### GEOCHEMICAL AND MINERALOGICAL CHARACTERISTICS OF SOME FINE POST-GLACIAL MARINE DEPOSITS IN THE ST. LAWRENCE LOWLANDS

by

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A Thesis submitted to the Faculty of Graduate Studies and Research, McGill University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Geological Sciences.

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In memory of my father

#### ABSTRACT

The post-glacial marine transgressive clays of the St. Lawrence Lowlands potentially constitute a source of chemical elements to the suspended and dissolved loads of the lower St. Lawrence River. In order to better understand the nature of this source and its contributions, the present study investigates the mineralogy and the geochemistry of fine-grained deposits from the Champlain Sea and Goldthwait Sea deep-water facies. Sediments from the land sites and from horizons submerged under the estuary, and suspended matter from the lower river and estuary, are analyzed. An attempt is made to reconsider the chemical nature, the concentration as well as the distribution and origin of an "amorphous" phase reported earlier in the sensitive marine clays. Two different extraction methods are applied to two distinct fine (<2µm) size fractions. The extraction capacity differs with particle size and with the method used. However, the results from both methods correlate well, indicating a total amorphous content below 5% to 6% by weight, mainly composed of silica and of Fe and Al hydroxides. This amorphous phase represents a nonnegligible contribution to the major element flux of the St. Lawrence. Long-term experiments keeping the sediments in suspension show that the release of silica, Fe and AI takes place preferentially in fresh water, and is inversely related to the salinity. In nature, contributions of dissolved silica by this mechanism would be minor (<3% of the total dissolved silica load). The relationships between the mineral content and the chemical composition of the post glacial clays, as well as their variations with depth, particle size and location are examined. In the colloid-size fraction, an increase in illite and a decrease in feldspars with depth along two sections and one core raise the possibility of mild weathering in situ. This supported by trends of indices for mineralogical and chemical maturity. Compared to indices calculated for sediments in other major rivers, those for the post-glacial marine clays of the St. Lawrence are low.

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RÉSUMÉ

Les arglies déposées sur les Basses Terres du Saint-Laurent au cours des trangressions marines post-glaciaires représentent une source potentielle d'éléments chimiques pour la charge en suspension et la charge dissoute du bas Saint-Laurent. Afin de mieux définir la nature de cette source, la présente étude examine la minéralogie et la géochimie des dépôts fins appartenant aux faciès profonds de la Mer de Champlain et de la Mer de Goldthwait. Des sédiments provenant de sites émergés et d'affleurements submergés sous l'estuaire, ainsi que de la matière en suspension prélevée dans le fleuve et dans l'estuaire, sont analysés. On réexamine la composition chimique et la concentration, ainsi que la répartition spatiale et l'origine, d'une phase "amorphe" antérieurement identifiée dans les argiles marines sensibles. Deux fractions fines (<2µm) sont traitées par deux différentes méthodes d'extraction. La capacité d'extraction, qui diffère pour chaque méthode, est fonction de la taille des particules. On observe cependant une bonne corrélation entre les résultats des deux méthodes, qui indiquent un poids de matières amorphes ne dépassant pas 5% à 6%, composées essentiellement de silice et d'hydroxides de Fe at Al. Cette phase amorphe représente une contribution non-négligeable au flux d'éléments majeurs fournis par le Saint-Laurent. Des expériences au cours desquelles on a gardé des sédiments en suspension pour des périodes prolongées jusqu'à équilibre, démontrent que la libération de silice, de fer et d'aluminium prend place de préférence dans l'eau douce, et est inversement reliée à la salinité. En nature, l'apport en silice dissoute par ce processus est mineur (<3% en poids de la charge totale en silice dissoute). On a examiné le rapport entre la minéralogie et la composition chimique des argiles, ainsi que les variations de ces propriétés avec la taille, la profondeur et le site géographique. Dans la fraction colloidale, une augmentation de l'illite et une diminution des feldspaths en fonction de la profondeur dans deux sections et une carotte suggèrent la possibilité d'une certaine altération chimique in situ. On calcule des indices de maturité chimique et minéralogique qui supportent cette interprétation. Ceux-ci sont faibles en comparaison de leurs valeurs pour les sédiments d'autres grands fleuves.

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#### **ACKNOWLEDGMENTS**

I am greatly indebted to Professor Bruno d'Anglejan, Department of Geological Sciences, McGill University, for his advice and scholarly guidance in preparing this thesis.

I am grateful to professors Reinhard Hesse, Alfonso Mucci and Robert F. Martin, of the Department of Geological Sciences, McGill University, for their advice rendered during this study and to Professor V. Subramanian, SES, J.N.U., for taking keen interest in this work. I thank Professor Andrew J. Hynes, Chairman, Department of Geological Sciences, McGill University, for providing the necessary facilities.

I am thankful to Dr. H. Kodama, Agriculture Canada, for providing experimental facilities and to Professor N.G. Pisias, Oregon State University, Corvallis, for providing the computer program for the quantitative estimation of minerals.

My sincerest thanks must also go to a large number of other scholars and friends, who have helped me in one way or another, while researching and writing this thesis. In this respect, Messers R. Srinivasan, G. Biksham, M. Lucotte, H. Vali, J. Ko, S. Lorrain, R. Jagadish, G. Zhang, as well as Dr Anne de Vernal, N. Gonthier, and Christiane Valentin deserve special mention.

The technical advice and assistance by Mr. S.T. Ahmedali, Mr.R. Yates and Ms. G. Keating respectively, facilitated the completion of this thesis on time. I am thankful to them.

Finally I would like to acknowledge the financial support of the Association of Universities and Colleges of Canada.

Above all, the love and affection of my wife Sudha, has been instrumental in the completion of this thesis.

### PREFACE

#### 1. Statement of originality

This thesis presents the first comprehensive investigation of the geochemistry and mineralogy of the fine-grained post-glacial marine clays in the St. Lawrence Lowlands, and of these deposits significance as sources to the dissolved load and to the suspended sediments of the St. Lawrence River Basin. Previous studies have considered the bulk chemistry as well as the amorphous and mineral contents of the marine clays in the perspective of their mechanical properties, not in term of their geochemical contributions to fluvial input into the ocean. The present one addresses the question of the relationship between size and composition. While documenting in more detail the nature and concentration of the "amorphous" material reported in the post-glacial clays, it demonstrates that this fraction accounts for a chemically significant component of the total suspended sediments. The mobility of the main labile elements present in the amorphous fraction is examined in a series of controlled experiments in the laboratory which attempt to replicate natural conditions in the region of river water and sea water mixing. An improved knowledge of the quantitative mineralogy of these marine deposits and of their degree of maturity is obtained. Some evidence of incipient weathering alteration is provided. The implication is that fine-grained sediments which are the results of glacial processes are far from being geochemically inert, in spite of the low rate of chemical weathering generally associated with high latitudes.

This thesis consists in a series of three manuscripts, each representing an original

contribution to scientific knowledge in terms of study design, experimental work and conclusions. Collectively, the manuscripts contribute new knowledge on the nature of the source material of the present-day suspended and dissolved load of the St.Lawrence River.

#### 2. Historical background of relevant work

An extensive historical background can be found in the General Introduction, and in the introduction and text of each chapter.

#### 3. Declaration of assistance

The candidate acknowledges the contribution of Prof. Bruno d'Anglejan, for his supervision, guidance and advice rendered during the study, and his critical review of the three manuscripts. In accordance with section 7 of the Thesis Guidelines, the candidate declares that the study design, field and laboratory works, data analyses and interpretation, and writing of the manuscripts were done by the candidate alone.

#### 4. Thesis format

In accordance with section 7 of the Thesis Guidelines, this thesis has been prepared as a series of three manuscripts suitable for submission to refereed scientific journals for publication. For this reason, each chapter contains its own Abstract, Introduction, Materials and Methods, Results, Discussion, Summary and Conclusions, References, and understandably contains a certain amount of repetition. The connections between the chapters are implicit in the text. The present thesis format has been approved by the thesis committee.

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## **CHAPTER I**

#### **GENERAL INTRODUCTION**

The St. Lawrence Lowlands in the eastern part of Canada can be subdivided into three regions: the West St. Lawrence Lowland, the Central St. Lawrence Lowland, and the East St. Lawrence Lowland. The latter two subdivisions are of interest to this study. The Central St. Lawrence Lowland includes the area between the Ottawa and St. Lawrence Rivers and straddles the St. Lawrence River as far east as Quebec city. The East St. Lawrence Lowland extends through the St. Lawrence River valley and estuary northeast of Quebec to the Strait of Belle Isle and the west coast of Newfoundland.

During the last deglaciation (13,000 to 9000 y BP), the East and Central St. Lawrence Lowlands underwent major environmental changes related to a major marine transgression which invaded the St. Lawrence valley, forming the Goldthwait and Champlain Seas. These were arms of the Atlantic Ocean which projected inland into the isostatically depressed lower Ottawa and upper St. Lawrence valleys (Fig. 1). The Goldthwait Sea refers to the marine waters which covered the region east of Quebec city. The Champlain Sea applies to its westward extension after 12,500 y BP over the present lake Champlain and the Ottawa valley (Dionne, 1988). During this submergence, marine deposits accumulated over large areas of the St. Lawrence Lowlands. Isostatic adjustment following ice retreat caused the progressive emergence of the Lowlands and led to partial Figure 1. Map showing maximum diachronic extent of the Champlain Sea and western arm of the Goldthwait Sea downstream from Quebec (modified from Parent and Occhietti, 1988). Numbers refer to relative elevations in meters of known marine terraces above present sea level.

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exposure of these deposits to erosion by run off and by fluvial processes. A considerable portion of these sediments remain concealed under the present terraces and submerged under the St. Lawrence Estuary. They consist of a marginal facies, made up of interlayered coarse sands and silty clays, and a deep-water facies represented by massive light grey, commonly sensitive, fine clays (Gadd, 1986). The deep water clays, which essentially consist of rock flour released from the retreating glaciers, have provided a major source to the suspended inorganic load of the St. Lawrence River in Holocene time. They consist of a stiff light grey pelite characterized by an extremely fine grain size, more than 50% of the particles being smaller than 2  $\mu$ m (Loring and Nota, 1973).

This chapter first reviews the development of our understanding of the geochemical and mineralogical characteristics of these marine clays, particularly regarding the presence, amounts and composition of an "amorphous phase", and their exact mineral composition. The general objectives of this thesis are then presented. The remainder of this chapter reviews information gathered over the last two decades on the Late Quaternary history and stratigraphy of the St. Lawrence Lowlands and as well as its physiographic and geologic setting.

#### 1. Review of the amorphous material in post-glacial sediments

Amorphous matter refers to substances that are extremely small in size, and arranged in a crystallographic disordered state, as evidenced by the lack of a characteristic X-ray diffraction pattern. The possibility of oxides and hydrous oxides of Al and Fe serving as cementing agents in the eastern Canadian marine clays, and thereby

contributing to their undisturbed strength, has been recognized since the mid- 1960's (Kenney et al. 1967; Quigley, 1968). However, the origin of the amorphous matter in the marine clays is not well established. Sangrey (1972) proposed that these oxides were produced after deposition by the weathering of the relatively unstable amphiboles and pyroxenes. The experiments of Jones and Uehara (1973) and Kodama and Jaakkimainen (1981) indicate that mechanical grinding on a variety of silicate minerals produces an amorphous component rich in Si, Al and Fe. This would support the origin of part of the amorphous fraction in the marine clays as related to rock grinding under ice loads. Some of the oxides produced also might have flocculated and sedimented during transportation into the transgressive seas. Finally, the skeletal remains of organisms such as diatoms, radiolaria, and siliceous sponges could contribute to the amorphous silica.

The amount of amorphous matter reported in the post-glacial marine clays of the St. Lawrence Lowlands ranges between 2% and 25% by weight, depending on the extraction techniques used. These include: (1) the pH-dependent dissolution technique developed by Segalen (1968) (used by Yong <u>et al.</u> 1979; Locat <u>et al.</u> 1984); (2) the ammonium oxalate procedure of McKeague and Day (1966) (used by Kroeker 1985); and (3) the dithionite-citrate-bicarbonate (DCB) procedure of Mehra and Jackson (1960) (used by Torrance <u>et al.</u> 1986).

Yong <u>et al.</u> (1979) reported approximately 19-24% of amorphous material by the Segalen extraction procedure. Various authors (Bentley <u>et al.</u> 1980; Locat <u>et al.</u> 1984; Torrance <u>et al.</u> 1986) concluded that the Segalen procedure, which consists of eight alternating washings with 8N HCl and 0.5N NaOH, overestimates the proportion of

amorphous material in these sediments.

Torrance <u>et al.</u> (1986) extracted 0.54%  $Fe_2O_3$ , 0.07%  $Al_2O_3$ , and 0.16%  $SiO_2$  by a single DCB extraction. They obtained values of 5.8%  $Fe_2O_3$ , 6.3%  $Al_2O_3$ , and 15.9%  $SiO_2$  on the same material by the first four extractions of the Segalen procedure. They also determined, by X-ray diffraction, that chlorite had been completely removed and the illite content greatly reduced by the partial Segalen extractions.

The studies on the amorphous content of the post-glacial clays reported above were done because of the role it plays in determining the sensitivity and other rheological characteristics of these sediments. There are well-established relationships between the amorphous content and geotechnical properties such as liquid limit, plastic limit, undisturbed and remoulded strength (Yong <u>et al.</u> 1979; Locat <u>et al.</u> 1984).

The results of the analyses made to date indicate that our understanding of the nature, abundance and distribution of the amorphous material reported still remains rudimentary, mainly because its determination relies on extraction procedures, the true effectiveness and selectivity of which are not well known. The evidence suggests that this amorphous component could consist of a continuum of poorly crystalline to truly amorphous matter mixed into the glacial "rock flour". Hence, its sensitivity to extracting solutions will depend on the strength of the reagents used.

So far, no attempt has been directed toward establishing the nature and the concentration of the amorphous material in the Goldthwait Sea clays, some of which are presently submerged under the St. Lawrence Estuary.

There remains a need to quantify the abundance of the "amorphous material" in

the post-glacial marine clays because: 1) the amorphous fraction appears to affect the mechanical properties of the so-called sensitive clays (Yong <u>et al.</u> 1979; Locat <u>et al.</u> 1984); 2) it could possibly represent, under present conditions of weathering, a significant source of major elements to the St. Lawrence drainage.

#### 2. Review of the mineralogy and mineral distribution in post-glacial sediments

The mineralogy of the Champlain Sea clays has been investigated by various researchers (Brydon and Patry, 1961; Liebling and Kerr, 1965; Brady and Dean, 1966; Gillot, 1971; Bentley and Smalley, 1978; Yong <u>et al</u>. 1979; Locat <u>et al</u>. 1984; Torrance, 1988) because of its influence on the geotechnical properties of the clays such as high sensitivity, liquidity index, etc.

Brydon and Patry (1961) examined Champlain clays from the Ottawa area. They reported no marked differences in mineralogy from one sample to another at a given site, or from one site to another. The main feature was that quartz, feldspars, amphiboles, micas and chlorites were found in the clay fractions as well as in the silt and sand fractions, and that the micas were not necessarily more abundant than the feldspars. Expanding lattice minerals present in most of their samples could not be precisely identified. Amphibole and feldspar were identified even in size fractions less than 0.2  $\mu$ m, and on this basis Brydon and Patry (1961) concluded that the samples had undergone little chemical weathering.

Liebling and Kerr (1965) concluded that quartz, albite, microcline and muscovite were predominant in the sand and silt fractions of the Champlain clays, and that

hornblende, biotite and calcite also occur in some samples. The principal minerals in the  $<2 \mu m$  fractions are illite, chlorite, vermiculite and montmorillonite.

Brady and Dean (1966), in more than 40 samples of clay and shale from Quebec, recorded a suite of minerals apparently similar to that identified by Liebling and Kerr (1965). They concluded that illite and chlorite were more abundant than quartz and feldspar.

Gillot's (1971) detailed mineralogical analyses of five samples of Champlain Sea clay revealed the same suite of minerals that had been recorded by previous investigators. Gillot confirmed the observation by Brydon and Patry (1961) that the material had undergone little chemical weathering.

Bentley and Smalley (1978) studied the mineralogy of six Champlain Sea clays from Quebec using X-ray diffraction, X-ray fluorescence, thermogravimetry and selective dissolution analyses. They conducted separate analyses on the >2  $\mu$ m and on the <2  $\mu$ m fractions. Bentley and Smalley reported the following approximate mineral distribution: 23-27% quartz, 36-70% plagioclase, 10-19% K-feldspar, 1-5% illite; 1-3% chlorite, and 9-18% amorphous material in the coarser fraction; and 2-30% quartz, 22-49% plagioclase, 9-13% K-feldspar, 3-13% illite, 1-10% chlorite and 15-50% amorphous material in the finer fraction. The amounts of "amorphous" material reported seem very high. This raises the questions of what is meant by "amorphous", and of what is extracted in the procedures used for the determinations.

From a boring at Gatineau (Quebec), Yong et al. (1979) reported approximately 7-12% quartz, 8-13% feldspar, 8-18% hornblende, 30-40% illite, 8-11% chlorite, and 19-

24% amorphous material above 12 m depth; and 19-17% quartz, 10-13% feldspar, 16-21% hornblende, 23-27% illite, 3-7% chlorite, and 13-17% amorphous material below 13 m.

Locat <u>et al.</u> (1984) examined the mineralogy of the samples from Champlain, Goldthwait, Tyrell, Laflamme marine sea clays by X-ray diffraction using potassium metaperiodate (KIO<sub>4</sub>) as an internal standard. They reported that the mineralogical composition of the soils studied were dominated, even in the clay fraction, by felsic minerals (plagioclase, quartz, microcline, and hornblende) whereas samples close to the Canadian Shield contained relatively more felsic minerals than those away from it.

Torrance (1988) reviewed the mineralogy of the Champlain Sea and related sediments, and concluded that our knowledge of the quantitative mineralogy is not sufficient to be confident of the relative mineral abundances in these sediments.

Scant attention has been directed toward the mineralogy of the Goldthwait Sea clays presently submerged under the St. Lawrence Estuary (Locat <u>et al.</u> 1984) and of the St. Lawrence River and its estuarine suspended sediments (d'Anglejan and Smith, 1973; Konta, 1985). d'Anglejan and Smith (1973) found temporal and spatial variations in the mineralogy and chemistry of the St. Lawrence estuarine suspended particulate matter (SPM). The average clay mineral composition of the <2  $\mu$ m fraction was reported as 60% illite; 31% chlorite; 8% kaolinite and 1.5% montmorillonite. On a total-sediment basis, Konta, (1985) reported about 47% illite; 11% chlorite; 15% quartz; 4% K-feldspar; 17% plagioclase and 6% amphibole for the St. Lawrence River SPM.

Apart from these results, relatively few quantitative estimates of the mineralogy

were attempted, some being made on the bulk sediment, others on the clay size (<2  $\mu$ m) fraction. None of these studies provided a detailed mineralogy of the Goldthwait and Champlain Sea sediments and of its variations with depth, size and location.

The sediments supplied to the estuary under the present transport regime form only minor deposits in the Upper St. Lawrence Estuary, covering no more than 10% of the floor area. Most fine sediments supplied in suspension from the river are exported at a fast rate into the Lower Estuary and the Gulf of St. Lawrence (d'Anglejan, 1990). At present, the major input of solids to the St. Lawrence Estuary is the discharge of SPM by the St. Lawrence River at Quebec city. The average yearly suspended solid discharge is estimated to be 4 x  $10^6$  metric tons (Milliman and Meade, 1983). Biscaye (1964) and Griffin <u>et al.</u> (1968) summarized the clay mineralogy of the North Atlantic Ocean sediments and demonstrated that the chlorite and illite concentrations in these sediments between lat. 35 and 55° N has been greatly influenced by the runoff from the St. Lawrence River basin. Hence, the mineralogical and chemical compositions of the source material of the present-day suspended load of the St. Lawrence River need to be better known.

#### 3. General Objectives

The present study was undertaken with the following general objectives:

 To better qualify the exact nature, distribution and composition of the so- called "amorphous material" present in both the exposed and submerged post-glacial clay deposits and examine the possibility of its alteration under present weathering conditions.

- 2). To determine whether the quantity and mobility of the elements held in this amorphous fraction are such as to influence the water composition of the St. Lawrence River and Estuary.
- 3). To better characterize the mineralogical and chemical properties of the post-glacial marine clays, considered to be main source of the present day suspended load of the St. Lawrence River.

Throughout this work, comparisons are made between the subaerially exposed and the submerged deposits, and between these two and the inorganic suspended particulate matter (SPM) in the lower river and estuary. It is postulated that the exposed deposits may have been somewhat altered over time by ground water weathering or leaching effects, which may have modified their composition relative to the permanently submerged marine clays. The SPM, representing the modern solid load of the St. Lawrence River, is considered to be the end product of their erosion and transportation. Minor but diagnostic differences in composition between the SPM and its sources in the marine deposits are expected.

The analyses are restricted to the finer components of these deposits, which are separated into two distinct size fractions: clay-size (1 to 2  $\mu$ m) and colloid-size (less-than 1  $\mu$ m), as together they constitute the bulk (> 50%) of the deposits, and regroup the most surface active particles. They constitute the essential part of the rock flour produced during glacier ice movement. These two size fractions are also believed to have made up most of the fine suspended load carried over large distances into the deeper parts of

the transgressive seas. They represent the main portion of the suspended load exported to the Gulf of St. Lawrence and the Atlantic Ocean under the present regime.

#### 4. Physiographic and Geologic Setting

The part of eastern Canada which includes the St. Lawrence River and Estuary, and the Gulf of St. Lawrence, consists of several physiographic regions: the Laurentian region (Canadian Shield), the St. Lawrence Lowlands and the Appalachian region. These exhibit distinct topographical and geological characteristics. The nature and distribution of Quaternary deposits, the patterns of ice flow and retreat, and the history of occupation and regression of the Late Glacial water bodies in the Central St. Lawrence Lowlands were strongly influenced by the bedrock lithology and by the regional physiographic framework (Fig. 2). The bedrock consists of two major types: Precambrian metamorphic and igneous rocks, and early Paleozoic carbonates, shales and sandstones (Bear et al. 1977). Precambrian rocks occupy highlands to the north, south and west, whereas the Paleozoic rocks occupy the St. Lawrence Lowlands (Fig. 2) that extend southwestward into the Lake Ontario basin and eastward down the St. Lawrence River valley and the Appalachian highlands. A major structural boundary, known as Logan's line, runs parallel to the St. Lawrence Estuary separating undisturbed Ordovician rocks overlying the basement to the north from highly distorted beds of the same age to the south. This boundary approximately follows the centre of the estuary.

The St. Lawrence River basin provides most of the run-off which flows over the Champlain and Goldthwait Sea deposits. In relation to the 58 major rivers of the world,

Figure 2. Physiographic and bedrock map of the Central St. Lawrence Lowlands. Physiographic subdivisions after Bostock (1970); Bedrock geology after Sanford <u>et al</u>. (1979).



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the St. Lawrence River ranks 14th in the drainage area, 11th in average discharge rate and 35th in its yearly suspended load (Inman and Nordstrom 1971; Milliman and Meade, 1983). Its drainage basin is about  $1.03 \times 10^6 \text{ km}^2$ , of which  $0.5 \times 10^6$  lie in the province of Quebec. On the north shore, there are 13 tributaries of more than 200 km long. On the south shore, four rivers upwards of 200 km long enter the St. Lawrence River (Loring and Nota, 1973). The average flow of the St. Lawrence River at its source is about 7,700 m<sup>3</sup>/s. By the time it enters the estuary near Quebec city, the flow has increased to an average of 12,000 m<sup>3</sup>/s and can reach a maximum of 18,000 m<sup>3</sup>/s (Allan, 1988). The St. Lawrence estuary is subdivided on the basis of depth, circulation and hydrography, into the Upper Estuary, between Quebec city and the Saguenay, and the Lower Estuary, between the Saguenay and the opening into the Gulf of St. Lawrence near Pointe-des-Monts. They cover areas of 3,470 km<sup>2</sup> and 9,350 km<sup>2</sup>, respectively and have an overall length of 400 km. The total area is about 1% of the St. Lawrence drainage basin.

