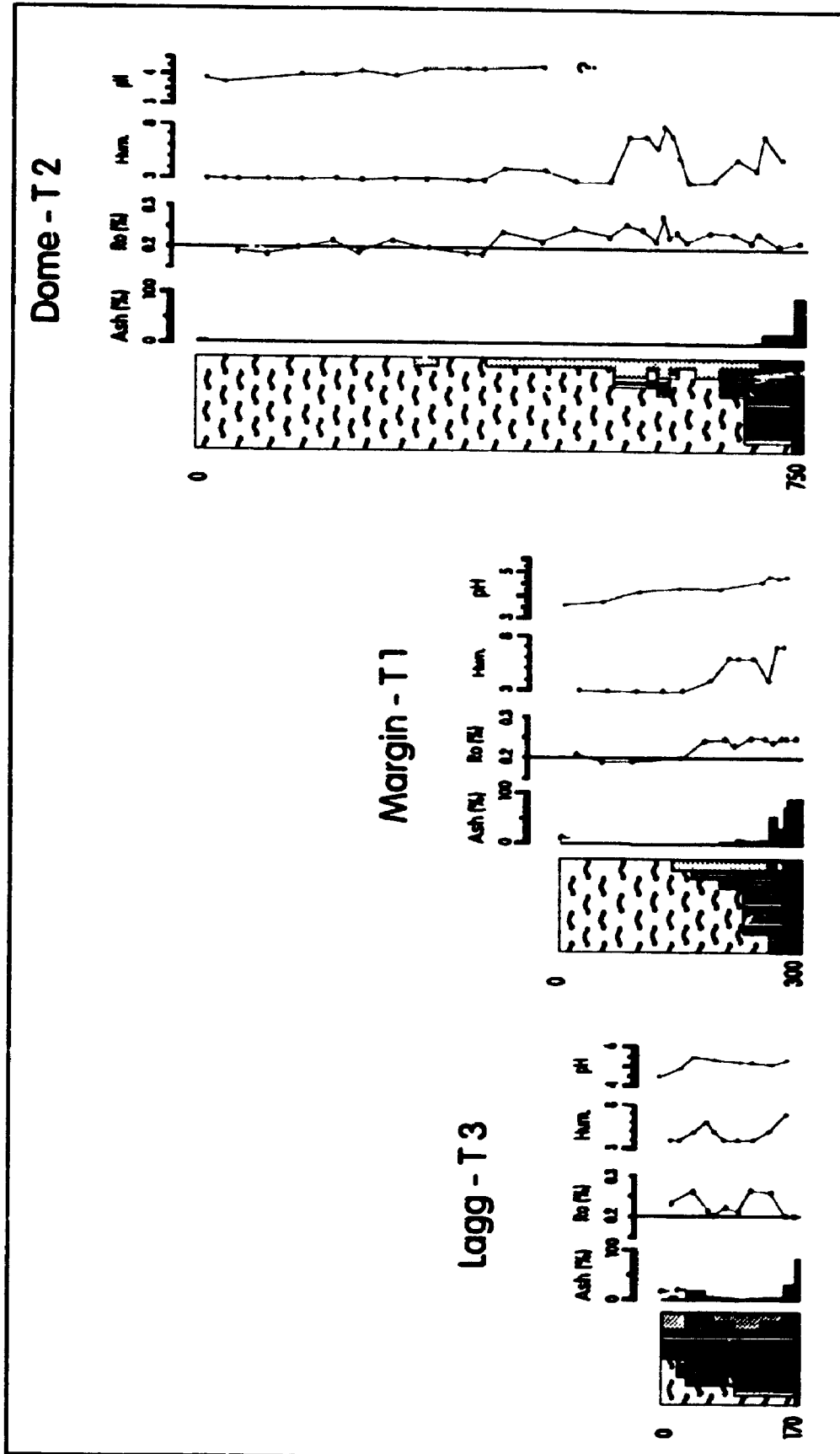


Figure 4.1 Variations in peat type, ash content, random reflectance (Ro%), degree of humification and pH in a fen to bog sequence (Lagg, margin, dome), Petite Bog, Nova Scotia. (Legend see Fig. 3.1)

it reaches 5.20 m near the center of the dome in core T2. The 5.20 m thick *Sphagnum* peat sequence is poorly humified ($H = 3$), as a result of limited microbial activity and oxygen supply. This shows that depth is not an essential factor for determining degree of humification, but rather microbial and bacterial activity, and oxygen and water availability.

Abundant precipitation, low evapotranspiration and low seasonality contribute to the formation of domed bogs, as the surface of the mires can rise above the influence of mineral- and nutrient-rich ground- and surface water (Tallis, 1983; Lottes and Ziegler, 1994). Oligotrophic conditions in the middle of the bog do not enhance rapid peat accumulation, but also inhibit peat decomposition due to low microbial activity and low oxygen availability. Furthermore, *Sphognum* species are poor in nitrogen, resulting in a low decay rate (Clymo, 1987). This results in the formation of a dome, since peat accumulates faster in the middle than near the margin. Towards the margin, seepage of nutrient- and mineral-rich waters, while enhancing peat formation, also increases peat decomposition, the net result being slower peat accumulation (Clymo, 1987).

Maceral analysis confirmed the changes occurring during bog development (Sections 3.2.1.1.1, 3.2.1.1.2 and 3.2.1.1.3). In the *Carex*-rich zones, ulminite was the dominant huminite maceral, reflecting the advanced degree of humification. This might also be related to higher pH and ionic supply, an indicator of groundwater influence earlier in mire formation (Calder, 1993). Attrinitic material and orange fluorescing liptinitic material are probably the result of groundwater movement in the lower part of the bog. A large component of phlobaphinite (and suberinite) reflected the abundance of

rootlet-bearing plants and trees in the nutrient-rich system. The shift toward oligotrophic conditions with decreasing depth is shown by a decrease in phlobaphinite. Oligotrophic peat material is composed mainly of rootless bryophytes, and trees are more rare in the nutrient-poor environment. In addition, peat is less humified and degraded as a result of limited microbial activity and low oxygen availability. This is indicated by an increase of textinite at the expense of ulminite. Towards the surface, textinite A is more common than textinite B, as peat becomes younger and less humified. Similar trend was reported by Calder *et al.* (1991) and Calder (1993) in a Westphalian coal deposit. They observed a dominance of the gelified vitrinite group macerals reflecting oxygen and groundwater availability under rheotrophic conditions (as opposed to ombrotrophic conditions).

Reflectance (measured on phlobaphinite) is generally higher in the minerotrophic peats than in the ombrotrophic peats (Figure 4.1). Although there are insufficient data to allow use of reflectance as a maturity indicator, the shift in reflectance appears to correlate with the changes in maceral composition. Lowest values are measured in the ombrotrophic peats where textinite A is abundant. The increase with increasing depth seems to be associated with an increase of textinite B, and then ulminite. Core reflectance values measured on textinite also decrease with decreasing depth.

The decrease of mineral matter content from the lagg zone to the center of the dome shows that the influence of the surrounding lithology decreases with increasing distance from the bog margin (Figure 4.1: Tables 3.1, 3.3 and 3.4). Cameron and Schruben (1983) suggest that surface and groundwater seeping toward the center of the bog lack the necessary gradient to reach the center of the bog, and as a result, mineral

matter supply is lower at the center of the bog (core T2) than near the margin (core T1). Near the margin, plants receive mineral matter from the surrounding terrain, while the only source of inorganic matter at the surface of the dome is from atmospheric input and from dead plants immediately beneath the living plants (Cameron and Schruben, 1983; Moore, 1987). However, ash content of the uppermost sample in core T2 is 4.1%, while underneath, the ombrotrophic peat contains less than 1.3% on average (Section 3.2.1.1.2, Table 3.3). This surficial enrichment appears to be caused by soil dust input, as suggested by Shotyk (1988), who reported similar surficial ash enrichment, especially in areas with high agricultural activity.

Charcoal was found at various depths in all three cores and is indicative of fire activity (Scott, 1989). Fires are frequent in peat-forming environments. They occur commonly during periods of drought, when the water table is lowered, and start usually either by spontaneous combustion or by lightning (Staub and Cohen, 1979; Rollins *et al.*, 1993). There are mainly two types of peat fires: surface fires and fires that burn into the peat. While the former are usually localized and do not provoke local species extinction, because the roots remain undamaged, the latter can burn for long periods of time and destroy the roots of most plant species in the peat-forming system. However, peat fires are usually a combination of both types and, due to heterogeneity within the peatland (such as the presence of pools and hummocks), peat fires develop and spread in an irregular pattern; Rollins *et al.* (1993) summarized the effects of peat fires on pH, nutrient availability, and resulting shifts in botanical and chemical composition.

In cores T1 and T3, charring intervals are not associated with a change in vegetation in the overlying layer. It can therefore be assumed that they were surface fires

or short-lived fires, that did not cause any detectable change in vegetation in the bog. Rollins *et al.* (1993) report the occurrence of severe peat fires in the Snuggedy Swamp, which resulted in major chemical changes but did not induce significant changes in botanical composition. However, a shift in vegetation is observed above a heavily charred interval in core T2. *Eriophorum* constitutes 20% of the peat material in this overlying interval (Figure 3.2, Table 3.3). The occurrence of *Eriophorum* on drained and burned British peatlands has been reported by Gorham (1982), suggesting that it may be present in this interval as a result of peat fire. Furthermore, *Eriophorum* has been found to dominate horizons at the boundary between minerotrophic and ombrotrophic peat (Gorham, 1949; DuRietz, 1950), and could be seen as a 'marker' of a shift in trophic status.

4.2.1.2 Mineralogy

Quartz is the major component of the bottom sediments in the bog, while mica, feldspars and clay minerals constitute a minor fraction. This mineralogical composition reflects the lithology of the surrounding and underlying Late Wisconsinan Lauwrencetown Tills (derived from sandstones and siltstones, and present as sandy-clayey loams).

Mineralogy of the peat in all cores is dominated by quartz, although mica comprises a large fraction in the lagg zone (core T3, Table 3.2) and near the margin of the bog (core T1, Table 3.2). The abundance of mica in the lagg zone (core T3) and in the minerotrophic section of core T1 is probably due to the input of sediment-laden groundwater. A low mica content in core T2 on the other hand is indicative of a decrease

in groundwater supply with increasing distance from the margin, as shown by the lower ash content at the center of the bog (Section 4.2.1.1). Mica comprises a large component of the mineralogical fraction of ombrotrophic peat in core T1 (1.00-1.40 m depth), suggesting that wind-blown mica may have been deposited at the time of peat formation. However, ash content is minimal in this interval (0.3%) and therefore mica is relatively insignificant.

Ombrotrophic peats receive their water and mineral supply either by precipitation or capillary action from below (Ingram, 1983). Thus, inorganic input is restricted to fine airborne particles or mature mineral grains carried upwards within the peat. As a result, ash content is low and contains mainly mature minerals, such as quartz (Raymond *et al.*, 1987). Although most of the quartz appears to be detrital in nature (i.e. windblown or waterborne), biogenic opaline material, primarily in the form of phytoliths, has also been reported in raised bogs in northern Minnesota (Malterer and Farnham, 1984). SEM analysis of the LTA of low-ash domed peats in Indonesia reveals the predominance of biogenic silica, mainly as siliceous chrysophyte cysts, phytoliths and organisms resembling testacid amoebae (Ruppert *et al.*, 1993; Ruppert, pers. comm., 1994). Therefore, it can be inferred that probably both detrital and authigenic quartz occur in the peats of Petite Bog.

Kaolinite is the most common clay mineral encountered in the peat, and because it forms at low pH (Staub and Cohen, 1978; Mason and Moore, 1982), it is likely to be authigenic, reflecting acidic conditions in the bog. Chlorite and mixed-layer clays are present in small amounts. The occurrence of chlorite in this acidic environment

suggests a detrital origin, since chlorite can not form and is unstable at $\text{pH} < 7$ (Kantorowicz, 1985). Mixed-layer clays also probably result from weathering and runoff.

Calcium oxalate minerals, weddelite and whewellite, are found in cores T1 and T2, respectively. Weddelite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) probably precipitates out during the growth of peat forming vegetation (Sawyer and Griffin, 1983). Frey-Wyssling (1981) suggests that it occurs in cells with plant fluid rich in calcium into which oxalate ions are brought. Whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) was observed in the LTA of marsh plants such as the water lily (*Nymphaea*) and neverwet (*Orontium*), that had been oven-dried at 105°C (Bardin and Bish, 1983). These authors suggest that whewellite may result from the transformation of weddelite during the drying process. In the present study, samples were dried at $100\text{-}105^\circ\text{C}$ before low temperature ashing. This may have resulted in the transformation of weddelite to whewellite in one of the samples (core T2, 4.50-5.00 m depth).

Calcite was found to constitute most of the LTA (71% calcite, 23% quartz) of one sample in core T2 (3.50-3.60 m depth), although it is not compatible with the oligotrophic conditions in this part of the core (100% *Sphagnum*, 0.5% ash). Furthermore, INAA analysis does not show any calcium enrichment in this sample, which may suggest that the high content of calcite is caused by contamination, such as a wind-blown particle. Peat is very heterogeneous, and although care was taken to homogenize samples before analysis, a single 'foreign' grain within a sample can cause such discrepancies between 2 different analyses.

Bassanite constituted a large fraction of the LTA, particularly in samples of core T2. However, it is an artifact of the low temperature ashing process, which forms

as a result of the oxidation of the organic sulfur to SO_3 and subsequent production of sulfuric acid in the presence of moisture, that reacts with exchangeable Ca^{2+} associated with carboxylic acid groups (Jenkins and Walker, 1978). Dehydration of gypsum during low temperature ashing may also result in bassanite production (Mitchell and Gluskoter, 1976). Raymond *et al.* (1990) report the presence of bassanite in 8 of 10 peat samples collected from different depositional and ecological settings. Relatively high Ca content in core T2 may explain production of bassanite, since it did not form in the LTA samples of cores T1 and T3, which have lower Ca levels. Although bassanite content in the samples alters the percentage of other mineral fractions present, it is an artifact and thus it will not be taken in consideration.

4.2.1.3 Geochemistry

4.2.1.3.1 Introduction

First, the distribution of major and trace elements is discussed, as related to the association of each element with the inorganic and/or organic fraction, and the influence of natural and anthropogenic factors. Second, lateral and vertical variations are interpreted in terms of the evolution from the fen to bog sequence.

4.2.1.3.2 Major elements

4.2.1.3.2.1 Al and Mg

A strong positive correlation between aluminum and ash content, and magnesium and ash content ($r=0.94$ in both cases); (Table 4.1) reflects the strong affinity of both elements with the inorganic fraction. Furthermore, a plot of Mg vs. Al

	Ash	Al	Br	Ca	Cl	Cr	Fe	I	Mg	Mn	Na	S	Se
Ash	1.00	0.94	-0.47	-0.07	-0.53	0.90	0.85	-0.52	0.94	0.72	0.94	0.13	-0.55
Al		1.00	-0.37	-0.14	-0.52	0.93	0.78	-0.45	1.00	0.70	0.77	0.17	-0.56
Br			1.00	-0.21	0.52	-0.33	-0.26	0.89	-0.39	-0.17	-0.50	0.37	0.21
Ca				1.00	0.28	-0.15	0.09	-0.06	-0.13	0.25	-0.04	0.02	0.09
Cl					1.00	-0.49	-0.43	0.60	-0.52	-0.39	-0.50	-0.05	0.24
Cr						1.00	0.86	-0.40	0.93	0.61	0.76	0.21	-0.50
Fe							1.00	-0.31	0.78	0.83	0.80	0.46	-0.52
I								1.00	-0.46	-0.22	-0.53	0.30	0.25
Mg									1.00	0.70	0.78	0.16	-0.56
Mn										1.00	0.67	0.56	-0.46
Na											1.00	0.07	-0.46
S												1.00	-0.11
Se													1.00

Table 4.1 Correlation coefficients of major and trace elements in Petite Bog, Nova Scotia.
(all samples, $n = 52$)

(Figure 4.2) suggests a similar occurrence for both of them. Mica and clays, which were identified by XRD, are probably the hosts of most Al and Mg. Correlation in surficial enrichments of Al, Mg and ash in core T2 can be attributed to atmospheric input (wet or dry deposition), as proposed by Shotyk (1988). Furthermore, both elements are slightly enriched in the charcoal-rich intervals (see Section 5.5.3). Variations in Al and Mg levels in the bottom sediments (5.9 to 10.8% Al, 1930 to 3380 ppm Mg) are probably due to variations in mineral composition.

4.2.1.3.2.2 Na and K

There is a strong positive correlation between sodium and ash ($r=0.94$), suggesting that most Na is associated with the inorganic fraction, such as clay minerals and feldspars (Wedepohl, 1978). Shotyk (1987a) reports a mean value of 353 ppm in a maritime bog (close to 320 ppm reported in Petite Bog), as opposed to 101 ppm in a continental bog, and attributes the higher concentration in the former one to oceanogenic influence. Petite bog is situated 10 km inland from an estuarine environment (Minas Basin), and thus, there may be some Na input from sea spray.

Local salt springs and an outcrop of the salt-rich Windsor Group (Section 2.2.1) could be a possible source of Na (and other elements associated with salt deposits, see also Section 4.2.1.3.3.2). Nevertheless, there is a strong negative correlation between Na and Cl ($r=-0.50$). Furthermore, analysis of filtrate water, which had been stirred with peat for a day (see also Section 4.2.1.3.3.2), yields Na concentration close to background (samples T1-6 and T2-9); (Table 4.2), suggesting that there is little or no soluble Na in the peat, i.e. in the form of salt.

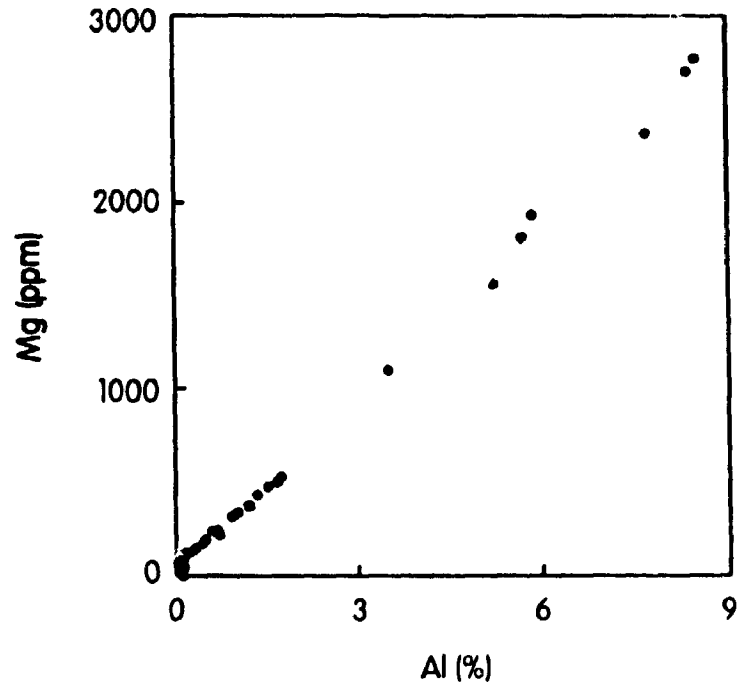


Figure 4.2 Plot of Mg vs. Al content of peat, Petite Bog, Nova Scotia.

element sample	Na (ppm)	Cl (ppb)	Br (ppb)	I (ppb)
T1-6	5.4	18 190	25	3.7
T2-9	5.6	26 762	34	7.8
CH1-1	719.0	>1%	7 311	27.9
CH1-2	444.0	815 549	3 316	24.1
distilled water	3.4	20 891	28	1.6

Table 4.2 Concentrations of Na, Cl, Br and I in distilled water and in filtrate water from peat (T1-6 and T2-9) and marsh muck (CH1-1 and CH1-2).

Na and K form highly soluble monovalent cations in aqueous solutions, which exhibit little affinity with peat and humic acids. Therefore they are readily lost from peat (Shotyk, 1988). Leaching from Na and K is evident in core T2, as higher levels are found in the upper section of the peat sequence. Furthermore, K is essential in plant systems and thus, enrichment at the surface has been attributed to plant bioaccumulation (Pakarinen and Gorham, 1983; Shotyk, 1988). Higher levels of Na and K in cores T1 and T3 are probably due to the higher inorganic content (feldspars, clay minerals and mica (illite)).

4.2.1.3.2.3 Ca

Variations in distribution of calcium in the bog (Figure 3.13) and the weak negative correlation with ash ($r=-0.07$) suggest that this element is associated with both organic and inorganic fractions. Ca concentration is lowest in the ombrotrophic peats and increases with depth, in the more minerotrophic peats. This concurs with the trophic status of the environment in which they grow. Plants need calcium for growth but they vary in their requirement and tolerability. While *Sphagnum* species usually do not tolerate high Ca concentration, other plants, such as sedges and grasses, are unable to grow in a Ca-deficient environment (Crum, 1988). Casagrande and Erchull (1976) postulate that a large component of Ca (and Fe and Mn) occupy cation-exchange sites from carboxyl and phenolic groups in humic and fulvic acids, particularly in humin. This may account for the occurrence of some Ca in peat, while the remaining fraction is associated with mineral components. There is no Ca enrichment at a depth of 3.50-3.60 m in core T2,

although mineralogy of peat is dominated by calcite (Section 4.2.1.2). This confirms the hypothesis of contamination by a single grain, possibly wind-blown.

In core T2, Ca levels increase considerably below a depth of 4.00 m to a maximum value of 1.17% in the basal peat layer. Ca content in the bottom sediments is low (0.10 to 0.42% overall, 0.37% in core T2), and thus it is unlikely that Ca concentration in the peat is derived from the underlying substratum. Furthermore, no other element studied exhibits similar increase in concentration in the lower 3.40 m of the peat sequence of core T2. Accumulation of Ca by peat-forming vegetation may cause the enrichment. For the purpose of this study, plant species were identified as *Carex*, *Sphagnum* and *Eriophorum* (in the bog), and not further divided in species. However, it can not be excluded that the peat-forming vegetation is different in this particular area of the bog. Furthermore, it has been shown in Section 4.2.1.1 that groundwater movement is impeded near the center of the bog, as suggested by a decrease in mineral matter content. Therefore, it is possible that the calcium accumulated by peat might not have been leached, due to lack of groundwater movement.

4.2.1.3.2.4 S

Total sulfur content is low in the peats of Petite Bog, and well within the range of freshwater peats (mean S <0.5%); (Lowe and Bustin, 1985; Bustin and Lowe, 1987). Recent studies show that, in low-sulfur peat-forming environments, organic sulfur is the dominant fraction of total sulfur (e.g. Altschuler *et al.*, 1983; Casagrande, 1984; Lowe and Bustin, 1985). This may explain the weak positive correlation coefficient between S and ash content ($r=0.13$). Furthermore, plant bioaccumulation has been

suggested as a mechanism for the incorporation of sulfur, particularly in acidic and nutrient-poor environments (Lowe and Bustin, 1985). Casagrande (1984) also postulates that plants or microbial sulfur-containing amino-acids may contribute to peat sulfur. Minor amounts of inorganic sulfate-S, elemental S, pyritic S and H₂S have been found to represent the remaining fraction of sulfur (Lowe and Bustin, 1985).

4.2.1.3.3 Trace elements

4.2.1.3.3.1 Cr

There is a strong positive correlation between chromium and ash ($r = 0.9$), indicating a strong affinity with the inorganic fraction. Cr enrichments in the charcoal-rich intervals in cores T1 (2.20-2.30 m and 2.60-2.70 m) and T2 (5.75-5.80 m) appear to be related to fire activity, as non-volatile Cr is likely to accumulate in charcoal and ash (see also Section 5.5.3).

4.2.1.3.3.2 Br, Cl and I

The distribution of Br, Cl and I in all cores and a strong negative correlation with the ash content (Table 4.1), suggest that they are not associated with ash-forming minerals but are concentrated in the organic fraction. Furthermore, as shown in Table 4.3, peat is enriched in Br, Cl and I when compared with the underlying mineral substrate.

Two samples of peat containing high Cl, Br and I levels (sample T1-6 at a depth of 1.65-2.00 m in core T1 and sample T2-9 at a depth of 2.70-3.00 m in core T2) were further analyzed to determine the mode of occurrence of the halogens. Distilled

	Bromine	Chlorine	Iodine
Concentrations in peat (ppm) ¹	12.4 to 62.0	257 to 1420	5.0 to 16.3
Concentrations in mineral substrate (ppm) ²	2.7	92	1.4
Typical crustal average (ppm) ³	2.5	130	0.5
Enrichment in peat vs. mineral substrate ⁴	+ 5 to + 23	+ 2 to + 15	+ 4 to + 12

¹Numbers represent the lowest and the highest levels measured in peat ($n = 48$)

²Number represents average concentration over the three cores

³Mason and Moore (1982)

⁴Number of times (based on the lowest and highest concentrations in peat vs. average concentration in mineral substrate)

Table 4.3 Relative enrichment of Br, Cl and I in peat, Petite Bog, Nova Scotia.

water was stirred with approximately one gram of peat material for 24 hours, and the filtrate submitted for ICP-MS. Results of ICP-MS are shown in Table 4.2. Cl, Br and I contents are low, just above the background concentrations, as are Na levels, suggesting that there are virtually no soluble compounds, such as salt. This confirms the strong negative correlation between Na and Cl contents ($r=-0.50$) indicating that Cl is probably not present as sodium chloride. Thus, it can be inferred that most Cl, Br and I present in the peats are bound with the organic fraction. Cox (1991) suggests that chlorine exists generally in the ionic state in coal, and is strongly bound to cationic sites of water-insoluble organic compounds in coal. This is supported by the work of Chou (1991), who shows that there are two forms of chlorine in Cl-rich coals associated with Cl-rich brines. One fraction occurs as sodium chloride dissolved in pore water associated with the coal seam, while the remaining occurs as chloride ions absorbed on the inner surfaces of micropores in macerals (particularly vitrinite). In the present study, there is virtually no Cl present as sodium chloride, and thus, an organic association (within the micropores of macerals) is most probable.