#### 5. Late Quaternary History of the St. Lawrence Lowlands

During late Wisconsinian, lobes from ice domes located to the north (Laurentian) and south (Appalachian) converged over the St. Lawrence valley (Dyke and Prest, 1987). The ice sheet attained its penultimate extent by 18,000 y BP. The northward retreat of the Wisconsin ice sheet led at about 14,000 y BP, to a marine transgression over the region of the Lower St. Lawrence Estuary known as the *Goldthwait Sea* stage (Dionne, 1977). Between 14,000 to 13,000 y BP, a calving margin retreated up the estuary to a stillstand position off the mouth of the Saguenay, thus leading to the separation of an Appalachian ice mass from the Laurentide ice. As this barrier disappeared near 12,800 y BP, the sea extended quickly over the present Upper St. Lawrence Estuary to Quebec city. The subsequent final retreat of the Laurentide ice sheet to the west at about 12,000 y BP caused the sea to spread over a basin of about 53,500 km<sup>2</sup> that occupied the isostatically depressed St. Lawrence Lowlands of Ontario, Quebec, New York and Vermont (Elson, 1969; Gadd, 1975; Cronin, 1977; Hillaire-Marcel, 1979). This submergence known as the *Champlain Sea* stage lasted for about 2000 years. The Laurentide ice withdrew from most of the Upper Estuary by 11,000 y BP and finally from the Laflamme Sea occupying the Saguenay region by 8400 y BP (Dyke and Prest, 1987).

The areal area extent of these marine basins underwent temporal changes that were controlled by three factors: 1) the retreat of the ice sheet; 2) the glacial isostatic recovery and, 3) the globally rising sea level (Parent and Occhietti, 1988). Since deglaciation, the isostatic recovery was very rapid. By 9000 y BP, about 85% of the coastal emergence had occurred (Dionne, 1990). Sea level curves from different locations along the south shore of the Estuary (Elson, 1969; Locat, 1977; Lortie and Guilbault, 1984; Dionne, 1988) indicate an exponential decrease in rates of emergence, from about 3 cm year<sup>-1</sup> between 13,000 to 9000 y BP, to less than 0.1 cm year<sup>-1</sup> at present. Dionne (1988) shows that emergence was not continuous on the south shore of the Upper Estuary, but included a sea level low stand of at least 5 m between 7000 to 6000 y BP, an 8 to 10 m transgression between 5800 to 4400 y BP. Sea level reached its present stand about 3000 y BP.

#### 6. Late Quaternary Stratigraphy of the St. Lawrence Lowlands

The Quaternary record of the east St. Lawrence Lowland was initially explored by boreholes on the south shore (Lee, 1962) and on the north shore (Chagnon, 1969; Rondot, 1974) of the Upper St. Lawrence Estuary. More comprehensive information has since been obtained by seismic reflection surveys (d'Anglejan and Brisebois, 1974; Syvitski and Praeg, 1989; Praeg <u>et al.</u> 1990).

In the North Channel of the Upper St. Lawrence Estuary, Syvitski and Praeg, (1989) and Praeg et al. (1990) found > 350 meters of glacial and post-glacial sediments. They have interpreted the acoustic data in term of four to five major stratigraphic units. These units relate to the advance and withdrawal of Late Wisconsin ice in the Estuary. They have interpreted these units as follows: Unit 1, as ice-contact sediments; Unit 2, as ice-proximal sediments; Unit 3, as Goldthwait Sea ice-distal fine-grained sediments which is 100's of meters thick; Unit 4, as glacial fluvio-deltaic sediments and Unit 5, as post-glacial estuarine muds and coarse lags. d'Anglejan and Brisebois (1978) identified exposed deep water marine clays of Goldthwait age in many regions of the Upper St. Lawrence Estuary.

The Late Quaternary stratigraphy of the glacial and post-glacial sediments of the Western St. Lawrence Lowlands, based on boreholes, microfaunal zones and textural analyses, has been described by Rodrigues (1987, 1988), Rodrigues <u>et al.</u> (1987), and Gadd (1977, 1986). The sediments are divided into four general stratigraphic units as follows: (1) a basal till; (2) rhythmically laminated silts and clays of freshwater origin ("varved sediments") (3) the Champlain Sea sediments and (4) post-Champlain Sea

deposits. At this stage, the relationships between the acoustic stratigraphy obtained under the estuary and the land stratigraphy are not well defined.

The origin of the rhythmites (unit 2), on land, is a subject of controversy. One interpretation favouring a glaciolacustrine origin is related to glacial lakes that expanded into the Ottawa Valley (Anderson <u>et al.</u> 1985). Another one supports a glaciomarine origin, probably without expansion of the glacial lakes (Gadd, 1988). The massive grey clay (unit 3) and the upper part of the gradational interval between units 2 and 3 were deposited during the Champlain Sea episode. The earliest marine deposits were deposited under conditions of highest salinity (30-34‰), with a gradual decrease in salinity (< 15‰) afterward. This conclusion is based on the distribution of salinity-dependent foraminiferal assemblages (Rodrigues and Richard, 1986).

Fine-grained sediments associated with deposition in the Champlain Sea reach thicknesses of about 100 m adjacent to and north of the present location of the Ottawa River (Fulton <u>et al.</u> 1986). These are located in the deeper parts of the basin, in areas where large quantities of fine grained sediment were supplied to the basin as ice retreated into the Laurentian Highlands.

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# **CHAPTER II**

### CONCENTRATION AND NATURE OF AMORPHOUS MATERIAL IN POST-GLACIAL SEDIMENTS OF THE ST. LAWRENCE LOWLANDS

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#### ABSTRACT

In order to document the concentration and chemical composition of amorphous material in the Champlain and Goldthwait Sea clays of the St. Lawrence Lowlands, sediment samples collected from the deposits exposed on land and from the deposits submerged under the Upper St. Lawrence Estuary, as well as samples of the present-day estuarine suspended matter were analyzed, using two different selective chemical extraction techniques. Si, Al, Fe, Ca, Mg, K, and Mn were extracted from the clay (2-1  $\mu$ m) and colloidal (<1  $\mu$ m) size fractions using dithionite-citrate-bicarbonate (DCB) and Alkali-Tiron solutions. Extractions capacity varies with grain size and also with the extraction method. Colloidal particles are enriched in amorphous matter by a factor of one to two, relative to clay-size particles. The sum of oxides of the elements measured (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, K<sub>2</sub>O and MnO) in the amorphous fraction varies from 0.66% to 4.88% and 1.49% to 6.60% by DCB and Alkali-Tiron chemical dissolution methods, respectively. Results obtained by the two methods correlate well. Transmission electron micrographs indicate the presence of irregular aggregates that are apparently amorphous in nature. These aggregates were absent after treatment with DCB and Alkali-Tiron reagents. The results suggest that the origin of the amorphous phase in the postglacial sediments is due to physical alteration of detrital minerals by grinding. Of the average 4x10<sup>6</sup> metric tons of suspended load introduced yearly by the St. Lawrence into the estuary, the amorphous fraction may account for a small, but non negligible amount (Si: 4 to 7x10<sup>3</sup> tons; Al: 3 to 7x10<sup>3</sup> tons; Fe: 25 to 45x10<sup>3</sup> tons; Ca: 25 to 27x10<sup>3</sup> tons; Mg: 2 to  $3x10^3$  tons; K:  $1x10^3$  tons).

#### I. INTRODUCTION

Post-glacial marine transgressive deposits of the Goldthwait and Champlain Seas (13,000 to 9000 y BP) constitute the main surficial material of the St. Lawrence Lowlands. These deposits consist of a marginal facies, made up of interlayered coarse sands and silty clays, and a deep-water facies represented by massive light grey, commonly sensitive fine clays. The fine-grained sediments of the Champlain Sea are derived predominantly from glacially ground Precambrian material from the Canadian Shield ("rock flour").

At about 12,000 to 10,000 y BP, the Champlain Sea flooded a basin of about 53,500 km<sup>2</sup> (Elson,1969) that occupied parts of the present-day lower St. Lawrence and Ottawa River valleys and of the modern Lake Champlain Lowlands (Fig. 1). The maximum depth of the sea varied between 250 meters north of Montreal and 55 meters south of Lake Champlain (Parent and Occhietti, 1988). Marine waters receded diachronously between 10,000 y BP in the Ottawa Valley, which is in the westernmost part of the basin, and 9,300 y BP, near Quebec City to the east. In the emerged portion of the St. Lawrence Lowlands, the deposits left by the former seas have thicknesses ranging from 10 to 61 meters. Seismic reflection surveys of the Upper St. Lawrence Estuary (Syvitski and Praeg, 1989) indicate accumulation of 200 meters or more of marine clays over glacial tills and the bedrock. These clays commonly lie under only a thin cover of Recent sediments. At some places they crop out on the channel floor. A

Figure 1. Map showing maximum extent of the Champlain Sea and sampling locations (\*)of the exposed deposits.


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thickness of more than 150 meters has been recorded under the Laurentian Trough of the lower estuary. Erosion of the post-glacial marine deposits as a result of the post-glacial isostatic rebound has provided a major source of fine suspended sediments for the St. Lawrence River in Holocene time.

The presence in the Champlain Sea clays of disseminated, poorly crystalline to amorphous matter, commonly referred to in the geotechnical literature as "amorphous matter", has been demonstrated by several workers (McKyes <u>et al.</u> 1974; Bentley and Smalley 1978; Yong <u>et al.</u> 1979; Locat <u>et al.</u> 1984). It has been proposed by these authors that the amorphous material functions as a bonding agent. Thus, a high content of amorphous matter correlates with low sensitivity. They have shown that this amorphous material profoundly affects the geotechnical properties of the transgressive marine clays, such as, liquid limit, plastic limit, undisturbed and remoulded strengths. Chemically, it appears to mainly consist of a mixture of silica and hydroxides of Al and Fe (Quigley, 1980).

However, the composition and the distribution of the amorphous component in the post-glacial sediments is not yet well determined, and there remains a need to do so because: 1) this component affects the mechanical behaviour of the so-called sensitive clays (Yong <u>et al.</u> 1979; Locat <u>et al.</u> 1984); 2) it could possibly represent, under present conditions of weathering, a significant source of major elements to the St. Lawrence drainage.

This paper reexamines the composition and distribution of the "amorphous" fraction in the Goldthwait Sea and Champlain Sea sediments by comparing results

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obtained by two "mild" extraction procedures. We chose to compare the DCB extraction of Mehra and Jackson (1960), the most selective of the previously used techniques, with the Alkali-Tiron dissolution technique of Biermans and Baert (1977). The latter was found by Kodama and Jaakkimainen (1981) to be the best method for the determination of the content of amorphous matter in mechanically ground mafic minerals (such as clinochlore, biotite, and hornblende).

These two methods of extraction were used on both the colloidal size (< 1  $\mu$ m) and clay size (1-2  $\mu$ m) fractions of the Champlain Sea sediments collected at three subaerially exposed sites in the Central Lowlands (Fig. 1). They were also applied to the analyses of the clay-size and colloidal fractions of Goldthwait deposits outcropping over the channel floor of the Upper St.Lawrence Estuary. Relict post-glacial marine clays of the Goldthwait or Champlain age mainly consist of a stiff light grey pelite characterized by an extremely fine grain size (more than 50% particles smaller than 2  $\mu$ m) representing a deep water depositional facies (Loring and Nota, 1973). The two fractions are believed to have made up the bulk of the suspended load introduced into the transgressive seas. They are chemically the most reactive, and constitute the essential part of the rock flour produced during movements of the ice caps.

Finally, similar analyses were obtained on fine estuarine suspended sediments, considered to be representative of the end products of the suspended load of the present St. Lawrence River.

# **II. PREVIOUS WORK**

Amorphous matter refers to substances that are extremely small in size, and arranged in a crystallographic disordered state, as evidenced by the lack of a characteristic X-ray diffraction pattern. The possibility of oxides and hydrous oxides of Al and Fe serving as cementing agents in the eastern Canadian marine clays, and thereby contributing to their undisturbed strength, has been recognized since the mid- 1960's (Kenney et al. 1967; Quigley, 1968). However, the origin of the amorphous matter in the marine clays is not well established. Sangrey (1972) proposed that these oxides were produced after deposition by the weathering of the relatively unstable amphiboles and pyroxenes. The experiments of Jones and Uehara (1973) and Kodama and Jaakkimainen (1981) indicate that mechanical grinding done on a variety of silicate minerals produces an amorphous component rich in Si, Al and Fe. This would support the origin of part of the amorphous fraction in the marine clays as related to rock grinding during migration of the ice caps. Some of the oxides produced might have flocculated and sedimented during transportation into the transgressive seas. Finally, the skeletal remains of organisms such as diatoms, radiolaria, and siliceous sponges could contribute to amorphous silica.

The amount of amorphous matter reported in the post-glacial marine clays of the St. Lawrence Lowlands ranges between 2% and 25% by weight, depending on the extraction techniques used. These include: (1) the pH-dependent dissolution technique developed by Segalen (1968) (used by Yong <u>et al</u>. 1979; Locat <u>et al</u>. 1984); (2) the ammonium oxalate procedure of McKeague and Day (1966) (used by Kroeker 1985); and (3) the dithionite-citrate-bicarbonate (DCB) procedure of Mehra and Jackson (1960) (used by Torrance <u>et al</u>. 1986).

Yong <u>et al.</u> (1979) reported approximately 19-24% of amorphous material by the Segalen extraction procedure. Various authors (Bentley <u>et al.</u> 1980; Locat <u>et al.</u> 1984; Torrance <u>et al.</u> 1986) concluded that the Segalen procedure, which consists of eight alternating washings with 8N HCl and 0.5N NaOH, overestimates the proportion amorphous material in these soils.

Torrance <u>et al.</u> (1986) extracted 0.54%  $Fe_2O_3$ , 0.07%  $Al_2O_3$ , and 0.16%  $SiO_2$  by a single DCB extraction. They obtained values of 5.8%  $Fe_2O_3$ , 6.3%  $Al_2O_3$ , and 15.9%  $SiO_2$  on the same material by the first four extractions of the Segalen procedure. They also determined, by X-ray diffraction, that chlorite had been completely removed and the illite content greatly reduced by the partial Segalen extractions.

The results of the analyses made to date indicate that our understanding of the nature, abundance and distribution of the amorphous material still remains rudimentary, mainly because little is known about the true effectiveness and selectivity of the extraction techniques used to identify and remove it from the sediment. The evidence suggests that it could consist of a continuum of poorly crystalline to truly amorphous matter mixed into the glacial "rock flour". Hence, its sensitivity to extracting solutions will depend on the strength of the reagents used.

# **III. MATERIALS AND METHODS**

#### **III. 1. Field Sampling**

Subaerially exposed deposits were sampled along three stratigraphic sections (Saint-Césaire, Sparrowhawk Point, and Casselman) in the Central St. Lawrence Lowlands (Fig. 1). Submerged deposits were collected by gravity coring in the Upper St. Lawrence Estuary (Fig. 2). The core samples are identified as being of Goldthwait age on the basis of the sediment characteristic colour (bluish-grey) and textural properties, including high plasticity and fine grain-size (more than 50% by weight of particles <2  $\mu$ m). These properties make these sediments very different from modern estuarine deposits.

The above sections and the cores were subsampled at intervals of 5 to 10 cm. Samples of the estuarine suspended matter (Fig. 2) were collected in the turbidity maximum zone of the Upper St. Lawrence Estuary by continuous flow centrifugation.

#### III. 2. Analyses

Prior to size separation, the calcium carbonate in the sediment samples was dissolved (Jackson, 1969) using a 1N sodium acetate buffer (82 g of sodium acetate and 27 mL of glacial acetic acid, per litre, adjusted to pH 5.0), and the suspension centrifuged until the supernatant liquid was clear. Jackson (1969) notes that this treatment has no deleterious effects on the main clay minerals, but research is needed to ascertain whether or not it is entirely safe for amorphous oxide minerals. The residue, considered to

Figure 2. The Upper St. Lawrence Estuary: location of the core and suspended-sediment sampling stations.



represent the carbonate-free fraction, was separated into a sand fraction (>62  $\mu$ m), a silt fraction (2-62  $\mu$ m), as well as a clay (1-2  $\mu$ m) and colloidal fraction (< 1  $\mu$ m) by wet sieving and centrifugation, as described by Harry <u>et al</u>. (1984). Due to this treatments, an unknown but likely minor amount of amorphous material might have dissolved.

Separate aliquots of the clay and colloidal fractions of the sediments and of the bulk estuarine suspended matter were extracted. The extraction methods of Mehra and Jackson (1960) and of Biermans and Baert (1977) as modified by Kodama and Jaakkimainen (1981) were applied and are described in brief below.

#### Dithionite-Citrate-Bicarbonate (DCB) method:

Fifty mg of the oven-dried sediment samples were treated with 20 mL of 0.3M sodium citrate and 2.5 mL of 1M sodium bicarbonate in a polypropylene centrifuge tube and mixed by ultrasonification. About 0.2 g of sodium dithionite  $(Na_2S_2O_4)$  was added and the tube placed in a water bath at 80°C for 15 minutes. The suspension was agitated by hand a few times. After cooling, 1 mL of saturated NaCl solution was added and the mixture was centrifuged for 15 minutes at about 2000 rpm. The supernatant was transferred into 50-mL volumetric flasks. The extraction was repeated and the extract added to the first. The volume was made up to 50 mL with doubly distilled water.

#### Alkali-Tiron Method :

An alkaline 0.1M Tiron (1,2-dihyroxybenzene, 3,5-disulfanic acid disodium salt) solution was prepared by dissolving 31.42 g of Tiron in approximately 800 mL distilled water in a plastic beaker and buffered to pH 10.5 by adding  $Na_2CO_3$  and a 4N NaOH solution. The volume was made to 1 litre. Fifty mg of the oven-dried (90°C) sample were treated with 30 mL of Tiron solution in a polypropylene centrifuge tube and kept in a water bath at 80°C for one hour. The suspensions were stirred several times throughout the extraction. After cooling, they were centrifuged for 15 minutes at 2000 rpm. The supernatant solution was transferred into 50-mL volumetric flasks. The extraction was repeated. The volume was made up to 50 mL by adding doubly distilled water.

Extracts containing suspended material were filtered through 0.45  $\mu$ m Millipore<sup>®</sup> HA filter. Concentrations of Si, Al, Fe, Ca, Mg, Mn and K in the extracts were determined on a Perkin Elmer Atomic Absorption Spectrophotometer 5100. The analyses are based on reference standards prepared using the same reagents and concentrations as in the sample extractions. Both extraction methods show good reproducibility among duplicates of the same sample: the precision is  $\pm$  3% at the 95% confidence level. The amount of amorphous content was expressed as sum of oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, MnO and K<sub>2</sub>O) of the elements present in this fraction.

In order to provide a control for the extraction of the amorphous fraction in sediments, both procedures were applied to a mineral mixture consisting of ground quartz and hematite. Prior to the analyses, the two minerals were pulverized in a ball mill and wet-sieved through a 230 mesh (0.063 mm) sieve to remove the fine fraction, thoroughly washed in distilled water and then dried overnight at 90°C.

The major-element chemistry of the bulk estuarine suspended sediments and of a limited number of samples of the clay and colloid size-fractions of the exposed and submerged sediment samples was analyzed by X-ray fluorescence. Non-crystalline materials are composed of very finely ground particles. The transmission electron microscope (TEM) is useful for the study of their microtextures. Both the treated (DCB and Alkali-Tiron) and untreated sediment samples of the exposed deposits were ultrasonically dispersed in distilled water and a drop of the suspension (with a concentration of 0.1 mg/mL) placed on carbon-coated copper grids and allowed to dry in air at room temperature. Micrographs were obtained with a JEOL 100 CX II transmission electron microscope operating at 100 kV.

# IV. STRATIGRAPHIC POSITION OF THE SAMPLES SELECTED FOR THE ANALYSES

The Late Quaternary stratigraphy of the glacial and post-glacial sediments of the Central St. Lawrence Lowlands, based on microfaunal zones and textural analyses, has been described by Rodrigues (1987, 1988), Rodrigues <u>et al.</u> (1987), and Gadd (1977, 1986). The sediments are divided into four general stratigraphic units as follows: (1) a basal till; (2) rhythmically laminated silts and clays of freshwater origin ("varved sediments") (3) the Champlain Sea sediments and (4) post-Champlain Sea deposits (Fig.3).

The coarse ice-contact deposits equivalent to unit 1 were not examined during the present study. The origin of the rhythmites (unit 2) is subject of Figure 3. Lithology, texture and distribution of the total amorphous content (sum of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, MnO and K<sub>2</sub>O) for sections at A) Sparrowhawk Point site; B) Saint-Césaire site and C) Casselman site. See text for details about stratigraphic units.



**Casselman Section** 

controversy. One interpretation favouring a glaciolacustrine origin is related to glacial Great Lakes that expanded into the Ottawa Valley (Anderson <u>et al.</u> 1985), another one supports a glaciomarine origin, probably without expansion of the glacial lakes (Gadd, 1988). The massive grey clay (unit 3) and the upper part of the gradational interval between units 2 and 3 were deposited during the Champlain Sea episode. The earliest marine deposits were deposited under conditions of highest salinity (30-34‰), with a gradual decrease in salinity (< 15‰) afterward (based on the distribution of salinity-dependent foraminiferal assemblages; Rodrigues and Richard, 1986). The position of the samples with respect to the stratigraphy determined at the three sampling sites is as follows :

# **Sparrowhawk Point site :**

A section of glacial and marine sediments about 10 m thick is exposed along the shore cliffs on the south side of the St. Lawrence River (Fig. 1). Figure 3a summarizes the stratigraphy. The contact between units 2 and 3 is gradational and the contact between units 3 and 4 is abrupt. Ostracodes are present in units 2, 3, and 4. Foraminifers are absent in unit 2 and are present in units 3 and 4 (Rodrigues, 1988). Radiocarbon ages of 11, 900  $\pm$  100 years BP (GSC-3767) and 11,300  $\pm$  100 years BP (GSC-3788) were reported for shells of <u>Portlandia arctica</u> from the lower part of unit 3 and for shells of <u>Macoma balthica</u> from the lower part of unit 4 respectively (Rodrigues and Richard, 1983). A 10-m section of glacial and fossiliferous Champlain Sea sediments is exposed on the eastern side of the Richelieu River (Fig.1). The contacts between units 2, 3 and 4 are gradational (Fig. 3b). <sup>14</sup>C dates of 10,500  $\pm$  140 years BP and of 10,970  $\pm$  60 years BP (QU-1059) were reported on shells of <u>Macoma balthica</u> from units 3 and 4, respectively (Fulton, 1986).

#### Casselman site :

About 17-m of glacial and post-glacial sediments are exposed along the west bank of the South Nation River (Fig.1). The sediments rest unconformably on Ordovician rocks. The contacts between units 2 and 3 and that between units 3 and 4 are gradational (Fig.3c). Foraminifers are most abundant in unit 3, and ostracodes are less prominent in units 2, 3, and 4. The fossiliferous sediments are locally overlain by red and grey banded silts and clays at the top of the section (unit 4). A radiocarbon date of 11,460  $\pm$  70 years BP (TO-702) was reported for foraminifers from the base of unit 3 (Rodrigues, 1988).

# V. RESULTS

The results of the various analyses are presented in Figures 3, 4, 5, and 6 and in Tables I, II, III, IV, and V. Table I gives the amount of the major elements

Element	DCB	Alkali-Tiron
Si	0.06	0.07
AI	0.16	0.17
Fe	0.58	0.76
Ca	0.02	0.05
Mg	0.01	0.02
к	0.04	0.14
Mn	0.007	0.007

Table I. Amounts of major elements (mg/g) extracted by DCB and Alkali-Tiron reagents on a mineral mixture of ground (> 62  $\mu$ m) quartz and hematite

extracted by the DCB and Alkali-Tiron methods on the mineral mixture of ground (> 62  $\mu$ m) quartz and hematite crystals. The results indicate that treatment with either the DCB or the Alkali-Tiron reagent attacks both minerals only slightly. Of the two methods of chemical dissolution, the Alkali-Tiron attacks more of the crystalline material (between 0.01 to 0.18 mg/g) compared to DCB.

Table II give the textural ratios (clay/colloid and silt/clay) in the Champlain and Goldthwait sea deposits. The changes in texture along the sections and cores (Figs. 3 and 4) are expressed as the weight ratios of sand versus silt and clay (textural index). Figures 3 and 4 also show the vertical distribution of the total content of amorphous matter extracted by DCB and Alkali-Tiron in the clay and colloid-size fractions of the exposed and submerged deposits. Tables III, IV, and V report the major-element composition of the total material and of the amorphous fraction in the fine size-fractions.

#### V. 1. Textural Relationships

The grain size exhibits large variations along the vertical sections at the three subaerially exposed sites. The Sparrowhawk Point section shows a continuous coarsening-upward suite in units 3 and 4, the textural index (sand%/(silt+clay)%) ranging from 0.14 to 0.84. This is interpreted as reflecting a progressive change from deep open marine conditions at the base of unit 3, to shallow freshwater conditions at the top of unit 4 (Fulton and Richard, 1987). In

unit 3 of the Saint-Césaire site, the textural index increases upward from 0.15 to a maximum of 1.2, then decreases sharply. The index remains constant throughout the Casselman section, with very low values (0.005 to 0.02), which suggests that these sediments may all represent deep-water marine deposits.

Examination of cores 87-3 #2 and 87-3 #12 from the Upper St. Lawrence Estuary indicates textural uniformity with depth (Fig. 4), except for the top few cm, which represent recently reworked lag deposits of fluvioglacial origin (d'Anglejan and Brisebois, 1978). Core 87-3 #14 shows a sharp upward increase of the textural index, from 0.03 to 0.21 at a depth of 30 cm, similar to that of Sparrowhawk Point section.

Both the exposed and the submerged deposits contain more colloid-size, then clay-sized material. The mean clay/colloid weight ratio ranges between 0.29 and 0.76 (Table II). Table II also indicates an increase of the clay/colloid ratio in the exposed deposits (ranges between 0.52 and 0.76) relative to submerged deposits (ranges between 0.29 and 0.40), which suggests that the latter deposits may all represent extremely fine grained deep-water facies (Gadd, 1986).

The particle size in the samples of suspended matter analyzed was not determined. However, earlier studies by Kranck (1979) indicate that the deflocculated suspended matter in the estuary has a modal size between 5 and 10  $\mu$ m, with minor contents in silt-size particles above 10  $\mu$ m. Because of sharp negative skewness, the median size is much smaller than the mode. Kranck (1979)

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Figure 4. Texture and distribution of the total amorphous content (sum of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, MnO and K<sub>2</sub>O) for cores A) 87-3 # 2; B) 87-3 # 14 and C) 87-3 # 12.



### 

Table II. Clay/colloid and silt/clay ratios in the exposed and submerged deposits

	cla	ay/colloids-		silt/total clay		
	Range	Mean	SD	Range	Mean SD	
Exposed Deposits						
<ol> <li>Saint-Césaire (n=16)</li> <li>Sparrowhawk Pt(n=12)</li> <li>Casselman (n=9)</li> </ol>	0.36-0.80 2) 0.45-0.85 0.53-1.08	0.52 0.54 0.76	0.14 0.11 0.18	0.15-1.33 0.34-1.27 0.82-1.45	0.81 0.30 0.66 0.25 1.08 0.20	
Submerged Deposits						
Core 87-3 #2 (n=6) Core 87-3 #14 (n=10) Core 87-3 #12 (n=9)	0.27-0.35 0.15-0.49 0.37-0.42	0.29 0.35 0.40	0.03 0.11 0.02	0.32-0.42 0.48-1.09 0.35-0.61	0.37 0.03 0.70 0.20 0.42 0.09	

n= number of samples SD Standard deviation found that both the natural and the deflocculated median sizes of the suspended particulate matter (SPM) tend to decrease downstream in the Upper St. Lawrence Estuary.

#### V. 2. Distribution of the total amorphous phase

Large variations in total content of amorphous matter were found at the three subaerially exposed sites (Fig. 3). The results of the DCB extraction range between 1.68% and 4.88% at Sparrowhawk Point, between 0.66% and 2.11% at Saint-Césaire, and between 1.77% and 3.00% at Casselman. The Alkali-Tiron extraction gives ranges between 2.72% and 6.60%, 1.49% and 3.81%, and 2.3% and 3.7%, respectively for the three above sites.

For the three submerged deposits (Fig. 4), the DCB extraction results range between 1.83% and 4.34% for core 87-3 # 2, between 2.04% and 3.83% for core 87-3 # 14, and between 2.13% and 3.88% for core 87-3 # 12. The Alkali-Tiron extraction gives ranges between 2.68% and 5.97%, 3.02% and 5.23%, 2.48% and 5.37%, respectively for the three cores.

For the fourteen samples of suspended sediment analyzed, the total content of amorphous matter ranges between 1.77% and 3.09% by DCB extraction and between 2.81% and 3.54% by Alkali-Tiron extraction.

These results indicate that the values obtained with the Alkali-Tiron method are systematically higher (by 0.4% to 1.7%) than those found by the DCB

procedure. However, results by both methods show strikingly parallel fluctuations in all sections and cores (Figs. 3 and 4). The plots of the total content of amorphous matter show no systematic trend with depth, except in cores 87-3 #14 and 87-3 #12 for which, below the top layer, there is a downward increase of the clay-size sediments with depth, and a decrease for the colloid-size fraction.

The content of amorphous matter increases upward by 0.1% to 2.1% near the surface for all sections and cores analyzed. No significant correlation was found between the changes in content of amorphous matter (weight % amorphous matter) and the changes in grain size (textural index), except in the St. Césaire section. In that section, which shows the highest textural variations, the two variables are inversely correlated (r = -0.63, at the 95% level).

The amounts of amorphous material, in both exposed and submerged deposits, increase in the colloidal as compared to the clay-size fraction. The total amounts of amorphous matter (Figs. 3 and 4) extracted by both methods is enriched by a factor of about two in the smaller size-fraction [range for the clay-size fraction: 0.66% to 3.62% (DCB), 1.49% to 4.4% (Alkali-Tiron), for the colloidal fraction: 1.44% to 4.88% (DCB), 2.39% to 6.6% (Alkali-Tiron)].

# V. 3. Distribution of the major elements in the size fractions and their respective amorphous phase

The concentrations of the major elements in the total fractions do not show

much variation with depth, either in the exposed sections or the cores. However, the element contents change with particle size: Si, Ca and Na are enriched in the clay-size sediment, whereas Al, Fe, Mg and Mn are enriched in the colloid-size fraction (Table III and IV). Loring and Nota (1973) also reported a similar relationship between composition and size for the coarser fractions in marine sediments from the Gulf of St. Lawrence.

Examination of Tables III and IV reveals that on average, the colloid-size fractions contain more amorphous Si, Al, Fe, Ca, Mg and K (by up 0.002% to 0.6%), than the clay-size sediments, both for DCB and Alkali-Tiron extracted material. From Tables III, IV and V, it may be seen that compared to the DCB-extracted amorphous fractions, the Alkali-Tiron-extracted amorphous fractions is significantly higher in Si (by 0.03% to 0.08%), Al (by 0.04% to 0.09%), Fe (by 0.4% to 0.6%), Ca (by 0.006% to 0.03%), Mg (by 0.006% to 0.031%) and K (by 0.002% to 0.003%). Mn is virtually identical in both extracts.

Tables III, IV, and V show that on average, the amorphous fraction from the submerged deposits have higher Si (by 0.14% and 0.18%) and Al (by 0.14% and 0.2%) concentrations, compared to the material from the exposed sites and the bulk estuarine SPM. Higher values in sediments which have remained permanently submerged as compared to those which have been subaerially exposed possibly reflect ground water weathering or leaching effects on the latter, also a cause of salt loss (Desaulniers and Cherry, 1989). The most striking observation between the

Element	X tot.sed.*	X amorpho (DCB)	us frac <sup>6</sup> .	X amorpho (TIROf	%" bus frac". N)	X tot. sed.*	X amorpho (DCB)	-> < 1 μm< % μs frac <sup>b</sup> .	X amorpho (TIRC	%° us frac <sup>ь</sup> . DN)
AI	<b>98.16</b> (3.02)	0.59 (0.16)	0.60	1.30 (0.18)	1.32	109.57 (3.27)	1.10 (0.25)	1.00	2.00 (0.35)	1.83
Si	276.41 (9.06)	0.91 (0.21)	0.33	1. <b>54</b> (0.24)	0.56	252.25 (2.77)	1.22 (0.36)	0.48	2.06 (0.43)	0.82
Fe	59.84 (5.15)	4.42 (2.24)	7.39	8.12 (2.01)	13.57	80.35 (5.44)	8.24 (2.19)	10.25	14.40 (2.25)	17.92
Ca	41.71 (5.54)	6.08 (6.84)	14.58	6.47 (6.91)	15.51	28.81 (3.02)	6.65 (6.89)	23.08	6.91 (6.95)	23.98
Mg	22.51 (2.65)	0.45 (0.27)	2.00	0.51 (0.28)	2.27	26.93 (1.60)	0.72 (0.38)	2.67	0.75 (0.37)	2.78
Na	15.69 (1.87)	-	-	•	-	10.64 (1.94)	-	-	-	
ĸ	32.27 (2.46)	0.30 (0.08)	0.93	0.32 (0.08)	0.99	30.01 (11.65)	0.35 (0.09)	1.17	0.37 (0.08)	1.23
Mn	0.83 (0.09)	0.15 (0.10)	18.07	0.15 (0.08)	18.07	1.00 (0.11)	0.15 (0.11)	15.00	0.17 (0.09)	17.00

Table III. Mean major-element composition (mg/g) of the total sediments and of the amorphous fraction in the clay (1-2  $\mu$ m) and in the colloid (<1  $\mu$ m) size particles of the exposed deposits

X = Arithmetic mean of individual analyses

Standard deviation given in brackets \* % of amorphous fraction to total sediments

average of 12 samples
average of 37 samples

tot. sed.- total sediments

***********		> 1-2 μ	m<	******	· · · · · · · · · · · · · · · · · · ·					
Element	X tot.sed.*	X amorpho (DCB)	%° us frac <sup>6</sup> .	X amorpho (TTF	%" bus frac <sup>ь</sup> . RON)	X tot.sed.ª.	X amorpho (DCE	%" us frac". ))	X amorpho (TIR	%* us frac <sup>»</sup> . ON)
N	95.32 (2.62)	2.42 (0.61)	2.54	2.79 (0.60)	2.93	105.00 (0.72)	3.09 (0.49)	2.94	3.57 (0.56)	3.40
3	265.31 (3.53)	2.71 (0.39)	1.02	3.03 (0.36)	1.14	249.40 (1.83)	3.06 (0.27)	1.23	3.44 (0.27)	1.38
:e	53.60 (3.96)	7.21 (1.87)	13.45	11.26 (2.92)	21.01	71.84 (0.72)	11.47 (2.50)	15.97	16.43 (3.86)	22.87
a	29.50 (4.20)	1.17 (0.24)	3.97	1.26 (0.22)	4.27	26.69 (3.73)	1.38 (0.27)	5.17	1.45 (0.24)	5.43
Ag	27.37 (0.89)	0.55 (0.08)	2.01	0.60 (0.08)	2.19	32.01 (0.62)	0.77 (0.14)	2.41	1.08 (1.64)	3.37
la	19.79 (2.34)	•	•	-	-	16.79 (1.77)	-	-	-	-
ζ.	28.69 (1.56)	0.19 (0.04)	0.66	0.21 (0.04)	0.73	31.29 (1.10)	0.26 (0.05)	0.83	0.28 (0.04)	0.89
<b>An</b>	0.90 (0.05)	0.09 (0.01)	10.00	0.09 (0.01)	10.00	1.03 (0.06)	0.10 (0.01)	9.71	0.10 (0.01)	9.71

Table IV. Mean major-element composition (mg/g) of the total sediments and of the amorphous fraction in the clay (1-2  $\mu$ m) and in the colloidal (<1  $\mu$ m) size particles of the submerged deposits

X = Arithmetic mean of individual analyses Standard deviation given in brackets \* % of amorphous fraction to total sediments \* average of 11 samples \* average of 24 samples

tot.sed.-total sediments

	>Bulk Estuarine SPM<									
Element	х	х	<b>%</b> *	X	%*					
	tot.sed.ª	amorpho (DCI	us fracª. B)	amorphous frac <sup>a</sup> . (TIRON)						
AI	74.39 (3.90)	1.19 (0.33)	1.60	1.79 (0.29)	2.41					
Si	253.56 (9.34)	1.55 (0.30)	0.61	2.12 (0.25)	0.84					
Fe	49.33 (3.55)	11.13 (2.73)	22.56	16.01 (2.36)	32.45					
Са	19.48 (1.51)	1. <b>46</b> (0.17)	7.49	1.52 (0.17)	7.80					
Mg	17.12 (1.57)	0.51 (0.05)	2.98	0.54 (0.05)	3.15					
к	20.76 (2.93)	0.25 (0.03)	1.20	0.28 (0.02)	1.35					
Mn	1.29 (0.17)	0.0 <del>9</del> (0.02)	6.98	0.10 (0.01)	7.75					

Table V. Mean major-element composition (mg/g) of the total sediments and of the amorphous fraction of the Upper St. Lawrence estuarine suspended sediments

X = Arithmetic mean of individual analyses
Standard deviation given in brackets
\* % of amorphous fraction to total sediments
\* average of 14 samples

tot.sed.-total sediments

exposed deposits and the estuarine SPM is the enrichment of amorphous Fe, from 0.16% to 0.79%, in the latter sediments. This reflects the addition of Fe to the solid phase by the precipitation of dissolved Fe, as has been shown to occur in the St. Lawrence Estuary by earlier researchers (Bewers and Yeats, 1978; Lucotte and d'Anglejan, 1988).

Correlation coefficients were computed for the DCB-and Alkali-Tironextracted elements. The interelemental relationship between pairs of elements in the combined exposed, submerged and suspended sediments (number of samples = 136) shows good positive correlation at the 95% level for Si-Al (r = 0.91 and 0.85); Fe-Al (r=0.65 and 0.70) and Ca-Mn (r = 0.43 and 0.74), respectively, for the DCB- and Alkali-Tiron-extracted samples. The percentage of an element in the amorphous fraction referred to the total material for the sections, cores and SPM are as follows : Si, 0.3-1.4%; Al, 0.6-3.4%; Fe, 7.4-22.9%; Ca, 4-24%; Mg, 2-3.4%; K, 0.7-1.4%; and Mn 7-18% (Tables III, IV, and V).

## V. 4. Electron micrographs of the treated and untreated post-glacial sediments

An attempt was made to image the amorphous material and to determine directly its forms of occurrence in the sediments by examining sediment particles under transmission electron microscope before and after treatment with the two reagents. Figure 5a shows an overview of untreated samples from the Sparrowhawk Point section. The larger, more abundant particles seem to consist Figure 5. TEM photomicrographs of the Sparrowhawk Point section before dissolution experiments:(a) and (b) bulk unsorted particles (x19,000);
(c) and (d) showing close up view (x100,000) of disseminated aggregates (indicated by arrows in (a) and (b)) which are amorphous. Scale: (a) and (b) 1 cm = 1 μm; (c) and (d) 1 cm = 0.2 μm.





mild procedures of extraction were examined and critically tested, using a variety of surficial sediments. The evidence that some success is achieved rests on the following experimental results.

A control sample consisting of a mineral mixture of pure hematite and quartz shows only minor attack by the two procedures (Table I). The amounts removed are only 3% to 15% of the amounts extracted from the sediments. The sensitivity of feldspar minerals to the reagents is unknown. However, in earlier studies, Kodama and Jaakkimainen (1981; Fig. 2) obtained values from 0 to 0.5% for Si and Al by the Alkali-Tiron method on feldspar minerals (albite, microcline) before grinding. Results of the control experiment indicate that the removal of crystalline material by DCB (0.88 mg/g) is less than by Alkali-Tiron extraction (1.22 mg/g) method. This suggests that the higher results obtained by Tiron in the sediments are due to partial attack of the crystalline phases. Therefore, the DCB method appears more reliable.

Even though the element concentrations found using the Alkali-Tiron procedure are about a factor of two higher than DCB, the covariances of the two lines of results obtained independently along vertical sections (Figs. 3 and 4) provide a strong indication that material of the same nature is being extracted in both cases. The correlation between results obtained by the two methods is good to excellent (Si, 91%; Al, 84%; Fe, 55%; Ca, 98%; Mg, 47%; Mn, 71%; K, 90%). They show better reproducibility and are more specific than other methods used in

previous studies (Locat et al. 1984; Kroeker, 1985).

The experiments put an upper limit (<6%) on the amounts of amorphous phase present in the Champlain and Goldthwait marine clays, much less than previously reported (Bentley and Smalley, 1978; Yong <u>et al</u>. 1979). The present study suggests that the amounts of amorphous material (10-20 wt.%) reported by earlier researchers (McKyes <u>et al</u>. 1974; Yong <u>et al</u>. 1979) in the post-glacial sediments have been greatly exaggerated as a result of misinterpretations of the effects of more aggressive procedures of chemical extraction.

It is postulated that this amorphous phase could consist of precipitates contemporaneously formed by flocculation and settling in the depositional environment of the post-glacial seas. As sedimentation proceeds in the brackish water environment of these seas, the double-layer repulsion between the suspended flocs is decreased and interparticle contacts lead to flocculation. An analogous situation arises during the precipitation of Fe oxides in the modern estuary, indicated by the high values of Fe in the SPM (Table V) and in previous studies (Bewers and Yeats, 1978; Lucotte and d'Anglejan, 1988). Some of the amorphous components could also conceivably be produced *in situ* by post-depositional diagenetic processes.

At this point, it would seem likely that the origin of some of the amorphous phase in the post-glacial clays may in part be related to crushing and grinding of rocks under ice pressure. This origin was first suggested by Jones and Uehara (1973) and is in agreement with the grinding experiments of Kodama and Jaakkimainen (1981) on kaolinite, clinochlore, biotite, hornblende, albite and microcline. These authors have demonstrated that the relative degree of crystallinity (ratio of peak intensities of a characteristic line before and after grinding) decreases from 1.00 before grinding to between 0 and 0.53 after grinding for about 150 hrs.

Whether the amorphous phase occurs as an independent matrix or as a surface alteration of particles of the product is also not yet established. The latter form of occurrence is suggested by the noted increase in content of amorphous matter with decreasing size (increasing surface-area) of the sediments. However, the electron micrographs support the presence of disseminated aggregates.

The chemical analyses of the extracted amorphous material from the postglacial sediments indicate that  $SiO_2$ ,  $Fe_2O_3$  and  $Al_2O_3$  are the main components, with small amounts of CaO, MgO, K<sub>2</sub>O and MnO. This amorphous fraction presumably consists of Fe and Al hydroxides and amorphous silica.

A high proportion of amorphous Ca (Ca<sub>amor</sub>/Ca<sub>tot</sub>) ratio varies between 0.15 to 0.24) was determined for the exposed deposits, more than 2-3 times the values found for the SPM, and 4 to 6 times that in the submerged deposits. For the three exposed deposits the total carbonate content varies between 4 and 10%, apparently randomly. Quigley (1980) estimated that carbonate contents of 1-4% originate from

planktonic remains during the accumulation of the marine clay. Some detrital carbonates may also be present. For the submerged deposits, the total carbonate content varies between 0.5 and 2%. The carbonate fraction was removed using acetic acid buffered with sodium acetate at a pH of 5.0 to preserve the XRD intensity of the clay minerals. However, the high Ca content noted in the exposed deposits, particularly for the Sparrowhawk Point section, suggests that Jackson's (1969) method has not completely removed the carbonate fraction. For future work, an alternative method, for example, ethylenediaminetetraacetic acid (EDTA) method of Bodine and Fernalld (1973), needs to be evaluated for the removal of carbonate during sample preparation.

A normative mineral composition was calculated from the major element composition of the amorphous material using the procedure of Garrels and Mackenzie (1971). It gives an average value of 23% quartz; 22% Ca-feldspar; 9% Na-feldspar and 14% K-feldspar. These results, which match the relative abundance of minerals in the sediments, support the interpretation that amorphous material in the post-glacial sediments are the result of the physical alteration by grinding of detrital minerals. The X-ray results for the exposed and submerged deposits (Ramesh and d'Anglejan, 1989) also indicate that feldspars are more abundant than quartz and that plagioclase is 2-4 times more abundant than Kfeldspar.

The limited research done on pore-water chemistry (major cations-Na, Mg,

Ca and K) of the Champlain clays of the Central St. Lawrence Lowlands has shown that the salt concentration has been reduced from an initial value of greater than 20 g/L at the time of deposition to less than 2 g/L at present (Torrance, 1975; 1988). Local factors such as leaching by ground water, and diffusion must have controlled the extent of salt removal (Torrance, 1979; Quigley <u>et al</u>. 1985), but no systematic investigation of the *in situ* pore water chemistry of an extensive area has been reported.

Using the average elemental composition of the total and amorphous fractions of the exposed deposits, as obtained in this study, a potential contribution of the amorphous matter to the total particulate load of the St. Lawrence River (4 x  $10^6$  tons year<sup>-1</sup>; Milliman and Meade, 1983) can be computed, assuming that these deposits are the main source of suspended solids to the river. Table VI shows the individual major elemental fluxes of total sediments and of the amorphous fraction transported out of the St. Lawrence River system into the estuary. The annual transport of elements ranges from  $1,057 \times 10^3$  tons for Si to  $4 \times 10^3$  tons for Mn. The percentages of the amorphous fraction to the total suspended flux are as follows : Si, 0.4-0.7%; Al, 0.7-1.7%; Fe, 9-16%; Ca, 18-19%; Mg, 2-3%; K, 0.8%; Mn, 15% . These amounts particularly for Fe and Ca, seem to be a significant fraction of the yearly St. Lawrence River input. Again, the high proportion of Ca may reflect the incomplete removal of carbonates in the samples analyzed.

For the Sparrowhawk Point, the weights of 12 samples at the end of the
Element	tot.sed. (1	DCB ext. 10 <sup>3</sup> metric tor	Alkali-Tiron ext. ns year <sup>-1</sup> )
Si	1057	4	7
AI	415	3	7
Fe	280	25	45
Са	141	25	27
Mg	99	2	3
K	125	1	1
Mn	4	0.6	0.6

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Table VI. Average major-element flux of total sediments and of the amorphous fraction transported out of the St. Lawrence River system into the estuary dissolution experiments was recorded after each sample had been washed using distilled water, centrifuged and the remaining solid dried at 100°C. Simple massbalance calculations show that the total mass of amorphous matter removed by the dissolution procedures (3% to 6% by DCB extraction; 4% to 8% by Alkali-Tiron extraction) is more or less equal to the sum of all the oxides recovered (2% to 5% by DCB extraction; 3% to 7% by Alkali-Tiron extraction).