A peak in concentration was observed for all three elements, at different depths in cores T1, T2, and T3, (at a depth of 2.10 m, 2.85 m and 0.65 m, respectively); (Figure 4.3). However, peat accumulates faster at the center of the bog than near the margin, and lagg zone (where microbial activity is the highest), thus resulting in the formation of a dome (Section 4.2.1.1). Consequently these peaks could represent a single 'event'. Relevant peat samples from cores T1 (2.10 m depth) and T2 (2.85 m depth) were dated by ^{14}C analysis. Ages obtained were 980 ± 60 years BP and 2570 ± 70 years BP, respectively. It appears that peat of core T2 is older than peat in core T1. The sample

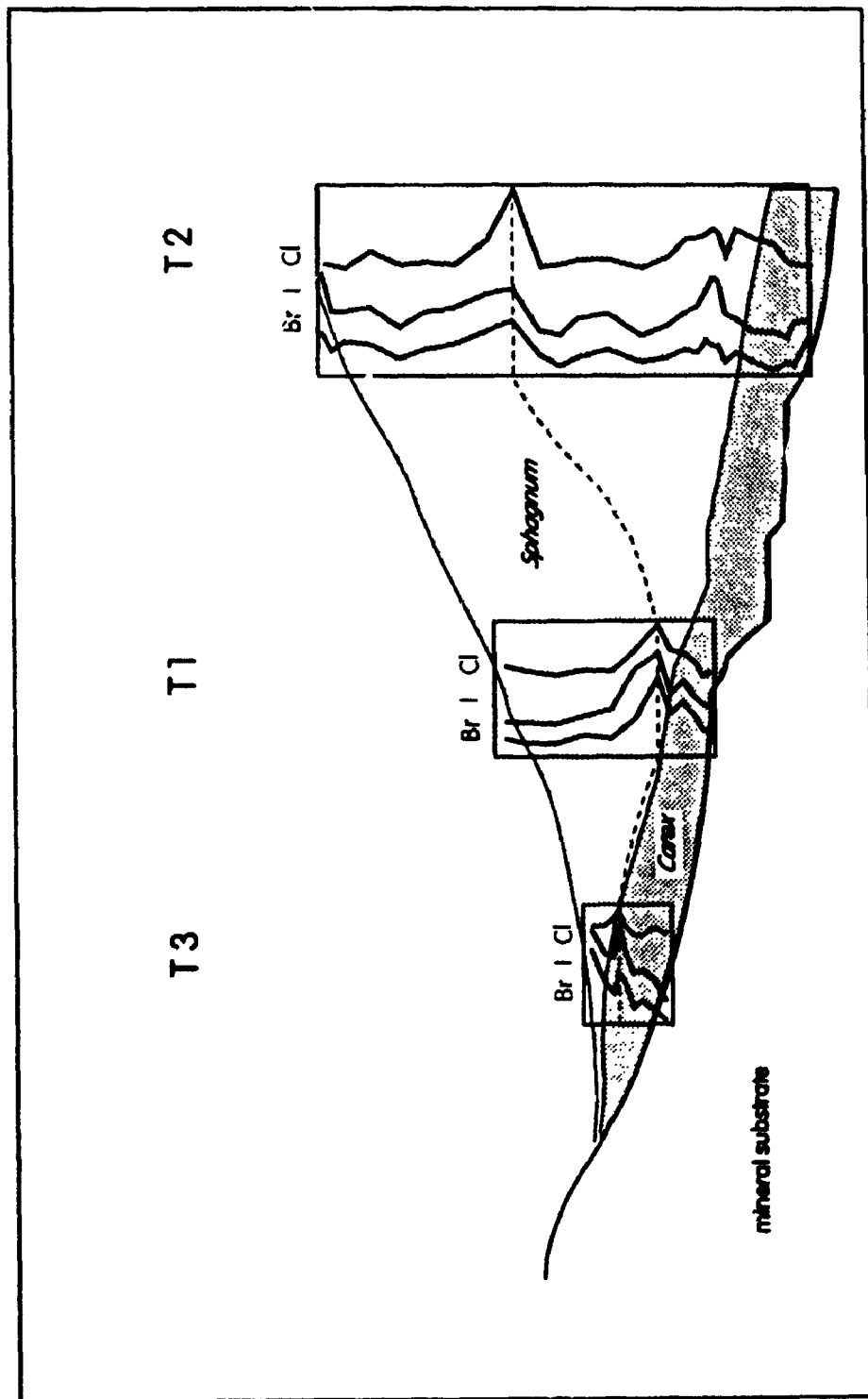


Figure 4.3 Br, I and Cl distribution in cores T1, T2 and T3, Petite Bog, Nova Scotia.

taken in core T2 is situated in the ombrotrophic section of the core, consisting exclusively of *Sphagnum* and with 0.4% ash content, obtaining its water and nutrient supply solely through precipitation. On the other hand, the sample in core T1 is situated in a transitional, mesotrophic zone, where the presence of *Carex* in the dominant *Sphagnum* peat, and the higher ash content (4%) indicate a relatively nutrient-rich environment. This is not totally independent of the influence of groundwater seepage. Therefore, contamination by seeping groundwater at a later stage of peat formation, bacterial activity, as well as incorporation of mobile secondary organic acids may have caused the more recent than expected ^{14}C date in core T1 (R. Sparks, pers. comm., 1994). This hypothesis is based upon the assumption that Cl, Br and I are immobile within the peat profile, which appears to be supported by the occurrence of Cl, Br and I enrichments at the same depth intervals in each core. On the other hand, Cameron *et al.* (1989) demonstrate the diachroneity of a mire base, also using ^{14}C dating. Mires expand, and thus the marginal base is likely to be younger than the central base, as suggested by the ^{14}C ages obtained in this study.

The origin of Cl, Br and I enrichment is uncertain. The evaporite-rich Windsor Group outcrops approximately 3 km SW of the bog, where a small karst area with a salt spring occurs (Boehner, 1986). Seepage of enriched groundwater may cause the generally high content of Cl, Br and I in the peat, but there are no comparative data available for bogs in the area to support or contradict this hypothesis. Mean Br (28 ppm) and I (9 ppm) levels in the bog fall within the values reported for raised bogs from Minnesota and Maine (9 and 34 ppm Br, 3 and 9 ppm I, respectively - Raymond *et al.*, 1990). However, Cl (mean = 529 ppm) is substantially higher in Petite Bog (198 and

288 ppm Cl in Minnesota and Maine bogs, respectively - Raymond *et al.*, 1990). In addition, Br, Cl and I concentrations in the bottom sediments do not show any substantial enrichment when compared to the crustal average (Table 4.3). Groundwater contaminated by salt-rich water does not appear to be the source of enrichment 2500 years BP. Enrichment is observed in the ombrotrophic section of core T2, where there is no evidence for detrital input by seeping groundwater (such as an increase in ash content as compared with adjoined intervals). Furthermore, halogen enrichment does not coincide with a sodium peak in the sample, although this may be due to the high solubility and resulting mobility of Na (Damman, 1978; Wedepohl, 1978).

Another source of Cl, Br and I is sea spray. Petite Bog is situated 10 km inland from an estuarine environment (Minas Basin); (Figure 2.1), and thus oceanogenic influence can not be excluded. Relatively high levels of Na (possibly related to sea spray input) were found in Petite Bog (Section 4.2.1.3.2.2). Wadleigh *et al.* (in press) report Cl and Na concentrations of up to 31 and 11 ppm respectively, in rain water samples collected less than 1 km from the coast in Nova Scotia. Based on sulfur isotope data, they show that almost all chloride contained in the rain is of marine origin, while Na does not appear to behave conservatively. This is in agreement with Wedepohl (1978), who infers that Cl is transported into the atmosphere as sodium chloride from the sea. While NaCl has a short residence time in the atmosphere, some of the chloride can be transported large distances in the form of aerosols. Marine-derived Cl appears to be the cause of high Cl levels in Petite Bog, as compared with raised bogs from Minnesota and Maine. Similarly, much of the Br and I in aerosols and rainwater are also derived from seawater (Wedepohl, 1978). Bearing in mind the strong influence of sea spray in the

composition of coastal rainwater, the peak concentration of Br, Cl and I in the bog appears to be derived from precipitation, and is possibly related to a major storm event in the Bay of Fundy.

Bromine is enriched at the surface (core T2) and appears to have an atmospheric origin. Br enrichment in top soils has been attributed to its precipitation in rain, due to the long retention period of Br from rainwater by soils (Kabata-Pendias and Pendias, 1992). Although the main anthropogenic source of Br is its release in vehicle exhaust, Br has also been used as a soil fumigant (methyl bromide), and is sometimes a component of K fertilizers (Kabata-Pendias and Pendias, 1992).

4.2.1.3.3.3 Fe and Mn

The strong positive correlation between Fe and ash ($r=0.85$), and Mn and ash ($r=0.72$) suggests the association of these elements mainly with the inorganic fraction of the peat. In soils, Fe occurs mainly in the form of oxides and hydroxides as small particles, but is also found in chelated form particularly in organic-rich soils (Kabata-Pendias and Pendias, 1992). Its occurrence on cation-exchange sites in the humin fraction of peat has been shown by Casagrande and Erchull (1976). Mn is an element essential in plant nutrition (Wedepohl, 1978), and thus its enrichment at the surface is probably due to plant bioaccumulation (Pakarinen and Gorham, 1983; Shoty, 1988). Its association with carboxyl groups has also been demonstrated (Brown and Swaine, 1964; Casagrande and Erchull, 1976).

Fe and Mn concentrations (normalized to 100% ash) show enrichment when compared to mineral substrate (e.g. core T2 - Figure 4.4). This can be attributed to humic

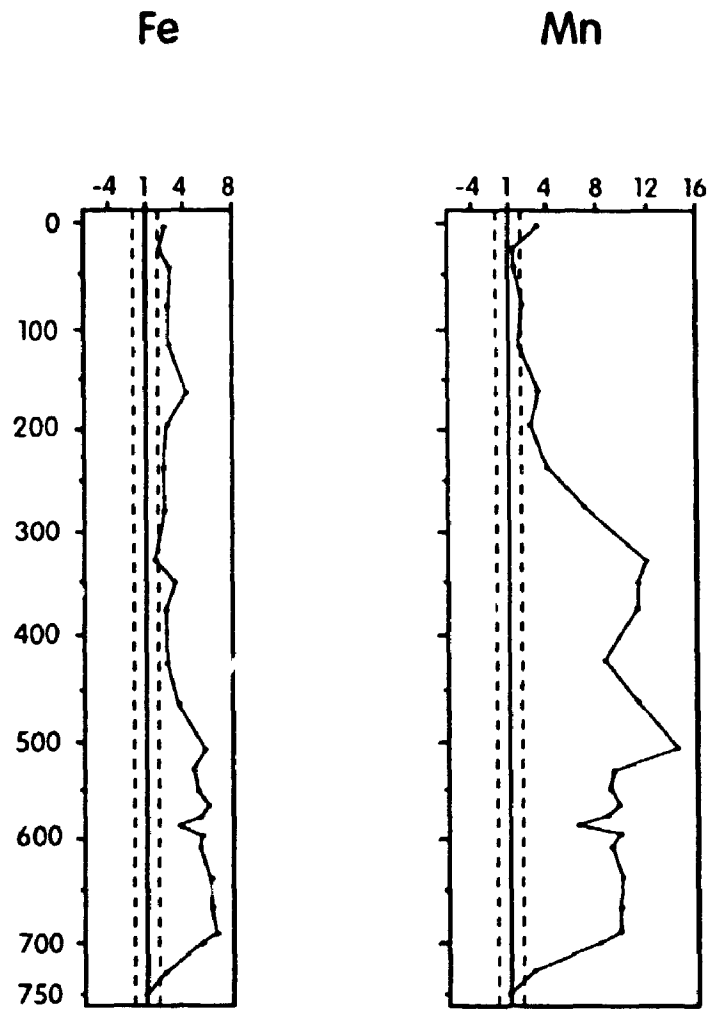


Figure 4.4 Relative enrichment of Fe and Mn in core T2, Petite Bog, Nova Scotia.

compounds, as their presence in organic-rich sediments has been shown to result in enhanced concentrations of many elements (Rashid, 1985).

4.2.1.3.3.4 Se

Measured selenium concentration in all cores shows that peat accumulates Se, as opposed to the mineral substrate (bottom sediments) which does not contain any detectable Se. Its distribution in the cores, supported by the negative correlation with ash ($r=-0.55$), suggests that it is bound mainly in the organic fraction of the peat. Due to its chemical affinity to S (Wedepohl, 1978), Se is able to replace S in amino-acids in plants (Kabata-Pendias and Pendias, 1992).

4.2.1.3.4 Geochemical variations in a fen to bog sequence

Analysis of three cores situated in the lagg zone (core T3), near the margin (core T1) and near the center of the dome (core T2), shows vertical and lateral variations in ash content and elemental composition. Decrease in ash content with increasing distance from the margin is attributed to the decreasing influence of the surrounding lithology and upland runoff. Vertical variations on the other hand reflect the trophic evolution of the peat sequence with time, as peat accumulates and becomes more independent of mineral-rich groundwater. As the bog surface rises above the water table, minerotrophic plant species are replaced by oligotrophic species which can thrive under nutrient-poor conditions. Ash content is also extremely low in these peats, since water, mineral and nutrient supply are obtained solely from precipitation and uptake from dead plants (i.e. "recycling"). Furthermore, the degree of humification decreases with

decreasing depth, and from the lagg zone to the center of the dome. This shows the relationship between ash content, trophic conditions, botanical composition and degree of humification. Changes of maceral composition (Section 4.2.1.1) also correlate with variations of trophic status (Figure 4.5). Similar trends of attributes of mire development (rheotrophic to ombrotrophic conditions) have been reported by Calder *et al.* (1991) and Calder (1993).

Al and Mg concentrations decrease laterally and vertically, being lowest in the ombrotrophic section at the center of the dome. This can be explained in terms of mineral (ash) abundance, since Al and Mg are main components in clays and mica, which are in low concentration at the center of the dome. Similar distribution is observed for Na, Cr, Fe and Mn. Considering the changes in vegetation in the fen to bog sequence, it can be inferred from these data that elemental concentrations are higher in minerotrophic *Carex* peats than in oligotrophic *Sphagnum* peats. There is also a strong positive correlation between the degree of humification and elemental composition, suggesting that peats accumulate metals with increasing decomposition. Thus, it can be demonstrated that, elemental concentration decreases, as the peatland develops from a fen to domed bog stage. It is a natural evolution for peat to become independent of the influence of surface and groundwater, resulting in a decrease of its inorganic content and level of degradation, and a shift in vegetation (Gore, 1983; Tallis, 1983; Calder, 1991, 1993).

However, this relationship is not demonstrated by elements having a strong organic affinity, such as Br, Cl, I and Se. As opposed to the elements associated with the inorganic fraction discussed above, their concentration is usually higher in oligotrophic

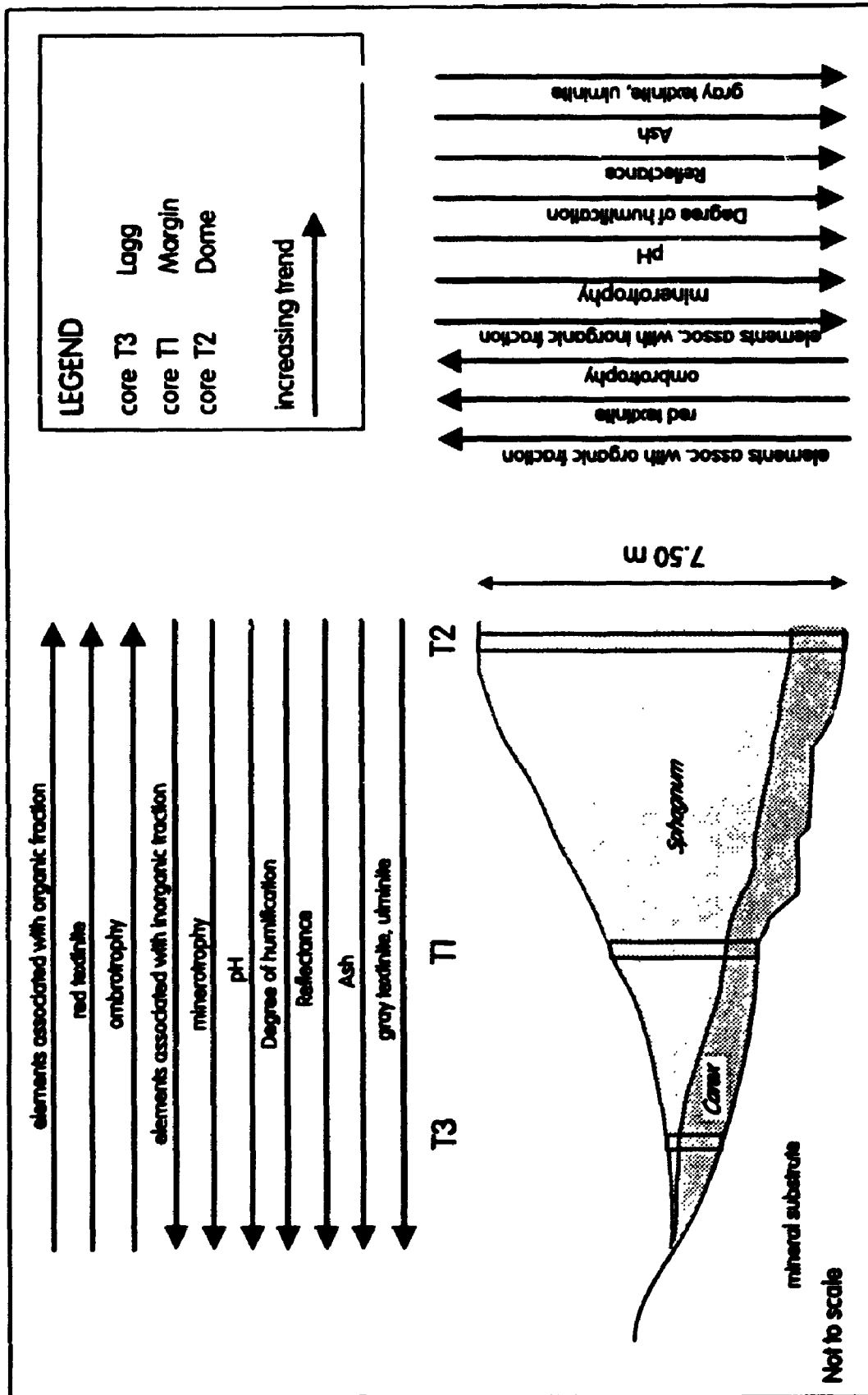


Figure 4.5 Summary of factors controlling peat geochemistry and organic petrology in a fen to bog sequence, Petite Bog, Nova Scotia.

peats having a lower ash content. Furthermore, Br, Cl and I seem to derive mainly from atmospheric deposition, and thus their supply to peat is the same over the whole bog. In addition, these elements are more likely to be leached by seeping groundwater near the margin of the bog, while water movement is very limited in the dome.

Although many elements decrease in concentration from the fen to bog sequence, as does the inorganic content of the peat, the trend is inverse for elements with strong organic affinity (Figure 4.5).

4.2.2 Salt marsh, Chezzetcook Inlet

4.2.2.1 Organic petrology

Maceral composition of the muck (Sections 3.2.1.2.2 and 3.2.1.2.3) reflects the influence of frequent flooding by nutrient- and sediment-loaded waters in the salt marsh. A predominance of ulminite over textinite is indicative of the advanced degree of degradation. Furthermore, the abundance of humodetrinite is probably due to flooding by oxygenated and sediment-rich tidal waters. Large oxyfusinite fragments were commonly observed, while pyrofusinite pieces are rare. This probably reflects alternate periods of flooding and drought in salt marsh environments subject to tidal influence, as opposed to fires. Abundance of mineral matter embedded in the organic material provides evidence of the effective trapping of fine particles by salt marsh plants.

Similar algae to those found in the muck have been observed in oil shales by Hutton (1987). He reported *Pediatrum* in lacustrine oil shales, while *Botryococcus* occurs in both lacustrine and marine oil shales. Therefore, the occurrence of *Pediatrum*,

Botryococcus, and freshwater and brackish Dinoflagellates in the salt marsh muck reflects the input of freshwater runoff in the brackish estuarine environment.

Relatively high reflectance values (>0.2%) appear to reflect the high degree of degradation in the marsh muck.

4.2.2.2 Rates of salt marsh accretion

The stratigraphic record suggests that salt marsh formation in the West Head of Chezzetcook Inlet started approximately 200 years ago, probably as a result of increased sedimentation related to settlement of European immigrants in the area (Scott, 1980). Furthermore, road construction in the late 1940's and early 1950's promoted an increase of marsh area in the inlet (Scott, 1980) and probably increased sedimentation rates in the salt marsh in the West Head (D. Scott, pers. comm., 1994).

Four surface cores (maximum 0.20 m depth) taken in the middle (CH1b and CH4) and high (CH2b and CH3) marsh were submitted for ^{137}Cs analysis in an attempt to determine recent changes in sedimentation rate throughout the marsh. Cores CH3 and CH4 were taken close to the new highway built in 1985-87. Core CH2b was extracted from the western tip of the West Head of Chezzetcook Inlet (approximately the same location as core CH2a), and core CH1b from the south side of the median channel in the middle marsh (approximately the same location as core CH1a); (Figure 2.3).

Temporal and lateral variations in rates of sedimentation are summarized in Table 4.4 and presented in detail in Appendix IV. There appears to be a decrease of sedimentation rate over the last 40 years, particularly in the middle marsh (cores CH1b and CH4). Based on the record of core CH2b, accumulation rates appear to decrease only

	High marsh	Middle marsh	
	Core CH2b	Core CH1b	Core CH4
Rates of sedimentation 1964-1993 ¹	0.36 ± 0.05 cm/yr	0.28 ± 0.07 cm/yr	0.28 ± 0.07 cm/yr
Rates of sedimentation 1953-1993 ²	> 0.37 cm/yr	> 0.37 cm/yr	> 0.45 cm/yr

¹based on 1964 fallout peak

²based on 1953 onset of fallout

Table 4.4 Rates of sedimentation in salt marsh, Chezzetcook Inlet, Nova Scotia.

slightly, if at all, in the high marsh. Increased sedimentation in the period 1945-1965 can probably be attributed to road construction (Scott pers. comm., 1994), resulting in a later decrease in accumulation rates. Core CH2b is located at the western tip of West Head and is probably more susceptible to additional terrestrial input, which may negate any apparent decrease in accretion rate.

Accumulation rates in the last 30 years vary from 0.28 ± 0.07 cm/yr in the middle marsh to 0.36 ± 0.05 cm/yr in the high marsh (Table 4.4). These values coincide with rates of accretion reported in Connecticut salt marshes (0.2 to 0.6 cm/yr from 1963-1973 - Harrison and Bloom, 1977). Delaune *et al.* (1978) on the other hand report higher sedimentation rates (0.75 to 1.35 cm/yr from 1954-1977), which they attribute to rapid subsidence of the Louisiana coast.

The influence of the most recent highway construction on sedimentation rates is probably not detectable in these samples, and would require further sampling in 2 to 4-mm intervals.

4.2.2.3 Mineralogy

4.2.2.3.1 Mineral varieties

As mentioned above (Section 4.2.2.1), the high inorganic content is probably mainly of detrital origin and comprised mostly quartz. Clay minerals are dominated by chlorite, reflecting the alkaline conditions in the salt marsh, while kaolinite was found only in one sample, and appears to be detrital, for it is usually an indicator of acidic conditions. Pyrite was found in almost all samples and occurs most commonly

as framboids. The occurrence and mode of formation of pyrite in salt marshes will be discussed in the next section. Plagioclase were the most common feldspars encountered and consisted essentially of Na-plagioclase.

Halite is abundant in the uppermost sample of core CH1a, while it is absent or only in small amounts in the underlying marsh muck and in the high marsh core site. It probably reflects important evapotranspiration and resulting oversaturation of Na and Cl at the marsh surface during drought periods between tidal flooding. The absence of halite in almost all other samples, as determined by XRD, can be attributed either to loss during low temperature ashing and/or dissolution *in situ* as a result of flushing or capillary action (at low tide). Furthermore, freshwater runoff is more significant at the western tip of West Head (location of core CH2a), and thus enhances dissolution of halite.

4.2.2.3.2 Pyrite

Pyrite formation is based on the generation of H_2S by the bacterial reduction of dissolved sulfate and a subsequent reaction with detrital iron minerals (Berner, 1972; 1984). Organic matter acts as a reducing agent and source of energy for sulfate reducing bacteria. Therefore, the major factors that determine the quantity of pyrite formed in a specific environment are the availability of organic matter, dissolved sulfate and reactive detrital iron minerals (Berner, 1984).

Brackish environments, such as salt marshes, represent ideal conditions for pyrite formation. Dissolved sulfate from sea water is readily available, reactive iron minerals are abundant in terrigenous material, and there is sufficient organic matter to

promote sulfate reduction (Altschuler *et al.*, 1983; Berner, 1984). Howarth (1979) shows that pyrite (in the form of minute euhedral crystals) can form in a very short period of time in salt marshes, and that it represents the major end product of sulfate reduction, which is the major form of respiration in salt marshes. Giblin and Howarth (1984) suggest that pyrite is formed directly and not by conversion from FeS since the solubility product of pyrite is always exceeded while the solubility product of amorphous FeS is not. However, framboidal pyrite is formed indirectly via iron monosulfide intermediates (Raiswell, 1982; Oenema, 1990). Furthermore, pyrite tends to be more frequent in brackish rather than in marine organic-rich material, as dissolved iron in freshwater is carried as stabilized organic colloids, which tend to flocculate out in brackish mixing zones (Sholkovitz *et al.*, 1978).

Microscopic analysis confirms the presence of pyrite in the salt marsh muck, as detected by XRD. Pyrite occurs in two forms, most commonly as framboids and rarely as small anhedral crystals (Sections 3.2.1.2.2 and 3.2.1.2.3). The association of framboidal pyrite with plant rootlets, which was observed in this study, has been reported elsewhere (e.g. Cohen *et al.*, 1983; Altschuler *et al.*, 1983; Oenema, 1990). Oenema (1990) suggests that roots and rootlets release metabolizable substrates, stimulating pyrite production at the interface of locally oxidizing and acidic conditions and surrounding reducing conditions. She reports pyrite forming at the interface of the oxidized and underlying reduced sediment.

4.2.2.4 Geochemistry

4.2.2.4.1 Major elements

4.2.2.4.1.1 Al, K, Mg and Si

There is a strong positive correlation between each of these elements and ash (Table 4.5), suggesting their association with the inorganic fraction, either as quartz (Si), mica or clay minerals. The abundance of K and Mg in sea-water promotes the formation of clay minerals, such as mica (illite) and chlorite. Potassium represents a major component in mica, while Mg is preferentially fixed in chlorite (Mason and Moore, 1982).

4.2.2.4.1.2 Na

The high sodium concentration in the muck is undoubtedly related to tidal flooding. Furthermore, there is a very strong positive correlation between Na and Cl (Figure 4.6); ($r=0.98$ - Appendix IV, Table 14), suggesting the occurrence of a sodium chloride mineral, such as halite, as confirmed by XRD (Table 3.6) and microprobe analysis. In the surface sample of core CH1a, it comprises 16% of the mineral fraction, and is probably the host of most of Na and Cl contained in the sample (3.4% Na; 4.8% Cl); (Figure 4.6). The occurrence of halite provides evidence of oversaturation of Na and Cl, and probably important evapotranspiration at the marsh surface (see Section 4.2.2.3.1).

	Ash	Al	Ca	K	Mg	Na	Si
Ash	1.00	0.63	-0.64	0.77	0.81	0.35	0.79
Al		1.00	-0.16	0.60	0.93	-0.18	0.61
Ca			1.00	-0.42	-0.29	-0.32	-0.44
K				1.00	0.79	0.06	0.67
Mg					1.00	-0.02	0.79
Na						1.00	0.29
Si							1.00

Table 4.5 Correlation coefficients of major elements, salt marsh, Chezzetcook Inlet, Nova Scotia. ($n = 13$).

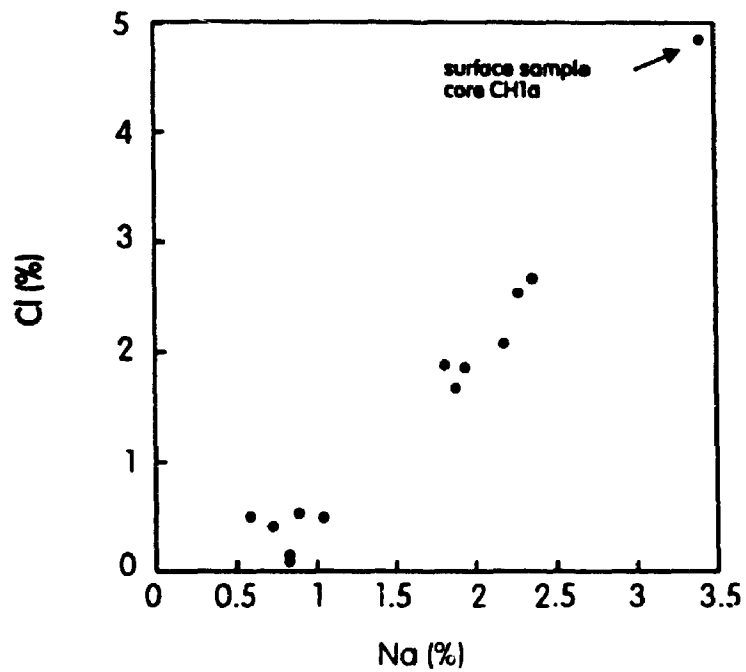


Figure 4.6 Plot of Cl vs. Na content of salt marsh muck, Chezzetcook Inlet, Nova Scotia.

The decrease with depth of Na and Cl concentrations in core CH1a (Figures 3.18 and 3.21) appears to result from flushing and subsequent dissolution of NaCl. In core CH2a, Na and Cl contents show little variation. The top sample represents an homogenized interval of 0 to 0.30 m depth, and variations, such as those observed near the surface in core CH1a, are probably not resolved.

4.2.2.4.1.3 Ca

There is a strong negative correlation between Ca and ash ($r=-0.64$), suggesting that this element is probably mainly associated with the organic fraction, such as humic acids and humin (Casagrande and Erchull, 1976). Laboratory experiments show that two fungi, which commonly colonize leaves of *Spartina alterniflora*, produce humic-like substances and thus contribute to the pool of humic substances in salt marshes (Filip and Alberts, 1993). Foraminiferal fauna present in the salt marsh consist of agglutinated foraminifera (Scott and Medioli, 1980a), and thus can not account for a Ca source.

4.2.2.4.1.4 S

Sulfur levels in the muck (mean value of 2%) fall within the values reported for brackish environments (e.g. 3.5%, Cohen *et al.*, 1983; up to 6%, Given and Miller, 1985; 3%, Lowe and Bustin, 1985; 2.38%, Raymond *et al.*, 1990), reflecting the seawater influence. Lateral and vertical variations of total sulfur content, similar to those observed in this study (Figure 3.19), were also reported by Given and Miller (1985). They infer that variations in sulfur distribution are mainly influenced by topochemical factors, such as the spatial distribution of bacterial colonies, rootlets, nutrients and

various insoluble and soluble chemical species. Organic sulfur was identified as being the main form of S in brackish peats, with a significant contribution of pyritic S, while inorganic sulfate, elemental S and H₂S constitute only minor fractions to total S content (Given and Miller, 1985; Lowe and Bustin, 1985; Price and Casagrande, 1991). The high S content in the muck reflects the availability of SO₄ (seawater) and the high pH in the brackish environment which favors bacterial reduction of seawater sulfate, and later incorporation of S in the marsh organic-rich material (Casagrande *et al.*, 1979; Lowe and Bustin, 1985). As shown by Casagrande *et al.* (1979), sulfur of H₂S can be incorporated into the humin fraction of the organic matter under anaerobic conditions.

4.2.2.4.2 Trace elements

4.2.2.4.2.1 Cr, Ni and Ba

Initial analyses of salt marsh samples (cores CH1a and CH2a) suggested that the high Cr levels at the surface were of anthropogenic origin. Differences in Cr concentrations in the middle and high marsh (almost twice the concentration in the middle marsh); (Figure 3.20), can be interpreted as the result of offshore pollution, for the high marsh is inundated only at higher tides. Similarly, Ni and Ba show enrichment in the surface samples of cores CH1a and CH2a, suggesting anthropogenic input. Nevertheless, the top sample in core CH2a represents an homogenized interval from 0 to 30 cm depth. Therefore the recent surface signature is not well resolved.

However, there was some concern regarding pollution resulting from highway construction (Highway 107) on the north part of the salt marsh (Figure 2.3). This led to sampling of surface cores at four locations situated in the middle and high

marsh, and on each side of the median channel (Figure 2.3). Cr and Ni levels do not exhibit any anomalies and appear to be correlated to ash contents, except in the top 3 cm of core CH2b, where there is a substantial enrichment in Ni (Figure 3.24). This supports the hypothesis of a recent anthropogenic source for Ni enrichment. Bearing in mind the rates of accumulation inferred from ^{137}Cs analysis (Section 4.2.2.2), the top 3 cm of core CH2b appear to have accumulated in approximately 8 years. Therefore Ni enrichment is probably associated with recent highway construction. Core CH2b was taken near the western tip of West Head, where freshwater runoff dilutes seawater, as indicated by low salinity values (Scott, 1977a). Thus, it is probable that heavy metals were transported in freshwater runoff in solution or in suspension, and then precipitated when entering the brackish environment. Furthermore, it is possible that heavy metals released in association with road construction (heavy equipments, paints, etc.) have accumulated at immediate proximity of the road. Thus, abnormal concentrations are not found in cores CH3 and CH4, located approximately 20 m from the highway, and core CH1b, which is further away.

A chromite grain was detected by microprobe analysis of the surface sample of core CH1a. It is possible that some chromite was present in the sample analyzed by INAA, which would explain the extremely high concentration of Cr in it (280 ppm). However, mean Cr levels were high in cores CH1a and CH2a. It is uncertain if they are due to contamination during sampling, or handling (e.g. crushing) in the laboratory.

4.2.2.4.2.2 Co and Mo

Cobalt and molybdenum exhibit surficial enrichment in core CH2b, similar to Ni, while their distribution follows ash content in the remaining cores (Figure 3.25). Their accumulation at the surface of core CH2b, which appears to have an anthropogenic origin can be attributed to transport in freshwater and later precipitation in the marsh (see Section 4.2.2.4.2.1). The enrichment at 1.15 m depth in core CH1a will be discussed in Section 4.2.2.4.2.4.

4.2.2.4.2.3 Br, Cl and I

Substantial levels of Br, Cl and I in the muck (Figures 3.21 and 3.26) appear to be directly related to oceanogenic influence, for similar data were reported in a brackish intertidal peat-forming environment (1120 ppm Br, 46900 ppm Cl and 65 ppm I - Raymond *et al.*, 1990).

Filtrate from distilled water stirred with muck samples taken from core CH1a (sample CH1-1 - 0 to 0.10 m and sample CH1-2 - 0.10 to 0.40 m depth) was analyzed by ICP-MS. Results are shown in Table 4.2. Very high Cl levels coincide with high concentrations of Na, suggesting that a large Cl fraction was present in soluble form in the muck, probably as halite (see Sections 4.2.2.3.1 and 4.2.2.4.1.2). Similarly, substantial levels of Br and smaller concentrations of I were observed in the filtrate, suggesting that they may be associated, at least in part, with the evaporite mineral in the muck. Br and I are commonly found in evaporites, particularly Br, which has a tendency to accumulate, while I is only present in smaller amounts (Wedepohl, 1978). Furthermore, it has been shown that a number of halophytic plants and salt marsh

grasses, such as *Spartina*, which grow in saline soils, accumulate Cl and have evolved salt glands which are able to excrete sodium chloride from the leaf surface (Lüttge, 1975). Cl distribution does not correlate with Br and I distribution, suggesting that, while most of Cl is present as sodium chloride (see also Section 4.2.2.4.1.2 and Figure 4.6), much of the Br and I exhibit a different association, probably with organic matter.

4.2.2.4.2.4 Fe

Iron concentrations in salt marsh sediments have been interpreted as being representative of the abundance of fine-grained matter in the marsh and therefore of flooding frequency (Thomas and Varekamp, 1991), since Fe occurs mainly as fine-grained oxides in coastal and estuarine environments (Coonley *et al.*, 1971). Low (and middle) marsh areas are flooded more frequently than high marsh areas, and thus trap more fine-grained material (clay, silt, hydrous iron oxides). Therefore, in the present study, higher Fe content in the middle marsh (mean Fe = 3.4%) than in the high marsh (mean Fe = 1.9%) can be interpreted as a result of more frequent flooding.

Furthermore, Fe enrichment at 1.15 m depth in core CH1a correlates with peak concentrations of S, Ni, As, Co and Mo (Figures 3.19, 3.20 and 3.22). Thomas and Varekamp (1991) report similar correlations in Fe-rich bands (except for As), and attribute this increased supply of trace elements in the pre-pollution period (before input of anthropogenic pollution) to an increase in flooding frequency, possibly as a result of fluctuations in the rate of true sea level rise.

On the other hand, surface enrichment in core CH2b (Figure 3.23) is more likely to be attributed to terrestrial input, as Fe colloids transported in freshwater runoff

flocculate when entering the brackish environment (Sholkovitz *et al.*, 1978). Fe enrichment correlates with Ni, Co and Mo anomalies (Figures 3.24 and 3.25) and thus, an anthropogenic source is possible.

4.2.2.4.2.5 As

It has been shown that arsenic enters estuaries in the inorganic form as a result of rock and ore weathering, and that it can adsorb onto precipitating iron oxides during mixing of fresh and salt water. This results in localized enrichments of As in the sediments (Bryan and Langston, 1992). Thus, the strong affinity of As for Fe-oxides is probably responsible for As enrichment at 1.15 m depth in core CH1a (Figure 3.22). Similarly, this affinity is probably responsible for the higher levels in the middle marsh (core CH1a) as opposed to the high marsh (core CH2a); (11 and 6 ppm, respectively). However, fine resolution of As contents in the surface cores CH1b, CH2b, CH3 and CH4 (Figure 3.26) shows large variations, which do not correlate well with Fe distribution. The cause of the variations is uncertain; nevertheless, changes in redox chemistry and post-depositional migration appear to influence As accumulation (Bryan and Langston, 1992). Furthermore, experiments show that *Spartina alterniflora* can incorporate soluble As^{5-} (Sanders and Osman, 1985).

4.3 ALBERTA

4.3.1 **Keephills Fen**

4.3.1.1 **Peat stratigraphy**

Variations in botanical composition (Section 3.2.2.1) reflect the trophic conditions in the peat-forming environment, which are controlled by a variety of factors, such as local lithology, hydrology, pH and nutrient availability. Brown mosses are dominant in the peat sequence, reflecting nutrient-rich conditions in the fen, which are supported by the high calcium levels found in the peat (see Section 4.3.1.3.4). The abundance of the moss *Tomenthypnum nitens* near the surface is characteristic of moderate-rich fens (Sjörs, 1950; Vitt and Kuhry, 1992), and is confirmed by pH values of 5.5 and 6.0, at the surface and 0.30 m depth, respectively, typical for transitional or moderate-rich fens. A study of rich patterned fens in Alberta (Slack *et al.*, 1980) show that *Tomenthypnum nitens* becomes dominant in drier string (narrow treed ridges) habitats, while *Carex* is more abundant in flarks (water-filled depressions). Therefore, the predominance of this brown moss species toward the surface is indicative of the evolution toward drier conditions (Kubiw *et al.*, 1989). At the surface of the peat core, brown moss is replaced by *Sphagnum*, which is dominant in the top 0.05 m. *Sphagnum* species are indicative of oligotrophic and acidic conditions. Therefore the shift in botanical composition reflects a change in trophic status in the peat-forming system. The general trend from rich to poor fen to bog appears to be primarily the result of the internal processes of peat accumulation, as peat surface becomes isolated from the mineral-rich groundwater, and eutrophic species are replaced by oligotrophic species, such as *Sphagnum* (see also Section 4.2.1.1)

At this stage, it is not possible to infer whether a *Sphagnum*-dominated peatland is developing. Kuhry *et al.* (1993) report the evolution from rich to poor fen to bog in five boreal continental peat-forming environments, and attribute the rapid transition to chemical factors. According to Gorham *et al.* (1984) few modern peatlands can be found with a pH in the range of 5.0-6.0, while the majority have either pH of 3.0-5.0 (bogs to poor fens) or pH of 6.0-7.0 (rich fens). The rarity of peatlands with this pH (5.0-6.0) has been attributed to a time component, for the transitional stage in the evolution sequence characterized by this pH occurs in a short period of time (Vitt and Kuhry, 1992; Kuhry *et al.*, 1993). While a number of *Sphagnum*-dominated peatlands developing from rich fens have been reported in Alberta (e.g. Zoltai and Johnson, 1985; Kuhry *et al.*, 1993), in others (e.g. Muskiki Lake), brown mosses are still dominant (Kubiw *et al.*, 1989). Kuhry *et al.* (1993) suggest that a continuous flow of mineral-rich groundwater delays the development of oligotrophic *Sphagnum*-dominated communities.

It can be inferred from petrological analysis (Section 3.2.2.1) that peat is still in the early stages of humification, supported by the abundance of textinite A through the entire peat sequence, and the relatively low reflectance values ($R_0 < 0.2\%$). Textinite B, which is rare in the top layers, increases with depth but is rarely dominant. Furthermore, it is common to observe variations from textinite A to textinite B in a single portion of peat material, indicative of low degree of humification. The abundance of large pyrofusinite fragments between 0.15 and 0.30 m depth is indicative of periods of drought and resulting fire activity in the latter stages of peat deposition in the fen. However, pyrofusinite is virtually absent in the rest of the peat sequence (except in the underlying marl sediments). Fens are wet environments characterized by a high water

table, and thus ground fires are rare. The occurrence of a thin layer of 'fresh' moss material between layers of marl, may suggest that peat accumulation in the fen was abruptly stopped due to flooding and deposition of lime-rich sediments, thus preserving the moss material. Observations of some plant material under the microscope showed cell wall material, displaying primary fluorescence under blue light excitation, and red internal reflection in reflected white light, giving evidence of the good state of conservation of the material.

4.3.1.2 Mineralogy

4.3.1.2.1 Mineral varieties

Calcite constitutes the dominant mineral fraction in the peat sequence, while quartz represents only a minor part, except in the upper layers of the section. The predominance of calcite in the peat reflects the influence of the surrounding and underlying calcareous lithology and resulting supply of cation-loaded seeping groundwater in the fen. The occurrence of gypsum is indicative of dissolved sulfate brought into the peat-forming system. As peat accumulates, it becomes isolated from the mineral-rich groundwater, reflected in a shift in botanical (see previous section) and mineralogical composition, for calcite decreases significantly in the upper layers and is replaced by quartz (Table 3.8). At the surface (0-0.05 m depth), the absence of calcite correlates well with the predominance of *Sphagnum* species, which enhance acidification of the environment. Bassanite is probably an artifact of low temperature ashing or a

dehydration product of gypsum (see Section 4.2.1.2). Whewellite and weddelite, which occur in some samples (Table 3.8) are authigenic minerals (see Section 4.2.1.2) forming in environments where calcium-rich fluids are present.

4.3.1.2.2 Pyrite

Although pyrite was not detected by XRD of low temperature ash, it was determined by optical methods. Microscopic analysis (reflected white light and blue light excitation) gives evidence of framboidal pyrite associated with plant tissues in the marl sediments (Plate 3.5a and 3.5b), while minute anhedral pyrite crystals were detected in peat using the microprobe after separation from the organic fraction (Plate 3.5c).

Pyrite is commonly associated with marine and brackish sediments and sedimentary rocks, since all the required conditions for the formation of pyrite are found in such environments (see Section 4.2.2.3.2). However, sedimentary pyrite formation occurs in freshwater environments as well (Davison *et al.*, 1985; Marnette *et al.*, 1993). The major factors controlling pyrite formation are the amounts of organic matter, and the availability of Fe and SO_4^{2-} , and the presence of oxidizing compounds such as O_2 or Fe^{3+} (Berner, 1984). While in marine and/or brackish systems, pyrite formation is usually limited by the amount and reactivity of organic matter buried in the sediment, in freshwater environments the availability of SO_4^{2-} is the limiting factor (Berner, 1984; Davison *et al.*, 1985). Marnette *et al.* (1993) observed pyrite framboids located within cell structures of partly decomposed organic matter in freshwater lake sediments, showing the association of pyrite formation with organic matter.

Framboidal pyrite was found in the marl sediments underlying the peat sequence, at 3.35 m depth. As mentioned above, a certain number of conditions have to be fulfilled to allow formation of pyrite. Easy metabolizable organic compounds are abundant, since the marl contains approximately 60% organic matter (Table 3.7), and iron reaches a concentration of 0.5% in this interval. High sulfur concentrations are found in most of the sequence, except near the surface (Section 4.3.1.3.5). The presence of free hydrogen sulfide was noticed while sampling (odor of rotten eggs), indicating reduction of sulfate by bacteria within the peat sequence and production of H_2S (Berner, 1984).

Pyrite formation occurred in the peat and marl as a consequence of the availability of sulfur and iron. Decomposing organic matter acts as a reducing agent in an oxidizing environment, and is often encountered in bottom lake sediments. According to Davison *et al.* (1985), pyrite formation occurs at the boundary of the oxic/anoxic zone, as it is created by decomposing organic matter in a rather oxidic environment. Furthermore, the occurrence of pyrite framboids within the cell structures may be due to organic compounds protecting pyrite against oxidation, as suggested by Marnette *et al.* (1993). Petraschek (1952) observed that most calcium-rich coals are higher in organic sulfur and syngenetic pyrite.

Analysis of groundwater in the Wabamun area (Ozoray, 1972) reveals that Keephills Fen is situated in an area where the hydrogeochemistry is dominated by Ca and Mg as major cations. The total dissolved solids content in groundwater is close to 1500 ppm, which is high when compared with the remaining map area, where levels average 500 ppm. Sulfate is found in significant amounts (up to 10% of anion content) in wells in the surrounding area. The fen is located SSW of an area characterized by

sulfate constituting 40% of the total anions, and since the area in question is situated at a higher hydraulic head than the fen, the high sulfur content in the lower section of the fen may be the result of sulfate-rich groundwaters seeping through the fen. Areas of coal and dark shale lithology appear to be the source of considerable SO_4 content (Ozoray, 1972).

4.3.1.3 Geochemistry

4.3.1.3.1 Introduction

Because of the nature of elemental concentration in the peat core (two enriched intervals), the distribution and affinity of most elements will not be discussed separately for each, but under two different headings, near-surface enrichment and tephra, respectively. Elements which do not follow any of these distribution patterns, will be addressed separately.

4.3.1.3.2 Near-surface enrichment

Elemental accumulation at shallow depth (0.15-0.30 m); (Figures 3.27, 3.28, 3.29, 3.30 and 3.31) appears to be associated with the zone of water table fluctuation (ZWTF). According to Damman (1978) and Pakarinen *et al.* (1980), mobility and fixation of elements in peat are closely related to water table level and fluctuation. These authors show that many elements accumulate in the ZWTF, and are removed from the peat before entering the permanently anaerobic zone. Chemical behavior of elements depends on redox conditions, which change in the ZWTF, situated at the interface between aerobic and anaerobic conditions.

Accumulation of iron in the ZWTF is a function of Eh-pH conditions. Reducing conditions lead to reduction of insoluble ferric compounds to ferrous ion, thus increasing solubility, while oxidizing conditions promote precipitation of iron (Wedepohl, 1978). Although insoluble Fe occurs mainly as oxides and hydroxides in mineral soils, it appears to be primarily in chelated form in soils rich in organic matter (Kabata-Pendias and Pendias, 1992).

Aluminum occurs in natural systems only in the trivalent form, which is insoluble within the natural pH range (Wedepohl, 1978). Nevertheless, Shotyk (1988) implies that solubility is enhanced by the presence of organic acids, which explains the higher than expected concentration of dissolved Al in peat waters. Damman (1978) suggests that, in the anaerobic peat, Al reacts with H_2S to form soluble Al_2S_3 , which is oxidized to $Al_2(SO_4)_3$ and precipitated above the water table.

Relatively high levels of As, Cl, Co, Cr, Sb, Th, Ti and V in the surficial layers (see Table 10, Appendix IV) as opposed to their low concentrations in the rest of the peat sequence do not appear to correlate with ash distribution. Thus, they are likely to indicate anthropogenic input (in addition to the accumulation effect caused by changes in redox chemistry in the ZWTF). To allow comparison between the surface layers and the rest of the peat sequence, concentrations of each element considered were normalized to 100% ash. As shown in Figure 4.7, all elements exhibit substantial enrichments near the surface, as compared with the peat underneath. Dominance of *Sphagnum* species in the top layers is indicative of oligotrophic conditions, as the peatland in the transitional stage receives its nutrient and water input mainly from dry or wet precipitation. An atmospheric source for the trace elements cited above is suggested. Highvale Mine and

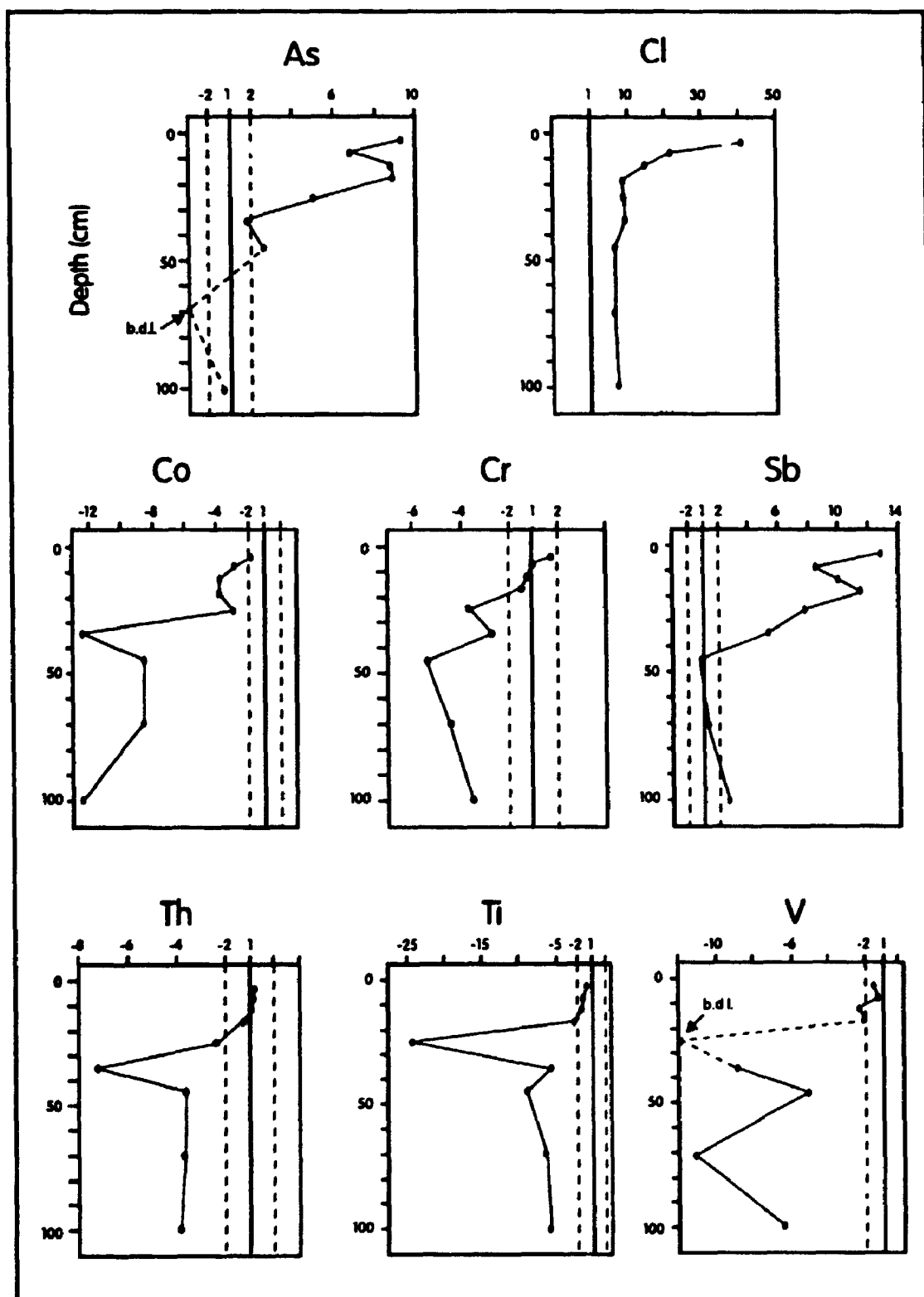


Figure 4.7 Relative enrichment/depletion of As, Cl, Co, Cr, Sb, Th, Ti and V, Keephills Fen, Alberta. (b.d.l. = below detection limit)

Transalta power station, which are situated on the south shore of Wabamun Lake, approximately 10 km upwind of Keephills Fen, may represent the origin of surficial concentration, for coal mining and combustion are the source of emissions into the environment. Coal mined and used for thermal-electric generation in Transalta power station is of subbituminous B rank and occurs in the Paleocene Ardley coal zone (Alberta Energy Resources Conservation Board, 1987). Elemental concentration of these coals has been analyzed by Gentzis and Goodarzi (in prep.). These authors report As levels ranging between 1.8 and 7.2 ppm, Cl concentrations 25 - 231 ppm, Co levels 0.5 - 10.2 ppm, Cr levels not exceeding 15 ppm, Mn concentrations 17 - 249 ppm, Sb levels not exceeding 2.8 ppm, Se concentrations below 6 ppm, Th levels below 26 ppm, Ti concentrations below 0.17%, and V levels below 88 ppm. Based on these data, near-surface enrichment in the peats seems likely to be related to atmospheric rainout enriched with coal dust.

Between 0.15 and 0.30 m depth, substantial Mn enrichment was observed (1020-2800 ppm); (Figure 3.31). It is unlikely that all Mn present is of anthropogenic origin, for Mn concentrations between 17 and 249 ppm have been found in coal from Highvale Mine (Gentzis and Goodarzi, in prep.). Mn is an essential element in plant nutrition and thus is usually concentrated in the top soil layers (Kabata-Pendias and Pendias, 1992). These authors report Mn concentrations of up to 2000 ppm in histosols from Poland. Mn compounds have a very low solubility under oxidizing conditions at pH near neutral, but are more soluble under reducing conditions (Wedepohl, 1978). Thus small shifts in Eh-pH can greatly influence their content in solution (Kabata-Pendias and

Pendias, 1992), and consequently in peat. Shotyk (1988) suggests that extreme insolubility of MnO_2 under aerobic conditions, plant accumulation and leaching from the anaerobic zone may result in Mn enrichment near the surface.

Although iodine levels in soils are known to derive mainly from atmospheric precipitation, they are highly dependent on the percentage of organic matter, due to the strong affinity of I for organic compounds (Wedepohl, 1978). Most iodine compounds are readily soluble in water (Wedepohl, 1978) Furthermore, it has been shown that while acidic conditions favor leaching of I, carbonate horizons in soils tend to act as natural barriers to I migration (Wedepohl, 1978). This may explain leaching in the top 0.10 m of the peat profile, which are more acidic, resulting in accumulation at 0.30 m depth (Figure 3.30).

4.3.1.3.3 Tephra

The association and ratio of elements showing substantial enrichment in the deeper zone suggest the occurrence of a volcanic-ash-rich layer. However, volcanic ash was not visible in the peat, and its presence was only inferred by chemical analysis, based on elemental enrichments. Between 2.40 and 2.64 m depth, substantial enrichments were reported for Al (0.9%), Si (4.5%), Na (3640 ppm), Mg (510 ppm), Fe (0.24%) and Ti (200 ppm); (Figures 3.27, 3.28 and 3.31). Detection of volcanic ash-rich peat layers is based upon the differences in elemental composition between bulk peat and volcanic ash (Westgate *et al.*, 1970). Ash consists mainly of SiO_2 and Al_2O_3 , with significant amounts of FeO, Na_2O , CaO and K_2O . High Ti contents are commonly associated with volcanic ash, in an area characterized by low background levels in Ti (Zoltai, 1989).

Three Quaternary pyroclastic layers have been identified in Alberta, occurring in peat, paleosol, alluvium and lake sediment (e.g. Westgate and Dreimanis, 1967; Westgate *et al.*, 1969; Zoltai and Johnson, 1985; Kubiw *et al.*, 1989; Zoltai, 1989). The most recent one, dated 2350 years BP, is the Bridge River tephra, originating in British Columbia. The middle layer is St. Helens "Y" tephra, dated 3500 years BP, which derived from Mount St. Helens, Washington, U.S.A. The lower ash is Mazama tephra, which originated from an eruption of Crater Lake, Oregon, U.S.A. and has been dated at 6800 years BP. In a recent study, based on the coring of 76 peatlands in Alberta (Zoltai, 1989), a large number of nonvisible volcanic-ash-rich zones were identified with microscopic and chemical means. This suggests a larger spatial distribution than supposed in previous studies. Furthermore, this author shows that volcanic ash continued to be deposited in peatlands for a prolonged period after (and possibly before) the main eruption, inferring younger (or older) dates than the generally accepted eruption date of 6600 years BP. The projected ages of ash-enriched zones related to Mazama tephra range between 5270 and 6970 years BP. Similarly, Westgate and Dreimanis (1967) report a date of 6020 ± 90 years BP for paleosol containing ash identified as Mazama tephra. This volcanic ash has the most widespread fall-out area, and has been identified in three locations near Edmonton (Westgate *et al.*, 1969). These authors report the presence of Mazama tephra within the A horizon of a paleosol covered by about 8 feet of aeolian sand in a locality five miles of Duffield ($53^{\circ}27'N$, $114^{\circ}21'W$), or in other words approximately 3 km SE of Keephills Fen.