The labile nature of the amorphous fraction raises the question of (i) its mobility under exposure to ground water and soil solutions, and to river water and sea water during transportation and (ii) whether the solubility and mobility of these post-glacial sediments are sufficient to influence the composition of St. Lawrence River and estuarine waters. Some of these questions will be examined separately (Ramesh & d'Anglejan, in preparation).

## **VII. SUMMARY AND CONCLUSIONS**

Of the two procedures of chemical dissolution applied to the extraction of amorphous material in the fine post-glacial transgressive marine deposits of the St. Lawrence Lowlands, the dithionite-citrate-bicarbonate (DCB) procedure (Mehra and Jackson, 1960) seems to be more selective than the Alkali-Tiron procedure (Biermans and Baert, 1977). The good covariance between the values along vertical sections provides some evidence that the two procedures are extracting material of the same nature, and are not attacking oxide and silicate minerals at greatly different rates. Therefore, it appears to confirm that the post-glacial marine clays indeed contain a minor fraction of noncrystalline components, which may be referred to as "amorphous matter". Although the percentage of "amorphous" (easily removable) constituents in the post-glacial marine deposits of the St. Lawrence Lowlands varies between the two mild extraction procedures used, it remains below 6%, much less than previously reported. Transmission electron micrographs indicate the presence of irregular aggregates which are amorphous in nature. Normative mineral calculations based on the analyses supports the possibility that the origin of the amorphous material can be traced to the physical alteration of the major detrital minerals by grinding, as suggested by the study of Kodama and Jaakkimainen (1981). The "amorphous fraction", however small, constitutes a significant amount of the total suspended flux discharged from the St. Lawrence River system into its estuary.

### ACKNOWLEDGMENTS

We would like to thank Professors Reinhard Hesse, Alfonso Mucci, Robert F. Martin and Dr. H. Vali for their helpful comments on the manuscript, and Ms. Glenna Keating for assistance during the chemical analyses.

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# **CHAPTER III**

# MOBILIZATION AND TRANSPORT OF SILICA, IRON AND ALUMINIUM FROM POST-GLACIAL SEDIMENTS OF THE ST. LAWRENCE LOWLANDS

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### ABSTRACT

The release of silica, iron and aluminium held in the labile "amorphous" fraction of the St. Lawrence Lowlands post-glacial marine transgressive clays was studied in the laboratory by keeping samples of these clays in suspension for 1000 hours in distilled water and in salt water of various salinities. The results show that SiO<sub>2</sub>, Al and Fe are released preferentially in zero salinity waters. For SiO<sub>2</sub>, the amounts released from subaerially exposed and submerged samples and from estuarine suspended particulate matter (SPM) are respectively at least 24%, 15%, and 20% of the total "amorphous silica" determined in these sediments. For Al and Fe, these amounts are much less. For all three elements, there is a sharp decrease in amounts released with increasing salinity. However, the  $SiO_2$  released from the SPM above a salinity of 7 are higher than for the sediments and remain constant, presumably because of the dissolution of diatom remains found to be present in the material. The release of  $SiO_2$  from the "amorphous" fraction, suggests that this process could provide a minor contribution (perhaps 2.6%) to the dissolved silica load of the St. Lawrence River. The Fe and Al appear to be released as microcolloids of hydrated oxides inherited from the original environment of deposition of the sediments.

#### I. INTRODUCTION

The inorganic component of the seston in the St. Lawrence River and Estuary is largely inherited from the post-glacial marine deposits of the St. Lawrence Lowlands. These deposits were formed during the Goldthwait and Champlain Sea (13,000 to 9000 YBP) transgressive events in the St. Lawrence valley. In these post-glacial deposits, the presence of disseminated, poorly crystalline to amorphous oxide minerals, commonly referred to in the geotechnical literature as "amorphous matter" has been demonstrated by several researchers (McKyes et al. 1974; Bentley and Smalley 1978; Yong et al. 1979; Locat et al. 1984; Ramesh and d'Anglejan, 1990 a). This so-called amorphous phase appears to consist mainly of a mixture of silica, and of hydroxides of Al and Fe (Quigley, 1980; Ramesh and d'Anglejan, 1990 a). In an earlier paper (Ramesh and d'Anglejan, id.), we determined the presence of a minor amorphous fraction (ranges between 0.7% and 6.6% by weight) in the Goldthwait and Champlain Sea fine-grained deposits and examined its composition and distribution by comparing results obtained using two mild extraction procedures, and by Transmission Electron Microscopy (TEM).

Some of the questions that the present research is designed to answer are: (i) could the main labile elements (Si, Al and Fe) in the amorphous fraction of the St. Lawrence fine-grained post-glacial sediments be released on exposure to river and estuarine waters? If so, how much?; (ii) could removal of these elements during transportation by river or estuarine waters or by ground water provide a significant contribution to the dissolved load of the St. Lawrence?

Previous experiments on the release of major elements from rock-forming silicate mineral suspensions in distilled water were reported by Keller <u>et al.</u> (1963). Similar experiments by Mackenzie <u>et al.</u> (1967) and Siever and Woodford, (1973) have shown that the release of silica from clay mineral suspensions in sea water takes place in solutions low in dissolved silica, whereas adsorption of silica onto the solid phase occurs at high silica concentrations.

The experiments reported in this paper were carried out to determine the reactivity of the amorphous fraction of sediments in fresh water and in sea water of different salinities. Sediment samples collected from subaerially exposed deposits of the Champlain Sea and from Goldthwait Sea deposits submerged under the St. Lawrence Estuary, and samples of estuarine suspended particulate matter (SPM), were used.

#### **II. MATERIALS AND METHODS**

The sediment samples were taken from a depth of 145-150 cm in the Sparrowhawk Point section of the subaerially exposed Champlain Sea deposits in western Quebec (A, Fig. 1), and from a depth of 28-33 cm of a gravity core from the Upper St. Lawrence Estuary (B, Fig. 1). The suspended particulate matter (SPM) sample (C, Fig. 1) was collected in the early mixing zone (salinity less than 1) of the Upper St. Lawrence Estuary by pumping and continuous flow centrifugation, kept frozen, then freeze-dried in the laboratory. These samples were selected in order to represent three distinct types of sediments in the St. Lawrence Lowlands. The assumption is that sediments of type A and Figure 1. Maximum diachronic extent of the Champlain Sea and western arm of the Goldthwait Sea downstream from Quebec (modified from Parent and Occhietti, 1988). Relative elevations in meters above present sea level are indicated by bold numbers. A, B, and C indicates sediment sample location used for the laboratory experiments.



B represent the proximate source of the type C, the SPM.

In the laboratory, the three samples (A, B and C) were sieved to remove the coarse fraction using a 230 mesh (0.063 mm) stainless steel sieve. Separate 1 g aliquots of the oven-dried sediment samples (A, B and C) were treated by the Dithionite-Citrate-Bicarbonate (DCB) procedure of Mehra and Jackson (1960) and by the Alkali-Tiron dissolution procedure of Biermans and Baert (1977) in order to extract amorphous Si, Al and Fe (Ramesh and d'Anglejan, 1990 a).

Synthetic sea water was prepared in the laboratory by dissolving 25 g of analytical reagent quality NaCl and 8 g of Mg SO<sub>4</sub>. 7H<sub>2</sub>O in one litre of distilled water. This is equivalent to sea water with a salinity of 28 (Strickland and Parsons, 1968). Varying amounts of synthetic sea water were added to fixed amounts of deionized double distilled water to obtain four solutions of salinities between 7 and 28. Aliquots of untreated samples A, B and C, each weighing 1 g (dry-weight), were placed in different polythene bottles containing 50 mL of synthetic sea water of various salinities, viz. 28, 21, 14, 7. In addition, 1 g of both the treated (by DCB and Alkali-Tiron) and untreated aliquots of A, B and C were suspended in 50 mL of deionized double distilled water (zero salinity). Samples of synthetic sea water of various salinities without added sediment samples were also monitored as controls.

The St. Lawrence River waters are always slightly basic (pH range between 7 and 8) above the salt intrusion (Chan, 1980). Hence, in the present study, the pH of all the water samples were initially buffered to pH 8 with either NaHCO<sub>3</sub> or HCl. No attempt was made to monitor the Eh. The containers were agitated on a Burrel wrist-action

shaker for about 1000 hours (42 days) at which time dissolution/precipitation appears to be fairly constant. Hurd (1977) studied the silica release and removal rates for various rock samples which were in contact with five different seawater solutions and observed that the concentrations of dissolved silica reached constant values of  $80 \pm 1 \mu$  mol/l after 44 days. The sediment suspensions were first centrifuged at 3000 RPM with an IE7 Centra-7<sup>®</sup> centrifuge for 15 minutes to remove the bulk of the suspended solids, and then filtered through a 0.45 $\mu$  Millipore<sup>®</sup> HA filter. The final pH (Table II) of the supernatants was measured with a Beckman Expandomatic<sup>®</sup> SS-2 pH meter. Table II gives the final weights of each sample at the end of the experiment, after each sample had been washed using distilled water, centrifuged, and the remaining solid dried at 110°C and re-weighed. The ambient temperature was approximately 25°C.

Reactive silica was determined colorimetrically using the method described by Strickland and Parsons (1968). The extinction of the silicomolybdate complex was measured in 10 mm cells at 650 nm using a Bausch and Lomb Spectronic 21. The precision based on two independent analyses of each sample is  $\pm 3\%$  (95% confidence level).

Iron and aluminium concentrations were determined by direct injection of samples and aqueous standards (prepared from 1000 ppm stock standards, Fisher Scientific company) on a flame Perkin Elmer Atomic Absorption Spectrophotometer 5100. All the samples were run at least twice and showed good reproducibility among duplicates. The overall precision of the analyses was better than  $\pm$  5% at the 95% confidence level. The original samples (A, B and C) were also analyzed by X-ray

#### III. RESULTS

Table I reports the Si, Al and Fe concentrations in the total material and in the amorphous fraction extracted by the DCB and Alkali-Tiron procedures. The extraction results indicate that the values obtained by the Alkali-Tiron method are higher by 0.3 to 7 mg/g than those obtained by the DCB method. This is in accord with the apparent relative effectiveness (more aggressive) of the reagents noted in previous studies on the amorphous phase (Ramesh and d'Anglejan, 1990 a). Table I also shows that the sample of submerged deposits contains more amorphous Si (by 0.9 and 1.3 mg/g) and Al (by 1.6 and 1.9 mg/g) and Fe (by 1.8 and 4.4 mg/g) than the sample of exposed deposits. Higher values in sediments which have remained permanently submerged as compared to those which have been subaerially exposed may reflect weathering effects on the latter, also a cause of salt loss (Desaulniers and Cherry, 1989). Amorphous Fe is higher, by 0.8 to 5.2 mg/g, in the estuarine SPM relative to the samples of the exposed and submerged deposits. This supports the well-established observation that estuarine mixing in the St. Lawrence results in the flocculation of Fe rich colloids (Bewers and Yeats, 1979; Lucotte and d'Anglejan, 1988).

The concentrations of dissolved silica, and of iron and aluminium in waters of various salinities at the end of the experiments are shown on Figs. 2, 3 and 4. Table II gives, for several salinities, the amounts of silica, iron and aluminium expressed as weight

	Exposed Deposits		Submerged Deposits			Estuarine suspended sediments			
EI.	tot.sed.	DCB	Tiron	tot.sed	DCB	Tiron	• tot.sed.	DCB	Tiron
Si	239.6	1.59	2.29	236.7	2.85	3.23	258.0	1.87	2.15
AI	96.7	0.79	1.69	89.6	2.65	3.33	76.7	1.64	1.96
Fe	67.8	6.50	11.02	54.6	8.32	15.39	53.4	9.10	16.16

Table I. Silicon, Aluminium and Iron concentration (mg/g) in the total sediments (< 62  $\mu$ m) and in the amorphous fraction extracted by DCB and Alkali-Tiron procedures.

El. - Element tot.sed. - total sediments % of the total element in the removable amorphous fraction obtained by either DCB or Alkali-Tiron extraction (Table I). The amounts of silica, aluminium and iron released in water of zero salinity from samples pretreated with the DCB and Alkali-Tiron reagents are given in Table III.

For both the exposed and the submerged sediments (Figs. 2A and 2B), the dissolution of silica is in excess of 20 ppm in zero salinity water. These values diminish with increasing salinity to less than 3 ppm in water of salinity of 28. In contrast, the release of silica from the SPM (Fig. 2C) showed little change with salinities above 7, remaining between 11 to 12 ppm, in salinities ranging from 7 to 28.

For the three types of sediments, the mobility of removable iron (Figs. 3A, B and C) and aluminium in waters of increasing salinities (Figs. 4A, B and C) follows trends similar to each other, levelling off at salinities above 7. In the present study, Millipore filters of 0.45  $\mu$ m pore size were used to separate the dissolved constituents. The relatively high amount of iron (2 to 3.8 ppm) and of aluminium (0.68 to 1.26 ppm) found in the zero-salinity waters could reflect the release from the sediments of hydroxides and hydrous oxides, which were transported and deposited contemporaneously as colloidal flocs of sizes below 0.45  $\mu$ m in the brackish environment of the post-glacial sediments (Boyle <u>et al.</u> 1977; Stumm & Morgan, 1981; Salomons & Förstner, 1984). In waters of salinities above approximately 7, the amounts of Al and Fe released remain virtually constant (Table II, Figs. 3 and 4).

In zero salinity waters, samples pretreated with DCB or Alkali-Tiron reagents released amounts of SiO<sub>2</sub>, Al and Fe, which are respectively 5% to 13% of the SiO<sub>2</sub>, 0.5%

s	Silic	a	Aluminium		ire	Iron		Final
	DCB	TIRON	DCB	TIRON	DCB	TIRON	pН	wt.(g)
Exp	osed Depo arrowhawk F	esit Point Section (		)				
				,				
0	35.15	24.39	7.97	3.73	1.58	0.93	7.6	0.753
7	24.56	17.04	2.87	1.34	0.67	0.39	7.7	0.889
14	18.97	13.16	2.69	1.26	0.61	0.36	7.7	0.920
21	8.68	6.02	2.47	1.15	0.52	0.31	8.0	0.950
28	4.26	2.96	2.47	1.16	0.52	0.30	7.9	0.966
<b>Sul</b> (87-	omerged De -3 #2; 28-33	e <b>posit</b> I cm)						
0	16.97	14.98	1.57	1.25	1.59	0.86	7.7	0.758
7	12.05	10.64	0.83	0.66	0.59	0.32	7.6	0.890
14	9.26	8.18	0.82	0.65	0.49	0.27	7.8	0.935
21	3.52	3.11	0.78	0.62	0.43	0.23	7.7	0.926
28	1.23	1.09	0.77	0.62	0.43	0.23	7.9	0.986
St.	Lawrence l	Jpper Estuar	ine Suspen	ded Sedimen	t			
			•					
0	22.88	19.89	2.06	1.72	2.13	1.20	7.6	0.778
7	15.25	13.26	1.16	0.97	0.56	0.32	7.7	0.815
14	14.63	12.72	1.14	0.95	0.54	0.31	7.7	0.853
21	14.50	12.61	1.11	0.93	0.47	0.27	7.8	0.940
28	13.88	12.07	1.11	0.93	0.48	0.27	8.0	0.946

Table II. Mobility of silica, aluminium and iron (in weight% of elements extracted by DCB and TIRON;Table I) in the exposed, submerged and suspended sediments of the St. Lawrence Lowlands.

S=Salinity

\* Initial pH was adjusted to 8.0

\*\* Initial weight was 1 g for all the samples

Figure 2. Dissolution of silica from untreated solid samples A, B and C at various salinities.



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Figure 4. Release of aluminium from untreated solid samples A, B and C at various salinities.

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to 2.3% of the Al and 0.2% to 0.5% of the Fe, determined in the amorphous fraction in the three sediments (Table III). The silica values obtained from the Alkali-Tiron and DCB treated samples could indicate that both extraction procedures were not fully effective in removing the labile fraction of these elements which is held in the amorphous matter. More likely, it indicates that additional amounts of silica were released in the water from the clay minerals or other detrital minerals kept in suspension during the experiments. This is in agreement with the observations of Siever and Woodford, (1973). If so, the amounts of released silica reported in Table II for the untreated samples represent maximum values.

Little changes in pH between the start and the end of the experiments were observed (Table II and III). We note that the total weight loss (Table II) in all cases, decreases with increasing salinity.

#### **IV. DISCUSSION**

The reproducibility of the overall salinity dependencies is not known since only one series of complete mixing experiments was run. However, the relationships between silica (linear), iron and aluminium (non-linear) and the salinity are analogous to those previously found in field and laboratory studies by several researchers working in different estuaries (Subramanian and d'Anglejan, 1976; Liss, 1976; Boyle <u>et al</u>. 1977; Sholkovitz, 1978; Hydes and Liss, 1979; Bewers and Yeats, 1979; Yeats, 1988).

Table III. Amounts of silica, aluminium and iron (in weight% of elements extracted by [	DCB	and
TIRON; Table I) released in water of zero salinity from the three types of sediments a	after [	CB
and TIRON extraction		

Sample <sup>®</sup>	Extraction Method	Silica	Aluminium	Iron	Final <sup>®</sup> pH	Final <sup>#</sup> wt.(g)
A	DCB	12.50	2.25	0.48	7.6	0.863
	TIRON	7.24	0.98	0.27	7.8	0.892
В	DCB	6.56	0.59	0.43	7.7	0.912
	TIRON	5.21	0.45	0.22	7.6	0.893
С	DCB	9.88	0.89	0.47	7.7	0.849
	TIRON	7.93	0.72	0.25	7.7	0.853

@ refer Figure 1 for sample location and text for description
\* Initial pH was adjusted to 8.0
\*\* Initial weight was 1 g for all the samples

#### IV. 1. Possible source and controls of the concentration of dissolved silica

Plagioclase, K-feldspar, quartz, amphibole, illite and chlorite are the main constituents of the post-glacial sediments of Champlain or Goldthwait age (Ramesh and d'Anglejan, 1990 b). Figure 5 shows the equilibrium concentrations of dissolved silica at 25°C obtained in the experiments for samples A, B and C, in both fresh water (FW) and sea water (SW). Also shown are the solubilities of various silicates and amorphous silica and quartz reported in the literature. Solubilities for amorphous silica and quartz are the two extremes in the range of values obtained for natural minerals. The solubility of quartz at room temperature is no higher than 8 ppm, while that of amorphous silica, is over 100 ppm (Fig. 5). Keller <u>et al.</u> (1963) report that K-feldspar releases more soluble silica than plagioclase in distilled water. Illite and chlorite release between 7 and 18 ppm and between 4 and 16 ppm SiO<sub>2</sub> in sea water respectively (Mackenzie <u>et al.</u> 1967).

The amounts of silica removable from post-glacial sediments in fresh water is higher than the known equilibrium values for detrital silicates, but lower than the value for amorphous silica (Fig. 5). A likely source for the silica, explaining the high values found, is the occurrence in the glacially reworked sediments of an unstable, "amorphous" phase. It is postulated that such a phase is produced by intergranular abrasion of rock fragments during glacier ice transport. This process gives rise to a powdery product, referred to as "rock flour". In the laboratory, the grinding of some rock-forming silicate minerals, i.e. feldspars, amphiboles, pyroxenes etc., has been found to produce an amorphous silica-rich phase (Kodama and Jaakkimainen, 1981). The study conducted by Keller et al. (1963) on dissolved products of artificially pulverized silicate minerals Figure 5. Range of dissolved silica concentrations in fresh water (FW, S=0) and sea water (SW, S=28) observed in post-glacial sediments based on this study (A, B, and C), compared to the solubility (at 25°C) of common silica-bearing minerals found in these post-glacial sediments.

Source of data : (1) Morey <u>et al</u>. (1962); (2) Keller <u>et al</u>. (1963); (3) Krauskopf (1956); (4) Mackenzie <u>et al</u>. (1967)



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reaches the same conclusion. These authors crushed a number of common silicate minerals in distilled water and determined the concentration of  $SiO_2$ , Al and Fe (Table IV) and other major and minor elements in the supernatant liquids after equilibration. Table IV indicates that, of the common detrital minerals, the pyroxenes supply the greatest amounts of soluble silica (35 to 50 ppm). The effects of sea water rather than distilled water on the dissolution process were not considered, and no attempts were made to determine the reactions involved.

The release of silica from the exposed sediments (A) as a function of salinity, follows the same trend as that from the submerged sediments (Fig. 2A & B). The plot for the SPM (Fig. 2C) shows that there is initially a lower amount of dissolution than for the exposed and submerged sediments, but that for salinity above 7 the values are higher than for the sediments and remain constant. This may be due to a higher proportion of biogenous silica in the SPM. Fragments of diatoms were observed in the SPM under Scanning Electron Microscopy (refer Fig. 1 in appendix). Dissolution of biogenic silica is quite rapid relative to that of other forms of amorphous silica (Hurd, 1972). Therriault et al., (1990) indicate that phytoplankton cells of freshwater origin occur in sometimes high numbers in the Upper St. Lawrence Estuary at salinity <1, with very low concentrations in the turbidity maximum zone (salinity below 10). Small cell numbers of brackish species are reported further downstream. Assuming that all silica released by the SPM at a salinity of 28 (SiO<sub>2</sub> = 12 mg/L; Fig. 2C) is due to dissolution of biogenous silica, its weight concentration in the SPM needs to be 0.06%. Using the analytical procedure of Hurd (1972), d'Anglejan (unpublished) determined the biogenous silica in

Mineral	SiO <sub>2</sub>	Al ppm	Fe
Quartz	5.5		
Labradorite	8.1	0.32	0.005
Microcline	15.8	0.86	0.00
Hornblende	10.7	0.26	0.15
Muscovite	14.8	0.40	0.59
Biotite	15.6	0.50	14.3
Enstatite	35.3	0.008	0.049
Augite	37.9	0.02	0.099
Diopside	49.8	0.04	0.12
Olivine	12.8	0.00	0.15
Nepheline	31.7	2.2	0.00

Table IV: Silica, AI and Fe released to solution by minerals wet ground in distilled water at room temperature (after, Keller et al. 1963)

Ten grams solid (except micas, 2.5 g), to 100 mL distilled water.

the SPM of the Upper St. Lawrence Estuary to be less than 1 %.

The decreasing amounts of silica released in solution at equilibrium with increasing salinities from both the exposed and the submerged sediments are in agreement with experiments carried out by Siever and Woodford (1973). They reported that the dissolution of kaolinite, illite and montmorillonite is considerably lower in sea water, than in distilled water. For example, they obtained about 42 ppm of dissolved silica from kaolinite suspended in distilled water against 10 ppm in sea water. They attributed the reduced dissolution to changes in pH, as well as to increasing ionic strength and changes in cation composition. The solubility of amorphous silica in sea water was found by Krauskopf (1956) to be the same as in distilled water. However, more recently Marshall (1980) observed a relative decrease in solubility with added electrolyte. He observed that in 6m NaNO<sub>3</sub> solutions, at 25°C, the solubility of amorphous silica is decreased by 60% from that in pure distilled water.