Since pyroclastic deposits investigated in previous studies have been identified based on the chemical composition of their volcanic glass, as determined by

electron microprobe, and expressed as oxides (e.g. Powers and Wilcox, 1964; Smith and Westgate, 1969; Westgate *et al.*, 1969; Westgate, 1977), it is impossible to make a direct comparison. Furthermore, no radiocarbon dates were available for Keephills Fen. However, the volcanic-ash-rich zone in Keephills Fen was found between 2.40 and 2.64 m, in accordance with Zoltai (1989), who reports a mean depth of 2.76 ± 0.14 m, and an average thickness of 23 cm for the lower ash layer identified as Mazama tephra. Also the occurrence of Mazama tephra in sites close to Keephills Fen (Westgate *et al.*, 1969) gives further evidence of deposition of this tephra in the area. Separation of magnetite for electron microprobe analysis (Brewster and Barnett, 1979) was attempted with a Frantz magnetic separator. However, no magnetite could be isolated.

Peat accumulation rates were calculated in various Albertan peatlands, based on radiocarbon dates and the occurrence of volcanic ash layers (Zoltai and Johnson, 1985; Zoltai *et al.*, 1988b; Kubiw *et al.*, 1989). These results show that rates of accumulation are controlled by various factors, such as peat type, depositional environment, and climate, and therefore they are not constant through time. Fluctuations between 0.43 and 0.58 mm/yr (Zoltai and Johnson, 1985), and between 0.34 and 0.79 mm/yr (Kubiw *et al.*, 1989) were reported. Radiocarbon ages of basal peat give further evidence of the variations between different peatland types (Lowdon and Blake, 1968; Zoltai *et al.*, 1988b), as the calculated peat formation rates vary between 0.36 and 0.81 mm/yr. Assuming a maximum depth of 2.64 m and a radiocarbon age of 6800 years BP for Mazama tephra, peat has accumulated at a rate of approximately 0.4 mm/yr. This is within the range of peat accumulation rates in Alberta determined in previous studies.

Bearing in mind that volcanic ash may have been deposited after the main eruption, as mentioned above, the age of the ash-enriched zone may be younger than 6600 years, inferring a slightly higher rate of peat accumulation.

4.3.1.3.4 Ca

Ca distribution closely follows ash content (Figure 3.28), suggesting that most of Ca is bound to the inorganic fraction, probably as calcite, which was detected by XRD analysis of the LTA. Calcite is the most widespread form of calcium in soils, and is highly dispersed (Kabata-Pendias and Pendias, 1992). A plot of Ca vs. ash (Figure 4.8) shows the presence of two populations, one representing marl sediments (ash>40%, Ca>30%), the other one peat (ash<30%, Ca<15%). Calcium appears to be the key indicator of the trophic status of peat. Low Ca levels near the surface coincide with a shift in vegetation, as eutrophic brown moss is replaced by oligotrophic *Sphagnum* moss, which can tolerate more acidic conditions. High Ca content underneath suggests a high pH, and is reflected by the predominance of brown moss. Ca does not accumulate in the ZWTF, which appears to be due to its high solubility.

4.3.1.3.5 S

Low sulfur concentrations near the surface (<0.5% in the top 0.40 m of the peat sequence), and high levels further down (ranging from 0.9 to 2% total S); (Figure 3.28) suggest that sulfur enters the peat-forming environment via seeping groundwater. Some S may derive from anthropogenic pollution, due to the proximity of Highvale Coal Mine. However, Ardley coals are low in S (Gentzis and Goodarzi, in

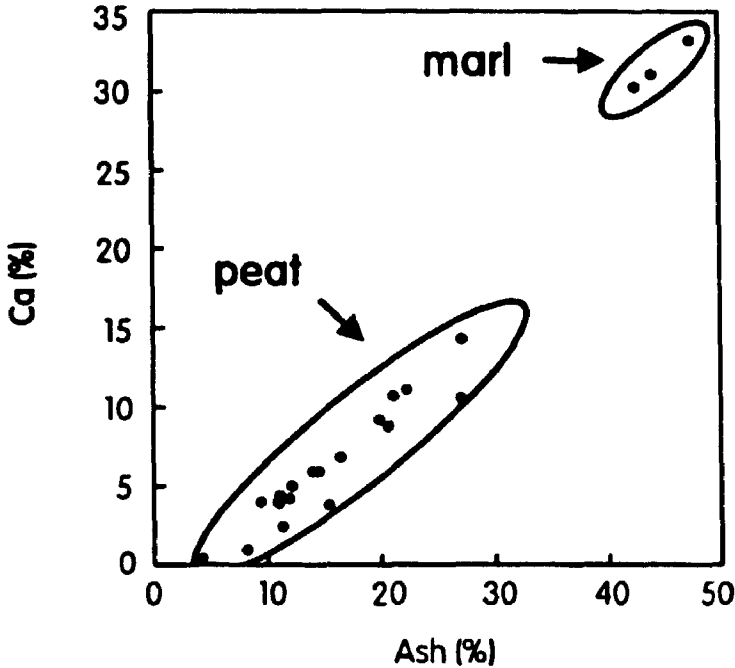


Figure 4.8 Plot of Ca vs. ash content, Keephills Fen, Alberta.

prep.), and it appears that the anthropogenic component, if any, is insignificant when compared with the natural component. Cohen *et al.* (1983) report total sulfur values between 0.3 and 0.9% for freshwater peats, thus the high concentrations in this peat appear uncommon. Nevertheless, the abundance of sulfate in groundwater of the Wabamun area has been reported (see Section 4.3.1.2.2) and appears to be the source of sulfur enrichment in peat. The presence of gypsum and pyrite are another evidence of high sulfur content.

4.3.1.3.6 K

Potassium is mainly below detection limit in the peat sequence, except at the surface (Section 3.3.2.1.1.2). Its concentration in the top layers is attributed to plant bioaccumulation (Shotyk, 1988), while it is readily leached in the underlying peat.

4.3.1.3.7 Se

Se distribution in the peat profile (Figure 3.31) suggests that this element is associated with both the organic and inorganic fractions. Se concentrations vary between 0.5 and 4 ppm (except in two intervals where it is below detection limit), averaging 1 ppm over the whole peat sequence. This corresponds to 3 times Se content in the underlying marl and 20 times the typical crustal average. Therefore, it can be inferred that peat accumulates Se, due to its high organic content. Furthermore, occurrence of relatively immobile selenides and Se-sulfides in soil rich in organic matter has been reported (Kabata-Pendias and Pendias, 1992). Similar association probably accounts for a fraction of Se in peat.

4.4 NORTHWEST TERRITORIES

4.4.1 **East Little Bear River deposit**

4.4.1.1 **Peat stratigraphy**

Variations in botanical composition between core 1 and core 2 (Figures 3.8 and 3.9, Table 3.9) reveal the heterogeneity in peat-forming environments, even within a short distance (approximately 10 m). However, brown moss and sedge are dominant in both peat cores, and are indicators of the influence of nutrient-rich seeping groundwater and resulting eutrophic conditions. In the Subarctic, wetlands generally go through an evolution from fen to bog to permafrost forms (Zoltai *et al.*, 1988a). Peat plateau bogs have been shown to form as ombrotrophic conditions develop. Furthermore, the presence of a *Sphagnum* cap over fen species shows that *Sphagnum* species play a role in the establishment of permafrost in many peatlands. In the summer, the dry *Sphagnum* mat acts as an insulator of underlying seasonal frost. When wet in the fall, *Sphagnum* is a good conductor and allows heat loss from the peat, thus enhancing formation and expansion of underlying permafrost (Railton and Sparling, 1973). Brown (1970) suggests that the insulating properties of peat are manifested by the fact that the permafrost table occurs within the peat (not beneath it). Thus, peat accumulation probably started in unfrozen fens and permafrost developed later after peat had accumulated a few meters, and oligotrophic conditions prevailed (Zoltai *et al.*, 1988a). Permafrost may have formed after a general cooling of the climate about 5,000 years ago (Ritchie *et al.*, 1983).

Fires are frequent in peat plateau bogs (Zoltai *et al.*, 1988a), as indicated by the abundance of charcoal in the surface layers of both cores. Phlobaphinite is more

abundant in core 1, due to the predominance of wood in this part of the bog. In the eutrophic peat sequence, inertinite is rare, reflecting the perennial presence of water within the peat deposit (and resulting lack of fire activity). The predominance of textinite A and B indicates the low degree of alteration of the peat, which may be associated with the dominance of brown moss. This is correlated with the fairly low reflectance values (R_o generally below 0.2%).

4.4.1.2 Mineralogy

Quartz is the dominant mineral fraction in the mineral substrate and in the peat sequence (Table 3.10). However, the abundance of feldspars and clay minerals is indicative of the detrital input by seeping groundwater. Evidence of calcium in seeping groundwater is given by the presence of whewellite, calcite, dolomite and bassanite (see also Section 4.2.1.2).

4.4.1.3 Geochemistry

4.4.1.3.1 Introduction

Although ash distribution does not display any significant difference between both cores, elemental concentration on the other hand appears to be affected by permafrost, for there is a strong enrichment immediately above the permafrost boundary in core 2, while no substantial accumulation was observed in core 1. Ash distribution, elemental enrichment associated with permafrost, and distribution of specific elements are discussed in the following sections.

4.4.1.3.2 Ash content

Ash content exhibits a similar distribution in C-shape in both cores (Figures 3.32 and 3.36). Surficial enrichment can be attributed to plant bioaccumulation, and atmospheric dust, as suggested by Shotyk (1988), as well as oxidation. The abundance of charcoal in the surface layers is indicative of fire activity, which probably contributes largely to mineral accumulation. This peatland is situated in a remote area, away from any anthropogenic source, and therefore, the anthropogenic input is insignificant. However, the peatland occurs at the top of the river bank and it is possible that fine sediments from the river bank are blown away and get trapped in *Sphagnum* moss and peat at the surface. Basal ash enrichment reflects the influence of mineral-rich groundwaters and the detrital input by surface and groundwater at the time of deposition.

4.4.1.3.3 Enrichment above the permafrost boundary

Vertical distribution of most elements (except Br, Ca, Cl, I, Se and S); (Figures 3.32, 3.33, 3.34, 3.36, 3.37 and 3.38) and a strong positive correlation with ash (Table 4.6), show that their concentration can be explained in terms of abundance of mineral matter in peat and reflects bedrock geochemistry. However, substantial enrichment occurs immediately above the permafrost boundary in core 2, independently of their affinity with the organic and/or inorganic fraction. Furthermore, elements show depletion below the permafrost limit (Figures 3.36, 3.37, 3.38 and 3.39).

Kadlec (1984) demonstrates that ice formation causes movement of soluble materials, because they are excluded from the crystal lattice, as water freezes. The experiment was conducted, based on ice formation from the surface downward, since it

	Ash	Al	Ba	Br	Ca	Cl	Cr	Fe	I	K	Mg	Na	S	Sc	Si
Ash	1.00	0.97	0.89	-0.63	0.08	-0.30	0.90	0.92	-0.43	0.96	0.97	0.97	-0.10	0.26	0.97
Al		1.00	0.96	-0.47	0.17	-0.13	0.96	0.96	-0.28	0.99	0.99	0.99	-0.19	0.22	0.99
Ba			1.00	-0.32	0.21	0.05	0.97	0.95	-0.08	0.94	0.94	0.94	-0.19	0.30	0.96
Br				1.00	0.40	0.58	-0.35	-0.41	0.58	-0.47	-0.48	-0.50	0.05	0.12	-0.48
Ca					1.00	0.03	0.20	0.26	-0.04	0.20	0.24	0.20	-0.03	0.28	0.15
Cl						1.00	0.01	-0.13	0.88	-0.17	-0.19	-0.19	-0.40	-0.11	-0.13
Cr							1.00	0.96	-0.15	0.92	0.93	0.94	-0.21	0.25	0.96
Fe								1.00	-0.28	0.92	0.91	0.95	-0.10	0.26	0.94
I									1.00	-0.30	-0.33	-0.34	-0.23	-0.21	-0.27
K										1.00	0.99	0.98	-0.18	0.19	0.98
Mg											1.00	0.99	-0.20	0.22	0.98
Na												1.00	-0.18	0.27	0.99
S													1.00	0.28	-0.20
Sc														1.00	0.25
Si															1.00

Table 4.6 Correlation coefficients of major and trace elements in East Little Bear River Deposit, Northwest Territories. (all samples, $n = 28$)

applies to northern temperate peatlands, which freeze from the top down in the winter. Although frost penetration originally takes place from above in subarctic peatlands, and results in establishment of permafrost within the peat itself (Zoltai and Tarnocai, 1975), the permafrost front advances upward. Furthermore, peat is affected by seasonal freezing from the surface downward. Assuming that the process described by Kadlec (1984) occurs, upward movement could be expected, resulting in depletion in the frozen peat and translocation followed by accumulation above the permafrost boundary.

Furthermore, leaching and seasonal freezing from the top may result in a downward movement of dissolved materials, which is stopped by permafrost, and therefore they contribute to elemental accumulation on the permafrost boundary. Similar to the zone of water table fluctuation, the limit between non-frozen peat and permafrost-affected peat represents an interface between aerobic (above) and anaerobic (below) conditions, where many elements tend to accumulate (see Section 4.3.1.3.2).

4.4.1.3.4 Ca

There is a weak positive correlation between Ca and ash ($r=0.08$), suggesting that some Ca is fixed on the organic matter, particularly the humic fraction (Casagrande and Erchull, 1976). The remaining fraction is associated with mineral matter, probably in the form of dispersed calcite and/or dolomite, which were determined by XRD analysis. Ca levels are lowest near the surface, indicating oligotrophic conditions in the active layer dominated by *Sphagnum* species (Figures 3.33 and 3.37).

4.4.1.3.5 Br, Cl, I and Se

Br, Cl and I exhibit a negative correlation with ash and positive correlation between each other (Table 4.6), suggesting that they display a strong affinity with organic matter. The weak positive correlation between Se and ash on the other hand ($r=0.26$) suggests its association with both the organic and inorganic fraction. However, all four elements are highly enriched immediately above the permafrost boundary, which shows that movement of ice favors elemental translocation, whatever the mode of bonding of the elements.

4.4.2 Mackenzie River deposit

4.4.2.1 Introduction

The sampled material was characterized by a very high ash content, averaging 53.5%, and is therefore termed muck (peaty and silty muck) instead of peat. However, the organic material consisted mainly of wood and peat, suggesting that the original material deposited was woody peat. This peat plateau bog occurs toward the upper part of the river bank, and appears to have been eroded by the Mackenzie River. Substantial inorganic enrichment is possibly caused by mineral-laden surface and groundwater seeping through the peat-forming system. Flooding by the Mackenzie River at earlier times is possible, resulting in a high detrital input. Furthermore, fine dissolved material in the ice may contribute to inorganic enrichment. Glacio-lacustrine sediments occurring in the Mackenzie River are fine grained, in the clay to silt fraction, and are likely to be wind blown, becoming trapped in peat at the time of deposition.

4.4.2.2 Muck stratigraphy

The abundance of wood remains within the muck is indicative of somewhat drier conditions at the time of deposition. Scarcity of pollen grains in frozen woody peats has been reported previously and attributed to oxidation favored by slow accumulation (Korpijaakko *et al.*, 1972). Drought, as revealed by the presence of inertinite fragments, and frost, probably delayed peat formation and accumulation.

A radiocarbon age of 6540 ± 80 years BP was obtained from a wood (*Picea*) fragment collected at a depth of 2.80 m. This suggests an average accumulation rate of 0.43 mm/yr, similar to those proposed by Korpijaakko *et al.* (1972), and Zoltai *et al.* (1988a). However, radiocarbon ages reveal changes in rates of peat accumulation with time. Accumulation rates are higher in the lower part of the subarctic wetlands, while there is a significant reduction towards the surface, which appears to correlate well with the onset of permafrost (see also Section 4.4.1.1). Similarly, rates of peat accretion in non-frozen peatlands are higher than in frozen peatlands (Zoltai *et al.*, 1988a). Chronologically and stratigraphically, the radiocarbon age of 6540 ± 80 years BP at 100 m asl correlates with ^{14}C ages of 6120 ± 120 years BP obtained from peat at 74 m asl further *downstream* ($65^{\circ}50'\text{N}$; $129^{\circ}05'\text{W}$); (Mackay and Mathews, 1973), and of 8650 ± 80 years BP obtained from basal peat at 145 m asl further *upstream* near Fort Norman (Smith, 1992).

4.4.2.3 Mineralogy

Quartz constitutes the main mineral fraction, with minor contributions of feldspars, mica and clays (Table 3.12), probably reflecting the mineral composition of the surrounding lithology. Calcite is present in small amounts, and is likely to have a detrital origin.

4.4.2.4 Geochemistry

Most elements studied (except Br, Ca, Cl, I and Se) display a strong positive correlation between each other and ash (Table 4.7), suggesting their association with the inorganic fraction. Elemental distribution can therefore be explained in terms of mineral matter distribution.

Selenium and iodine were below detection limit or absent in most samples, probably due to the low organic content. Similarly, low Br and Cl levels were recorded.

In this core, no enrichment related to permafrost was detected, probably due to the lack of resolution (large sampling interval)..

	Ash	Al	Ba	Br	Ca	Cl	Fe	K	Mg	Na	Si
Ash	1.00	0.71	0.63	-0.16	0.23	-0.07	0.66	0.73	0.72	0.79	0.68
Al		1.00	0.88	-0.36	0.13	0.14	0.95	0.92	0.92	0.90	0.96
Ba			1.00	-0.50	0.27	0.16	0.91	0.89	0.81	0.81	0.85
Br				1.00	-0.01	0.22	-0.54	0.36	-0.42	-0.30	-0.37
Ca					1.00	0.22	0.19	-0.01	0.10	0.17	0.11
Cl						1.00	0.11	0.14	0.28	0.29	0.13
Fe							1.00	0.94	0.87	0.88	0.91
K								1.00	0.85	0.90	0.93
Mg									1.00	0.90	0.89
Na										1.00	0.90
Si											1.00

Table 4.7 Correlation coefficients of major and trace elements in Mackenzie River Deposit, Northwest Territories. ($n = 15$)

CHAPTER FIVE

SUMMARY DISCUSSION

5.1 INTRODUCTION

Data presented and interpreted in previous chapters are discussed and compared below. Petrographic characteristics of the various 'peat' types are addressed. Elemental affinity is determined, based on the concentration of major and trace elements in the peats, and enrichment and depletion of the elements are discussed. A variety of peat-forming environments were studied, thus the geochemical behavior of major and trace elements is controlled by a number of different factors, which are addressed below. Occurrence of pyrite in fresh- and brackish water peat-forming environments is briefly reviewed. Peat deposits as modern analogues for coal seams are discussed. Finally, an assessment of the significance of wetlands and peat to global climate change will be made, based on this study.

5.2 ORGANIC PETROLOGY

In all peatlands studied, analysis reveals similar vertical changes in maceral composition. Near the surface, green or yellow fluorescing peat material is observed (Plate 3.1a). This does not exhibit any reflectivity but appears brown in reflected white light. Underneath, fluorescing properties diminish and the peat material displays red

internal reflection (red textinite A); (Plates 3.2a and 3.4a). Textinite A is progressively replaced by gray reflecting textinite B (Plates 3.2b and 3.4a) and ulminite with increasing depth and degree of degradation (Figure 5.1).

The major components of peat are lignin, cellulose and lipids (i.e. waxes, resins). Each component is altered differently during humification. While lignin is quite resistant to degradation, cellulosic components are easily decomposed (Teichmüller, 1982; Stout *et al.*, 1989). Loss of fluorescence and red internal reflection with increasing depth can be attributed to loss of cellulosic compounds (Teichmüller, 1982; Stout and Spackman, 1987). A comparative study of peat and lignite confirms this hypothesis. Red reflecting material is abundant in peat, while the cell walls of tissue in the lignite are characterized by a loss of red coloration (Moore and Hilbert, 1992). With an increasing degree of decomposition, textinite B is replaced by gelified ulminite, which is free of cellulose (Teichmüller, 1982), as shown by the gray reflectivity and the absence of red reflection (Plate 3.6d).

A distinct lateral and vertical shift of maceral composition was observed in Petite Bog. Loss of fluorescence and red coloration is observed downcore and from the center of the dome (core T2) to the margin (core T1) and the lagg zone (core T3). The proportion of wood fragments and rootlets exhibits an inverse trend. It is lowest in *Sphagnum* peat, and increases downcore and towards the margin (correlating with an increase of minerotrophy). Similar trends were reported in a domed peat deposit in Sarawak, Malaysia (Esterle *et al.*, 1989); (loss of red coloration and increase of woody components with depth and towards the margin).

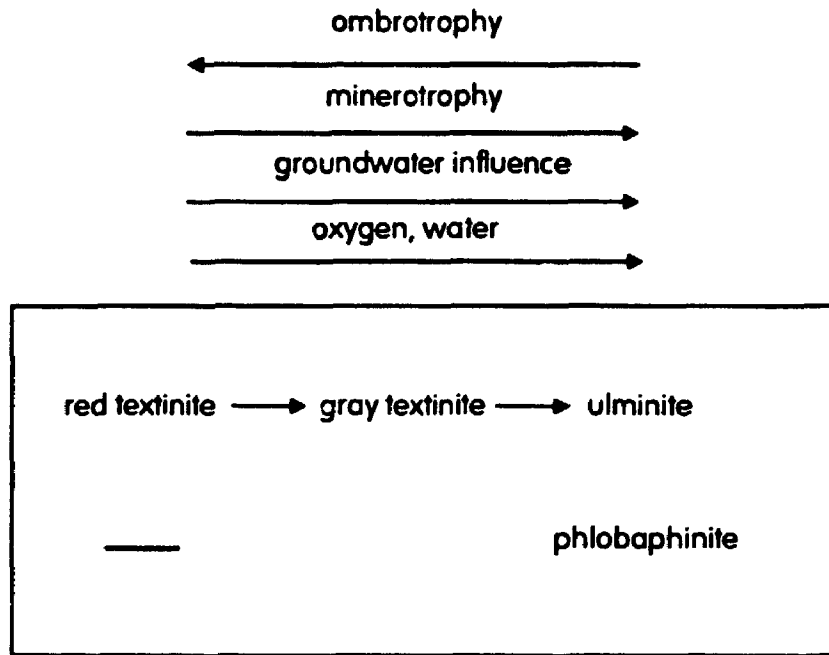


Figure 5.1 Summary of changes in maceral composition as related to trophic status

Furthermore, changes in maceral composition correlate with shifts in reflectance values and degree of humification (see Section 4.2.1.1). There appears to be a strong relationship between trophic conditions (and botanical composition) and changes in maceral composition and degree of decomposition (Figure 5.1).

In the other peatlands (Keephills Fen, East Little Bear River deposit and Mackenzie River deposit), which are minerotrophic peat-forming environments, changes in maceral composition and reflectance are subdued. However, a similar trend is observed; red reflecting textinite A is generally more abundant in the upper sections of the cores, while textinite B is abundant in the lower sections. It is tentatively suggested that a difference in botanical composition seems to be the most likely reason for the generally lower reflectance values in the brown moss-dominated peatlands (Keephills Fen and East Little Bear River deposit), as opposed to the *Carex*-dominated minerotrophic sections in the domed bog. More research needs to be carried out on this problem.

In Keephills Fen, higher reflectance was determined near the surface (Figure 3.7, Table 3.7). These high levels can probably be attributed to wild fires and peat oxidation, which are more likely to occur at that stage of peatland development (shift to oligotrophic conditions), where the water table is lower. Intervals rich in pyrofusinite are not always characterized by higher reflectance values, probably due to peat heterogeneity. Abundance of pyrofusinite in certain intervals coincide with the occurrence of charcoal, and thus is indicative of periods of drought and fire activity in the peat-forming environments.

Maceral composition of the salt marsh muck differs from that of the other peatlands studied. Oxyfusinite prevails over pyrofusinite, reflecting the influence of

oxidized conditions in the marsh. Abundance of ulminite is indicative of the advanced degree of degradation in this environment, which is affected by frequent tidal flooding.

5.3 ELEMENTAL AFFINITY WITH THE ORGANIC AND/OR INORGANIC FRACTION

Elements which exhibit a strong affinity with the inorganic fraction are those which have a strong positive correlation with the ash content, since they are primarily associated with the mineral matter in peat. Thus, they are in higher concentrations in minerotrophic peats as opposed to ombrotrophic peats (Figure 4.5). However, other factors also affect elemental concentrations (see Section 5.5). Redox changes associated with the zone of water table fluctuation, incorporation of tephra, anthropogenic pollution, and the occurrence of permafrost, all result in significant changes in the concentration of elements. Consequently, correlation coefficients are altered, such as for the peats of Keephills Fen (Appendix IV, Table 15). The correlation coefficient between Al and ash content, for example, is -0.18. Other factors affect Al concentration in the peat (not only ash content), such as volcanoclastics input and redox changes. Thus, these data can not be included in statistical analyses to determine the affinity of most elements. Furthermore, data from the salt marsh are not taken into consideration in this statistical analysis, since it represents a brackish non-peat-forming environment.

Correlation coefficients were calculated for peat samples from Petite Bog and East Little Bear River deposit ($n=73$). Results are shown in Table 5.1 (and Appendix IV, Table 16). There is a strong positive correlation between most major elements studied (Al, Mg and Na) and ash content, reflecting their association with mineral matter, such

Elements	Corr. coeff.
Al	0.86
Br	-0.18
Ca	0.11
Cl	-0.37
Cr	0.86
Fe	0.41
I	-0.25
Mg	0.87
Mn	0.48
Na	0.83
Se	-0.09
V	0.93

Table 5.1 Correlation between element concentration and ash content in peat.
(n=73)

as clays, feldspars and mica. Si and K are not included in the statistics, because they are below detection limit or not detected in more than half of the samples, which are characterized by very low ash content. However, their distribution follows ash content, suggesting their association with the mineral fraction (quartz (only Si), feldspars, mica and clays). Ca displays only a weak positive relationship with ash ($r=0.11$). Some Ca is present in mineral matter, such as in calcite, dolomite or calcium oxalate minerals, but another fraction of Ca is combined with organic matter.

Cr is strongly associated with the inorganic fraction ($r=0.86$), as shown by Shotyk (1988) and Shotyk *et al.* (1992). They infer that Cr concentrations can be explained in terms of mineral matter abundance, and that Cr behaves conservatively in peat.

The small positive correlation coefficient between Fe and Mn, and ash content ($r=0.41$ and 0.48 , respectively) suggests rather a scattering of data, and does not suggest any definite association. The association of Fe and Mn with both the inorganic and organic fraction (on cation-exchange sites of humic acids (Casagrande and Erchull, 1976)).

Halogens Br, Cl and I exhibit a negative correlation with ash ($r=-0.18$, -0.37 and -0.25 , respectively) suggesting that they are mainly associated with the organic fraction of peat. Furthermore, they show considerable enrichment in peat (see Table 4.3 and Section 5.4), while they are depleted in the mineral substrate of each peat sequence studied (when normalized to 100% ash). In the salt marsh, Na and Cl exhibit a very strong positive correlation due to the presence of halite (Figure 4.6). However, Cl is usually not associated with the mineral fraction.

There is a weak negative correlation between Se and ash ($r=-0.09$), suggesting that much of the Se is associated with the organic matter. Another fraction occurs in association with mineral matter, as selenides or sulfides. The association with sulfur, probably as sulfides, is suggested by the positive correlation between both elements ($r=0.42$); (Appendix IV, Table 16). This can be attributed to the chemical similarity between S and Se (Wedepohl, 1978). Se associated with both the organic fraction and with sulfides (sometimes pyrite) has been reported in coals (Swaine, 1990).

In the salt marsh muck, Al, Mg, Si and K appear to be associated mainly with the inorganic fraction, as shown by their high positive correlation with ash (Table 4.5). Na, on the other hand, is primarily associated with Cl forming sodium chloride (Figure 4.6 and Appendix IV, Table 14), and thus has a lower correlation with ash ($r=0.35$). Cr appears to be mainly combined with the inorganic fraction, but because of input of anthropogenic Cr near the surface, the correlation coefficient with ash is lower ($r=0.43$); (Appendix IV, Table 14). Correlation coefficients between halogens (Br, Cl and I) and ash content ($r=-0.46, 0.20$ and 0.19 , respectively); (Appendix IV, Table 14) give evidence of seawater influence and incorporation of halogens in evaporite minerals and in salt marsh plants (see Section 4.2.2.4.2.3).

5.4 ELEMENTAL ENRICHMENTS AND DEPLETIONS IN PEAT

To determine if a certain element was enriched or depleted in peat, its concentration was recalculated by normalizing to 100% ash, so that it can be compared to typical crustal abundance (Shotyk, 1987a; Shotyk *et al.*, 1992). This calculation is based on data obtained from peats from Petite Bog, Keepphills Fen and East Little Bear

River, and results are shown in Table 5.2. Here, data from the salt marsh and Mackenzie River Deposit were not taken in consideration, because of the high ash values (generally >50% ash).

Elements associated with the organic fraction are strongly enriched in peat (Se, I, Br and Cl in decreasing order). Ca enrichment (+6) can be attributed to both its combination with carboxyl groups of the humic fraction and the calcareous nature of substratum in Keephills Fen. Omitting data from Keephills Fen results in an enrichment of 3 times (instead of 6) relative to crustal abundance. Na and Mg depletions in peats are probably related to their depletions in the substratum of the peatlands studied, and to leaching by groundwater in the minerotrophic peats. Only enrichments or depletions greater than twice the typical crustal average are considered significant, thus Al, Cr and Fe are neither enriched nor depleted in peat. However, the relatively low value for Fe appear to be caused by depletions in the substratum of the peatlands studied. As shown in Figure 4.4, Fe is enriched in peat when compared to the mineral substrate (however, the mineral substrate is depleted when compared with typical crust average). There is a slight enrichment of Mn (+2), which can be attributed to its affinity with carboxyl groups of humic acids. Enhanced concentrations of many metals in organic-rich sediments have been attributed to humic compounds (Rashid, 1985). Humic substances react with a variety of elements, forming organo-metal complexes, and resulting in increased solubility of the metallic cations, which in turn influences their mobility and redistribution.

	Average concentration in peats * (n=92)	Calculated composition of peat ash * ¹	Typical crustal abundance ²	Enrichment or depletion relative to crustal abundance ³
Ash (%)	9.35%	100%		
Al (%)	0.68%	7.3%	8.1%	---
Ca (%)	1.9%	20.4%	3.6%	+6
Mg	309	3302	20900	-6
Na	509	5446	28300	-5
Br	23	249	2.5	+100
Cl	334	3570	130	+27
Cr	12	127	100	---
Fe	3095	33092	50000	---
I	7	77.5	0.5	+155
Mn	163	1740	950	+2
Se	1	12.5	0.05	+249

*in ppm unless otherwise noted.

¹average concentration in peat normalized to 100% ash

²Mason and Moore (1982).

³Number of times is given only when greater or smaller than twice the typical crustal abundance.

Table 5.2 Elemental enrichments and depletions in peat relative to typical crustal abundance.

5.5 FACTORS AFFECTING THE GEOCHEMISTRY OF PEAT

5.5.1 Introduction

In Sections 5.3 and 5.4 it has been shown that most elements associated with the inorganic fraction (mineral matter) are usually only slightly depleted or enriched in peat, while elements with a strong affinity for organic matter are considerably enriched. However, as seen in Chapter Four, natural and anthropogenic factors influence the geochemical behavior of major and trace elements, causing minor or major changes in concentration and distribution in peat.

5.5.2 Geology

Lithology of surrounding and underlying bedrock and till is a major factor controlling the type of wetland. While an oligotrophic peatland (such as Petite Bog) develops in a felsic environment, a minerotrophic peatland (such as Keephills Fen) forms over a calcareous substratum. This is directly related to the solubility of the rock-constituting minerals (Shotyk, 1988). Quartz and feldspars are relatively insoluble, and therefore groundwater seeping through a felsic substratum will be oligotrophic. Groundwater seeping through limestone on the other hand will be eutrophic, due to the high solubility of calcite, and results in development of a rich fen. Calcium levels in peat are indicative of the trophic status in the peatland, which in turn determines the type of vegetation.

Furthermore, elemental concentration in the peat is a good indication of local bedrock geochemistry, particularly in the minerotrophic peats. Ombrotrophic peats, on the other hand, obtain their nutrient and mineral input only from precipitation.

However, soil chemistry reflects the mineral composition of the bedrock, from which it derives, and thus the geochemistry of ombrotrophic peats is also influenced by soil dust input.

Inter-site comparisons are difficult because of the interference of various other factors which cause enrichments in the peat, such as permafrost, atmospheric dust, tephra, sea spray, anthropogenic pollution and redox changes associated with water table fluctuation. However, concentrations of some elements in different wetlands can be attributed to the local lithology. Barium and titanium contents, for example, are significantly higher in the sub-arctic wetlands studied (substratum consisting of shale, sand and mudstone) than in the peatland of Alberta (calcareous substratum). Ba content averages 178 ppm in core 1 of East Little Bear River deposit (mean ash content = 11%), and 1465 ppm in the mineral substrate (mean ash content = 89%). In Keephills Fen it averages 67 ppm in peat (mean ash content = 15%), and 80 ppm in marl (mean ash content = 45%). Ti levels average 268 ppm in core 1, East Little Bear River deposit, and 3840 ppm in the mineral substrate. In Keephills Fen, Ti concentrations are below detection limit (< 50 ppm) in the marl and average 113 ppm in the peat. These values are indicative of the geochemistry of the local substratum: mean Ba and Ti contents in limestone are 90 ppm and 300 ppm, respectively; mean Ba content is 320 ppm in sandstone and 550 ppm in shale, while Ti averages 3500 ppm in sandstone and 4600 ppm in shale (Bowen, 1979).

5.5.3 Peat fires

Fires are common in peatlands and may have a drastic effect on vegetation and deposition patterns (Staub and Cohen, 1979; Rollins *et al.*, 1993). However, in this study it appears that fires were never severe enough to significantly affect the vegetation. The most drastic change in peat-forming vegetation was observed in core T2, Petite Bog, Nova Scotia (Section 3.2.1.1.2), where the presence of *Eriophorum* probably reflects changes in peatland (such as water level and trophic status) as a result of relatively extensive fire activity.

The percentage of inorganic material (ash content) is usually higher in intervals containing charcoal and fusinitized material, since residual ash from fires is usually high in inorganics. Some of the ash may be leached into the deposit, blown away or transported by flowing water (Rollins *et al.*, 1993). However, it seems that a large part remains in site, as shown in all intervals containing pyrofusinite and charcoal.

Although elemental enrichment is commonly observed in direct association with peat fire activity, it appears that it is mainly due to the increase of ash content, resulting in higher levels of elements associated with the inorganic fraction. It is shown by normalizing to 100% ash content and comparing with concentrations in intervals immediately above or below, such as in core T1, Petite Bog, Nova Scotia, where two intervals rich in fusinite were identified (Figure 5.2). However, there are some exceptions, such as a considerable Cr enrichment at depth of 5.75-5.80 m in core T2, Petite Bog, in which 90% of organic material gives evidence of charring (Figure 5.3).

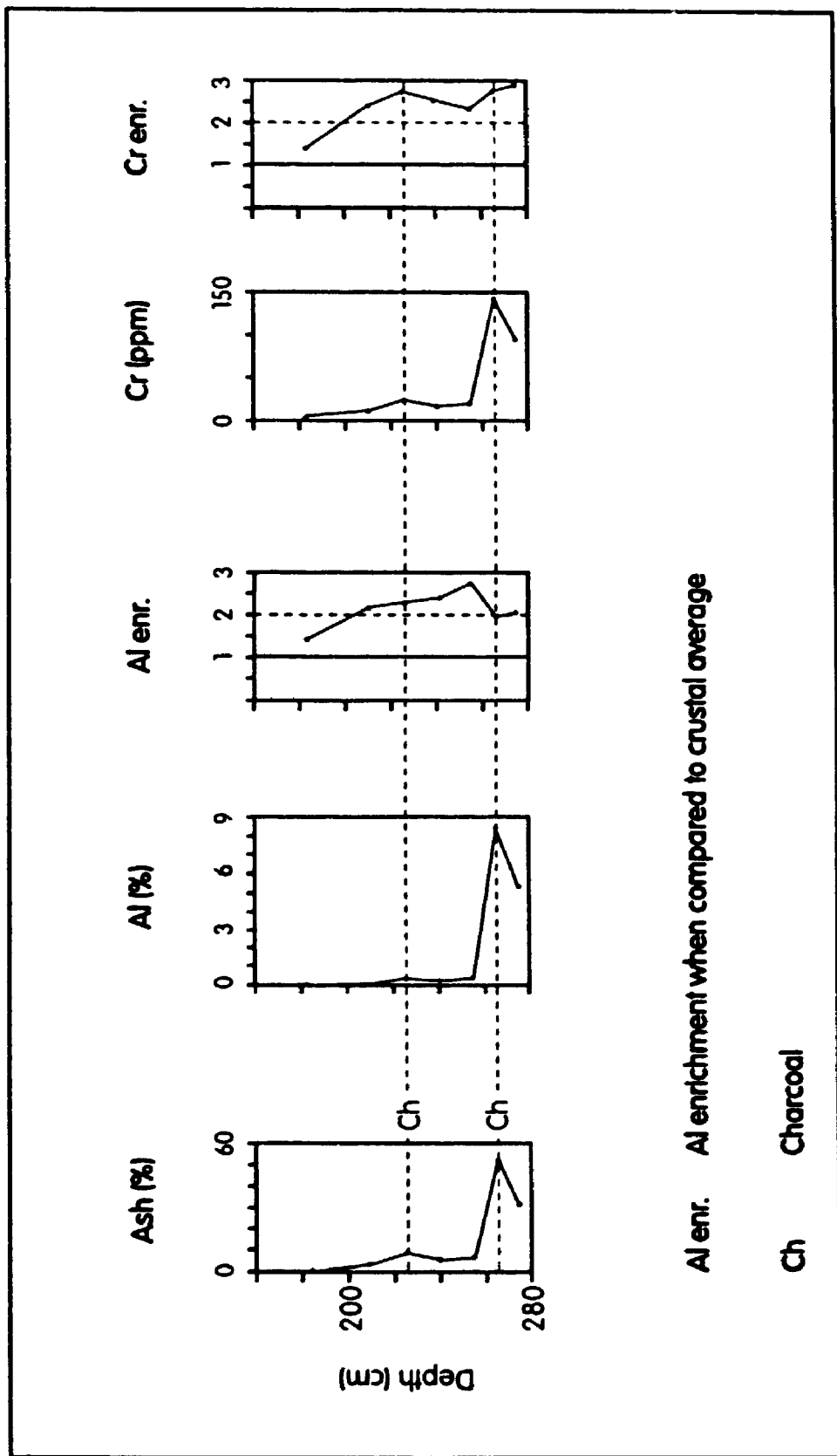


Figure 5.2 Relative enrichment of Al and Cr in core T1 (charcoal-rich intervals), Petite Bog, Nova Scotia.

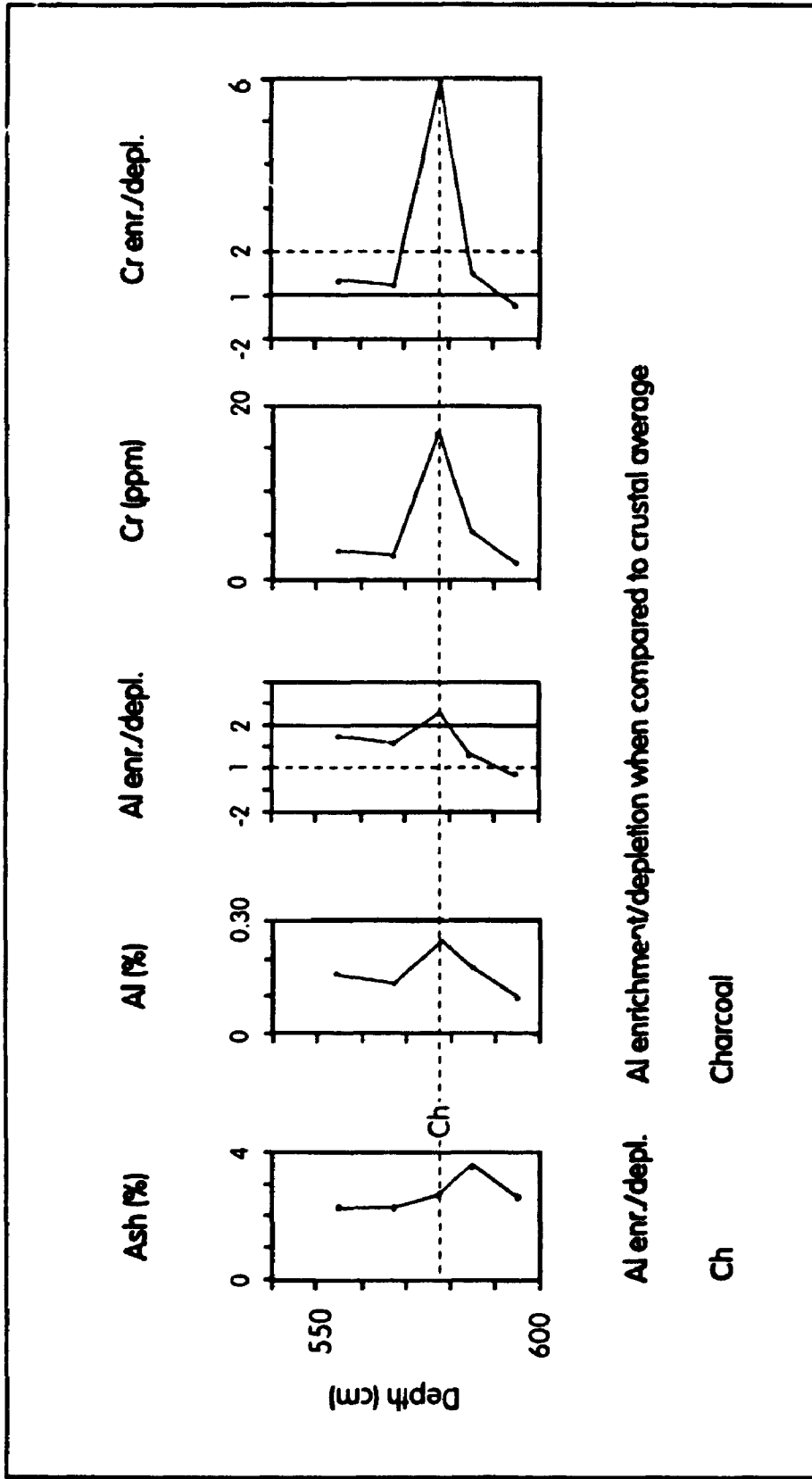


Figure 5.3 Relative enrichment/depletion of Al and Cr in core T2 (charcoal-rich interval), Petite Bog, Nova Scotia.

Similar enrichment was observed for Al, Na, Mg and Ti in this interval. Even Si content, which is below detection limit in most samples, is high (1.8%), corresponding to more than twice the crustal average (when normalized to 100% ash).

Pyrofusinite gives evidence of recent fire activity in Keepphills Fen (at 0.15-0.20 m depth), although charcoal fragments were scarce in the rest of the core. Substantial elemental enrichment was observed at that depth. However, other factors, such as redox changes associated with the zone of water table fluctuation and anthropogenic pollution (Section 4.3.1.3.2), appear to have a major control on the distribution and accumulation of the elements, so that the influence of fire on peat geochemistry is probably minimal and not easily identifiable.

Similarly, fire activity does not appear to affect elemental distribution in peats of East Little Bear River deposit, Northwest Territories. Surficial enrichment appears to be caused mainly by dry and wet deposition (Section 4.4.1.3.2), while leaching associated with seasonal freezing probably affects element mobility.

5.5.4 Redox changes associated with the zone of water table fluctuation

The role of the water table in controlling the geochemical behavior of the elements is substantial, since it represents the boundary between reducing and oxidizing conditions. Solubility, mobility and precipitation of most elements are strongly dependent upon the redox chemistry, and thus they are likely to accumulate in the ZWTF (Damman, 1978; Pakarinen *et al.*, 1980). In the present study, enrichment in the ZWTF associated

with depletion underneath was observed only in Keephills Fen. This is probably due to the sampling interval, which resulted in homogenization of anomalies in elemental concentration (in the other peatlands investigated).

As shown in Section 4.3.1.3.2, most elements are substantially enriched in the ZWTF, although the enrichment effect may be enhanced by an additional anthropogenic input (a coal mine and coal-fired power plant). However, Ca does not accumulate in the ZWTF, probably due to its high solubility.

5.5.5 Permafrost

The influence of permafrost on elemental distribution is illustrated in the peat deposit of East Little Bear River, Northwest Territories (Section 4.4.1.3.3). While major and trace element concentrations follow ash distribution (except for some elements with a strong affinity for the organic fraction) in the core not affected by permafrost, a substantial enrichment (independent of elemental affinity) occurs immediately above the permafrost boundary in the core affected by permafrost.

These results are in contradiction to those of Coker and DiLabio (1979) and DiLabio and Coker (1982), who studied uraniferous peat bogs affected by permafrost in Manitoba. They described low trace element levels in *Sphagnum* above the permafrost table, as opposed to high concentrations below in the humified peat. However, these authors conducted a study to evaluate peat as a sampling medium for geochemical exploration in permafrost terrain and analyzed only one sample in each core above the permafrost boundary (Table 3 - DiLabio and Coker, 1982). Thus, it is probable that the unfrozen peat sample was not collected immediately above the permafrost table, where

substantial enrichment was observed in core 2 of East Little Bear River deposit. Furthermore, most of the peat bogs investigated by DiLabio and Coker (1982) are associated with uraniferous bedrock, which results in concentration of U and associated trace metals in the peat (below the permafrost boundary). On the other hand, elemental distribution in cores taken in peatlands not associated with uraniferous bedrock appears to follow ash content, similar to the present study.

Based on their data, DiLabio and Coker (1982) postulate that the onset of permafrost stops humification and thus trace metal accumulation. Although it is probable that permafrost inhibits further humification, it appears that a critical aspect of the influence of permafrost on element concentration has been overlooked. This represents an important issue when considering the effects of the variations of the permafrost table on the global geochemical cycle.

5.5.6 Tephra deposition

Peatlands are passive depositional environments, in which the stratigraphic record is well preserved. Furthermore, they represent excellent sinks for airborne elements, because they are wet and well vegetated, and thus can efficiently trap wind-blown volcanic ash. Thus, the occurrence of volcanic-ash-rich layers in peatlands has been widely reported in Western North America. These have been associated with eruptions in Washington, Oregon, Alaska and British Columbia (Zoltai, 1989).

The volcanic-ash-rich layer identified in this study at the site of Keepphills Fen, Alberta (Section 4.3.1.3.3), is enriched in Al, Fe, Na, Si and Ti, and many trace elements. Although the amount of volcanic ash deposited in the peatland is minor and

does not appear to alter local vegetation, nor cause drastic changes in peatland evolution, it results in a significant elemental concentration. On a larger scale, enrichments caused by deposition of volcanic ash in peat can profoundly alter the geochemistry of the peat-forming environment and the composition of the resulting coal.

5.5.7 Plant bioaccumulation

Many elements are essential for plant growth, and thus are concentrated at the surface of peat sequences, where the proportion of moss is greatest. Surface enrichments of Mn and K in peatlands are mainly attributed to plant bioaccumulation. Similar enrichments were observed in the surface samples of core T2, Petite Bog, and of Keephills Fen, which can not be explained simply in terms of ash distribution (Figure 5.4 - Mn and K levels are normalized to 100% ash to show relative enrichment/depletion when compared to typical crustal average). In Keephills Fen, Mn and K levels are higher at the surface than in the sample immediately below, although there is twice as much ash in the latter (the substantial Mn accumulation at a depth of 0.15-0.30 m has been discussed in Section 4.3.1.3.2). In Petite Bog (core T2), surficial Mn enrichment also appears to be out of proportion with the surficial ash increase. K levels are only detected at the surface, while they are below detection limit in the samples below. This can be attributed to both a higher ash content and plant bioaccumulation.

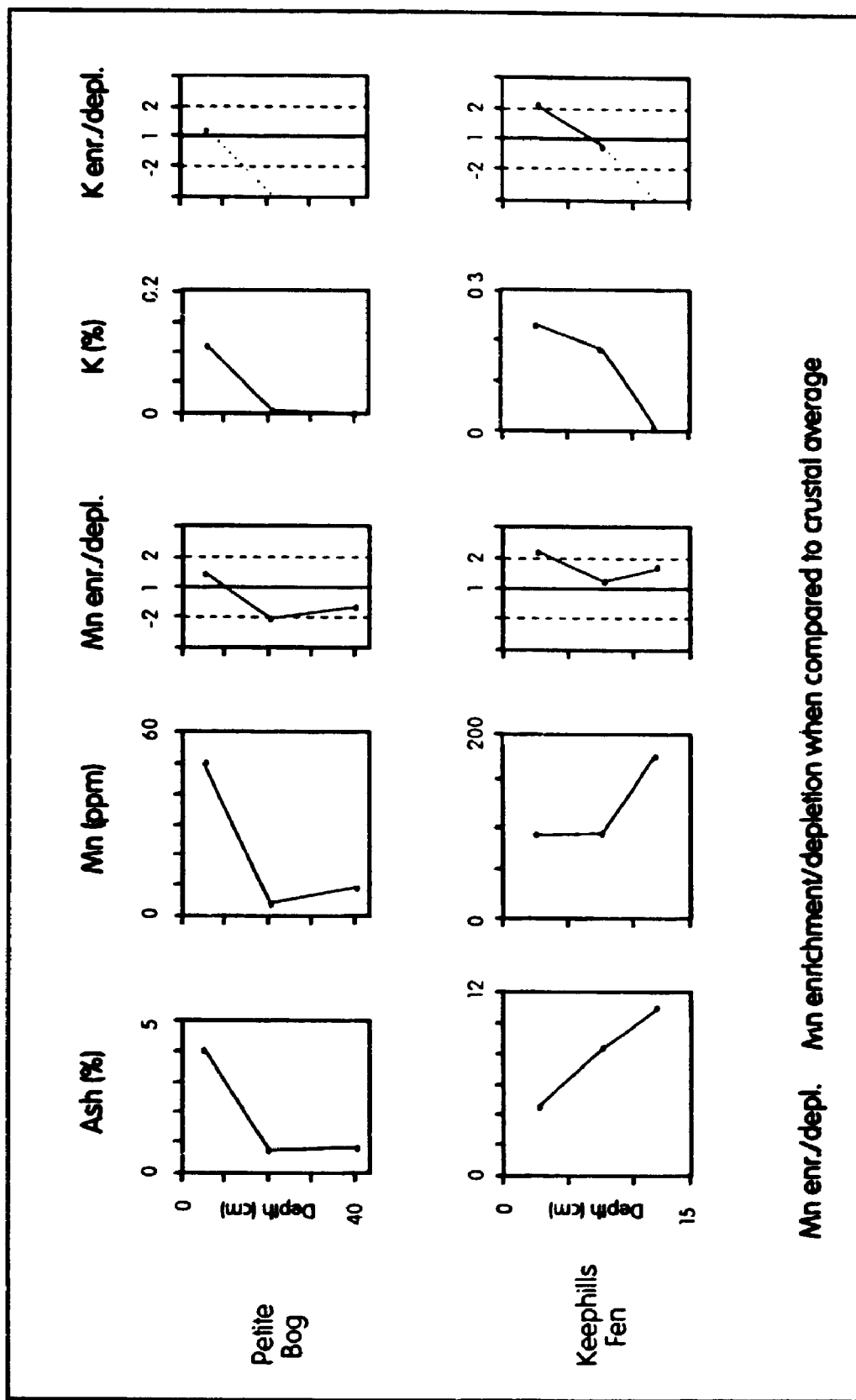


Figure 5.4 Relative surficial enrichment/depletion of Mn and K in Petite Bog, Nova Scotia and Keephills Fen, Alberta.

5.5.8 Ash content

Since most elements appear to show a strong affinity with the inorganic fraction (Section 5.3), their concentration in peat will depend greatly on ash content, which represents the percentage of inorganic matter in peat (remaining after combustion at high temperature). Biophilic elements on the other hand, will decrease with increasing ash content, while elements associated with both the organic and inorganic fraction exhibit a more random behavior. Thus, the concentration of elements showing a strong positive correlation with ash (e.g. Al, Cr, Mg, Na and V - Table 5.1) can be explained in terms of mineral matter abundance.

5.5.9 Oceanogenic influence

Although Petite Bog, Nova Scotia, is situated 10 km inland from an estuarine environment (Minao Basin), there appears to be a significant oceanogenic influence on peat geochemistry. Na appears to be enriched when compared with continental peats (101 ppm, Ontario - Shotyk, 1988; 119 ppm, Maine and Minnesota - Raymond *et al.*, 1990). Furthermore, high levels of Br, Cl and I in peat seem to be related to the composition of rainfall in the coastal area, which is likely to be strongly influenced by seaspray (see Section 4.2.1.3.3.2).

Salt marsh geochemistry is directly dependent on salt water influence, because of frequent flooding. Thus, high levels of Na (1.6%), Cl (1.5%), S (2.03%), Br (274 ppm) and I (38 ppm) reflect the marine influence, while high ash contents (mean ash 58.5%) are indicative of frequent flooding and trapping of fines by salt marsh plants. Although I concentration in sea water is less than the typical crustal average (0.06 ppm

as opposed to 0.5 ppm - Mason and Moore, 1982), high I concentration in the muck is most likely attributed to tidal flooding and subsequent bonding of I with the organic matter and in evaporite minerals. Similar to I, Br has been reported in evaporite minerals (Bowen, 1979). While Na and Cl combine to form halite (see also Section 4.2.2.3.1), the availability of Fe and S in the presence of organic matter results in the formation of pyrite (see also Section 4.2.2.3.2). However, as discussed below in Section 5.6, brackish environments do not represent the only optimal site for pyrite formation.

5.5.10 Botanical composition

For the purpose of this study, plant species have been divided in two main groups, eutrophic and oligotrophic. Eutrophic plants, such as sedge, grass and brown moss grow under alkaline and minerotrophic conditions. Therefore, they dominate the peat-forming vegetation in the lagg zone and in the lower minerotrophic section of raised Petite Bog (sedge), in the salt marsh in Chezzetcook Inlet (grass), both in Nova Scotia, as well as in Keephills Fen, Alberta (mainly brown moss), and in the peat plateau bog, East Little Bear River deposit, Northwest Territories (mainly brown moss). *Sphagnum* species on the other hand are virtually the only plants surviving in acidic and oligotrophic conditions. They are only present at the surface of the wetlands studied in Alberta and Northwest Territories, while they constitute the main part of the peat sequence in the dome of Petite Bog (particularly core T2), reflecting the independence from nutrient and mineral-rich ground- and surface water, as peat accumulates above the groundwater table.

Thus, oligotrophic peats are characterized by low ash content and low elemental concentrations, since they obtain their water and mineral supply almost solely through precipitation. Minerotrophic peats, on the other hand, have a higher ash content and are enriched in most elements, when compared to oligotrophic peats, because they are largely influenced by ground- and surface water rich in minerals and ions. This was well illustrated in the case of the domed bog (Petite Bog), in which many elements (i.e. K, Si) were below detection limit in the oligotrophic peats composed entirely of *Sphagnum*, while they were in measurable concentrations in the minerotrophic peats dominated by *Carex*. However, there are many variations to this general rule. Elements with a strong affinity for the organic fraction are present in higher levels in low-ash (oligotrophic) peats, while they are rather depleted in ash-rich (minerotrophic) peats. Furthermore, pedogenic dust and anthropogenic activity contribute to elevated concentrations in surface peats (which were, in the present study, dominated by *Sphagnum* species).