The factors that keep the concentration of silica below the equilibrium solubility value for amorphous silica and even for quartz in brackish and saline waters (Fig. 5) are not completely understood. Reaction kinetics, inorganic adsorption by detrital particles, change in ionic strength, all play a part. Bien <u>et al.</u> (1958) and Liss and Spencer (1970) showed that the presence of electrolytes results in maximum uptake of dissolved silica by sediments. Another adsorption process has been reported by Harder (1965) and by Harder and Flehmig (1970), who found in laboratory studies that considerable quantities of dissolved silica could be adsorbed on X-ray amorphous hydroxides of iron, aluminium and magnesium from solutions containing as little as 0.5 ppm silica. Moreover, the

"amorphous" phase studied, believed to be produced by disordering of the crystal structures of detrital silicates subject to high pressure grinding, could be chemically quite different from opaline amorphous silica (SiO<sub>2</sub>:nH<sub>2</sub>O). Finally, the release of silica from the mineral mixture in the sediments, which contain a variety of detrital silicates is not likely to be the same as that of the pure amorphous phase.

#### IV. 2. Potential silica contribution to the St. Lawrence dissolved load

According to Livingstone (1963), the St. Lawrence River water contains 180 ppm dissolved solids on average, which correspond to an annual supply of 80.46 x 10<sup>6</sup> tons. The dissolved silica concentration is 5.5 ppm, equivalent to a yearly output of 2.5 x  $10^6$ Based on (i) the average silica concentration in the waters of the lower St. tons. Lawrence River, (ii) on an SPM average concentration of 20 mg/L (d'Anglejan, 1990), and (iii) on the concentrations of total and amorphous silica determined by us in the SPM, a first order estimate is that up to 2.62% of the total dissolved silica in the lower St. Lawrence River water could be accounted for by the release of amorphous silica from their suspended load (Table V). In the present laboratory experiments, the weight-volume ratios (1g/50mL) are considerably above the natural concentrations of the SPM (20 mg/L). Hence, this calculation assumes that all the amorphous silica in the SPM is released. Therefore, the amounts of amorphous silica reported in Table V represent maximum values. Because of the long residence time, several months, and high concentrations (up to 400 mg/L) of the SPM in the low brackish environment of the turbidity maximum zone (d'Anglejan, 1990), the potential contribution of the SPM amorphous matter to the total

Table V. Amount of silica released by the amorphous fraction from the suspended particulate matter (SPM) to the St. Lawrence dissolved load.

Average SPM concentration in the St. Lawrence River (upstream of Quebec city)	= 20 mg/l (d'Anglejan, 1990)
Silica concentration in SPM	= 552 mg/g (Table I)
Silica concentration in amorphous fraction of SPM (by DCB extraction)	= 4 mg/g (Table I)
Amount of amorphous SiO <sub>2</sub> released in freshwater experiment per gram of SPM (Table II)	= 4/552 x 100 = 0.72%
Amount of amorphous $SiO_2$ released by 20 mg SPM	= 0.72  x  20/100 = 0.144  mg
Average $SiO_2$ concentration in the St. Lawrence River	= 5.5 mg/l (Livingstone, 1963; Yeats, 1988)
% contribution of the amorphous silica to the total dissolved silica concentration	$= 0.144/5.5 \times 100 = 2.62\%$
input of dissolved  $SiO_2$  into the estuary may well exceed considerably the value calculated above. Yeats (1988) observed that during the spring freshet, a time of peak delivery of SPM, the  $SiO_2$  concentrations (6.5 mg/L) are much higher in the lower St. Lawrence River than in the estuary, a fact which he found puzzling. The above calculations also neglect any contribution of amorphous silica from resuspended bottom sediments in the river and the estuary.

At first sight, the compact and massive post-glacial clays would appear to be too impervious to ground water solutions to make a significant contribution to the dissolved chemical load of the drainage waters. However, it has been reported that, due to frequent fracturing, the near-surface zone (1 to 2 m thick) of the Champlain Sea deposits is moderately permeable (Lafleur and Giroux, 1983). Hence, the transport of dissolved silica by ground water flow cannot be ruled out, although no evidence for it has as yet been reported.

Meybeck (1980) observed that dissolved silica in rivers from cooler climatic regions is typically less than in rivers from warmer regions. He suggested that this is at least partly caused by a decrease in the intensity of chemical weathering in cooler areas. Comparison of the dissolved silica concentrations in a number of major world rivers (Table VI) is consistent with this interpretation, indicating that the lower silica concentration in the St. Lawrence River is a reflection of climatic factors.

Differences in rock types in river basins determine differences in the concentrations of dissolved silica between rivers of the same climatic zone. In the Amazon basin, Stallard (1980) found greater silica concentrations in rivers flowing over

River	SiO <sub>2</sub> mg/L	Fe μg/L	Al μg/L	References	
St. Lawrence	5.5	56	64	Livingstone (1963); Yeats (1988)	
Saguenay	-	52	78	Yeats (1988)	
Amazon	11.2	30	40	Gibbs (1972; 1977)	
Zaire	9.8	250	36	Meybeck (1978)	
North American Rivers	9.0	300	400	Livingstone (1963); Durum & Hafty (1963)	
Global average	12.4	670	400	Sarin & Krishnaswami (1984); Riley & Chester (1971)	

Table VI. Average dissolved silica, iron and aluminium concentrations in the St. Lawrence and other major rivers of the world.

igneous and metamorphic terrains than in those cutting through sedimentary rocks. His explanation is that sedimentary silicates release less silica because they consist largely of detrital minerals that are basically resistant to weathering. At odds with this conclusion, Livingstone's (1963) analyses for the St. Lawrence waters indicate a systematic increase in silica concentration as the river moves eastward, from regions underlain by the crystalline basement of the Canadian Shield to the Lowlands, underlain by the Champlain Sea sediments. The average concentrations of dissolved silica reported for Lake Erie and Lake Ontario which extend over Precambrian igneous and metamorphic basement are between 2.1 to 3.7 ppm SiO<sub>2</sub>, as opposed to concentrations of 3.9 to 9.9 ppm for the St. Lawrence River between Kingston and Sorel where it flows over exposed Champlain Sea deposits. Based on the experimental evidence reported here, it would seem that the increasing dissolved silica load of the St. Lawrence River as it flows downstream could well be accounted for, at least partly, by the release of amorphous silica from the finegrained post-glacial deposits. Meybeck (1980) suggest that the presence of diatoms in the Great Lakes may lower the silica concentration there.

# IV. 3. Removal processes of iron and aluminium

The amorphous Fe and Al in post-glacial sediments appear to be present as hydrated oxides which take the form of discrete particles and coatings (Bentley <u>et al.</u> 1980; Quigley, 1980). The trends in removal of iron and aluminium are similar (Figs. 2 and 3). This suggests that they respond to the same process. The amounts of iron and aluminum released at zero salinity (Fig. 3 and 4) are significantly higher (Fe, by 1.99 to

3.81 ppm and Al, by 0.61 to 1.20 ppm) than those reported for the St. Lawrence River water (Table V). This may reflect in part an abundance of microcolloidal flocs within the samples studied. The "dissolved" fraction was defined here as that passing a Millipore filter 0.45  $\mu$ m nominal pore diameter. Abundant Fe and Al-rich colloids smaller than this size are known to exist in river waters (Boyle <u>et al.</u> 1977; Sholkovitz, 1978; Figuéres <u>et al.</u> 1978). Possibly, the Eh, which was not monitored, may have become low or even negative in the suspensions at the end of the experiments, creating conditions favourable to the dissolution of some of the Fe colloids.

A possible origin of these elements is the alteration of Fe and Al containing detrital minerals by glacial crushing and grinding under pressure. This is in agreement with grinding experiments conducted by Keller <u>et al.</u> (1963) on rock-forming silicate minerals (Table IV). They demonstrated that up to 0.9 ppm of Al (nepheline, 2.2 ppm), and up to 0.6 ppm of Fe (biotite, 14.3 ppm) were released from silicate minerals in distilled water due to grinding. They attributed the significantly higher release of Al from nepheline to change in pH, and that of Fe from biotite to the release of Fe from octahedral and interlayer ions.

Deposition may have followed flocculation during transportation by glacial meltwaters to the transgressive seas during ice retreat. The formation of flocs as river water enters the sea is caused by the neutralization of electrostatic repelling forces at mineral grain surfaces by sea water cations. The particles are held together at close range by Van der Waals forces. Fe and Al colloidal hydroxides occur as colloidal and subcolloidal flocs which are incorporated in the sediments by settling out. The Fe in the colloidal aggregates may have been released by reduction in the suboxic to reducing pore water environment. It has been shown that because of the presence of enough organic matter disseminated through the sediments, the alkaline ground waters percolating through the Champlain Sea deposits are reducing. Eh values of -276 to -343 mV have been determined (Donovan and Lajoie, 1979). The reduced iron may therefore be transported in solution and reprecipitate around detrital grains in the oxidizing environment of the vadose zone, forming a component of the labile "amorphous" coating. The present experiments suggest that some of these Fe and Al hydroxide precipitates, may have been released presumably as fine colloids, by stirring in zero salinity water. The possibility of releasing significant amounts of Fe and Al from surface coatings on residual sands of glacial origin by stirring in distilled water has been demonstrated by d'Anglejan, et al. (1990).

At zero salinity, the Fe/Al ratio in the filtrate obtained at the end of the experiment was essentially the same for the three samples (A, 1.75 and 1.79; B, 2.29 and 2.28; C, 2.95 and 2.86) after pretreatment with both DCB and Alkali-Tiron reagents. The interelemental relationship of iron and aluminium with silica released from the post-glacial clays shows positive correlation (r SiO<sub>2</sub>-Fe = 0.47; SiO<sub>2</sub>-Al = 0.53). Such a covariance may point to a common origin, in the "amorphous" material of the post-glacial marine clays.

The weight losses recorded on the three types of sediments at the end of the experiment are inversely related to the salinity (Table II). Simple mass-balance calculations show that the loss of inorganic material in post-glacial sediments accounts

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for between 22% and 26% of the original material in zero-salinity water, and between 1% and 5% at a salinity of 28. These amounts are in close agreement with the observed losses of dissolved silica, and of iron and aluminium.

# **V. SUMMARY AND CONCLUSIONS**

This study indicates that silica as well as the hydrated oxides of iron and aluminium which are held in the "amorphous" fraction of the post-glacial marine deposits of the St. Lawrence Lowlands may represent a potential source of SiO<sub>2</sub>, Al and Fe to the St. Lawrence River waters. Laboratory experiments show a significant release of silica from the sediments in fresh water within a six week reaction time. The equilibrium concentration of silica in fresh water is higher than the solubility of silica from quartz, plagioclase, K-feldspar, amphibole, illite and chlorite, which are common in these postglacial sediments, but lower than for a pure amorphous silica phase. This observation may help to explain, at least partly, the increase in silica concentration in the St. Lawrence River waters reported by Livingstone (1963), as they flow over the Champlain Sea deposits in the St. Lawrence Lowlands. It is postulated that physical alteration of detrital minerals by grain-to-grain grinding during glacier ice movement at the end of glaciation is the main source of the amorphous silica, and of the iron and aluminium present in the fine post-glacial marine deposits (Keller et al. 1963; Kodama and Jaakkimainen, 1981). The present experiments show that the ionic concentrations of sea salts have a negative effect on the release of soluble silica, particularly for samples from

the exposed and submerged deposits, in agreement with laboratory observations by Siever and Woodford (1973). Larger amounts of dissolved silica released from the SPM in the brackish environment of the estuary is attributed to the presence of biogenic silica, mainly diatoms frustules which were observed under SEM. This material dissolves more readily than the amorphous silica in the sediments. The relatively high concentrations of iron and of aluminium in the filtrate following long term stirring in zero salinity water reflect the release of colloidal and subcolloidal particles of Fe and Al hydrated oxides which are held as surface coatings and matrix precipitates in the marine clays.

# ACKNOWLEDGMENTS

We would like to thank Professors Alfonso Mucci and Reinhard Hesse for their helpful criticisms of this paper, and Ms. Glenna Keating for assistance during chemical analyses.

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# **CHAPTER IV**

# MINERALOGY, CHEMISTRY AND PARTICLE SIZE INTERRELATIONSHIPS IN SOME POST-GLACIAL MARINE DEPOSITS OF THE ST. LAWRENCE LOWLANDS

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# ABSTRACT

In order to better characterize the nature of the source material of the present-day suspended load of the St. Lawrence River, we have examined the mineralogy and chemistry of the clay and colloid-size fractions of subaerially exposed Champlain Sea deposits and of submerged Goldthwait Sea deposits under the Upper St. Lawrence Estuary. Similar analyses were obtained on lower St. Lawrence River and estuarine suspended sediments. The mineralogical composition, obtained from semi-quantitative X-ray studies, changes with particle size. Primary minerals (feldspar and quartz) are predominant in the clay-size fraction, while layer silicates (illite and chlorite) are abundant in the colloid-size fraction. The chlorite is Fe-rich. The mineralogical composition of the clay-size material in the Champlain and Goldthwait Sea deposits is similar to that found in suspension. Since the marine deposits of the St. Lawrence Lowlands contain the lowest mineral maturity (M<sub>M</sub>) and chemical maturity (Ch<sub>M</sub>) values, when compared to some of the major rivers of the world, it appears that mineralogically and chemically immature material is still being supplied by the St. Lawrence River under the present climatic conditions. An increase in illite content, M<sub>M</sub>, Ch<sub>M</sub> and a decrease in primary minerals in the colloid-size fraction with increasing depth is observed in some of the profiles investigated. This suggests the possibility of post-glacial diagenetic alteration. Higher chemical index of alteration (CIA) values in sediments which have been subaerially exposed as compared to those which have remained permanently submerged may be due to leaching or weathering by ground water effects on the exposed deposits, also a cause for the removal of the more labile minerals.

# I. INTRODUCTION

Post-glacial marine transgressive deposits of the Goldthwait and Champlain Seas (13,000 to 9000 y BP) constitute the main surficial material of the St. Lawrence Lowlands. These deposits consist of a marginal facies, made up of interlayered coarse sands and silty clays, and a deep-water facies represented by massive light grey, frequently sensitive, fine clays. Due to erosion and transportation as a result of the post-glacial isostatic uplift, these relict post-glacial marine clays have provided a major source to the suspended inorganic load of the St. Lawrence River in Holocene time. At present, the major input of solids to the St. Lawrence River at Quebec City. The yearly input is estimated to be about  $4 \times 10^6$  metric tons (Milliman and Meade, 1983).

The mineralogy of the Champlain Sea clays (now mostly subaerially exposed) has been investigated by various researchers (Brydon and Patry, 1961; Gillot, 1971; Bentley and Smalley, 1978; Lebuis and Rissmann, 1979; Yong <u>et al</u>. 1979; Locat <u>et al</u>. 1984; Torrance, 1988) because of its influence on their geotechnical properties (of the clays such as sensitivity, liquidity index, etc.). The different methodologies used by various researchers make it difficult to compare results. For example, the results of Brydon and Patry (1961), Gillot (1971), and Lebuis and Rissmann (1979) are based on X-ray diffraction. Bentley and Smalley (1978) and Yong <u>et al</u>. (1979) used X-ray diffraction, X-ray fluorescence, thermogravimetry and selective-dissolution analyses. Locat <u>et al</u>. (1984) used X-ray diffraction to estimate quartz, feldspars, amphiboles and calcite contents. Total phyllosilicates were determined by the difference between the total dry weight of the sediment and of these primary minerals. The mica group (illite) was evaluated by analyzing for K with a correction for the presence of microcline. However, general agreement now exists that the primary minerals: feldspars, quartz, and amphiboles are the main constituents of the sediments. Phyllosilicates, mainly illite and chlorite; amorphous oxides and carbonates are present as accessory components.

Some attention has been directed toward the mineralogy of the Goldthwait Sea clays (now in part submerged under the St. Lawrence Estuary) and of the St. Lawrence River and its estuarine suspended sediments (d'Anglejan and Smith, 1973; Konta, 1985). d'Anglejan and Smith (1973) found temporal and spatial variations in the mineralogy and chemistry of the St. Lawrence estuarine SPM. The average clay mineral composition of the <2  $\mu$ m fraction was reported as 60% illite; 31% chlorite; 8% kaolinite and 1.5% montmorillonite. On a total-sediment basis, Konta (1985) reported about 47% illite; 11% chlorite; 15% quartz; 4% K-feldspar; 17% plagioclase and 6% amphibole for the St. Lawrence River SPM.

Apart from these results, relatively few quantitative estimates of the mineralogy were attempted. In particular, these studies did not provide a detailed mineralogy of the Champlain and Goldthwait Sea sediments and of its variations with depth, size and location.

Both mineralogy and particle size control the elemental composition of riverborne sediments. Hence, the fine particle sizes of the source sediments and the SPM need to be compared as to their mineralogical and chemical compositions. This paper examines

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the variations in mineralogical and chemical compositions with depth and size (clay and colloidal fractions) along six profiles in Goldthwait and Champlain Sea deposits. The mineralogy was studied by X-ray diffraction using the most recent method available for quantitative mineralogical analyses (Heath and Pisias, 1979; latter modified by Pisias, 1989 unpublished). The sediment chemistry was obtained by X-ray fluorescence. Similar work was carried out on samples of the SPM from the lower river and from the estuary. Attempts have also been made to ascertain the environment of deposition of the post-glacial clays by analyzing the boron content in some of these samples. It is hoped that these analyses will help to better characterize the nature of the source material of the present-day suspended load of the St. Lawrence.

# **II. GEOLOGICAL ENVIRONMENT**

The Goldthwait Sea occupied the St. Lawrence Estuary and Gulf from approximately 13,500 y BP on (Dionne, 1988). The Champlain Sea (Fig. 1) flooded a basin of about 53,500 km<sup>2</sup> that occupied the isostatically depressed St. Lawrence Lowlands of Ontario, Quebec, New York, and Vermont during the final retreat of the Laurentide Ice sheet (between 12,000 to 10,000 y BP) from eastern North America (Elson, 1969; Gadd, 1975; Cronin, 1977; Hillaire-Marcel, 1979). The surface area of these marine basins underwent temporal changes that were controlled by three factors: 1) retreat of the ice sheet; 2) glacial isostatic recovery and 3) globally rising sea level (Parent and Occhietti, 1988). Since deglaciation, isostatic recovery was very rapid. By 9000 y BP,



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about 85% of the coastal emergence had occurred (Dionne, 1990). The mean rate of isostatic uplift decreased from 3 cm year<sup>-1</sup> at 13,000 y BP to less then 1 mm year<sup>-1</sup> today (Dionne, 1988). Marine maximum depth of about 250 meters north of Montreal and about 55 meters south of Lake Champlain have been established (Parent and Occhietti, 1988). During the isostatic rebound, part of the associated marine deposits were lifted above sea level, while others remained submerged under the St. Lawrence River and its Estuary.

The St. Lawrence River drains a basin of approximately 1.2 x 10<sup>6</sup> km<sup>2</sup> consisting largely of crystalline rocks of the Canadian Shield. The surficial cover of much of the area immediately bordering the Great Lakes and north and south of the St. Lawrence River valley is composed to a large extent of the fine-grained sediments of the Champlain Sea. These are derived predominantly from ice-ground Precambrian material from the Canadian Shield ("rock flour"). Lithofacies of the Champlain Sea deposits have been described from boreholes in the Ottawa Valley (Gadd, 1986). The stratigraphically lowest marine deposits consist of massive to weakly stratified blue-grey clays and silty clays which apparently were deposited at the time of deglaciation, while the upper Champlain Sea horizons show a marked decrease in salinity as indicated by salinity-dependent foraminiferal assemblages (Rodrigues and Richard, 1986). The top unit consists of rhythmically bedded couplets of grey, silty clays and red clays, that are considered to represent deltaic deposits. The sequence indicates upward coarsening in a gradation from open marine conditions at the base, to freshwater conditions at the top. The stratigraphically highest unit associated with deposition in the Champlain Sea ranges from

clay to sand in texture.

Seismic reflection surveys of the Upper St. Lawrence Estuary (Praeg et al. 1990) indicate accumulation of 200 meters or more of marine clays over glacial tills and the bedrock. Most of these consist of seismically transparent deep water marine clays of Goldthwait age. These clays often lie under a thin cover of Recent sediments, at some places outcropping on the channel floor (d'Anglejan and Brisebois, 1978).

### **III. MATERIALS AND METHODS**

# **III. 1. Sampling**

Subaerially exposed deposits were sampled along three stratigraphic sections (Saint-Césaire, Sparrowhawk Point, Casselman) outcropping in the Central St. Lawrence Lowlands (Fig. 1). Submerged deposits were collected by gravity coring in the Upper St. Lawrence Estuary (Fig. 2). The core samples are identified as being of Goldthwait age on the basis of the sediment characteristic colour (bluish-grey) and textural properties, including high plasticity and fine grain-size (more than 50% by weight of particles <2  $\mu$ m). These properties make these sediments very different from modern estuarine deposits.

The above sections and cores were subsampled at intervals of 5 to 10 cm. Suspended sediment samples were collected in the lower St. Lawrence River and in the turbidity maximum zone of the Upper St. Lawrence Estuary by continuous flow centrifugation. Figure 2. The Upper St.Lawrence Estuary: location of the core and suspended-sediment sampling stations.



# **III. 2. Laboratory analyses**

Prior to size separation, the calcium carbonate in the sediment samples was dissolved (Jackson, 1969) using a 1N sodium acetate buffer (82 g of sodium acetate and 27 mL of glacial acetic acid, per litre, adjusted to pH 5.0) and the suspension centrifuged until the supernatant liquid was clear. The residues, considered to represent the carbonate-free fraction were separated into a sand fraction (>62  $\mu$ m), a silt fraction (2-62  $\mu$ m), as well as a clay (1-2  $\mu$ m) and a colloidal fraction (<1  $\mu$ m) by wet sieving and by centrifugation, as described by Harry <u>et al</u>. (1984). The present study deals only with the clay and colloidal fractions, which constitute more than 50% of the total sediments (Ramesh and d'Anglejan, 1990).

Due to the limited quantity of material available, the samples of SPM were not size-fractionated. However, earlier studies by Kranck (1979) indicate that the SPM is composed primarily of fine silts and clays with modal sizes between 5 and 10  $\mu$ m, but lower median sizes.

Aliquots of the clay and colloidal size fractions of the sediments as well as the bulk SPM were treated by the Dithionite-Citrate-Bicarbonate (DCB) procedure of Mehra and Jackson (1960) in order to remove amorphous oxides.

Using X-ray powder diffractometry, precise clay mineral concentrations that accurately reflect sample to sample variations can be determined by adding a 10% talc internal standard (Heath and Pisias, 1979). For the X-ray powder diffraction analyses, 100 mg of sample were dispersed in 5 ml of deionized distilled water. A similar suspension of talc (obtained from Alberene, Virginia), prepared by wet-grinding and Stoke's law settling was also made. A homogenized mixture of 1.8 ml of clay suspension and 0.2 ml of talc suspension was transferred to a 15 ml test tube and stirred with a Deluxe mixer or a Branson ultrasonic cleaner. The suspension was then immediately transferred on to a 37.5 mm x 25 mm glass slide by pouring directly from the test tube. No washings were applied to the test tube, as this might disturb the homogeneity of the suspension on the slide (Kodama <u>et al.</u> 1977). Due to this, a small loss (1-2 mg) of sample was therefore unavoidable. Selected samples were heated at 550°C for 1 hour. Other samples were glycolated overnight before X-ray analyses.

All samples were analyzed using a Siemens D 500 X-ray diffractometer at 1° 20 per minute. CuK $\alpha$  radiation was generated using settings of 40 kV and 20 mA. Diffractogram peak areas were determined using the peak height times peak width at half height method (Segall <u>et al.</u> 1987).