5.5.11 Degree of humification

Increase of degree of humification can be determined in the field, using the Von Post humification scale (Appendix III) or microscopically, based on maceral analysis and reflectance measurements. This is particularly well illustrated in the case of the domed bog (Petite Bog., Nova Scotia), in which both macroscopic and microscopic methods were used. The low degree of humification in the oligotrophic peats (generally $H = 3$ or 4) coincides with low random reflectance values ($\leq 0.2\%$), while higher reflectance values ($\geq 0.2\%$) are measured in the more humified ($H > 4$) minerotrophic

peats (Figure 4.1). Furthermore, red textinite A is progressively replaced by gray textinite B with increasing depth, reflecting the increasing degree of humification. Near the bottom of the peat sequence, ulminite becomes more dominant, and is correlated with higher reflectance values. Lateral variations from the dome to the lagg zone, similar to those downcore are also observed. These reflect the increase of degradation with increasing minerotrophy. In the other wetlands studied, smaller vertical variations were observed microscopically, probably because peats are mainly minerotrophic and thus generally more decomposed.

Humification, which includes compaction, dewatering and decomposition of organic matter, results in an increase of the inorganic fraction at the expense of the organic fraction. Higher elemental concentrations were generally observed in humified (minerotrophic) peats, while levels were substantially lower in poorly humified (oligotrophic) peats. However, since increasing humification usually correlates with increasing ash content, increases of metal concentration may be essentially caused by higher ash contents and only indirectly related to increases in humification.

Whether organically bound elements accumulate or are lost during the process of organic matter decomposition can not be determined for certain from this study. As shown in Figure 5.5, peaks in degree of humification ($H \geq 7$) do not always coincide with peaks in concentration of Br, Cl and I (independent of ash content). However, when considered on a larger scale, elements having a strong organic affinity (Br, Cl, I and Se) are usually in lower concentrations in humified minerotrophic peats (in the lower part of the peat profiles); (Figures 3.15 and 3.16). Nevertheless, this may be essentially related to higher ash contents.

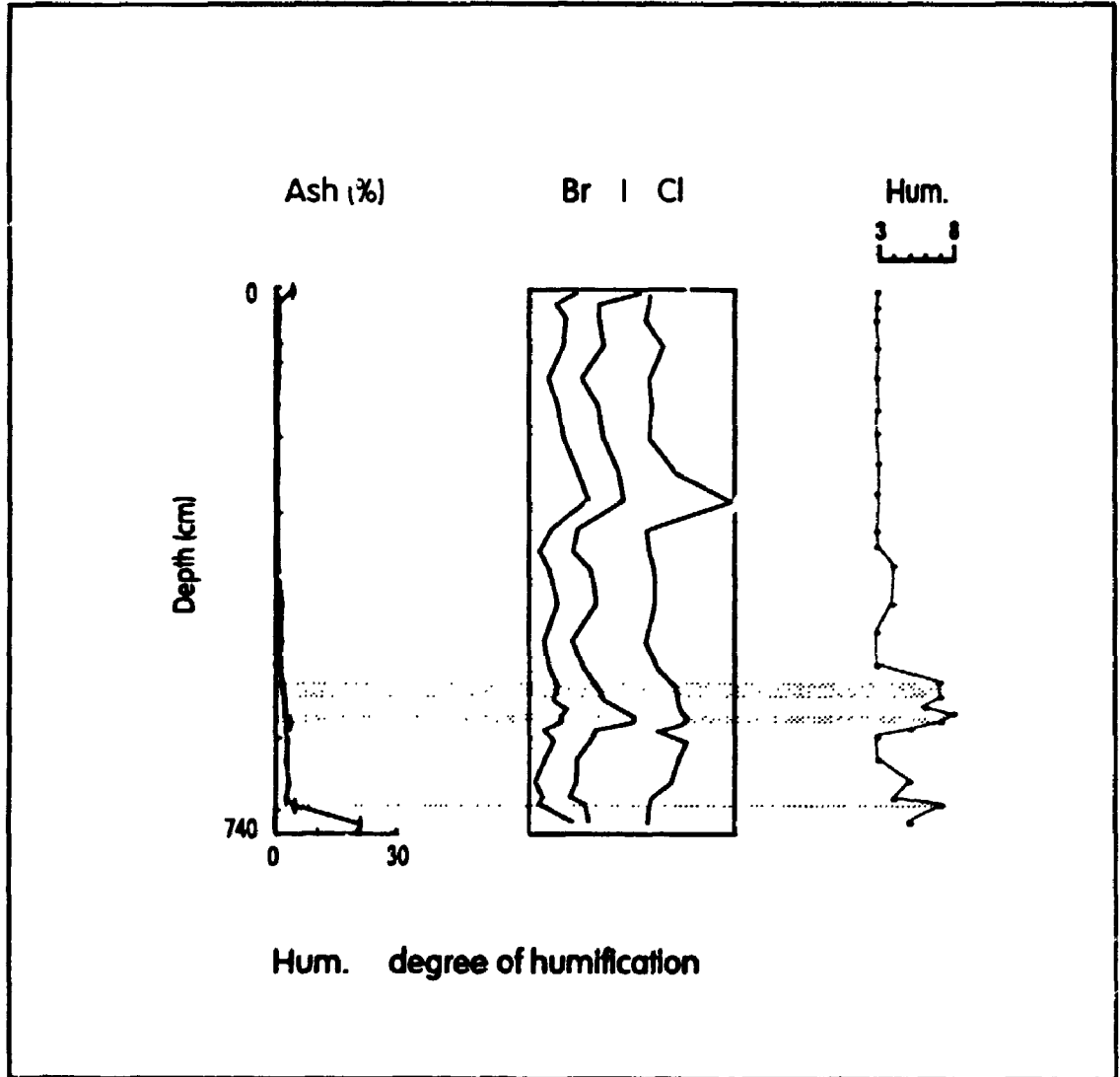


Figure 5.5 Relationship between ash, Br, I and Cl distribution, and degree of humification, core T2, Petite Bog, Nova Scotia.

5.5.12 **Anthropogenic pollution**

Metal enrichments were observed in the upper zone of the peat sequence in Keephills Fen as well as in the surface layer of muck in the salt marsh of Chezzetcook Inlet. These do not correlate with ash enrichments and thus can not be attributed to increase in ash content. Surface enrichments caused by input of pedogenic dust can be differentiated, since they correlate well with ash enrichment (i.e. Al enrichment in core T2, Petite Bog - Figure 3.11). Elevated surface levels caused by plant bioaccumulation were observed (see Section 5.5.7) but are also different, since enrichments are limited to the surface layer, in which the amount of living moss is greater (although fluctuations of the water table result in considerable accumulations at depths down to 0.40 m, and thus alter the general pattern). Furthermore, they are restricted to elements essential for plant nutrition, such as K and Mn.

Despite being taken up in plants, As, Sb, Th and V, for example, are not essential for plant growth (Kabata-Pendias and Pendias, 1992). Thus, unless growing in contaminated soils, plants usually do not accumulate these metals. As shown in Figure 4.7, surface enrichments of As, Sb, Th and V (and other elements) in Keephills Fen, are most likely to derive from coal mining and coal burning in Highvale mine and Transalta Power station respectively (located approximately 10 km upwind from the fen). Many elements are released into the atmosphere in the form of fine particulates or vapor, and transported by wind action before being deposited by wet or dry precipitation. Peats are very efficient in trapping atmospherically deposited particles, and thus their elemental composition can be used as a tool for monitoring the extent of atmospheric pollution.

Similarly, in the salt marsh, Chezzetcook Inlet, localized enrichments of Ba, Ni, Cr, Co and Mo were observed, which can probably be attributed to anthropogenic pollution (see Sections 4.2.2.4.2.1 and 4.2.2.4.2.2).

5.6 PYRITE OCCURRENCE IN FRESH- AND BRACKISH WATER PEAT-FORMING ENVIRONMENTS

Although it is generally believed that pyrite forms only in brackish and marine-influenced environments, the present study provides evidence of pyrite formation in a freshwater environment. While pyrite is often observed in brackish peats (e.g. Howarth, 1979; Raiswell, 1982; Altschuler *et al.*, 1983; Cohen *et al.*, 1983; Giblin and Howarth, 1984; Oenema, 1990), it has only rarely been reported in freshwater peats (see Shotyk, 1988, for a review). However, pyrite formation in freshwater lake sediments has been the subject of several studies (e.g. Davison *et al.*, 1985; Nriagu and Soon, 1985; Marnette *et al.*, 1993).

The main factors controlling pyrite formation are, availability of iron, sulfur and organic matter (see Sections 4.2.2.3.2 and 4.3.1.2.2). Furthermore, pH appears to be a limiting factor in pyrite production, as sulfate reducing bacteria are known to grow best at pH 6.5 to 8, although some have been found at pH 5.5 (Casagrande *et al.*, 1977). In brackish and marine environments, formation of pyrite is generally limited by the availability of organic matter (although it appears that Fe represents the limiting factor in salt marsh (Thomas and Varekamp, 1991)). In freshwater environments on the other hand, the availability of sulfur appears to be the major limiting factor.

In Keephills Fen, all conditions required for pyrite formation are satisfied in the organic-rich marl underlying the peat sequence: alkaline conditions, supply of

sulfate (groundwater), iron and organic matter availability, and the presence of oxic-anoxic surfaces. Marine-influenced peats generally have a higher sulfur content than freshwater peats (Casagrande *et al.*, 1977; Casagrande, 1984). However, in Keephills Fen, mean total S is approximately 1%, and ranges from 0.9% to 2.05% from a depth of 0.40 m downcore.

Therefore, this study provides evidence that pyrite formation is not only restricted to brackish peats, although pyrite does not appear to be as abundant in freshwater peats. Furthermore, the example of Keephills Fen shows that freshwater peats can result in high-sulfur coals, as opposed to the general belief that high-sulfur coals are usually directly associated with a brackish depositional environment.

5.7 PEAT AS A PRECURSOR OF COAL

The study of modern peat-forming environments helps in the interpretation of ancient coal deposits, and in the determination of coal characteristics. Many factors control the composition and preservation of peat (e.g. depositional environment, botanical composition, mineral matter, hydrology, fires, oceanogenic influence, etc.), and their interpretation is significant to the understanding of variations in coal deposits.

In the present study, five peat-forming environments were investigated. However, two of them, the salt marsh (Chezzetcook Inlet, Nova Scotia) and the Mackenzie River deposit, Northwest Territories, do not represent good precursors for coal, particularly due to their high inorganic content (and therefore low organic matter content). As postulated by Cohen *et al.* (1987), the precursor of a good coal should consist of at least 70% organic matter (on a dry weight basis), and the inorganic supply

and rate of decomposition should be low. The three other peat deposits on the other hand are theoretically more likely to produce coal. However, coal resulting from minerotrophic peat deposits (Keephills Fen and East Little Bear River Deposit) will have a relatively high ash content. Furthermore, Keephills peats will result in high sulfur coal (not desirable for combustion).

Based on the geochemical and petrographical data, it seems likely that the ombrotrophic peat deposit (Petite Bog, Nova Scotia) will produce a generally low-ash and low-sulfur humic coal. Although maceral analysis was qualitative rather than quantitative, it was shown that huminite (particularly textinite) was the dominant maceral, with only minor inertinite and liptinite. Therefore, it can be inferred that the resulting coal will be composed mainly of huminite or vitrinite, depending on coal rank (vitrinite is the bituminous equivalent of huminite in lignite and peat - Teichmüller, 1982).

Vertical and lateral variations in botanical (and petrographical), chemical and mineralogical composition, as well as pH, are interpreted as representative of changes from minerotrophic to ombrotrophic conditions within the deposit (see Sections 4.2.1.1 and 4.2.1.3.4). As shown by Calder *et al.* (1991), the evolution from minerotrophic to ombrotrophic conditions is also reflected in maceral composition of the resulting coal. Maceral composition is interpreted using a *groundwater influence index* (and *vegetation index*). The observed trend in maceral composition (based on vitrinite maceral determination) correlates with a reduction in ash content, and is indicative of decrease in groundwater influence. Thus, it can be inferred that variations within a single peat deposit may result in similar variations within the resulting coal bed (Figure 4 - Calder *et al.*, 1991). Furthermore, due to the strong relationship between peat

geochemistry and trophic status (and all dependent factors, such as botanical and mineralogical composition, pH and ash content - see Figure 4.5), the geochemical characteristics of peat are most likely to be reflected in the resulting coal. Petite Bog is of limited size and the resulting coal seam would be of limited extent, however, it can be used as a model for extensive peat deposits.

5.8 WETLANDS AND GLOBAL CLIMATE CHANGE

It has been shown in this study that peats act as sinks for airborne and waterborne elements. Due to their high content of humic compounds, peats are able to accumulate a number of elements, in concentrations higher than the mineral substrate on which they form. Furthermore, elevated elemental concentrations have been observed immediately above the permafrost boundary (Section 4.4.1.3.3) and in the zone of water table fluctuation (Section 4.3.1.3.2). Near-surface accumulations are also attributed to anthropogenic pollution (Sections 4.2.2.4.2 and 4.3.1.3.2).

Wetlands are fragile ecosystems, which are sensitive to exogenous variables (e.g. changes in temperature, fluctuations of the water table, and anthropogenic activities). Increases in temperature and decreases in water level (and permafrost table) have been shown to result in the evolution of wetlands from carbon sinks to carbon sources (see Section 1.4.3). Prolonged periods of drought resulting from a lowering of the water table may result in increased peat oxidation, fire activity and removal by eolian processes. Thus, elements associated with the organic fraction (such as Br, Cl, I and Se) are most

likely to be released into the atmosphere. Heavy metals on the other hand, which are mainly associated with the inorganic fraction, will be concentrated in the residual ash and may contaminate groundwater.

It is probable that lowering of either the water or permafrost table may cause the associated zones of elevated elemental concentrations to follow a similar pattern and migrate downcore. Wetlands cover a large portion of the land surface and represent major accumulations of elements. Thus, continued global warming may eventually result in a release of these concentrated elements into the environment (a changing role from sink to source), leading to fluctuations in the geochemical cycle.

CHAPTER SIX

CONCLUSIONS

Based on the organic petrological, mineralogical and geochemical study of five different peat-forming environments, the following conclusions can be drawn:

- 1) It is possible to develop a model based on the study of a domed bog, which shows the relationship between peat geochemistry and pH, botanical composition, degree of humification, reflectance and ash content: all of them being dependent on trophic conditions.
- 2) Lateral and vertical trends in degree of humification are reflected by similar changes in maceral composition and reflectance. Loss of fluorescence and red internal reflection of huminite macerals reflects an increase of the degree of degradation and generally correlates with increases of reflectance. While a distinct shift is recognized between ombrotrophic and minerotrophic peats in a domed bog, changes appear to be subdued in minerotrophic peat-forming environments. Abundance of pyrofusinite in certain intervals is indicative of periods of seasonal or episodic drought, and fire activity.

- 3) Peat acts as a sink for airborne and waterborne elements. Incorporation of tephra, which can be inferred from geochemical evidence, can help estimate the rate of peat accumulation. Anthropogenic pollution is particularly pronounced close to industrial areas. An oceanogenic influence is significant in coastal areas, and can also be recognized in wetlands at least 10 km inland.

- 4) The distribution of elements associated with the inorganic fraction (i.e. Al, Mg, Na, Si, K, Cr, V, Ba, Fe) can generally be explained in terms of mineral matter distribution. Elements associated with the organic fraction (Br, Cl, I and Se) are enriched in peat and usually decrease in concentration with increasing ash content. However, these general rules can be altered as a result of the interaction of a variety of natural and anthropogenic factors.

- 5) Elemental concentration and distribution are affected by many natural factors, such as depositional environment (i.e. geology and proximity to the marine environment), redox changes in the zone of water table fluctuation, permafrost, tephra incorporation, plant bioaccumulation, botanical composition, degree of humification, and to a limited extent, fire activity.

- 6) Br, Cl and I exhibit a strong affinity with the organic fraction of peat in freshwater peat-forming environments. As shown in Petite Bog, peat can accumulate Cl, Br and I from atmospheric sources in significant amounts. In the coastal salt marsh,

most of the Cl combined with Na to form halite, while Br and I appear to be present both in organic association and in evaporite minerals.

- 7) This study provides evidence of pyrite formation in both fresh- and brackish water peat-forming environments. Pyrite occurs as framboids and anhedral crystals in combination with organic matter. Associated fen peats are characterized by high sulfur levels, which are not typical for freshwater peats. This shows that high-sulfur coals can result from high-sulfur peats not necessarily associated with a brackish environment.
- 8) Substantial elemental enrichments are observed immediately above the permafrost boundary in perennially frozen peats demonstrating the influence of permafrost on peat geochemistry. Bearing in mind that more than 50% of the total wetland surface in Canada is perennially frozen, alterations of these environments could have serious implications for the geochemical cycle. It is therefore necessary for more research to be carried out in these areas.
- 9) Organic petrological, mineralogical and geochemical characteristics of a salt marsh differ greatly from those of freshwater peat-forming environments, due to an oceanogenic influence. Freshwater and brackish algae are abundant, and oxyfusinite constitutes the main inertinite maceral. Evaporite minerals and pyrite are common. Elemental distribution is mainly controlled by tidal flooding and anthropogenic influence.

- 10) Peatland processes are crucial to an understanding of coal formation. Peatlands represent modern analogues of ancient coal deposits, when considered from the standpoint of hydrological and trophic status, thus the study of the hydrological, mineralogical and geochemical variability can provide important insight into the spatial variability of ancient coals.

APPENDICES

APPENDIX I

GLOSSARY

- Aerobic:** Living or taking place in the presence of oxygen.
- Amorphous peat:** Highly decomposed peat which has no evident structure.
- Anaerobic:** Living or active in the absence of free oxygen.
- Ash content:** Percentage of inorganic matter remaining after combustion at high temperature ($> 750^{\circ}\text{C}$ in this study).
- Bog:** Peatland with the water table at or near the surface. The surface may be raised or level with the surrounding terrain. Bogs are hydrologically unique in that their surface waters have become isolated from the influence of nutrient-rich groundwater and surface water. As a result, bogs are oligotrophic acidic environments, dominated by *Sphagnum* peat.
- Brown moss peat:** Peat composed of various proportions of brown mosses, such as Amblystegiaceae, *Hypnum* and *Tomenthypnum*.
- Clayey/silty muck:** Mineral-rich well-decomposed organic sediment, accumulated under waterlogged conditions, characterized by a mineral matter content between 50 and 75%.
- Domed (raised) bog:** Oligotrophic peatland which has grown above its site of origin (sometimes several meters) whose center is higher than the margin and whose surface is convex.
- Eutrophic:** Refers to peatlands with high levels of plant nutrients (with correspondingly high primary productivity).
- Fen:** Peatland with the water table at or just above the surface. Minerotrophic environment "fed" by nutrient-rich groundwater and surface water. Acids produced via decomposition of organic matter are neutralized by dissolved mineral bases and a relatively high pH can be maintained. Fen peat consists mainly of moderately to well decomposed sedge and/or brown moss peat.
- Lagg:** (swedish term) Wet margin around a raised bog, characterized by eutrophic plant species.

- Marl:** Loose, earthy deposit of mainly calcium or magnesium carbonate, apparently accumulated in freshwater basins fed by carbonate rich groundwater or runoff.
- Marsh:** Mineral or organic wetland that is periodically inundated by standing or slowly moving waters varying from fresh water to highly saline. Nutrient-rich milieu, dominated by sedges, grasses, rushes and reeds.
- Mesotrophic:** Refers to peatlands with moderate nutrient availability and biological activity.
- Minerotrophic:** Nourished by mineral water. Refers to wetlands which receive nutrients from ground- and surface water in addition to precipitation.
- Mire:** Freshwater wetland system in which peat accumulates (equivalent of freshwater peatland).
- Muck:** Generally a mineral-rich, gyttja-like, well decomposed organic material, dark in color and accumulated under conditions of imperfect drainage, containing as little as 26% ash to as high as 75% ash (Jarrett System). In the OSRC (Organic Sediments Research Center of the University of South Carolina) System, the term muck is replaced by carbonaceous sediment.
- Muskeg:** Canadian term applied to natural and undisturbed areas covered more or less with *Sphagnum* mosses, sedges, and an open growth of stunted black spruce. The word muskeg is of Indian (algonquin) origin.
- Oligotrophic:** Refers to peatlands formed of plants growing under nutrient-poor conditions.
- Ombrotrophic:** Refers to peat and peatlands which receive their nutrient solely from precipitation (*ombros* = rain in Greek).
- Ooze:** Soft, soupy mud or slime, typically found covering the bottom of a river, estuary or lake.
- Oxalate:** Salt or ester of oxalic acid.
- Oxalic acid:** A crystalline solid (COOH)₂, that is slightly soluble in water. Oxalic acid is strongly acidic and very poisonous, and occurs in certain plants.

- Peat:** Unconsolidated deposit, consisting largely of organic residues, forming under waterlogged and anaerobic conditions through the incomplete decomposition of plant and animal constituents.
- Peatland:** Organic wetland, in which the rate of accumulation of organic matter exceeds the rate of decomposition, and that is characterized by a minimum thickness of 40 cm of peat (Canadian classification).
- Peat plateau bog:** Perennially frozen peatland with a low and generally flat surface, which is elevated above the water table of the surrounding wetlands.
- Peaty muck:** Organic material high in clay and silt, characterized by an ash content greater than 25% and less than 50%, and in which the original constituents are usually not recognized.
- Redox potential:** Measures the ability of an environment to supply electrons to an oxidizing agent or to take up electrons from a reducing agent.
- Rheotrophic:** Refers to wetlands which receive recharge from both groundwater and rainfall (see also minerotrophic)
- Sedge peat:** Peat material composed mainly of *Carex* plant material, or cotton grass *Eriophorum*, which are plants growing under minerotrophic conditions.
- Silty muck:** See clayey/silty muck.
- Sphagnum* peat:** Peat material composed mainly of *Sphagnum* plant remains, often poorly humified. Other plant material includes *Carex*, *Eriophorum*, shrub and wood fragments.
- Wetland:** Land that has the water table at, near or above the land surface or which is saturated with water for a long enough period to promote wetland or aquatic processes as indicated by hydric soils, hydrophytic vegetation and various kinds of biological activity, which are adapted to a wet environment (Tarnocai, 1980).
- Woody sedge/
brown moss peat:** Sedge/brown moss peat containing many woody remains of trees and shrubs.

APPENDIX II**SAMPLING AND ANALYTICAL METHODS**

- a) Sampling
- b) Sample preparation
- c) Ashing
- d) Sulfur analysis
- e) Organic petrology
- f) X-ray diffraction
- g) Instrumental Neutron Activation Analysis (INAA)
- h) Inductively Coupled Plasma-Mass Spectrometer (ICP-MS)
- i) Radiocarbon dating
- j) Cesium dating

a) **SAMPLING**

In all sites but one, samples were collected using an auger. The Macaulay, or Russian-type auger was used to collect samples from sites in Nova Scotia and Alberta. This type of auger is commonly used for sampling since it allows the collection of undisturbed samples at any depth, and contamination is prevented because the shuttle is closed when the auger is inserted into the peat and when withdrawn after sampling (Jowsey, 1966). Samples of perennially frozen peat from the bank of the Mackenzie River near Norman Wells, Northwest Territories, were collected using a 2 cm diameter modified Hoffer probe (Zoltai, 1978).

At the East Little Bear River deposit, Northwest Territories, peat blocks of approximately 10 cm³ were cut from the river bank by knife. Sampling of core 1 was performed by Dr. A. Duk-Rodkin in August 1990, while core 2 was taken by the author with the assistance of Dr. A. Duk-Rodkin in August 1991. In Keephills Fen, within-core samples were taken at intervals corresponding to naturally-occurring changes in peat composition, except for the top 50 cm, which were sampled at 5 cm intervals. Dr. L. Turchenek assisted the author for sampling. Three peat cores, varying in length from 1.70 to 7.50 m, were collected in Petite Bog, Nova Scotia. Dr. J. Calder, A. Anderson, W. Broughm and A. Beaton performed the sampling in July 1990. Samples vary between 10 and 60 cm thickness. In the salt marsh of the Chezzetcook Inlet, 2 cores were taken through the marsh sequence, and the size of within-core samples varies between 5 and 60 cm. Cores were taken by Dr. J. Calder and A. Beaton. Furthermore, 4 surface cores to a maximum depth of 20 cm were collected in August 1993 by the author. Samples vary between 2 and 5 cm thickness. At the Mackenzie River deposit, a core of 280 cm

length of mainly woody peat was taken, the sizes of within-core samples ranging from 5 to 10 cm. Dr. A. Duk-Rodkin assisted the author for sampling (August 1991).

All samples were subsequently packed in plastic bags and stored at room temperature prior to analysis.

b) SAMPLE PREPARATION

In the laboratory, samples were first dried at room temperature and then in a furnace at 50°C for approximately 16 hours.

A split of the samples was prepared for chemical analysis by crushing using a pestle and mortar, and were then ground using a Brinkman grinder to -100 mesh (149 µm). Another split was prepared for organic petrology: samples were crushed to -20 mesh (<850 µm), mounted in epoxy resin and polished according to the method of Mackowsky (1982).

c) ASHING

Both high and low temperature ashing were performed by B. Gorham at the Geological Survey of Canada in Calgary.

1. High temperature ashing

Prior to ashing, samples were dried in an oven at 105°C for 16 hours and the dry weight determined. Samples were then placed in the oven and the temperature was increased gradually by increments of 200°C every 2 hours up to a maximum of 1000°C.

in a oxygen rich environment to enhance combustion. The ash content was determined as the difference between the dry weight and the loss of weight on ignition. This represents the ash content on a dry weight basis.

High temperature ashing at 1000°C was undertaken in order to remove the organic content and therefore determine the mineral matter content of the peat, ooze, clay and silt material.

2. Low temperature ashing

Samples were dried at 105°C for 16 hours prior to ashing. Low temperature ashing consists of passing oxygen through a microwave field which creates a plasma field of activated oxygen (Andrejko *et al*, 1983). Peat material is oxidized at low temperature (approximately 110°C) by the activated oxygen without combustion. Samples were ashed for approximately 100 hours. Alteration and decomposition of the mineral matter are minimal with this method, allowing determination of the mineralogy by X-ray diffraction (clay minerals and naturally occurring reactive minerals); (Andrejko *et al*, 1983). However bassanite occurs in a number of samples as a result of the oxidation of the organic sulfur to SO₃ and subsequent production of sulfuric acid in the presence of moisture, that reacts with exchangeable Ca²⁺ (Jenkins and Walker, 1978) or due to dehydration of gypsum during low temperature ashing (Mitchell and Gluskoter, 1976).

d) SULFUR ANALYSIS

Prior to analysis, the samples were dried overnight at 105°C, in order to obtain the subsequent results on the dry weight basis. Analysis was performed by B. Gorham,

at the Geological Survey of Canada in Calgary. Total Sulfur analysis was carried out using a LECO SC-32 Sulfur Determinator, at a temperature of 1500°C, for a minimum acquisition time of 120 sec. The machine was calibrated using $1.68 \pm 0.04\%$ Sulfur coal standard. The samples were run in duplicate and the average of the two is reported, as % total sulfur on a dry weight basis.

e) **ORGANIC PETROLOGY**

Polished pellets were examined under a reflected light Zeiss MPM II microscope fitted with white (halogen 12V, 100W) and fluorescent (HBO 100) light sources, for reflectance measurements and maceral analysis.

1. Maceral analysis

Maceral analysis was carried out by using both white and HBO light (reflector FL05, blue violet excitation filter B.P. 400-440, chromatic beam splitter 460, barrier filter LP 470).

Macerals are in part coalified plant remains whose form and structure are usually still well preserved at the peat stage. The same terminology is used for both peat and lignite (Teichmüller, 1982). Macerals are divided in three groups, huminite, inertinite and liptinite macerals. In this study, a simplified classification will be given (Table II.1), for further details, the reader is referred to Teichmüller (1982).

The maceral group huminite (corresponding to the vitrinite for coals of bituminous and higher ranks) derives mainly from phlobatannin, lignin and cellulose of the plant material, and is divided into three maceral subgroups: humotelinite, humocollinite and

MACERAL GROUP	MACERAL SUBGROUP	MACERAL	MACERAL TYPE
HUMINITE	humotelinite	textinite A	phlobaphinite
		ulminite B	
	humocollinite	corpohuminite	
	humodetrinite	attrinite	
INERTINITE	fusinite	pyrofusinite	
	sclerotinite	oxyfusinite	
	inertodetrinite		
LIPTINITE	alginite		
	cutinite		
	sporinite		
	suberinite		

Table II.1 Maceral classification used in this study.
(Modified after Teichmüller, 1982).

humodetrinite. Humotelinites derive from intact cell walls, and humocollinite from cell fillings, while humodetrinites originate from cell detritus (Teichmüller, 1982).

In the humotelinite subgroup, textinite and ulminite can be distinguished, depending upon their degree of gelification. Textinite tissues are poorly humified and still resemble the original plant cell walls. According to Teichmüller (1982), 2 types of textinite can be distinguished: textinite A and textinite B. Textinite A is observed particularly in the samples of the peat surface layers, where the degree of humification is low. It is characterized by a extremely weak reflectivity under white light. This partially degraded plant material is often associated with a red internal reflection under reflected light (Plate 3.2a). Some cell wall material exhibits yellow-green fluorescence and no reflectivity at all in reflected white light (Plate 3.1a). This represents probably another type of textinite A (indicating a very early stage of humification). As humification progresses, the reflectivity is stronger and the fluorescence decreases (Textinite B); (Plate 3.2b). However, due to heterogeneity in the peat material and microbial attack, it is not unusual to observe in the same pellet humotelinite maceral at different stages of humification. Gelification results in the transformation of textinite to ulminite (Teichmüller, 1982). In general, humification of the peat material hardly reaches the gelification stage, so that ulminite is observed only in rare cases (Plate 3.6d).

Cell infillings at the peat stage are described as corpohuminites, which are part of the humocollinite subgroup. In this study the only corpohuminitic maceral identified was phlobaphinite. Phlobaphinite derives from phlobatannins that are found particularly in bark tissues and roots (Teichmüller, 1982). Therefore phlobaphinite is abundant in

woody peat (Plate 3.6e). Wood, roots and stems are usually better preserved than leaves, due to their content of highly resistant substances such as tannins and suberin (cork).

Humodetrinite macerals derive from humic detritus. In this study attrinite, which consists of loosely packed detrital particles in a humic gel, was identified.

The macerals of the inertinite group originate mainly from lignin and cellulose, similar to the huminite group. However, they undergo fusinitization caused by charring, oxidation, fungal attack or mouldering in the peat swamp (Teichmüller, 1982). In the peat material, pyrofusinite, oxyfusinite, sclerotinite and inertodetrinite were observed. Pyrofusinite formed as a result of ground fires in the peat deposit, and is characterized by thin cell walls, a yellow tint due to the very high carbon content and a very high reflectivity (Plates 3.1b and 3.1c). Oxyfusinites differ from pyrofusinites in that their cell structures are poorly preserved, and they are white in reflected light (Teichmüller, 1982); (Plates 3.3a and 3.3.b). They apparently form through dehydration and oxidation, or as a result of mouldering by wood-mouldering fungi (Teichmüller, 1982). The term sclerotinite is used for all strongly reflecting fungal remains, such as hyphae, mycelia, spores and *Sclerotia* (Teichmüller, 1982). As a protection against moisture and cold, fungi develop resistant bodies exhibiting multicelled rounded to elliptical shapes (Stach, 1982); (Plate 3.1d). Teichmüller (1982) postulates that *Sclerotia*, a form of fungal mycelia, attacks particularly *Graminae* and *Cyperaceae*. Therefore, sclerotinite is more abundant in sedge and reed peats, as observed in this study. Inertodetrinite consists of debris of other macerals of the inertinite group and of small plant remains decomposed and fusinitized within the peat (Teichmüller, 1982).

Liptinite macerals derive from hydrogen-rich plant materials, such as spores and pollen, cuticles, suberin, fats and oils. They are relatively stable during the coalification stage, since they do not undergo humification and gelification. The difference with the liptinite macerals in the coal is that they are usually preserved in their original form, because they were not compressed. Spores, pollen grains, algae, suberinite and cutinite were observed in this study. They show a high fluorescence under blue-violet excitation, due to their high hydrogen content. Cutinite (Plates 3.2c and 3.2d) originates from the cuticles of leaves and stems. Suberinite derives from suberin, which occurs mainly in bark, and at the surface of roots. It forms the cortex of roots and barks, while phlobaphinite represents the cell fillings (Plates 3.6a and 3.6b). Algae displays a strong green-yellow fluorescence (Teichmüller, 1982), and is distinguished by its particular shape (Plate 3.3c). Thin-walled microspores are common in all types of peat, as are thick-walled pollen grains (Plate 3.4b).

2. Reflectance measurements

Random reflectance measurements were taken using an oil-immersion objective ($n_{oil} = 1.518$ at 546 nm, 23°C), based on the procedure outlined in the International Handbook of Coal Petrography (ICCP, 1971). Macerals of the humotelinite group are commonly used for reflectance measurements in order to determine the degree of maturity of the organic matter. However, due to scarcity of macerals of the huminite group, most measurements were taken on phlobaphinite. Comparison measurements on huminite and phlobaphinite show that random reflectance measured on phlobaphinite is higher than that for huminite, as stated by Goodarzi (1987) and Cohen *et al.* (1987).

Goodarzi (1987) identified two types of corpohuminite in sub-bituminous coals of the Hat Creek deposit. One of them, called phlobaphinite type 2, is similar to the type of phlobaphinite found in the peat samples and has a higher reflectance than eu-ulminite. He concluded that, in absence of eu-ulminite, phlobaphinite type 2 could be used for random reflectance ($R_o\%$) measurements. However, the R_o values can not be used for rank determination based on the classification of Teichmüller and Teichmüller (1982), since they are higher than comparative data obtained on huminite, and would therefore suggest a higher rank.

Furthermore, reflectance data are usually based on 50 measurements. In this study, the number of measurements was limited to the availability of phlobaphinite and/or textinite, and therefore the reflectance values reported are merely indicative of a certain degree of oxidation or maturity.

f) X-RAY DIFFRACTION

The mineralogy of the samples was determined semi-quantitatively using X-ray diffraction at two different laboratories, Geological Survey of Canada (Calgary) and the University of Western Ontario (London). Samples submitted to XRD were either low temperature ash or unashed raw samples, as indicated (LTA or unashed sample). At the GSC, low temperature ashes were prepared on slides and were analyzed by a Philips PW1700 automated powder diffraction system using Cobalt radiation. The samples were scanned from 2 degrees to 64 degrees 2theta with a setting of 40KV-30 mA and with recording speed of 1 deg/cm/min. At UWO, the samples were prepared on slides and analyzed by a Rigaku Geigerflex D/Max-IIa automated X-ray diffractometer with a

curved single crystal graphite monochromator, Ni filter and a Cu-K alpha radiation source, (wavelength = 1.54178 angstroms), where they were scanned from 5 to 60 degrees 2theta. Below is a brief description of the method after Bloss (1971) and Zoltai and Stout (1984).

The powder method is based on the use of a polycrystal sample in the form of a powder and is performed primarily for identification of unknown minerals. A powder diffractometer records and converts the diffraction effects by an electronic detector. Each diffracted ray is recorded on diffractometer chart paper as a discrete peak, each height is proportional to diffraction intensity, whereas the peak's location on the chart corresponds to the ray's 2θ value. Since every mineral has a distinct chemical composition and structure, every mineral will have a distinct powder pattern. The locations of the diffraction peaks on the diffractogram provide the information necessary to calculate the interplanar spacings, and therefore identify the different minerals present in the sample. The peak heights are recalculated to 100% using the ASF (absolute scale factor), which allows the conversion of relative intensities to relative amounts of each mineral in a mixed powder pattern, thus providing semi-quantitative results in mineral percent (Zoltai and Stout, 1984).

g) INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

Neutron activation analysis is a method which allows the simultaneous determination of up to 36 elements on whole samples. The method is based on the instrumental measurement of the emissions from radioactive isotopes formed by various

elements following irradiation of the samples with neutrons. Irradiation was performed at the University of Illinois and counting in the Department of Earth Sciences at UWO. The method is briefly described below.

Small samples are encapsulated and submitted most commonly to thermal neutron irradiation, resulting in the formation of radioactive nuclei, which then decay to stable nuclei and emit decay gamma rays. These gamma rays, which are specific for each radionuclide, are measured and quantified using high resolution germanium detectors, and thereby allow identification and accurate quantification of the radionuclides present in the samples. Different isotopes decay with different half-lives, thus permitting the resolution of peaks which may have overlapping gamma-rays (Hoffman, 1992).

One of the main advantages of the method is the minimal requirement for sample preparation, which reduces the risk of contamination and errors.

h) INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETER (ICP-MS)

Analysis was performed at the ACT-labs in Mississauga. The ICP-MS instrument consists of an inductively coupled argon plasma interfaced to a quadrupole mass spectrometer. Samples, which are usually in solution form, are introduced into the plasma, where they are vaporised, atomised and ionized. A small portion of the ion stream passes through an interface into the mass spectrometer, where it is analyzed according to its mass. The mass spectrometer has a resolution between 0.5 and 1.0 atomic mass units (amu), so all isotopes are separated.

Simultaneous determination of most of the chemical elements, high sensitivity, short analysis time and ability to measure individual isotopes are the main advantages of this method.

i) RADIOCARBON DATING

Radiocarbon analysis of peat samples (T1-7 and T2-9) were carried out at Beta Analytic Incorporate (Beta), Florida, U.S.A., while the wood sample was analyzed at the Radiocarbon Dating Laboratory of the Geological Survey of Canada.

Radiocarbon dating is based on the formation of a radioactive isotope, ^{14}C , by the reaction of cosmic ray secondary neutrons with nitrogen of the atmosphere. The ^{14}C combines with oxygen to form radioactive carbon dioxide, which is taken up by living plants (and eventually animals). The living material has the same radiocarbon content as the atmosphere for as long as it is alive. The half-life of radiocarbon is taken to be 5568 years.

Peat samples were initially saturated with hot de-ionized water and subjected to hot acid washes to ensure the absence of carbonates. Furthermore, sample T2-9 was subjected to hot alkali washes to remove mobile secondary organic acids. Sample T1-7 was too small for this additional pretreatment. Samples were then combusted and the carbon dioxide obtained from combustion of the samples carbon was concentrated to benzene and measured for ^{14}C content. The wood sample (*Picea*) was submitted to hot base, hot acid and distilled water rinses before analysis.

After death, plants lose ^{14}C by radioactive decay, but cannot replenish it from the atmospheric reservoir. However, downward-migrating humic acids and variable ^{14}C

production in the upper atmosphere (DeVries effect) can cause age ranges of hundreds of years on samples which differ in calendar years by only decades (Stuiver and Pearson, 1986; Nelson, 1992).

Age obtained for sample T1-7 (980 ± 60 years BP) appears to be erroneous. Contamination by seeping groundwater (sample T1-7 is situated in the mesotrophic section of the core), bacterial activity (R. Sparks, pers. comm., 1994) may have caused the more recent than expected ^{14}C age in the sample. Furthermore, incorporation of mobile secondary organic acids can not be excluded.

j) CESIUM DATING

Analysis of marsh samples was performed by Dr. T. Hamilton at the Pacific Geoscience Center in Victoria, B.C. Caesium-137 is an artificial radio-isotope, and is the result of fallout from atomic-bomb testing and the occasional nuclear accident. It has a half-life of 30.2 years. Detectable concentrations can be dated to 1953-1954, and the peak of activity to 1963-1964, although other peaks can sometimes be resolved (e.g. 1956-1957, 1986-1987: Chernobyl - not recorded in Canada to date; Stihler *et al.*, 1992). A time lag of six to twelve months has been observed between fallout and deposition in sediments. Some corrections need to be made, such as variations in rainfall and delays in hemispheric exchange. The ^{137}Cs dating technique appears to be a useful dating tool in determining sedimentation rates over the past forty years in salt marshes. Sediment deposited on the marsh surface is stabilized by the dense vegetation. There appears to be little reworking and disturbance by bioturbation in this type of sediment (Delaune *et al.*,

1978). However, it has been shown in a few studies (Sholkovitz *et al.*, 1983; Varekamp, 1991) that post-depositional Cs mobility in the saline pore waters, diffusion and exchange may result in Cs redistribution in the sediment.

Counting the concentration of ^{137}Cs in sediments is by correlation as opposed to the conventional dating technique based on half-lives. Variations in concentration versus depth is compared to the fallout record with time, the best correlations coming from closely-spaced samples counted on a gamma ray spectrometer using the procedures after the method of Lewis (1974). ^{137}Cs concentrations are measured in picocuries per gram (pCi/g) of dried sediment (see Appendix IV). Counting errors were about 10% and concentrations of up to 3.26 picocuries per gram of dried sediment (marsh muck) were recorded.

Sedimentation rates based on the variable concentrations of ^{137}Cs in the sediment cores have been calculated based upon data shown in Appendix IV.

APPENDIX III

MODIFIED VON POST HUMIFICATION SCALE

(after Anderson and Broughm, 1988)

- H 1: Completely undecomposed peat which, when squeezed, releases almost clear water. Plant remains are easily identifiable. No amorphous material present.
- H 2: Almost completely undecomposed peat which, when squeezed, releases clear or yellowish water. Plant remains are still easily identifiable. No amorphous material present.
- H 3: Very slightly decomposed peat which, when squeezed, releases muddy brown water, but does not pass between the fingers. Plant remains are still identifiable and no amorphous material is present.
- H 4: Slightly decomposed peat which, when squeezed, releases very muddy dark water. No peat passes between the fingers but the plant remains are slightly pasty and have lost some of the identifiable features.
- H 5: Moderately decomposed peat which, when squeezed, releases very muddy water while a very small amount of amorphous granular peat escapes between the fingers. The structure of plant remains is quite indistinct although it is still possible to recognize certain features. The residue is strongly pasty.
- H 6: Moderately strongly decomposed peat with a very indistinct plant structure. When squeezed, about 1/3 of the peat escapes between the fingers. The residue is strongly pasty but shows the plant structure more distinctly than before squeezing.
- H 7: Strongly decomposed peat. Contains significant amounts of amorphous material with very faintly recognizable plant structure. When squeezed, about 1/2 of the peat escapes between the fingers. The water, if any is released, is very dark and almost pasty.
- H 8: Very strongly decomposed peat with a large quantity of amorphous material and very indistinct plant structure. When squeezed, about 2/3 of the peat escapes between the fingers and a small quantity of pasty water may be released. The plant material remaining consists of residues such as roots and fibres that resist decomposition.

- H 9: Practically fully decomposed peat in which there is hardly any recognizable plant structure. When squeezed, almost all the peat escapes between the fingers as a fairly uniform paste.
- H 10: Completely decomposed peat with no discernible plant structure. When squeezed, all the wet peat escapes between the fingers.

APPENDIX IV**a) Geochemical data**

In Tables 1 to 13, INAA data and ash contents are given versus depth in each core.

n.d. = non determined

<0.10 (% or ppm) = below detection limit of 0.10 (% or ppm).

Tables 14, 15 and 16 give the correlation coefficients of major and trace elements for the salt marsh, Chezzetcook Inlet (Nova Scotia), Keephills Fen (Alberta), and peat samples (Petite Bog, Nova Scotia and East Little Bear River deposit, Northwest Territories - $n = 73$), respectively.

Table 1 Core T1, Petite Bog, Nova Scotia

Depth cm	Ash %	Al %	Br ppm	Ca %	Cl ppm	Cr ppm	Fe ppm	I ppm	K %	Mg ppm	Mn ppm	Na ppm	Se ppm	S %	Si %
10-35	0.9	0.10	20.8	0.08	408	9.1	590	5.4	<0.10	81	21.5	287	2.0	0.13	0.0
35-70	0.4	0.08	18.1	0.04	342	2.9	488	5.3	0.00	40	13.6	203	1.6	0.06	0.0
70-100	0.3	0.05	17.3	0.03	278	2.3	368	5.0	<0.08	75	25.6	217	0.8	nd	1.5
100-140	0.3	0.06	23.2	0.05	353	2.9	750	6.4	0.00	70	20.3	188	<0.6	nd	0.0
140-165	0.5	0.05	20.8	0.07	334	2.5	1688	7.3	0.00	35	29.1	188	0.6	0.00	0.0
165-200	1.2	0.14	33.3	0.08	617	1.7	3680	13.6	0.00	44	61.3	137	0.3	nd	0.0
200-220	4.2	0.73	58.5	0.07	980	9.9	3160	15.9	0.14	220	58.6	232	0.7	0.17	1.4
220-230	9.1	1.73	37.1	0.09	619	24.7	4470	9.7	0.36	528	120.5	473	0.8	0.13	1.9
230-250	6.2	1.22	43.7	0.10	582	16.3	5190	11.7	0.14	374	94.5	252	0.8	0.23	1.9
250-260	7.6	1.67	34.5	0.11	459	17.8	6550	9.2	0.20	503	123.2	273	0.8	nd	1.7
260-270	53.4	8.40	25.7	0.11	257	142.4	13480	8.2	1.42	2700	139.1	1760	0.0	0.10	14.0
270-280	31.3	5.23	26.3	0.11	329	91.0	8970	7.4	0.87	1559	135.8	1140	1.4	0.24	9.7
280-285	72.7	7.71	5.9	0.10	126	111.1	10160	2.6	1.88	2370	141.6	3730	0.0	0.10	27.5
285-300	88.2	8.53	<5.1	0.10	100	133.3	21610	<1.3	2.12	2770	279.7	5000	0.0	0.27	33.9

Table 2
Core T2, Petite Bog, Nova Scotia

Depth cm	Ash %	Al %	Br ppm	Ca %	Cl ppm	Cr ppm	Fe ppm	I ppm	K %	Mg ppm	Mn ppm	Na ppm	Se ppm	S %	Si %
0-10	4.1	0.33	36.8	0.11	420	13.9	2150	14.9	0.11	149	50.2	425	2.3	0.09	1.0
10-30	0.7	0.08	24.6	0.05	401	4.1	329	9.0	0.00	79	3.6	186	0.7	0.12	0.0
30-50	0.8	0.11	30.7	0.07	390	2.5	493	9.0	0.00	86	4.7	203	0.8	0.08	0.0
50-102	0.8	0.12	28.8	0.12	582	3.9	515	9.6	0.00	104	6.2	270	3.2	nd	0.0
102-140	0.6	0.08	19.9	0.08	400	1.5	372	6.6	0.00	72	4.3	185	1.4	0.07	0.0
140-175	0.4	0.05	25.7	0.07	444	1.9	430	8.9	0.00	89	5.3	235	1.0	nd	0.0
175-225	0.4	0.10	28.7	0.07	401	<1.6	220	9.5	0.00	60	3.2	228	0.8	0.05	0.0
225-270	0.5	0.08	37.3	0.09	750	1.4	273	11.7	0.00	97	7.8	186	0.9	nd	0.0
270-300	0.4	0.08	43.6	0.10	1420	0.0	225	12.5	0.00	93	10.6	189	0.9	0.10	0.0
300-350	0.4	0.05	21.7	0.10	370	<1.4	149	6.0	0.00	90	16.8	203	1.6	nd	0.0
350-380	0.5	0.08	15.0	0.13	407	2.3	320	5.4	0.00	84	19.5	244	2.0	nd	0.0
380-400	0.6	0.05	20.6	0.16	477	2.2	329	7.9	0.00	98	25.8	181	1.5	0.08	0.0
400-450	1.3	0.08	25.2	0.30	475	3.1	775	8.6	0.00	113	43.8	196	0.6	0.07	0.0
450-500	1.3	0.06	17.7	0.48	364	0.0	990	5.3	0.00	66	54.1	178	1.4	nd	0.0
500-520	1.0	0.04	20.3	0.53	513	1.4	1301	8.8	0.00	69	58.5	151	1.8	0.05	0.0
520-550	1.7	0.05	25.4	0.67	749	1.8	1770	8.7	0.00	76	58.9	152	0.9	nd	0.0
550-580	2.2	0.16	23.0	0.88	770	2.9	2520	9.7	0.00	116	77.7	155	1.2	0.09	0.0
580-575	2.3	0.13	31.2	0.78	811	2.7	3030	12.1	0.00	97	84.6	157	1.3	nd	0.0
575-580	2.6	0.25	27.2	0.75	887	15.6	2980	14.0	0.00	130	87.1	192	1.6	0.13	1.8
580-590	3.7	0.17	27.6	0.82	837	5.4	2900	13.8	0.00	126	88.9	189	1.1	nd	<0.9
590-600	2.5	0.09	17.8	0.89	533	1.6	2890	8.6	0.00	100	91.6	163	1.1	0.11	0.0
600-620	2.7	0.11	23.1	0.89	873	2.3	3090	7.8	<0.08	87	81.2	216	1.1	nd	0.0
620-650	2.6	0.07	17.9	0.94	769	1.6	3470	5.9	0.00	87	95.9	145	0.8	0.12	0.0
650-680	3.1	0.11	12.4	0.97	690	1.4	4280	5.8	0.00	92	116.1	187	1.1	nd	0.0
680-690	2.5	0.10	16.9	0.77	427	1.7	3710	5.0	0.00	75	94.9	179	1.0	0.15	0.0
690-700	4.6	0.45	14.8	0.99	403	6.3	5620	7.1	0.08	179	139.3	254	1.0	0.24	<1.0
700-740	21.0	1.52	34.8	1.17	388	33.9	10990	7.6	0.27	479	225.7	1760	1.7	nd	8.1
740-750	92.1	5.86	0.0	0.37	81	94.0	20370	1.7	1.37	1930	365.4	8100	0.0	0.17	38.3

Table 3 Core T3, Petite Bog, Nova Scotia

Depth cm	Ash %	Al %	Br ppm	Ca %	Cl ppm	Cr ppm	Fe ppm	I ppm	K %	Mg ppm	Mn ppm	Na ppm	Se ppm	S %	Si %
10-20	8.9	1.20	62.0	0.21	451	12	7080	16.3	0.13	372	316	307	1.0	0.40	3.4
30-50	17.6	3.50	39.2	0.21	450	37	6030	12.4	0.40	1097	160	647	1.0	0.31	4.4
50-60	6.8	1.35	34.0	0.23	544	14	4350	12.1	<0.08	432	119	278	1.2	0.27	1.2
60-70	5.3	1.02	46.9	0.23	650	12	4320	17.3	0.00	336	115	203	1.3	nd	0.0
70-85	3.3	0.71	39.2	0.28	442	6	4320	12.7	0.00	244	127	155	1.1	0.29	<1.2
85-100	2.8	0.49	24.8	0.33	322	5	4860	9.5	0.00	195	171	119	0.9	nd	0.0
100-115	3.5	0.61	29.0	0.36	328	7	5680	10.1	0.00	241	195	141	0.9	nd	0.0
115-140	4.8	0.93	22.6	0.33	413	12	5710	8.6	0.11	317	187	200	0.8	0.25	0.0
140-160	30.8	5.69	16.0	0.38	337	74	12620	5.2	0.65	1810	285	1020	0.0	0.25	5.6
160-170	80.4	10.77	0.0	0.42	61	66	6440	0.0	1.41	3380	347	4100	0.0	0.06	31.6

Table 4 Core CH1a, Chezzetcook Inlet, Nova Scotia

Depth cm	Ash %	Al %	As ppm	Ba ppm	Br ppm	Ca %	Cl ppm	Co ppm	Cr ppm	Fe %	I ppm	K %	Mg ppm	Mo ppm	Na %	Ni ppm	S %	S %
0-10	65.4	4.9	4.3	610	363	0.67	48500	137	281	3.1	58	1.9	2440	15.2	3.4	87	1.5	27.4
10-40	68.9	6.0	9.0	390	242	0.51	26700	12.5	109	3.5	45	1.6	2480	6.9	2.4	31	1.7	20.7
40-100	51.0	5.1	8.7	350	368	0.67	5280	11.7	83	3.5	44	1.7	2080	14.7	0.9	27	3.0	11.5
100-120	47.1	4.4	25.9	320	298	0.45	4100	18.2	69	4.9	43	1.5	1920	47.2	0.7	41	4.6	18.6
120-150	68.1	6.1	3.5	390	279	0.71	4900	11.9	103	3.1	46	2.1	2540	4.5	1.0	21	1.4	23.1
150-170	65.6	6.4	4.9	410	274	0.66	1460	10.2	99	3.0	47	2.2	2680	6.1	0.8	18	1.6	21.9
170-195	71.5	11.8	16.1	407	265	0.77	870	18.5	106	4.3	57	2.0	3360	<3.4	0.8	32	1.9	26.8
195-200	28.0	2.7	17.4	170	600	1.19	4980	14.1	44	2.2	49	1.0	1480	<5.0	0.8	0	2.9	8.2

Table 5 Core CH2a, Chezzetcook Inlet, Nova Scotia

Depth cm	Ash %	Al %	As ppm	Ba ppm	Br ppm	Ca %	Cl ppm	Co ppm	Cr ppm	Fe %	I ppm	K %	Mg ppm	Mo ppm	Na %	Ni ppm	S %	S %
0-30	77.2	5.6	7.9	520	241	0.51	20800	11.2	149	2.9	30	1.8	2440	<3.8	2.2	51	1.0	21.3
30-50	56.4	4.4	4.1	260	161	0.66	16600	7.3	68	1.7	19	1.2	1950	0.0	1.9	18	1.6	22.4
50-65	64.8	4.9	4.7	270	185	0.52	16700	9.2	75	2.3	26	1.8	2080	0.0	1.9	20	1.6	18.6
65-85	48.2	4.1	7.4	260	163	0.72	25400	5.1	48	0.7	15	1.1	1700	0.0	2.3	15	2.0	9.5
85-90	48.0	4.9	7.1	<230	94	0.84	18800	8.5	85	1.7	13	0.9	2000	0.0	1.8	27	1.4	16.5

Table 6 Core CH1b, Chezzetcook Inlet, Nova Scotia

Depth cm	Ash %	As ppm	Br ppm	Co ppm	Cr ppm	Fe %	Mo ppm	Ni ppm
0-4	22.8	14.9	910	3.5	3	0.65	8	12
4-8	48.9	6.6	474	5.9	37	1.26	18	16
8-12	53.2	7.9	543	6.7	36	1.57	15	19
12-15	60.5	9.2	477	8.3	44	2.11	23	27

Table 7 Core CH2b, Chezzetcook Inlet, Nova Scotia

Depth cm	Ash %	As ppm	Br ppm	Co ppm	Cr ppm	Fe %	Mo ppm	Ni ppm
0-3	56.6	48.4	496	77.7	37	3.54	56	63
3-6	58.8	56.5	538	25.2	42	3.59	31	25
6-9	69.9	18.6	307	9.7	51	2.54	15	23
9-12	61.7	13.8	556	9.9	52	1.92	16	32
12-15	69.7	22.7	451	13.1	54	2.39	18	29

Table 8 Core CH3, Chezzetcook Inlet, Nova Scotia

Depth cm	Ash %	As ppm	Br ppm	Co ppm	Cr ppm	Fe %	Mo ppm	Ni ppm
0-5	41.8	27.6	472	6.6	31	2.06	8	23
5-9	55.0	34.6	605	9.7	35	1.98	18	23
9-13	60.3	46.8	583	8.1	45	1.83	15	27
13-17	69.5	31.3	391	9.8	51	2.50	15	43
17-20	72.3	24.5	476	11.3	60	2.85	26	46