The 10 Å, 7 Å, 8.4 Å, 3.34 Å, 3.19 Å and 3.25 Å peaks were used to identify illite, chlorite, amphibole, quartz, plagioclase and K-feldspar, respectively. No smectite was found. Heating kaolinite to 550°C for 1 hour causes it to become amorphous to Xrays and its diffraction pattern disappears (Moore and Reynolds, 1989). This test suggests that kaolinite is absent in post-glacial sediments. No attempt was made to resolve and quantify more complex mixed-layer clay mineral phases, minor amounts of which appear to be present in some samples.

To simplify processing, all peak areas were normalized to the area of the 9.3 Å peak of the 10% talc internal standard. Linear programming (Heath and Pisias, 1979; latter modified by Pisias, 1989 unpublished) was used to generate factors for converting

talc-normalized peak areas to weight percentages. This procedure minimizes residuals (non diffracting or poorly crystalline components), but its accuracy is untested. Although this procedure results in an average residual of about 35% for post-glacial sediments, other peak-area to weight conversion schemes (Biscaye, 1965) generate even larger values. The percentages calculated for these samples are semi-quantitative and reflect only the relative abundances of identified minerals. Duplicate analyses show generally good reproducibility. Overall analytical precision is estimated to be  $\pm 5\%$ .

The major, minor and trace element chemistry of the bulk estuarine suspended sediments and a limited number of the clay and colloid-size fractions of the exposed and submerged sediment samples were analyzed by X-ray fluorescence (Philips BW 1400). The accuracy was checked by analyses of two certified soil-samples, SO1 and SO2 from Canadian Centre for Mineral and Energy Technology (CANMET, 1979). The results were within the 95% confidence limits of the recommended values given for these two certified materials. Overall analytical precision was  $\pm 2\%$  for the major and  $\pm 5\%$  for the minor and trace elements.

# **IV. RESULTS AND DISCUSSION**

#### IV. 1. Mineralogy and mineral distribution

The mineralogical composition of the clay and colloidal size fractions from the exposed and submerged deposits are shown on Figures 3 and 4. The relative mineral abundances change with particle size in both the exposed and the submerged deposits.

Figure 3. Semi-quantitative mineralogy of marine clay and colloid-size fractions from the Champlain Sea deposits.

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Figure 4. Semi-quantitative mineralogy of marine clay and colloid-size fractions from the Goldthwait Sea deposits.

















<1µm



87-3 # 12 (1 µm





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The proportion of phyllosilicates (illite and to a lesser extent chlorite) increases, and tectosilicates (plagioclase, K-feldspar and to a lesser extent quartz) decreases in the finer (<1  $\mu$ m) size fractions (Table I and Fig. 5). Feldspars exceed quartz in both the 2-1  $\mu$ m and the <1  $\mu$ m size fractions. The presence of plagioclase feldspar and amphibole in the smaller size fraction indicates that the post-glacial sediments are mineralogically immature, as would be expected in mechanically ground "rock flour", derived mainly from the crystalline rocks of the Canadian Shield.

The  $<1 \mu m$  fractions from the Saint-Césaire and the Sparrowhawk Point sections and from core 87-3 #12 all exhibit a downward decrease in the relative percentages of the four primary minerals: plagioclase, K-feldspar, and, to a lesser extent, amphibole and quartz. A corresponding increase in illite content is also noted along these three profiles. As sample preparation and experimental conditions were identical, this decrease may be the result of post-depositional diagenetic alteration. Based on <sup>14</sup>C dating (Rodrigues, 1988), the depth interval over which the decrease in primary minerals and the increase in illite are noted, correspond to a time interval of about 600 years. Due to isostatic rebound these Champlain Sea clays have been lifted up to 200 m above the present sea level, and have been exposed to subaerial weathering for the last 9000 years. Phyllosilicates with a dioctahedral 2:1 layer structure are known to be more resistant to chemical weathering than feldspar and quartz (Rueslåtten and Jørgensen, 1977; Pederstad and Jørgensen, 1985). Konta et al. (1970) found dioctahedral illite in the clay fraction from strongly weathered soils where all other primary minerals are absent. Pederstad and Jørgensen (1985) also found an increase in dioctahedral illite and a decrease in quartz, K-

feldspar, and plagioclase with depth in the fine fraction of the Norwegian post-glacial clays as a result of weathering. No attempt was made in this study to identify the exact nature of the illite. Since weathering intensity depends on the surface area of the mineral particles in contact with the liquid phase, the effects of weathering are most easily observed in the colloid-size fractions. Similar vertical trends in the mineralogy were not found in the Casselman section and two of the estuary cores (87-3 # 2 and 87-3 # 14). The observed mineral distribution and the textural index (sand%/silt+clay%; Ramesh and d'Anglejan, 1990) remains constant throughout the Casselman section, suggesting that these sediments may all represent deep-water marine deposits with no indication of weathering. It appears that the extent and pattern of post-depositional alteration in the Central St. Lawrence Lowlands is strongly influenced by local factors and that no broad spatial trends exist.

Diffractograms obtained on material from the cores and from some samples in the subaerially exposed sections indicate a change with size in the intensity ratio of the 001 (14.2 Å) to the 002 (7.10 Å) reflections for chlorite. This ratio decreases in the <1  $\mu$ m and the enhancement of the 002 (7.10 Å) reflection coincides with a marked reinforcement of the 004 (3.55 Å) reflection. This suggests an Fe increase in octahedral positions with decreasing size. It has been demonstrated that an increase in Fe or in other heavy metal causes weakening of the 001, 003, and 005 reflections relative to the 002 and 004 reflections ( Brown and Brindley, 1980; Moore and Reynolds, 1989). The results suggest the possibility that the relatively large Fe/Mg ratio in the Champlain beds is caused by particularly high percentages of Fe-rich chlorite. The results of this study do not preclude the formation of Fe-rich chlorite by diagenesis.

No systematic regional differences in mineralogy seem to exist between the marine clays from the exposed (Champlain) and from the submerged (Goldthwait) deposits. However, analyses of the sediment core samples from the submerged deposits (Table I) show a slight (2-5%) but significant increase in chlorite over the subaerially exposed sediments, both in the clay and in the colloid-size fractions. This suggests that the Appalachian sedimentary rocks or the soil horizons developed over the Appalachian bedrock, which are known to be enriched in chlorite (Kodama, 1979) may have represented the dominant source for the submerged deposits in the estuary region. This source would have been active during the retreat of the Appalachian ice dome. Seismic profiling of the estuary provides evidence for sediment transport from the south at that time (Praeg et al. 1990).

The illite-to-chlorite ratio in the samples analyzed ranges between 2 and 5 in the submerged deposits of the estuary, and between 3 and 7 in the exposed deposits of the Lowlands in clay and colloidal size fractions. Kodama (1979; Fig. 2) reported an average illite-to-chlorite ratio of 3 in the subsoils of the St. Lawrence Lowlands. The somewhat higher proportion of illite in the exposed deposits may well also reflect a closer proximity to sources in the Precambrian Shield, whose rocks contain abundant micas, but a relatively small amount of chlorites (Kodama, 1979).

In the fourteen samples of suspended sediment analyzed, the illite-to-chlorite ratio varies between 3 to 4. No conclusive trends are observed across the salt gradient at the head of the estuary, suggesting that flocculation exerts no sorting effect on the clay

Goldthwait Sea deposits											
a	PF	KF	A	1	с	Q	PF	KF	A	1	с
			μ						μη		
Deposi	s										
ésaire (n	=22)										
07-12	28-39	09-16	07-13	24-31	05-11	06-08	10-16	03-07	05-11	52-66	08-11
1.64	3.11	2.19	1.85	28 2.00	1.90	0.75	1.67	1.29	1.80	36 4.33	0.78
whawk F	oint (n=24	4)									
12-16	32-34	12-15	08-12	20-26	05-07	06-10	13-17	04-08	06-11	47-60	07-11
14 1.40	33 0.55	13 0.95	10 1.19	24 1.61	06 0.72	08 1.08	14 1.44	06 1.50	09 1.50	54 3.83	09 1.15
man (n=	18)										
13-17	25-28	08-10	09-13	27-37	05-07	06-09	15-21	06-09	09-12	45-53	07-09
14 1.17	26 1.07	09 0.74	1.20	33 3.31	06 0.79	07 0.94	18 1.69	08 0.96	11 0.83	48 2.70	08 0.74
ed Depo	sits										
7-3 # 2 (	(n=10)										
06-08	31-36	07-10	10-16	26-31	11-13	04-05	21-24	06-08	11-17	40-42	08-15
07 0.75	32 1.85	09 1.02	12 2.23	28 1.83	12 0.75	05 0.49	22 1.26	07 0.89	12 2.33	42 1.36	12 2.65
7-3 # 14	(n=20)										
06-09	28-35	08-12	11-15	26-30	09-13	05-07	17-22	08-10	10-13	41-44	11-14
07 0.80	30 2.24	10 1.41	13 1.14	28 1.08	11 1.22	06 0.75	20 1.27	09 0.77	11 0.94	42 0.89	12 1.02
7-3 # 12	(n=18)									-	
09-15	26-37	06-11	08-13	17-39	07-10	05-09	16-24	06-10	08-14	32-51	10-14
11	30	08	10	32	09	07	19	08	10	42	12
	Q Depositi ésaire (n 07-12 09 1.64 whawk F 12-16 14 1.40 man (n= 13-17 14 1.17 ed Depo 7-3 # 2 ( 06-08 07 0.75 7-3 # 14 06-09 07 0.80 7-3 # 12 09-15 11 2.08	Q         PF           Deposits         ésaire (n=22)           07-12         28-39           09         34           1.64         3.11           whawk Point (n=24)           12-16         32-34           14         33           1.40         0.55           man (n= 18)           13-17         25-28           14         26           1.17         1.07           ed Deposits           7-3 # 2 (n=10)           06-08         31-36           07         32           0.75         1.85           7-3 # 14 (n=20)           06-09         28-35           07         30           0.80         2.24           7-3 # 12 (n=18)           09-15         26-37           11         30           2.08         3.14	Q         PF         KF           2-1           Deposits           ésaire (n=22)         07-12         28-39         09-16           09         34         12         1.64         3.11         2.19           whawk Point (n=24)         12-16         32-34         12-15         14         33         13           1.40         0.55         0.95         man (n= 18)         13-17         25-28         08-10           14         26         09         1.17         1.07         0.74           ed Deposits           7-3 # 2 (n=10)         06-08         31-36         07-10           07         32         09         0.75         1.85         1.02           7-3 # 14 (n=20)         06-09         28-35         08-12         07         30         10           0.80         2.24         1.41         14         14         14         14         14           7-3 # 12 (n=18)         09-15         26-37         06-11         06         08         2.08         3.14         1.57	Q         PF         KF         A           2-1 $\mu$ m           Deposits           ésaire (n=22)         07-12         28-39         09-16         07-13           09         34         12         10         1.64         3.11         2.19         1.85           whawk Point (n=24)         12-16         32-34         12-15         08-12         14         33         13         10           1.40         0.55         0.95         1.19         man (n= 18)         13-17         25-28         08-10         09-13         14         26         09         11         1.17         1.07         0.74         1.20           ed Deposits           7-3 # 2 (n=10)         06-08         31-36         07-10         10-16         07         32         09         12           0.75         1.85         1.02         2.23         7-3 # 14 (n=20)         06-09         28-35         08-12         11-15         07         30         10         13         0.80         2.24         1.41         1.14           7 3 # 12 (n=18)           09-15         26-37         06-11         08-13         10         2.08	Q         PF         KF         A         I $2-1 \mu m$ $2-1 \mu m$ $2-1 \mu m$ Deposits         staire (n=22)         O7-12         28-39         O9-16         O7-13         24-31           09         34         12         10         28         1.64         3.11         2.19         1.85         2.00           whawk Point (n=24)         12-16         32-34         12-15         08-12         20-26         14         33         13         10         24           1.40         0.55         0.95         1.19         1.61         nan (n= 18)         13.10         24           1.40         0.55         0.95         1.19         1.61           man (n= 18)         13.17         1.07         0.74         1.20         3.31           1.47         1.07         0.74         1.20         3.31         1.17           1.07         0.74         1.20         3.31         1.28         1.33           0.60-08         31-36         07-10         10-16         26-31         07         32         09         12         28           0.75         1.85         1.02         2.23         1	Q         PF         KF         A         I         C $2-1 \ \mu m$ $2-1 \ \mu m$ $2-1 \ \mu m$ $2-1 \ \mu m$ Deposits         6saire (n=22)         07-12         28-39         09-16         07-13         24-31         05-11           09         34         12         10         28         07           1.64         3.11         2.19         1.85         2.00         1.90           whawk Point (n=24)         12         10         24         06           1.40         0.55         0.95         1.19         1.61         0.72           man (n= 18)         13-17         25-28         08-10         09-13         27-37         05-07           14         26         09         11         33         06         1.17         1.07         0.74         1.20         3.31         0.79           ed Deposits         7-3 # 2 (n=10)         06-08         31-36         07-10         10-16         26-31         11-13           07         32         09         12         28         12           0.75         1.85         1.02         2.23         1.83         0.75           <	Q         PF         KF         A         I         C         Q           2-1 $\mu$ m           Deposits           ésaire (n=22)           07-12         28-39         09-16         07-13         24-31         05-11         06-08           09         34         12         10         28         07         07           1.64         3.11         2.19         1.85         2.00         1.90         0.75           whawk Point (n=24)           12-16         32-34         12-15         08-12         20-26         05-07         06-10           14         33         13         10         24         06         08           1.40         0.55         0.95         1.19         1.61         0.72         1.08           man (n= 18)         13-17         25-28         08-10         09-13         27-37         05-07         06-09           14         26         09         11         33         0.6         07           1.17         1.07         0.74         1.20         3.31         0.79         0.94           of Deposits	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Q         PF         KF         A         I         C         Q         PF         KF           2-1 $\mu$ m         2-1 $\mu$ m         2-1 $\mu$ m	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

 Table I. Mean and range of mineral composition (in % by weight) in marine clay and colloid-size fractions from the Champlain and

 Goldthwait Sea deposits

Q-quartz; PF-plagioclase feldspar; KF-potassium feldspar; A-amphibole; I-IIIite; C-chlorite.

n= number of samples analyzed

SD-Standard deviation

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minerals. Since the mineralogical composition of the clay-size material in the post-glacial deposits is similar to that found in the bulk SPM (Table I and II), it appears that immature (both mineralogically and chemically) material continues to be supplied by the St. Lawrence River under the present improved climatic conditions and, that the residence of this material in soil profiles is either too short or is ineffective to produce any appreciable diagenetic transformation.

Sorting processes during erosion and transportation result in a SPM product which is significantly coarser than the source. It has a deflocculated size mode between 5 and 10  $\mu$ m (Kranck, 1979) and carries a lesser proportion of the colloid-size material. A decrease in illite content and an increase in primary minerals within the SPM as compared to the colloid-sizes of the exposed and submerged deposits (Table I and II) is in agreement with Kranck's observation. It suggests that the finest detrital products introduced by the St. Lawrence drainage system into the upper estuary are transported downstream toward the lower estuary and the Gulf of St. Lawrence on a time scale which is shorter than the slightly coarser particles. The latter tend to be retained within the estuary by the residual non-tidal circulation.

# **IV. 2. Chemical Composition**

Table III summarizes the major, minor and trace element composition of the three sediment types studied. The data do not show any systematic variation with depth either in the exposed sections or in the cores. However, an examination of the chemical composition of the clay and colloid-size materials reveals small but significant differences

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sample" number	Q	PF	KF	A	I	с	M	Chu
1	14	21	07	09	37	12	1.32	1.72
2	12	21	09	10	37	11	1.20	1.74
3	13	23	08	10	36	10	1.12	1.51
4	15	21	09	09	33	13	1.18	1.04
5	14	22	09	10	33	12	1.10	1.36
6	10	19	07	07	42	15	1.73	1.65
7	11	20	06	09	40	14	1.54	1.68
8	11	20	06	08	45	10	1.62	1.69
9	12	21	09	07	39	12	1.38	0.97
10	12	20	08	09	38	13	1.38	1.16
11	10	17	07	06	49	11	2.00	1.24
12	10	17	07	09	46	11	1.73	1.39
13	12	23	06	08	39	12	1.38	1.34
14	12	21	06	09	40	12	1.44	0.99
Range	10-15	17-23	06-09	06-10	33-49	10-15	1.10-2.0	0.97-1.74
Mean	12	20	07	09	40	12	1.44	1.39
SD	1.51	1.76	1.18	1.18	4.48	1.36	0.25	0.27

Table II. Semi-quantitative mineralogy (in % by weight) of the bulk lower St. Lawrence River and its estuarine suspended sediments

Q-quartz; PF-plagioclase feldspar; KF-potassium feldspar; A-amphibole; I-illite; C-chlorite. M<sub>M</sub>-Mineral maturity; Ch<sub>M</sub>-Chemical maturity; SD- Standard deviation

\* Sample numbers correspond to Fig. 2
		Expose	d Deposit	Deposits			rged Depo	SPM		
Element	Mean	Range	Mean	Range	Mean	Range	Mean	Renge	Meen	Range
<b>h=</b>	12	µm	12	і µ <b>m</b>	2·1 11	µm	11	і µm	Bu 14	IX
sio.	59.13	54.78-	53.97	52.58-	56.76	55.69-	53.37	52.68-	60.60	<b>57.19</b> -
•	(1.94)	62.57	(0.59)	54.73	(0.75)	58.29	(0.39)	54.19	(2.29)	63.79
TIO,	0.95	0.79-	0.92	0.80-	0.72	0.69-	0.76	0.74-	1.00	0.88-
-	(0.07)	1.03	(0.07)	0.99	(0.02)	0.75	(0.02)	0.79	(0.05)	1.11
AI,O,	18.55	17. <b>59</b> -	20.70	19.34-	18.01	17.19-	19.84	19.5 <del>9-</del>	15.63	15.04-
	(0.57)	19.40	(0.62)	21.48	(0.50)	18.56	(0.14)	19.99	(0.38)	16.36
Fe <sub>2</sub> O,	8.56	7.06-	11.49	10.46-	7.66	6.84-	10.27	10.0 <del>9-</del>	7.80	7.13-
	(0.74)	9.68	(0.78)	13.06	(0.57)	8.27	(0.1)	10.43	(0.39)	8.48
MnO	0.11	0.09-	0.13	0.10-	0.12	0.11-	0.13	0.12-	0.18	0.16-
	(0.01)	0.12	(0.01)	0.14	(0.01)	0.13	(0.01)	0.15	(0.02)	0.24
MgO	3.73	3.18-	4.47	4.23-	4.54	4.20-	5.31	5.08-	3.13	2.42.
	(0.44)	4.81	(0.27)	5.14	(0.15)	4.74	(0.1)	5.49	(0.36)	4.07
CeO	2.73	2.27-	2.34	1.85-	5.84	4.92-	4.03	3.26-	3.06	2.60-
	(0.59)	4.49	(0.52)	3.84	(0.78)	7.27	(0.42)	4.83	(0.32)	3.54
Na <sub>z</sub> O	2.12	1.75-	1.43	1.09-	2.67	2.22-	2.26	1.94-	5.50	2.38-
	(0.25)	2.59	(0.26)	2.12	(0.32)	3.05	(0.24)	2.62	(2.81)	10.31
K <sub>2</sub> O	3.46	3.12-	3.62	1.09-	3.89	3.13-	3.77	3.55-	2.73	2.27.
	(0.30)	4.30	(1.40)	4.55	(0.19)	3.68	(0.13)	3.93	(0.43)	3.52
P,O,	0.22	0.15-	0.24	0.13-	0.22	0.18-	0.23	0.19-	0.37	0.33-
	(0.04)	U.27	(0.00)	0.31	(0.02)	0.23	(0.02)	0.23	(0.04)	0.40
/	112	91- 142	138	115-	<b>92</b>	79-	115	104-	•	•
	(13.1)	176	(13.7)	101	(5.5)	20	(5.7)	124		
Cr	219 (47 E)	140-	246	177-	227	121-	305	154-	•	•
	(47.5)	201	(44.2)	235	(70.1)	335	(00.0)	3/8		
	63 (11 7)	46- 85	82 A9 29	72-	71 (9.3)	56- 25	<b>87</b>	66- 90	<b>44</b> (10.19)	33- 70
_	()	~	(*.~)	••	(8.3)	8	(10.0)		(10.10)	/0
30	1067 (266.8)	571- 1340	10009 (263.6)	495- 1244	787 (153.6)	554- 1038	704 (109.8)	540- 824	•	•
<b>`</b>	40	17-	64	50-	38	17-	58	38-	16	13-
	(14.3)	66	(9.4)	79	(14.6)	58	(15)	82	(2.1)	21
λ <b>ι</b>	130	28-	150	15-	73	10-	83	14-	42	29-
	(69.1)	229	(67.4)	215	(58.73)	170	(57.4)	182	(12.1)	77
ъ	37	25-	50	30-	28	18-	33	27.	•	•
	(8.9)	52	(14.8)	71	(9.1)	52	(4.5)	42		
'n	142	102-	238	132-	102	79-	136	127-	188	131-
	(28.3)	192	(205.1)	907	(13.1)	115	(5.6)	147	(34.7)	240

Table III. Mean and range of elemental composition<sup>®</sup> (corrected to L.O.I) of fine grained sediments from the St. Lawrence Lowlands

@ Major element analyses are given in wL%; minor element anlayses in  $\mu g/g$ ; L.O.I. = Loss of ignition n= number of samples analyzed; Standard deviation given in brackets

in composition which are also apparent in the mineralogical studies. For example, the depletion of Si, Na, and Ca in the colloid-size fraction reflects diminishing amounts of quartz and plagioclase. Similarly, enrichment in Al, Fe and Mg in the same fraction reflects an increasing abundance in clay minerals and Fe hydroxides. Loring and Nota (1973) also reported change of major elemental composition with particle size for the coarser fractions of marine sediments from the Gulf of St. Lawrence. An increase of Fe/Mg ratio (by 0.3) in the colloid-size compared to the clay-size fractions, may be due to an increase in Fe-enriched chlorite in that fraction.

Table III indicates that, compared to sediments from the exposed sites, the clay and colloid-size fractions in the cores are significantly higher in Ca, Na, K and Mg and lower in Si, Ti, Al and Fe. Mobilization of these elements by soil solutions in the vadose zone may partly explain this difference. It has been reported that the near-surface zone in the Champlain Sea clays is moderately permeable, as a result of fracturing and other weathering effects (Lafleur and Giroux, 1983). Thus Ca, Na and K could be partly removed from the feldspars and Mg from the amphibole or the chlorite by soil solutions and ground water from the upper horizons of the exposed deposits.

The average Mn, Ni, Co and Cu concentrations (Table III) in the Champlain and Goldthwait Sea clays are considerably higher than in the samples of suspended sediments. The post-glacial deposits may therefore be a source of dissolved trace metals to the river.

# IV. 3. Evidence of mild weathering

The mineral maturity  $(M_M)$  can be expressed as the ratio of the sum of the more

stable minerals, to that of the less stable minerals in aqueous environments (Konta, 1988). The  $M_M$  reflects the mechanical to chemical weathering ratio of sediments in a river basin.

The mineral maturity of the St. Lawrence River and its estuarine SPM and of the sediment samples from the sections and cores were computed from the X-ray data as the ratio of the sum of the percentages of the phyllosilicates, relatively more stable in aqueous environments, to the sum of percentages of the less stable clastic primary minerals:

 $M_{M} = \%$ (illite + chlorite)/ % (plagioclase + K-feldspar + amphibole)

Quartz is not included in the ratio, because it only dilutes the sum of the more stable phyllosilicate minerals (Fig. 5).