Table 9 Core CH4, Chezzetcook Inlet, Nova Scotia

Depth cm	Ash %	As ppm	Br ppm	Co ppm	Cr ppm	Fe %	Mo ppm	Ni ppm
0-3	44.2	13.9	532	4.8	29	0.98	13	17
3-6	58.7	73.0	4	7.0	40	1.53	14	21
6-10	58.5	16.6	426	8.5	40	2.06	25	21
10-14	56.7	15.3	414	8.3	42	2.09	30	21
14-18	63.0	16.8	359	9.9	43	2.58	27	28

Table 10 Keephills Fen, Alberta

Depth cm	Ash %	Al %	As ppm	Ba ppm	Br ppm	Ca %	Cl ppm	Co ppm	Cr ppm	Fe %	I ppm	K %	Mg ppm	Mn ppm	Na ppm	S %	Sb ppm	Se ppm	Si %	Th ppm	Ti ppm	V ppm
0.5	4.2	0.26	0.7	65	5	0.43	222	0.55	7.1	0.09	0.0	0.23	147	90	664	0.16	0.11	1.4	0.00	0.33	140	3.4
5-10	8.2	0.49	1.0	90	8	0.97	228	0.76	8.2	0.18	0.0	0.17	265	91	879	0.19	0.14	0.7	1.78	0.67	220	8.4
10-15	11.3	0.55	1.8	78	11	2.40	216	0.82	9.0	0.20	2.9	0.00	372	173	790	0.18	0.23	1.1	2.28	0.82	290	6.6
15-20	15.5	0.61	2.4	43	18	3.80	182	1.07	9.9	0.27	11.3	0.00	405	1060	1050	0.21	0.36	0.8	3.79	0.91	300	10.0
20-30	14.0	0.11	1.3	130	43	5.90	168	1.25	3.8	0.11	25.9	0.00	300	2820	555	0.34	0.22	0.8	0.00	0.37	<50	0.0
30-40	9.4	0.10	<0.6	42	53	4.00	118	0.23	3.4	0.05	18.3	0.00	289	132	384	0.47	0.10	1.0	0.00	0.14	70	1.4
40-50	12.1	0.13	0.5	41	30	5.00	104	0.41	2.2	0.07	11.3	0.00	273	56	439	1.17	0.02	1.3	0.00	0.22	65	3.2
50-90	11.0	0.11	0.0	44	33	4.40	101	0.28	2.7	0.04	12.2	0.00	286	93	413	1.28	0.03	0.0	0.00	0.21	78	<1.7
90-110	11.9	0.14	0.2	32	26	4.20	115	0.26	3.4	0.04	8.6	0.00	292	139	395	1.26	0.06	0.9	<1.19	0.20	85	2.5
110-150	10.9	0.12	<0.4	65	25	4.00	96	0.25	2.8	0.04	6.2	0.00	273	188	546	1.45	0.07	0.6	0.00	0.16	80	<1.5
150-171	14.5	0.16	<0.7	72	23	5.90	76	0.30	3.6	0.05	7.5	<0.19	325	323	700	1.28	<0.07	4.0	0.00	0.21	<50	<2.7
171-181	16.5	0.11	0.0	63	25	6.80	116	0.30	2.3	0.02	8.4	0.00	477	713	545	n.d.	0.05	0.7	0.00	0.07	<50	2.0
181-200	11.0	0.08	<0.5	43	19	3.90	64	0.30	3.4	0.02	3.5	0.00	315	202	715	1.45	<0.05	0.6	0.00	0.12	<50	1.4
200-224	19.9	0.08	0.0	88	15	9.20	58	0.22	2.5	0.03	4.1	0.00	312	390	716	1.49	0.05	0.0	0.00	0.13	47	<1.5
224-240	20.7	0.29	<0.3	56	11	8.80	64	0.32	2.7	0.06	5.7	0.00	356	492	1050	2.05	0.05	0.5	0.00	0.22	120	2.3
240-264	27.2	0.92	0.0	95	16	10.60	137	0.77	4.4	0.24	0.0	0.00	519	480	3640	1.42	0.19	0.8	4.46	0.43	200	<2.4
264-270	27.3	0.15	0.0	<30	18	14.30	119	0.33	2.2	0.04	<3.6	0.00	319	970	1120	n.d.	0.08	0.7	0.00	0.10	181	<2.5
270-280	22.3	0.10	<0.4	99	24	11.10	70	0.30	1.8	0.03	2.9	0.00	267	668	716	n.d.	0.10	0.8	<2.18	0.10	<50	0.0
280-290	21.1	0.06	0.0	97	16	10.70	111	0.28	2.9	0.02	4.2	0.00	301	599	1060	n.d.	0.13	2.1	0.00	0.06	<50	<2.1
290-306	44.1	0.04	0.5	134	9	31.10	290	0.14	2.5	0.02	<3.2	0.00	371	1070	565	0.91	0.04	0.4	0.00	0.05	<50	0.0
306-335	47.4	0.04	0.4	38	10	33.30	152	0.15	1.4	0.09	3.2	0.00	504	503	509	0.91	0.03	<0.2	0.00	0.06	<50	0.0
335-345	42.6	0.06	1.9	61	13	30.30	75	0.79	1.4	0.56	3.0	0.00	337	775	787	1.79	0.05	<0.3	0.00	0.09	<50	<1.6

Table 11 Core 1, East Little Bear River Deposit, Northwest Territories

Depth cm	Ash %	Al %	Ba ppm	Br ppm	Ca %	Cl ppm	Cr ppm	Fe %	I ppm	K %	Mg ppm	Na ppm	S %	Se ppm	Si %	Ti ppm
0-10	34.4	2.6	650	14.0	0.44	126	36.6	1.15	2.5	0.61	697	1790	0.12	1.4	11.3	1630
10-20	11.2	0.7	209	16.6	1.22	216	8.9	0.27	7.1	0.10	267	591	0.15	0.6	4.2	428
20-30	8.1	0.4	200	13.4	1.66	167	7.6	0.23	4.9	<0.06	224	298	0.19	0.7	1.2	220
30-40	13.2	0.7	282	11.8	1.61	144	9.8	0.24	5.5	0.18	303	516	0.16	0.8	4.2	570
40-50	8.3	0.4	194	9.3	1.94	80	6.8	0.15	3.6	0.00	238	235	nd	1.3	2.0	217
50-60	4.6	0.1	133	18.2	2.29	60	2.0	0.10	2.1	0.00	154	173	0.16	2.4	0.0	0
60-70	5.6	0.2	0	17.8	1.97	69	2.6	0.13	2.9	0.00	172	199	nd	0.0	0.0	0
70-80	6.2	0.2	111	12.8	2.03	123	3.3	0.13	2.1	0.00	147	233	0.19	1.3	0.0	0
80-90	5.5	0.1	0	19.2	2.26	62	2.8	0.11	<1.6	0.00	212	155	nd	1.2	0.0	0
90-100	8.0	0.3	116	19.3	1.42	99	4.5	0.16	2.0	0.00	178	234	0.77	1.5	1.7	230
100-110	8.5	0.2	130	23.6	2.03	126	4.6	0.11	1.7	0.10	178	151	nd	2.3	<1.5	<150
110-120	7.7	0.2	<60	20.1	2.11	84	5.2	0.13	2.3	0.11	118	201	1.21	2.7	<2.3	0
120-130	10.1	0.3	193	19.4	2.17	89	5.1	0.34	2.6	0.00	194	217	nd	2.5	2.8	0
130-140	25.9	0.5	223	5.4	0.69	32	7.2	0.41	1.3	0.12	177	344	1.47	2.1	2.0	301
150-160	88.7	5.5	1400	0.0	1.39	71	90.6	2.14	0.0	1.44	2070	5300	0.14	4.9	32.4	3350
170-180	91.9	6.7	1530	0.0	2.91	<50	82.3	2.41	0.0	2.29	2820	5820	0.14	1.0	34.8	4330

Table 12 Core 2, East Little Bear River Deposit, Northwest Territories

Depth cm	Ash %	Al %	Ba ppm	Br ppm	Ca %	Cl ppm	Cr ppm	Fe %	I ppm	K %	Mg ppm	Na ppm	S %	Se ppm	Si %	Ti ppm
0-10	26.0	2.0	570	9.7	0.41	141	44.7	0.76	3.5	0.48	641	1300	0.12	<0.6	11.9	1180
10-20	9.8	0.7	280	11.6	0.70	160	21.5	0.49	4.2	0.15	257	439	0.16	0.0	3.8	440
20-30	12.9	0.8	331	16.1	0.61	184	15.6	0.44	5.3	0.13	248	750	0.18	1.0	4.7	560
30-40	15.3	1.0	415	9.0	0.79	155	25.0	0.38	5.9	0.17	307	584	0.24	1.3	4.8	720
40-50	10.8	0.6	304	11.7	1.02	87	16.9	0.31	4.2	0.17	204	381	0.32	0.6	2.5	350
50-68	5.0	2.0	1000	43.9	3.81	336	58.5	1.06	10.8	0.48	710	1360	0.12	2.7	9.8	1020
68-70	3.0	0.2	0	11.8	1.95	68	4.5	0.15	0.0	0.00	179	397	0.15	1.4	0.0	0
70-90	5.2	0.1	0	13.1	1.98	83	7.0	0.18	2.7	0.00	228	438	0.23	1.2	0.0	0
90-110	9.4	0.3	108	14.7	2.24	116	13.0	0.35	<1.6	0.00	266	610	nd	1.4	0.0	220
110-115	11.1	0.3	324	14.4	2.97	93	16.2	1.15	1.9	0.00	219	378	0.58	2.1	0.0	0
115-120	20.8	1.8	515	7.8	1.76	80	33.4	1.23	2.5	0.43	663	1560	1.32	1.9	8.9	1040
120-125	62.4	5.4	1120	3.2	2.20	72	82.1	2.13	1.3	1.14	14.44	4240	0.68	1.5	24.3	2310
125-130	88.1	6.2	1310	24.6	2.64	66	108.3	2.71	0.0	1.62	2310	5070	0.13	1.0	34.4	3300

Table 13 MacKenzie River Deposit, Northwest Territories

Depth cm	Ash %	Al %	Ba ppm	Br ppm	Ca %	Cl ppm	Fe %	I ppm	K %	Mg ppm	Na ppm	S %	Se ppm	Si %
0-10	71.0	3.8	820	7.9	3.01	83	1.88	2.0	1.14	1840	5750	0.07	0.0	26.8
10-33	69.6	3.3	710	10.6	2.69	54	1.63	0.0	1.02	1400	4670	nd	<0.7	21.8
33-45	63.4	2.9	720	<6.0	3.44	62	nd	0.0	0.89	1400	3870	nd	nd	17.9
45-59	63.3	3.7	830	11.6	2.75	75	nd	<1.8	1.11	1580	4490	nd	nd	22.0
59-75	50.1	2.7	630	18.2	3.17	83	1.48	<2.2	0.83	1220	3840	nd	0.0	16.5
75-90	73.3	3.8	850	10.8	4.59	67	1.81	0.0	0.98	1580	5020	nd	0.0	24.5
90-131	44.3	3.1	650	10.9	3.24	63	1.53	1.6	0.80	1288	3170	nd	0.0	19.1
131-144	57.2	3.1	650	10.1	2.80	49	1.49	2.1	0.80	1280	3510	0.12	0.0	18.3
144-162	50.6	2.6	690	9.1	3.12	52	1.48	1.0	0.71	1165	2980	nd	0.0	14.1
162-183	24.3	2.2	620	11.3	3.23	70	1.09	1.8	0.52	1023	2030	nd	<0.7	12.3
183-203	34.3	3.4	750	6.6	2.67	62	1.75	0.0	0.95	1460	3970	nd	0.0	21.9
203-216	58.4	3.4	740	8.4	3.12	66	1.72	<1.5	0.90	1590	3710	nd	0.0	19.5
216-232	55.8	3.3	730	10.3	2.81	51	1.58	1.8	0.95	1363	3440	nd	0.0	22.6
232-250	52.2	2.5	530	15.1	2.82	52	1.16	2.5	0.55	1250	2700	0.11	0.0	14.0
250-280	35.3	2.5	530	12.0	3.19	76	1.24	2.0	0.50	1156	2850	0.11	0.0	13.5

Table 14 Correlation coefficients of major and trace elements, Chezzetcook Inlet, Nova Scotia

	Ash	Al	As	Ba	Br	Ca	Cl	Co	Cr	Fe	I	K	Mg	Mo	Na	Ni	S	Si
Ash	1.00																	
Al	0.63	1.00																
As	-0.00	0.06	1.00															
Ba	0.76	0.49	-0.19	1.00														
Br	-0.46	-0.20	0.10	0.05	1.00													
Ca	-0.64	-0.16	0.10	-0.44	0.52	1.00												
Cl	0.20	-0.28	-0.43	0.36	-0.22	-0.21	1.00											
Co	0.09	0.45	0.38	0.37	0.07	-0.00	-0.32	1.00										
Cr	0.43	0.18	-0.36	0.66	-0.37	-0.24	0.67	0.01	1.00									
Fe	0.45	0.50	0.10	0.49	-0.21	-0.37	-0.35	0.48	0.42	1.00								
I	0.19	0.41	0.31	0.57	0.69	0.08	-0.16	0.79	0.45	0.74	1.00							
K	0.77	0.60	-0.23	0.77	0.08	-0.42	-0.13	0.35	0.49	0.55	0.63	1.00						
Mg	0.81	0.93	-0.13	0.71	-0.18	-0.29	-0.12	0.42	0.44	0.53	0.51	0.79	1.00					
Mo	0.04	-0.11	0.47	0.17	0.28	-0.42	-0.11	0.62	-0.23	0.38	0.35	0.10	-0.08	1.00				
Na	0.35	-0.18	-0.53	0.39	-0.38	-0.32	0.98	-0.39	0.64	-0.37	-0.24	-0.08	-0.02	-0.20	1.00			
Ni	0.48	0.15	0.09	0.61	-0.11	-0.45	0.65	0.47	0.68	0.49	0.34	0.37	0.35	0.39	0.62	1.00		
S	-0.60	-0.24	0.83	-0.30	0.44	0.01	-0.41	0.51	-0.37	0.48	0.24	-0.24	-0.38	0.80	-0.53	-0.12	1.00	
Si	0.79	0.61	-0.23	0.73	-0.29	-0.44	0.21	0.33	0.65	0.44	0.38	0.67	0.79	0.07	0.29	0.60	-0.41	1.00

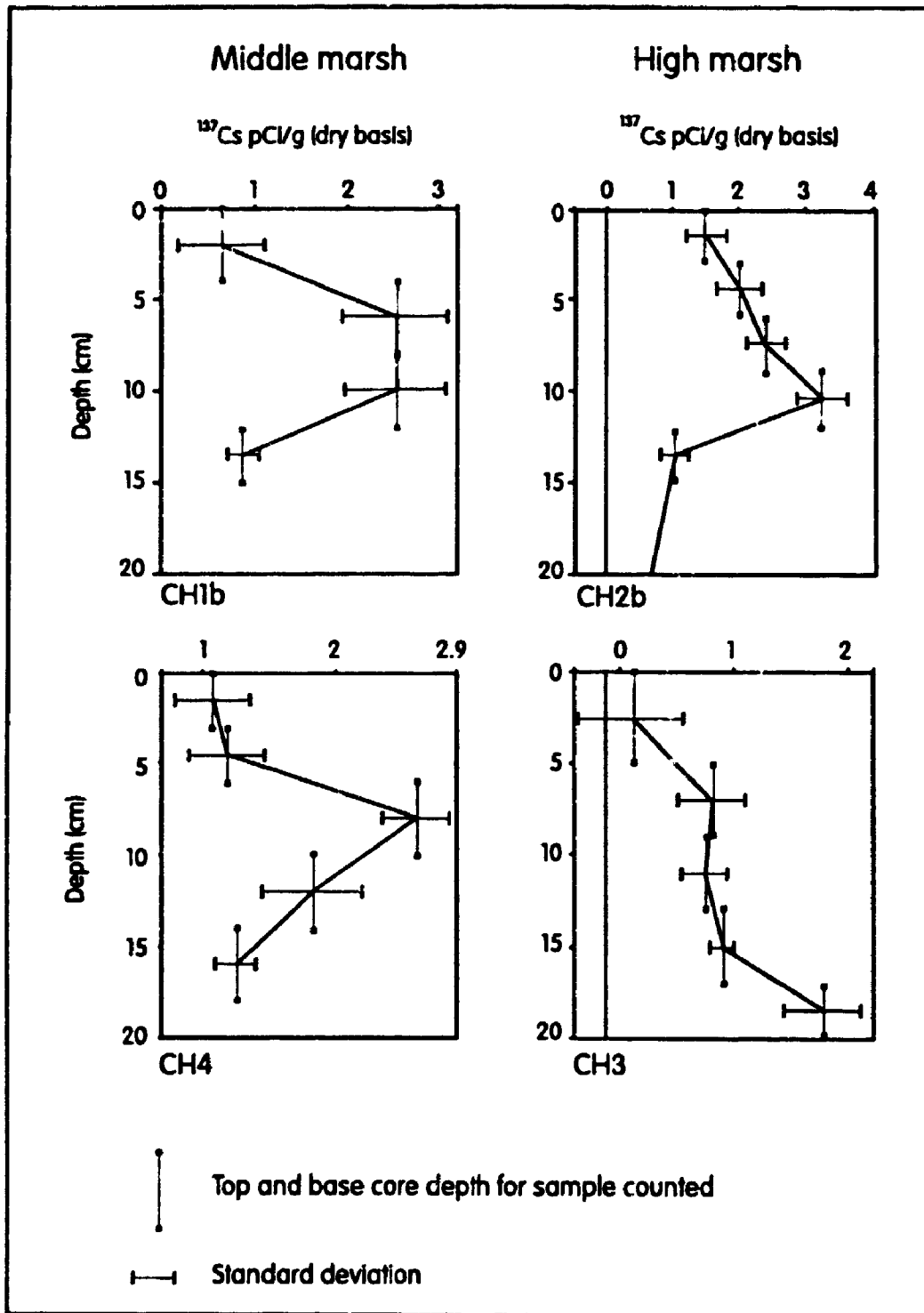
Table 15 Correlation coefficients of major and trace elements, Keechikwa Fen, Alberta

	Ash	Al	As	Ba	Br	Ca	Cl	Co	Cr	Fe	I	K	Mg	Mn	Na	Sb	Se	Si	Th	Ti	V	S	
Ash	1.00																						
Al	-0.18	1.00																					
As	0.02	0.33	1.00																				
Ba	0.17	0.08	0.09	1.00																			
Br	-0.36	-0.28	-0.15	-0.12	1.00																		
Ca	0.98	-0.31	0.02	0.16	-0.32	1.00																	
Cl	0.07	0.32	0.40	0.37	-0.32	0.10	1.00																
Co	-0.17	0.57	0.77	0.28	0.01	-0.22	0.34	1.00															
Cr	-0.48	0.70	0.63	0.05	-0.28	-0.51	0.58	0.62	1.00														
Fe	0.31	0.41	0.73	0.04	-0.26	0.29	0.10	0.64	0.28	1.00													
I	-0.31	-0.24	0.15	-0.01	0.85	-0.27	-0.12	0.30	-0.08	-0.15	1.00												
K	-0.37	0.16	0.08	0.08	-0.35	-0.31	0.36	0.12	0.45	0.02	-0.30	1.00											
Mg	0.55	0.37	0.02	0.01	-0.16	0.44	0.05	0.07	-0.07	0.22	-0.11	-0.46	1.00										
Mn	0.28	-0.09	0.30	0.48	0.23	0.25	0.19	0.53	-0.08	0.12	0.53	-0.26	0.17	1.00									
Na	0.18	0.76	-0.09	0.19	-0.25	0.03	0.02	0.30	0.16	0.32	-0.35	-0.05	0.48	0.03	1.00								
Sb	-0.22	0.66	0.05	0.23	0.01	-0.31	0.43	0.80	0.77	0.36	0.21	0.01	0.16	0.39	0.36	1.00							
Se	-0.33	0.89	0.62	0.06	-0.20	-0.43	0.44	0.72	0.80	0.42	-0.03	0.21	0.19	0.00	0.42	0.83	1.00						
Si	-0.29	0.04	-0.02	0.07	0.07	-0.06	-0.06	-0.00	0.15	-0.15	0.05	0.43	-0.18	-0.10	0.02	0.06	1.00						
Th	-0.08	0.90	0.38	0.12	-0.19	-0.20	0.27	0.54	0.62	0.41	-0.20	-0.04	0.41	-0.01	0.69	0.74	-0.03	1.00					
Ti	-0.38	0.79	0.70	0.06	-0.18	-0.45	0.48	0.75	0.94	0.40	0.04	0.25	0.09	0.04	0.25	0.83	0.06	0.73	1.00				
V	-0.27	0.83	0.49	-0.18	-0.31	-0.37	0.44	0.53	0.84	0.34	-0.20	0.19	0.13	-0.13	0.40	0.71	-0.05	0.73	0.87	1.00			
S	-0.41	0.67	0.61	-0.18	-0.29	-0.48	0.39	0.53	0.89	0.38	-0.13	0.33	0.01	-0.21	0.13	0.64	0.09	0.60	0.89	0.85	1.00		
	0.33	-0.27	-0.49	-0.19	-0.08	0.30	-0.76	-0.48	-0.74	0.01	-0.19	-0.41	0.18	-0.20	0.16	-0.64	-0.13	-0.29	-0.64	-0.51	-0.53	1.00	

Table 16 Correlation coefficients of major and trace elements in peat (n = 73)

	Ash	S	Al	Ba	Br	Ca	Cl	Cr	Fe	I	Mg	Mn	Na	Ni	Se	Ti	V
Ash	1.00																
S	0.34	1.00															
Al	0.86	0.06	1.00														
Ba	0.61	0.19	0.44	1.00													
Br	-0.18	-0.17	0.10	-0.15	1.00												
Ca	0.11	0.32	-0.09	0.38	-0.33	1.00											
Cl	-0.37	-0.38	-0.14	-0.18	0.59	-0.49	1.00										
Cr	0.86	0.05	0.96	0.55	0.05	0.02	-0.18	1.00									
Fe	0.41	-0.11	0.67	0.21	0.39	-0.33	0.26	0.57	1.00								
I	-0.25	0.35	0.05	-0.16	0.83	-0.54	0.74	-0.00	0.41	1.00							
Mg	0.87	0.07	0.99	0.46	0.06	-0.02	-0.17	0.96	0.63	-0.01	1.00						
Mn	0.48	0.24	0.54	0.41	0.29	-0.08	0.07	0.44	0.75	0.23	0.52	1.00					
Na	0.83	0.21	0.70	0.79	-0.08	0.19	-0.28	0.77	0.24	-0.18	0.73	0.42	1.00				
Ni	0.85	0.22	0.74	0.61	0.17	0.12	-0.19	0.82	0.75	0.10	0.74	0.50	0.91	1.00			
Sb	0.41	0.27	0.17	0.64	-0.27	0.62	-0.49	0.29	-0.39	-0.40	0.21	-0.03	0.57	0.47	1.00		
Se	-0.09	0.42	-0.22	0.12	-0.03	0.39	-0.16	-0.14	-0.32	-0.19	-0.20	-0.12	0.04	-0.08	0.17	1.00	
Ti	0.91	0.08	0.95	0.57	0.03	-0.04	-0.18	0.97	0.56	-0.01	0.96	0.46	0.82	0.83	-0.17	0.96	1.00
V	0.93	0.15	0.95	0.61	0.01	0.02	-0.24	0.94	0.50	-0.06	0.95	0.53	0.86	0.76	-0.15	0.96	1.00

b) Cesium data



Concentration of ^{137}Cs vs. core depth, cores CH1b, CH2b, CH3 and CH4, Chezzetcook Inlet, Nova Scotia.

High marsh, core CH2b

Sample#	Top (cm)	Base (cm)	Depth (cm)	¹³⁷ Cs pCi/g	s.d. %	Cs. max	Cs. min	dry wt. (g)
CG16	0.0	3.0	1.5	1.50040	18.05	1.77122	1.22958	4.50
CG17	3.0	6.0	4.5	2.03397	15.24	2.34395	1.72399	3.98
CG18	6.0	9.0	7.5	2.38913	10.04	2.62901	2.14927	6.10
CG19	9.0	12.0	10.5	3.25900	11.01	3.61782	2.90018	2.56
CG2'	12.0	15.0	13.5	1.05884	20.04	1.27103	0.84665	5.80
CH.-2	30.0	50.0	40.0	-0.02724	192.17	-0.07959	0.02511	31.70

Peak fallout concentration is >3.259 pCi/g of sediment.

Final sedimentation rate estimate based on 1964 fallout peak.

(10.5 ± 1.5) cm/(1993-1964) yr 0.362 ± 0.052 cm/yr 0.414 max

Sedimentation rate estimate based on 1953 onset of fallout

(22.5 ± 7.5) cm/ (1993-1953) yr 0.563 ± 0.188 cm/yr 0.375 min

Onset of fallout poorly constrained. Sedimentation could have been constant or slightly decreasing for the last 40 years.

High marsh, core CH3

Sample#	Top (cm)	Base (cm)	Depth (cm)	¹³⁷ Cs pCi/g	s.d. %	Cs. max	Cs. min	dry wt. (g)
CG7	0.0	5.0	2.5	0.10848	432.54	0.57770	-0.36074	2.07
CG8	5.0	9.0	7.0	0.81461	35.23	1.10160	0.52762	3.75
CG9	9.0	13.0	11.0	0.75219	26.66	0.95272	0.55166	5.82
CG10	13.0	17.0	15.0	0.90707	11.90	1.01501	0.79913	12.65
CG11	17.0	20.0	18.5	1.77479	18.73	2.10721	1.44237	3.62

Peak fallout concentration measured is >1.775 pCi/g of sediment.

Apparently neither the peak nor base of fallout was obtained. Deeper sampling required.

Minimum sedimentation rate, assuming 1964 = base of core,

rate > 0.690 ± 0.103 cm/yr.

s.d.% = standard deviation in %

dry wt. (g) = dry weight in g.

Middle marsh, core CH4

Sample#	Top (cm)	Base (cm)	Depth (cm)	¹³⁷ Cs pCi/g	s.d. %	Cs. max	Cs. min	dry wt. (g)
CG1	0.0	3.0	1.5	1.08126	26.22	1.36477	0.79775	3.90
CG3	3.0	6.0	4.5	1.19291	24.00	1.47921	0.90661	5.52
CG4	6.0	10.0	8.0	2.60656	9.88	2.86409	2.34903	5.50
CG5	10.0	14.0	12.0	1.82658	20.62	2.20322	1.44994	2.20
CG6	14.0	18.0	16.0	1.25554	12.11	1.40759	1.10349	8.50

Peak fallout concentration measured is >2.607 pCi/g of sediment.

Final sedimentation rate estimate based on 1964 fallout peak.

(8.0 ± 2.0) cm/(1993-1964) yr 0.276 ± 0.069 cm/yr 0.345 max

Sedimentation rate estimate based on 1953 onset of fallout

> 18.0 cm / (1993-1953) yr >0.450 cm/yr

The rate of sedimentation has apparently decreased in middle marsh.

Middle marsh, core CH1b

Sample#	Top (cm)	Base (cm)	Depth (cm)	¹³⁷ Cs pCi/g	s.d. %	Cs. max	Cs. min	dry wt. (g)
CG12	0.0	4.0	2.0	0.64213	74.38	1.11975	0.16451	1.59
CG13	4.0	8.0	6.0	2.53548	22.95	3.11737	1.95359	1.98
CG14	8.0	12.0	10.0	2.53126	21.54	3.07649	1.98603	1.99
CG15	12.0	15.0	13.5	0.86995	19.19	1.03689	0.70301	7.31

Peak fallout concentration measured is >2.53 pCi/g of sediment.

Final sedimentation rate estimate based on 1964 fallout peak.

(8.0 ± 2.0) cm/(1993-1964) yr 0.276 ± 0.069 cm/yr 0.345 max

Sedimentation rate estimate based on 1953 onset of fallout

> 15.0 cm / (1993-1953) yr >0.375 cm/yr

The rate of sedimentation has apparently decreased in middle marsh.

Equal rate to site CH4 near highway 107.

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