The chemical maturity  $(Ch_M)$  can be expressed by a simple ratio %  $Al_2O_3$  : %  $(Na_2O + MgO + CaO^*)$  (Konta, 1985), where CaO<sup>\*</sup> is the amount of CaO incorporated in the silicate fraction of the rocks. The Ch<sub>M</sub> reflects the intensity of weathering in a river basin.

Table II and IV present the computed values of  $M_M$  and  $Ch_M$  for the SPM, and for the samples from the exposed and from the submerged deposits. As might be expected,  $M_M$  and  $Ch_M$  increase in the fine-grained (<1 µm) fractions, which have a larger surface area. In the Saint-Césaire, and Sparrowhawk Point sections and in core 87-3 # 12,  $M_M$  and  $Ch_M$  increase with depth in the colloid-size fractions (refer Table A-19 to A-22 in the appendix). The  $M_M$  increases from 1.94 to 4.22 at Saint-Césaire; from 1.50 to 3.09 at Sparrowhawk Point, and from 0.98 to 2.06 in core 87-3 # 12. The  $Ch_M$  increases from 2.24 to 2.81; from 2.26 to 2.74, and from 1.70 to 1.76 respectively, for the two Figure 5. The triangular plot of the sum of the percentages of the phyllosilicates (illite and chlorite), the sum of percentages of clastic primary minerals relatively less stable in aqueous environment (plagioclase, K-feldspar, amphibole) and the percentage of quartz in clay and colloid-size fractions of the Champlain and of the Goldthwait Sea deposits and in the bulk suspended sediments of the St. Lawrence River and its Estuary.



Location	M	Ch <sub>M</sub>	M	Ch <sub>M</sub>	
n=	2-1 µ 56	ـm 23	< 1 µ 56	um 23	
Exposed Deposits					
1.Saint-Césaire	0.64	2.25	2.52	2.61	
	(0.12)	(0.16)	(0.71)	(0.23)	
2. Sparrowhawk Point	0.53	2.18	2.25	2.53	
	(0.04)	(0.11)	(0.46)	(0.15)	
3.Casselman	0.86	2.09	1.56	2.45	
	(0.10)	(0.25)	(0.17)	(0.37)	
Submerged Deposits					
1. Core 87-3 # 2	0.76	1.30	1.31	1.69	
	(0.04)	(0.13)	(0.09)	(0.12)	
2. Core 87-3 # 14	0.74	1.45	1.37	1.74	
	(0.04)	(0.05)	(0.06)	(0.04)	
3. Core 87-3 # 12	0.85	1.48	1.46	1.73	
	(0.22)	(0.05)	(0.28)	(0.03)	

Table IV. Mean mineral and chemical maturity in marine clay and colloid-size fractions from the Champlain and Goldthwait Sea deposits

n= number of samples analyzed; Standard deviation given in brackets

M<sub>M</sub> - Mineral maturity; Ch<sub>M</sub> - Chemical maturity

sections and the core. The downward increase in both  $M_M$  and  $Ch_M$  in the colloid-size fraction supports the interpretation, already suggested by the mineral concentration profiles, that mild weathering may have taken place since deposition. Pederstad and Jørgensen (1985) have demonstrated similar changes due to weathering in Norwegian post-glacial clays. These clays were deposited in marine or brackish environments, similar to those of the Champlain Sea deposits, immediately after glacial retreat and were subsequently elevated above sea level by isostatic readjustment of the land surface.

Table V gives the average  $M_M$  and  $Ch_M$  in post-glacial sediments of the St. Lawrence Lowlands and in sediments from other major world rivers (Konta, 1985 and 1988). The St. Lawrence post-glacial sediments show the lowest values, indicating that these sediments are mineralogically as well as chemically immature when compared to other large river basins. Both the  $Ch_M$  and the  $M_M$  of suspended sediments in rivers depend on several factors: climate, relief, geology of the drainage basin, source of the sediments and vegetation. However, the values shown in Table V suggest that climate is the major controlling factor. Tropical and subtropical rivers (Niger, Orinoco, Orange, Parana) contain suspended sediments having higher  $M_M$  and  $Ch_M$ . The lower values of  $M_M$  and  $Ch_M$  are typical of the suspended inorganic sediments in rivers draining cold or warm arid regions (St. Lawrence, Mackenzie, Nile), where rates of erosion are relatively high.

Another measure of the degree of weathering can be obtained by calculation of the chemical index of alteration (CIA) using molecular proportions (Nesbitt and Young, 1982).

River	М <sub>м</sub>	Ch <sub>₩</sub>
St. Lawrence Lowlands <sup>®</sup>		
a) Exposed Deposits	1.39	2.35
b) Submerged Deposits	1.08	1.57
c) St.Lawrence River & Estuarine SPM	1.44	1.39
Mackenzie	3.22	2.50
Orinoco	17.84	4.80
Parana	5.91	5.30
Nile	1.84	1.20
Niger	34.15	5.50
Orange	12.64	1.60
indus	3.71	1.50
Ganges	6.88	1.30
Brahmaputra	2.75	2.60

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Table V. Mineral and chemical maturity in the St. Lawrence Lowland sediments and other major rivers of the world

@ average values from present study

For other river basins data were computed from Konta, (1985) and (1988)

M<sub>M</sub> - Mineral maturity; Ch<sub>M</sub> - Chemical maturity

# $CIA = [Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O]x100]$

where CaO<sup>•</sup> is the amount of CaO incorporated in the silicate fraction of the rock. The index is a measure of the percentage of  $Al_2O_3$  versus all labile oxides in the analyzed sample. Values of the index are 50 for unaltered albite, anorthite and K-feldspars, whereas the value for diopside is 0. Fresh basalts have values between about 30 and 45 and granites and granodiorites have higher values, ranging between 45 and 55. Idealized muscovite has a value of 75 and illite ranges between 75 and 85, as do montmorillonites and beidellites. Kaolinite and chlorite yield the highest values, very close to 100.

To facilitate the interpretation of the CIA values obtained from the clay and colloid-size fractions of the exposed and submerged deposits, values were also calculated for a variety of other rocks and sediments (Fig. 6). Chemical analyses of the clay and the colloid-size portion of the 24 Champlain Sea exposed deposits yielded CIA values ranging from 65 to 71 and from 69 to 85, respectively. These values are higher than those obtained from the average Canadian Precambrian Shield rocks (CIA value of 52; computed from Shaw <u>et al</u>. 1967). CIA for the 22 Goldthwait Sea sediment samples analyzed ranges from 56 to 63 and from 63 to 69, for the clay and colloid-size fractions, respectively. These values are comparable to the CIA for Pleistocene glacial clays (between 60 and 65) computed from Church, (1967) and Young, (1981), and slightly higher than the average value for the Shield. The relatively higher CIA values for the exposed sediments analyzed, as compared to the same index for those which have remained permanently submerged in the estuary further supports the possibility of removal of labile minerals (eg., feldspars) due to ground water weathering or leaching effects in

Figure 6. Chemical index of alteration (CIA) for clay and colloid-size fractions of Champlain and Goldthwait Sea deposits and various other rocks and sediments. Each square in the lower part of the diagram represents a single chemical analyses. Dots in the upper part of the diagram are either individual analyses or averages.
source of data: (a) Shaw <u>et al</u>. 1967; (b) Martin and Meybeck (1979); (c) Nesbitt and Young (1982); (d) Church (1967); (e) Young (1981); (f) Chandler <u>et al</u>.(1969).



the exposed deposits. Data from the lower St. Lawrence River and its Estuarine SPM gave values in the 51 to 64 range, close to the range of values obtained from the Goldthwait Sea clay-size sediments.

### **V. SUMMARY AND CONCLUSIONS**

Grain-size exerts the primary control on the mineralogy of the fine-grained postglacial marine sediments. Feldspar and quartz are abundant in the clay-size, while illite and chlorite are predominant in the colloid-size fraction. There is no significant regional variation in the mineralogy of the post-glacial sediments examined. A slight variation in clay mineral content generally corresponds with variation in bedrock lithology of the source area: fine clays from the exposed St. Lawrence Lowlands sections tend to be richer in illite, while those from the estuary, closer to Appalachian sources are richer in chlorite. Sorting processes during erosion and transportation result in a SPM product which is significantly coarser than the source. The mineralogical evidence supports the view that the finest detrital products are exported out of the estuary on a time scale which is shorter than the slightly coarser particles. These tend to be retained within the estuary by the residual non-tidal circulation.

In three of the six profiles studied, vertical trends in the mineral maturity  $(M_M)$  and chemical maturity  $(Ch_M)$ , as well as changes in the mineralogy and chemical composition of the colloid-size fraction, support the possibility of mild weathering (dissolution of plagioclase, K-feldspar, and to a lesser extent, amphibole and quartz). The

St. Lawrence Lowland sediments contain the lowest  $M_M$  and  $Ch_M$  values when compared to some of the major rivers of the world. This indicates that immature (both mineralogically and chemically) material is still being supplied by the St. Lawrence River under the present climatic conditions and that its residence in soil profiles is either too short or is ineffective in producing any appreciable diagenetic transformation. The Chemical Index of Alteration (CIA) values suggest a higher degree of alteration of the exposed deposits as compared to those which have been remained permanently submerged.

# ACKNOWLEDGMENTS

We thank Professors Reinhard Hesse and Alfonso Mucci for critically reviewing the manuscript. We are grateful to Prof. N.G. Pisias for providing the linear program for the quantitative estimation of minerals and to Mr. Jagadish for help in computer work.

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# CHAPTER V

# SUMMARY AND CONCLUSIONS

The studies presented in this thesis were done in order to improve our understanding of the geochemical and mineralogical characteristics of the fine-grained post-glacial marine clays extensively found in the St. Lawrence Lowlands, as these deposits constitute an important source of dissolved and particulate substances to the St. Lawrence drainage waters. The composition, distribution and mobility of an "amorphous" phase of glacial origin, previously reported in these sediments are examined to determine its potential role as a source of major elements, particularly Si, Fe and Al, to the St. Lawrence chemical load. The distribution, the stability and the chemical composition of the minerals present in the post-glacial marine clays are also studied in detail in order to search for evidence, if any, of alteration due to weathering, and in order to ascertain the degree of maturity of these sediments. Marine clays subaerially exposed following land emergence are analyzed, as well as similar ones which have remained submerged since deposition in the brackish environment of the estuary. These two kinds of deposits of contrasting post-depositional histories are in turn compared with the river and estuary suspended particulate matter (SPM), which is to a large extent a by-product of their present erosion. Two fine size fractions, the one-to-two microns and the less-than-one micron fractions, are analyzed separately, as together they constitute the bulk of the

deposits and regroup the most surface active particles. The main findings of this research presented in the chapters II, III, and IV are summarized here.

The problem of defining the "amorphous content" of post-glacial transgressive marine clays, in terms of a reliable procedure of chemical dissolution, was first examined. Two mild chemical extraction procedures commonly used for the extraction of labile amorphous material from sediments were compared. A procedure using, the dithionitecitrate-bicarbonate (DCB) reagents of Mehra and Jackson (1960) seems to be more selective than the Alkali-Tiron method developed by Biermans and Baert (1977). However, a high degree of covariance between the two series of results along vertical sections supports the conclusion that both procedures are extracting material of the same nature, and are not attacking randomly oxide and silicate minerals. The sum of oxides measured (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, K<sub>2</sub>O and MnO) in the amorphous fraction varies from 0.66 to 4.88% and from 1.49% to 6.60% by the DCB and by the Alkali-Tiron dissolution method, respectively. This is several times less than the values reported previously using other extraction procedures. Colloidal particles are enriched in amorphous components by a factor of one to two relative to the clay-size fraction.

Transmission electron micrographs indicate the presence of irregular aggregates which are amorphous in nature. These were absent in samples treated with the DCB and the Alkali-Tiron reagents. This material may correspond to the amorphous substances, shown to be produced in the laboratory by grinding of minerals under pressure (Kodama and Jaakkimainen, 1981). The implication is that amorphous substances in the marine clays studied are inherited from the rock flour, resulting from the pulverization of rock

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outcrops by the flowing glaciers.

The amorphous fraction accounts for a significant fraction of the 4 x  $10^6$  metric tons of suspended sediments introduced yearly by the St. Lawrence River into the estuary. Its contributions to the overall chemical composition of the suspended flux are as follows: 4 to 7 x  $10^3$  metric tons Si (0.4 to 0.7% of the total flux); 3 to 7 x  $10^3$  tons Al (0.7 to 1.7%); 25 to 45 x  $10^3$  tons Fe (9 to 16%); 25 to 27 x  $10^3$  tons Ca (18 to 19%); 2 to 3 x  $10^3$  tons Mg (2 to 3%); 1 x  $10^3$  tons K (0.8%) and 0.6 x  $10^3$  tons Mn (15%).

The release by weak reagents of some important major elements (Si, Al and Fe) which are held in the "amorphous" fraction raises the question of its mobility under exposure to river water and estuarine waters during erosion and transportation. This was examined by a series of controlled experiments in the laboratory, in which samples of marine clays, collected at both subaerially exposed and submerged sites, are kept in suspensions for a 1000 hour period in distilled water and in waters of increasing salinity. The experiments demonstrate a significant release of SiO<sub>2</sub>, Al and Fe in zero salinity water. For all three elements, there is a sharp decrease in amounts released with increasing salinity. These observations are in agreement with laboratory experiments carried out by Siever and Woodford (1973). However, the dissolved silica released from the SPM in the brackish environment (S, > 7) are higher than the sediments and remain constant, presumably because of the dissolution of incorporated biogenous silica. This is suggested by the presence of diatom fragments in SPM samples examined under scanning electron microscopy. Assuming that all silica released by the SPM at a salinity of 28 is due to dissolution of biogenous silica, its weight concentration in the SPM needs

to be 0.06%, which agrees with previous observations.

The release of SiO<sub>2</sub> from the "amorphous" fraction, indicates that in nature this processes could provide a minor, but non negligible contribution (at least 2.6%) to the dissolved silica load of the St. Lawrence River. Because of the long residence time, several months, and high concentrations (up to 400 mg/L) of the SPM in the low brackish environment of the turbidity maximum zone (d'Anglejan, 1990), the potential contribution of the SPM amorphous matter to the total input of dissolved SiO<sub>2</sub> into the estuary may exceed the value computed here. The relatively high concentration of iron and of aluminium in the filtrate following long term stirring in distilled water reflect the release of fine colloidal and subcolloidal particles of Fe and Al hydrated oxides, both of which may also be produced from the crystalline bedrock by grinding under ice loads. These oxides are held as surface coatings or matrix precipitates in the marine clays, having presumably settled out from the transgressive seas, with possible migration of Fe in the reducing to suboxic pore environment of the deposits.

The relationship between the mineralogy, the particle size and the chemical composition of deposits exposed on land, of other submerged under the Upper St. Lawrence Estuary and of river and estuarine SPM was examined. The presence of feldspar and amphibole in clay-size and even in colloid-size material indicates that these fine-grained sediments are mineralogically immature. They consist essentially of "rock flour" derived from the crystalline rocks of the Canadian Shield to the north and from the Appalachian Cambro-Ordovician sedimentary rocks to the south.

The relative mineral abundance was found to change with particle size. In the

clay-size (2-1  $\mu$ m) material, the minerals, in decreasing order of abundance, are feldspars, illite, amphibole, quartz and chlorite. No smectite was detected. In the finest fraction (<1  $\mu$ m), the order of abundance is illite, feldspars, chlorite, amphibole and quartz. A decrease in the 001/002 basal reflection intensity ratio for the less-than one-micron fraction indicates that chlorite is of a Fe-rich variety. The mineralogical composition of the clay-size material in the exposed and submerged deposits is similar to that of the suspended matter, which contains less colloid-size particles than the marine clays as a result of estuarine sorting processes.

In three of the six profiles investigated, the colloid-size fraction exhibits a downward decrease in the relative percentages of the four primary minerals (plagioclase, K-feldspar, and to a lesser extent, amphibole and quartz) and an increase in illite content. Similar vertical trends were observed in the mineral maturity index  $(M_M)$  and chemical maturity index  $(Ch_M)$  of these profiles. This suggests that mild weathering has taken place since deposition. The average  $M_M$  and  $Ch_M$  values were computed in post-glacial sediments of the St. Lawrence Lowlands and compared to some of the major rivers of the world. The particulates of the tropical and subtropical rivers (for example, Niger, Orinoco, Orange, Parana) display the greatest  $M_M$  and  $Ch_M$ , whereas the rivers draining over typical cold or warm arid basins (for example, St. Lawrence, Mackenzie, Nile) are characterized by low values. This can be explained primarily by differences in climate and weathering regimes between river basins. In the case of the St. Lawrence, which displays the lowest  $M_M$  and  $Ch_M$  values, the results probably reflect the influence not only of climatic factors but also of continued erosion of the transgressive marine clays as result

of isostatic uplift, presently estimated to be 1 mm year<sup>-1</sup>. High chemical index of alteration (CIA) values in sediments which have been subaerially exposed as compared to those which have remained permanently submerged may be due to post-depositional weathering of the exposed deposits, also a cause for the removal of the more labile minerals.

The present study represents a useful contribution to the understanding of the nature, distribution and composition of the "amorphous material" present in post-glacial marine transgressive clays, and of its significance as a contributor to the present-day dissolved load of the St. Lawrence River. It also provides additional knowledge on the nature and evolution of the source material for the present-day suspended load of the St. Lawrence. A detailed appraisal of diagenetic alterations possibly at work in the transgressive clays of the St. Lawrence Lowlands should include a comparative analyses of the chemistry of pore waters in both aerially exposed and submerged deposits.

# APPENDIX

Sample number	Si	AI	Fe	Ca	Mg	Mn	К
1	1.40	0.95	4.69	0.66	0.10	0.03	0.33
2	0.93	0.42	3.99	1.98	0.06	0.08	0.36
3	0.84	0.37	3.01	1.24	0.09	0.04	0.28
4	0.61	0.26	2.59	0.81	0.13	0.05	0.31
5	0.56	0.26	1.89	1.03	0.19	0.07	0.35
6	0.89	0.48	2.94	2.37	0.12	0.11	0.42
7	0.75	0.48	2.73	1.67	0.09	0.15	0.27
8	0.89	0.58	3.15	2.29	0.10	0.18	0.35
9	0.89	0.58	3.15	0.80	0.10	0.03	0.23
10	1.12	0.69	3.36	0.88	0.13	0.03	0.25
11	0.93	0.64	3.29	0.60	0.27	0.08	0.28
12	0.93	0.58	3.36	0.50	0.35	0.07	0.34
13	0.75	0.53	2.45	0.67	0.39	0.09	0.38
14	0.93	0.64	3.29	0.79	0.33	0.08	0.35
15	1.12	0.85	3.64	0.41	0.45	0.14	0.38
16	0.84	0.64	3.08	0.49	0.40	0.13	0.33
17	1.36	0.58	3.57	17.09	0.65	0.35	0.25
18	0.93	0.48	2.87	14.90	0.65	0.25	0.26
19	0.98	0.42	2.24	17.47	0.73	0.22	0.30
20	1.26	0.53	3.43	17.58	0.74	0.22	0.31
21	1.12	0.58	3.43	17.01	0.72	0.17	0.34
22	0.47	0.37	2.24	7.37	0.59	0.20	0.23
23	1.03	0.58	3.43	16.10	0.80	0.36	0.37
24	1.03	0.69	4.34	15.95	0.23	0.41	0.41
25	1.22	0.85	7.13	5.29	0.84	0.26	0.42
26	0.84	0.53	4.13	18.35	0.58	0.28	0.34
27	0.98	0.58	3.29	17.91	0.77	0.24	0.45
28	0.75	0.32	3.22	17.46	0.51	0.25	0.27
29	0.89	0.79	9.79	5.01	0.50	0.13	0.18
30	0.75	0.64	8.32	1.06	0.66	0.17	0.21
31	0.79	0.69	7.27	1.88	0.55	0.16	0.22
32	0.79	0.69	6.64	2.96	0.40	0.09	0.25
33	0.70	0.74	5.18	4.86	0.46	0.06	0.32
34	0.65	0.64	5.81	4.33	0.33	0.08	0.24
35	0.70	0.79	6.50	3.43	0.62	0.10	0.18
36	0.98	0.69	10.35	0.86	0.97	0.13	0.09
37	0.93	0.69	9.79	0.77	1.00	0.13	0.08

Table A-1. Amounts of major elements (mg/g) extracted by DCB reagents in the clay (2-1  $\mu$ m) size particles of the exposed deposits.

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Sample number	Si	Al	Fe	Ca	Mg	Mn	К
1	1.68	1.96	8.18	0.95	0.20	0.05	0.37
2	1.26	0.95	7.69	2.37	0.13	0.08	0.37
3	1.12	0.79	6.92	1.70	0.17	0.05	0.31
4	0.70	0.74	5.25	1.17	0.22	0.60	0.34
5	0.65	0.69	3.99	1.33	0.28	0.08	0.39
6	1.08	1.11	5.74	2.86	0.21	0.12	0.45
7	0.98	1.06	5.25	2.19	0.18	0.14	0.36
8	1.08	1.16	6.22	2.79	0.19	0.17	0.39
9	1.17	1.27	6.36	1.15	0.18	0.04	0.29
10	1.36	1.38	6.78	1.22	0.31	0.04	0.26
11	1.08	1.22	6.22	0.92	0.67	0.07	0.32
12	0.98	0.95	7.27	0.98	0.88	0.07	0.36
13	0.89	0.79	4.27	1.02	0.97	0.09	0.45
14	0.98	0.90	6.99	0.88	0.94	0.09	0.37
15	1.26	1.22	7.27	1.16	0.98	0.14	0.39
16	0.93	0.90	6.99	1.26	0.48	0.11	0.40
17	1.92	1.11	10.98	17.41	0.78	0.21	0.29
18	1.40	1.01	7.97	15.35	0.75	0.13	0.30
19	1.36	0.90	6.22	18.17	0.76	0.20	0.31
20	1.92	1.06	9.58	18.22	0.80	0.20	0.34
21	1.64	1.16	9.79	17.20	0.95	0.19	0.37
22	0.98	0.74	6.71	7.91	0.67	0.21	0.27
23	1.87	1.27	9.23	17.73	1.12	0.32	0.41
24	1.82	1.32	11.05	16.95	0.67	0.29	0.45
25	2.15	1.38	12.87	6.73	1.23	0.29	0.51
26	1.17	1.01	10.98	18.97	0.84	0.25	0.38
27	1.31	1.11	9.23	18.13	0.98	0.22	0.58
28	1.22	0.74	8.74	17.81	0.72	0.22	0.33
29	0.93	0.90	10.63	5.36	0.51	0.08	0.27
30	0.79	1.06	9.72	1.72	1.17	0.12	0.25
31	0.93	1.11	9.09	2.73	1.02	0.14	0.30
32	1.17	1.22	9.65	4.63	0.71	0.07	0.34
33	1.03	1.16	7.90	5.10	0.87	0.05	0.34
34	1.17	1.53	10.63	5.19	0.94	0.07	0.37
35	0.93	1.27	9.30	4.29	1.16	0.09	0.23
36	1.03	1.22	12.38	1.26	1.48	0.10	0.15
37	1.08	1.38	10.77	1.15	1.53	0.11	0.14

Table A-2. Amounts of major elements (mg/g) extracted by DCB reagents in the colloidal (<1  $\mu$ m) size particles of the exposed deposits.

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Sample number	Si	Al	Fe	Ca	Mg	Mn	K
1	1.92	1.75	9.23	0.72	0.13	0.04	0.35
2	1.54	1.27	8.04	2.02	0.09	0.08	0.40
3	1.45	1.11	7.27	1.25	0.10	0.04	0.34
4	1.17	1.06	8.25	0.91	0.17	0.07	0.33
5	1.12	1.06	5.67	1.08	0.20	0.09	0.38
6	1.54	1.43	6.22	2.45	0.14	0.11	0.46
7	1.54	1.16	7.62	1.72	0.11	0.14	0.32
8	1.54	1.27	8.25	2.39	0.12	0.18	0.38
9	1.54	1.32	9.16	0.85	0.12	0.06	0.27
10	1.73	1.48	10.07	0.92	0.16	0.06	0.28
11	1.64	1.32	9.93	0.72	0.28	0.09	0.32
12	1.87	1.27	10.14	0.52	0.38	0.09	0.37
13	1.50	1.11	8.74	0.65	0.42	0.10	0.39
14	1.59	1.16	7.27	0.85	0.39	0.10	0.38
15	1.96	1.43	8.88	0.49	0.49	0.16	0.39
16	1.54	1.32	7.90	0.52	0.43	0.15	0.35
17	1.92	1.38	7.13	18.12	0.72	0.32	0.31
18	1.45	1.22	4.55	15.93	0.73	0.25	0.29
19	1.54	1.22	4.55	18.12	0.78	0.23	0.32
20	1.87	1.32	6.43	17.93	0.81	0.22	0.34
21	1.78	1.48	6.57	17.56	0.79	0.21	0.38
22	1.12	1.16	4.27	10.57	0.66	0.21	0.26
23	1.87	1.48	6.43	15.65	0.85	0.33	0.39
24	1.73	1.59	6.64	17.13	0.54	0.29	0.41
25	1.92	1.80	9.72	10.22	0.90	0.27	0.43
26	1.59	1.38	7.76	15.65	0.66	0.26	0.35
27	1.64	1.43	5.81	17.73	0.79	0.26	0.47
28	1.59	1.16	5.53	17.93	0.63	0.27	0.33
29	1.31	1.27	11.26	5.62	0.56	0.12	0.20
30	1.36	1.01	9.93	2.03	0.69	0.17	0.22
31	1.40	1.32	9.23	2.58	0.66	0.14	0.25
32	1.50	1.22	9.58	3.17	0.51	0.07	0.28
33	1.12	1.22	8.60	4.98	0.57	0.06	0.33
34	1.17	1.06	9.93	4.57	0.41	0.07	0.26
35	1.22	1.32	10.00	3.88	0.67	0.09	0.21
36	1.40	1.22	13.43	1.02	1.05	0.11	0.11
37	1.40	1.16	10.28	1.08	1.07	0.11	0.11

Table A-3. Amounts of major elements (mg/g) extracted by Alkali-Tiron reagents in the clay (2-1  $\mu$ m) size particles of the exposed deposits.

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Sample number	Si	Al	Fe	Ca	Mg	Mn	К
1	2.57	2.86	16.23	0.98	0.24	0.05	0.39
2	1.96	1.80	14.20	2.42	0.17	0.09	0.41
3	2.06	1.64	15.25	1.72	0.20	0.04	0.40
4	1.54	1.96	13.50	1.20	0.25	0.22	0.39
5	1.45	1.64	10.21	1.42	0.29	0.09	0.41
6	2.06	2.01	13.29	2.92	0.24	0.12	0.51
7	1.87	2.12	12.80	2.22	0.20	0.16	0.39
8	2.10	2.22	14.76	2.69	0.22	0.18	0.41
9	2.29	2.70	15.81	1.16	0.20	0.08	0.33
10	2.76	2.75	15.95	1.24	0.27	0.07	0.31
11	2.10	2.65	14.97	0.93	0.65	0.10	0.36
12	2.29	1.80	16.58	0.95	0.91	0.09	0.39
13	1.92	1.64	10.91	1.07	0.98	0.12	0.43
14	1.87	1.85	15.60	0.92	0.96	0.10	0.42
15	2.57	2.12	17.28	1.17	0.98	0.15	0.42
16	1.96	1.69	15.95	1.32	0.52	0.16	0.41
17	2.57	2.06	19.16	18.77	0.85	0.33	0.31
18	2.06	1.80	13.92	16.25	0.82	0.26	0.33
19	2.01	1.64	11.75	18.72	0.82	0.23	0.35
20	2.71	2.06	15.60	18.13	0.85	0.22	0.38
21	2.66	2.17	16.23	17.98	0.87	0.22	0.39
22	1.54	1.64	11.54	10.94	0.75	0.28	0.31
23	2.66	2.17	15.25	16.12	0.98	0.35	0.45
24	2.71	2.38	18.05	17.88	0.70	0.39	0.45
25	2.94	2.49	18.88	10.53	1.12	0.29	0.49
26	2.10	2.17	16.09	15.92	0.94	0.29	0.39
27	2.20	2.06	15.25	18.23	0.99	0.25	0.52
28	2.10	1.69	14.20	18.57	0.83	0.28	0.39
29	1.82	1.59	12.59	5.92	0.59	0.13	0.26
30	1.45	1.53	11.82	2.25	1.21	0.17	0.27
31	1.68	1.80	11.26	3.13	1.11	0.16	0.31
32	1.82	1.69	11.96	4.26	0.91	0.09	0.35
33	1.45	1.64	11.47	5.23	0.89	0.07	0.37
34	1.73	2.06	13.78	5.42	0.95	0.08	0.36
35	1.50	1.85	13.08	4.52	1.19	0.10	0.25
36	1.54	1.91	15.18	1.30	1.36	0.12	0.17
37	1.59	2.01	11.33	1.22	1.64	0.12	0.15

Table A-4. Amounts of major elements (mg/g) extracted by Alkali-Tiron reagents in the colloidal (<1  $\mu$ m) size particles of the exposed deposits.

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Sample number	Si	Al	Fe	Ca	Mg	Mn	К
1	2.15	1.75	10.98	1.42	0.38	0.08	0.15
2	1.73	1.38	5.60	1.95	0.57	0.10	0.18
3	2.01	1.80	6.22	1.56	0.52	0.09	0.20
4	2.57	1.64	6.50	0.97	0.47	0.07	0.29
5	3.13	3.28	10.21	0.85	0.63	0.08	0.12
6	2.29	2.06	11.40	1.16	0.41	0.09	0.15
7	2.43	1.53	6.36	1.44	0.52	0.09	0.16
8	2.71	2.49	6.22	1.00	0.53	0.12	0.20
9	2.76	2.59	6.50	1.04	0.46	0.09	0.23
10	2.94	2.81	6.64	1.13	0.66	0.10	0.24
11	2.94	2.91	6.09	1.21	0.62	0.12	0.25
12	3.09	2.81	6.22	1.14	0.59	0.09	0.19
13	3.23	3.02	5.95	1.06	0.67	0.10	0.19
14	3.23	3.23	5.95	0.92	0.49	0.09	0.18
15	3.32	3.33	5.67	0.88	0.71	0.09	0.15
16	2.48	2.49	12.24	1.26	0.48	0.08	0.12
17	2.38	1.27	7.55	1.35	0.52	0.09	0.15
18	2.85	1.96	7.34	1.14	0.58	0.10	0.19
19	2.52	2.17	6.99	1.09	0.52	0.09	0.22
20	2.71	2.59	6.92	1.13	0.61	0.10	0.22
21	2.85	2.81	6.36	1.24	0.62	0.11	0.20
22	2.94	2.59	6.50	1.12	0.51	0.10	0.20
23	2.71	2.70	6.36	1.09	0.55	0.09	0.19
24	2.94	2.96	6.22	1.02	0.62	0.10	0.18

Table A-5. Amounts of major elements (mg/g) extracted by DCB reagents in clay (2-1  $\mu$ m) size particles of the submerged deposits



Sample number	Si	Al	Fe	Ca	Mg	Mn	К
1	2 90	4 23	17.77	1.87	0.45	0.09	0.24
2	2.62	2.75	9.93	2.02	0.77	0.11	0.22
3	3.69	3.44	10.42	1.92	0.85	0.10	0.28
4	2 71	1 69	6.85	1.28	0.95	0.08	0.33
5	3.18	3.55	11.19	1.13	0.94	0.10	0.15
6	3.13	3.86	14.90	1.48	0.50	0.10	0.22
7	2.66	3.12	13.78	1.68	0.62	0.11	0.24
8	2.94	3.23	12.45	1.32	0.68	0.10	0.25
9	3.09	3.07	12.52	1.24	0.73	0.10	0.29
10	3.13	3.23	11.40	1.32	0.90	0.11	0.31
11	3.13	3.12	10.98	1.38	0.75	0.15	0.32
12	3.23	2.91	9.72	1.30	0.87	0.10	0.25
13	3.32	3.33	9.86	1.12	8.92	0.10	0.22
14	3.37	3.39	8.46	1.12	0.72	0.09	0.22
15	3.55	3.39	7.13	1.04	0.93	0.09	0.20
16	3.23	3.23	15.46	1.73	0.55	0.09	0.22
17	2.71	2.17	13.92	1.53	0.62	0.10	0.26
18	2.99	2.75	13.08	1.30	0.69	0.10	0.29
19	2.76	2.96	12.66	1.16	0.69	0.09	0.34
20	2.94	2.86	11.54	1.32	0.80	0.10	0.32
21	2.99	2.91	10.98	1.30	0.81	0.12	0.31
22	2.99	2.81	10.56	1.19	0.74	0.09	0.25
23	2.94	3.02	10.42	1.13	0.73	0.09	0.23
24	3.23	3.23	9.23	1.25	0.78	0.09	0.21

Table A-6. Amounts of major elements (mg/g) extracted by DCB reagents in colloidal (<1  $\mu$ m) size particles of the submerged deposits

Sample number	Si	Al	Fe	Ca	Mg	Mn	К
1	2.66	2.38	18.26	1.54	0.41	0.06	0.17
2	2.34	2.06	9.58	1.99	0.62	0.09	0.21
3	2.38	2.59	11.26	1.62	0.56	0.10	0.22
4	3.18	2.22	10.35	1.07	0.54	0.08	0.29
5	3.69	3.81	15.32	0.96	0.72	0.09	0.18
6	2.62	2.38	15.53	1.18	0.45	0.09	0.16
7	2.85	1.59	12.52	1.39	0.57	0.09	0.18
8	3.13	3.07	12.03	1.15	0.58	0.10	0.21
9	2.94	2.81	12.66	1.17	0.51	0.09	0.24
10	3.23	3.23	13.29	1.21	0.72	0.10	0.26
11	3.13	3.12	11.54	1.29	0.68	0.11	0.27
12	3.23	3.33	11.96	1.23	0.62	0.10	0.23
13	3.55	3.39	11.75	1.15	0.71	0.10	0.23
14	3.69	3.65	11.89	1.03	0.62	0.10	0.21
15	3.60	3.70	12.80	1.01	0.73	0.11	0.19
16	2.76	2.70	14.83	1.36	0.50	0.09	0.13
17	2.62	1.53	10.35	1.43	0.55	0.09	0.15
18	2.99	2.17	9.51	1.30	0.57	0.09	0.19
19	2.85	2.33	8.04	1.16	0.57	0.09	0.23
20	2.94	2.86	8.11	1.25	0.62	0.10	0.23
21	3.18	3.07	7.83	1.29	0.63	0.11	0.22
22	3.04	2.96	6.92	1.22	0.62	0.10	0.21
23	2.94	2.86	6.99	1.19	0.62	0.09	0.19
24	3.13	3.12	6.78	1.13	0.67	0.10	0.19

Table A-7. Amounts of major elements (mg/g) extracted by Alkali-Tiron reagents in the clay (2-1  $\mu$ m) size particles of the submerged deposits

Sample number	Si	Al	Fe	Ca	Mg	Mn	К
1	3.55	5.24	26.79	1.90	0.49	0.09	0.23
2	3.23	3.65	17.98	2.15	0.79	0.11	0.25
3	4.07	4.02	19.44	1.88	0.89	0.11	0.30
4	3.51	3.02	12.73	1.30	0.99	0.09	0.34
5	3.88	4.08	19.30	1.18	0.97	0.10	0.22
6	3.51	4.29	23.43	1.36	0.53	0.10	0.21
7	3.23	3.23	20.00	1.60	0.69	0.12	0.25
8	3.37	3.86	18.74	1.46	0.71	0.12	0.27
9	3.23	3.33	19.09	1.34	0.72	0.10	0.32
10	3.41	3.65	18.26	1.40	0.92	0.10	0.34
11	3.32	3.55	17.00	1.42	0.79	0.12	0.35
12	3.55	3.65	16.65	1.41	0.88	0.11	0.29
13	3.69	3.86	16.86	1.27	0.92	0.11	0.27
14	3.88	3.86	15.04	1.23	0.84	0.11	0.25
15	3.97	3.97	15.04	1.19	0.96	0.12	0.22
16	3.41	3.33	16.44	1.72	0.55	0.09	0.23
17	2.94	2.28	15.46	1.61	0.61	0.09	0.27
18	3.23	2.91	14.83	1.37	0.66	0.10	0.30
19	3.18	3.12	13.43	1.24	0.67	0.09	0.33
20	3.23	3.12	13.08	1.42	0.78	0.10	0.32
21	3.32	3.33	12.10	1.37	0.81	0.11	0.33
22	3.23	3.55	11.40	1.32	0.76	0.11	0.29
23	3.32	3.23	10.98	1.29	0.75	0.09	0.24
24	3.37	3.49	10.28	1.30	0.79	0.10	0.23

Table A-8. Amounts of major elements (mg/g) extracted by Alkali-Tiron reagents in the colloidal (<1  $\mu$ m) size particles of the submerged deposits

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Sample number	Si	Al	Fe	Ca	Mg	Mn	К
1	1.22	0.79	7.83	1.52	0.47	0.08	0.21
2	1.51	1.06	9.30	1.74	0.44	0.08	0.25
3	1.55	0.79	7.97	1.62	0.52	0.08	0.25
4	1.22	0.90	9.51	1.49	0.52	0.08	0.22
5	1.55	1.38	11.12	1.46	0.54	0.09	0.28
6	1.31	1.59	14.27	1.28	0.48	0.11	0.29
7	1.68	1.38	14.55	1.35	0.52	0.12	0.29
8	2.02	1.64	14.48	1.19	0.62	0.10	0.23
9	1.68	0.93	12.34	1.27	0.51	0.09	0.25
10	1.87	1.21	11.65	1.57	0.49	0.08	0.23
11	1.49	1.01	12.34	1.23	0.59	0.09	0.24
12	1.53	0.87	9.12	1.04	0.51	0.08	0.26
13	1.64	1.27	8.58	1.07	0.39	0.10	0.29
14	1.43	1.15	10.91	1.12	0.45	0.09	0.21

Table A-9. Amounts of major elements (mg/g) extracted by DCB reagents in the lower St. Lawrence River and estuarine suspended sediments

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Sample number	Si	Al	Fe	Ca	Mg	Mn	К
1	1.78	1.38	12.73	1.61	0.49	0.08	0.25
2	2.10	1.64	15.32	1.69	0.49	0.08	0.27
3	1.78	1.43	13.01	1.71	0.52	0.09	0.27
4	2.01	1.59	15.74	1.62	0.55	0.09	0.26
5	2.24	2.06	16.16	1.59	0.56	0.10	0.29
6	2.57	2.17	19.37	1.32	0.52	0.11	0.31
7	2.34	2.06	19.58	1.37	0.56	0.12	0.31
8	2.15	1.96	16.16	1.25	0.65	0.10	0.28
9	2.12	1.79	15.94	1.45	0.54	0.09	0.28
10	1.98	1.85	14.57	1.76	0.57	0.08	0.27
11	2.24	2.02	15.94	1.53	0.62	0.09	0.30
12	2.08	1.78	16.14	1.44	0.53	0.08	0.31
13	2.14	1.79	14.23	1.34	0.49	0.11	0.29
14	1.97	1.99	18.24	1.61	0.54	0.09	0.28

Table A-10. Amounts of major elements (mg/g) extracted by Alkali-Tiron reagents in the lower St. Lawrence River and estuarine suspended sediments.

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Location	Depth in cms	size	SiO2	TiO2	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na₂O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
Saint Cer	saire					_						
	70-75	2-1μm < 1μm	58.46 53.57	0.94 0.97	18.14 19.34	08.88 13.06	0.12 0.14	3.73 4.25	2.95 2.78	2.49 1.60	4.02 3.99	0.27 0.30
	210-215	2-1μπ < 1μπ	59.82 54.10	1.00 0.96	18.40 20.20	08.46 11.95	0.10 0.14	3.45 4.25	2.27 2.29	1.95 1.22	4.29 4.62	0.25 0.26
	325-330	2-1μπ < 1μm	59.56 54.63	1.02 0.96	18.70 20.95	08.32 10.93	0.10 0.13	3.60 4.34	2.37 1.91	2.05 1.26	4.05 4.64	0.23 0.25
	375-380	2-1μm < 1μm	62.57 53.87	0.98 0.97	17.59 21.48	07.06 10.97	0.09 0.14	3.18 4.51	2.34 1.92	2.21 1.22	3.77 4.67	0.22 0.24
Sparrowhawk Point												
	10-15	2-1 μm < 1 μm	59.18 53.98	0.94 0.98	18.59 20.13	08.58 12.08	0.12 0.14	3.59 4.25	3.03 2.52	2.59 2.12	3.12 3.48	0.26 0.31
	75-80	2-1μm < 1μm	59.40 53.62	0.96 0.96	18.06 20.21	09.06 12.46	0.09 0.13	3.56 4.39	2.48 2.04	2.43 1.60	3.73 4.31	0.23 0.26
	255-260	2-1μm < 1μm	58.11 52.56	1.03 0.99	18.58 20.95	09.03 11.99	0.11 0.13	3.77 4.50	2.92 2.34	1.93 1.38	4.30 4.88	0.24 0.27
	465-470	2-1μm < 1μm	59.76 54.61	1.00 0.95	18.67 21.31	08.32 10.46	0.10 0.14	3.42 4.23	2.59 2.08	2.03 1.47	3.87 4.49	0.23 0.25
	575-580	2-1μm < 1μm	62.10 54.35	1.00 0.95	17.80 20.98	07.22 10.69	0.12 0.14	3.30 4.33	2.46 2.26	2.07 1.55	3.70 4.51	0.23 0.26
Caseima	n											
	45-50	2-1μm < 1μm	57.89 54.16	0.84 0.80	19.17 21.05	08.86 11.30	0.12 0.11	4.27 4.85	2.54 2.19	2.03 1.25	3.98 3.97	0.16 0.18
	145-150	2-1μm < 1μm	54.78 53.40	0.79 0.79	19.47 20.42	09.68 10.66	0.11 0.11	4.81 5.14	4.49 3.84	1.75 1.45	3.84 3.91	0.17 0.16
	310-315	2-1μm < 1μm	57.97 54.73	0.85 0.81	19.40 21.42	09.20 11.31	0.10 0.10	4.10 4.55	2.30 1.85	1.85 1.09	3.97 3.88	0.15 0.13

Table A-11. Major-element analyses (in wt%) of the clay and colloid-size fractions from the Champlain Sea sediments

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Location	Depth in cms	size	v	Cr	Ni	Ва	Co	Cu	Рb	Zn
Saint Cesaire										
	70-75	2-1μm < 1μm	125 141	281 224	67 81	1340 1217	30 63	209 189	45 63	159 907
	210-215	2-1μπ < 1μπ	108 144	228 231	58 67	1238 1140	34 54	104 215	29 32	127 176
	325-330	2-1μπ < 1μπ	118 144	197 292	56 76	1180 1190	37 50	196 170	28 34	121 160
	375-380	2-1μm <1μm	111 140	228 295	42 83	1284 1244	17 55	91 213	43 60	102 168
Sparrowt	awk Point	t								
	10-15	2-1μm < 1μm	142 161	274 292	69 92	1248 1195	42 79	229 209	52 71	192 273
	75-80	2-1μm < 1μm	119 157	268 288	65 84	1215 1152	37 64	215 198	47 68	187 215
	255-260	2-1μm < 1μm	115 142	249 269	58 79	1190 1147	35 61	159 167	45 61	162 194
	465-470	2-1μm < 1μm	112 139	249 275	57 78	1192 1141	37 66	132 177	38 58	159 177
	575-580	2-1μm < 1μm	98 125	215 246	46 72	1054 978	22 53	112 143	32 47	143 168
Caselman										
	45-50	2-1μπ < 1μπ	97 120	144 185	74 97	666 571	60 78	34 48	26 30	114 142
	145-150	2-1μm <1μm	108 115	160 177	85 77	571 495	66 68	28 15	31 30	125 132
	310-315	2-1μm < 1μm	91 123	140 179	74 99	622 639	58 75	48 55	25 44	114 139

Table A-12. Minor-element analyses (in µg/g) of the clay and colloid-size fractions from the Champlain Sea deposits
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Location	Depth in cms	size	SiO2	TiO₂	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K₂O	P <sub>2</sub> O <sub>5</sub>
87-3 # 2					_							
	03-08	2-1μm <1μm	58.29 54.19	0.75 0.79	17.81 19.96	07.32 10.22	0.13 0.15	4.20 5.08	4.92 3.26	2.92 2.38	3.45 3.72	0.22 0.23
	13-18	2-1μm <1μm	57.72 53.65	0.71 0.77	17.44 19.84	06.84 10.23	0.11 0.13	4.46 5.36	6.29 3.69	2.98 2.40	3.26 3.73	0.19 0.21
	28-33	2-1 μm < 1 μm	57.13 53.07	0.70 0.75	17.22 19.68	06.90 10.14	0.11 0.13	4.45 5.49	7.11 4.38	3.01 2.57	3.20 3.60	0.18 0.19
	48-53	2-1μm < 1μm	57.00 52.68	0.69 0.74	17.19 19.59	06.84 10.20	0.11 0.13	4.53 5.44	7.27 4.83	3. <b>05</b> 2.62	3.13 3.55	0.20 0.21
	68-73	2-1μm < 1μm	57.02 53.89	0.69 0.74	18.13 19.89	07.62 10.09	0.12 0.14	4.60 5.24	5.25 3.61	3.04 2.57	3.32 3.61	0.21 0.22
87-3 # 14	4											
	05-10	2-1μm < 1μm	55.89 53.40	0.73 0.76	18.19 19.64	08.23 10.36	0.12 0.13	4.71 5.31	6.09 4.35	2.32 1.94	3.51 3.77	0.23 0.22
	30-35	2-1μm < 1μm	56.84 53.29	0.75 0.78	18.13 19.95	07.85 10.35	0.11 0.13	4.51 5.30	5.43 3.85	2.46 2.08	3.57 3.92	0.23 0.25
	50-55	2-1μm < 1μm	56.17 53.30	0.75 0.77	18.50 19.91	08.22 10.25	0.12 0.14	4.69 5.33	5.20 3.99	2.37 2.04	3.63 3.89	0.23 0.25
87-3 # 12	2											
	10-15	2-1μm < 1μm	55.69 53.22	0.72 0.75	18.39 19.82	08.24 10.39	0.12 0.13	4.60 5.25	6.20 4.41	2.22 2.01	3.61 3.84	0.23 0.22
	40-45	2-1μm < 1μm	56.42 53.19	0.74 0.76	18.55 19.99	07.97 10.43	0.11 0.12	4.43 5.31	5.32 3.86	2.57 2.18	3.68 3.93	0.22 0.24
	70-75	2-1μm <1μm	56.16 53.19	0.74 0.76	18.56 19.97	08.27 10.32	0.12 0.13	4.74 5.27	5.12 4.11	2.41 2.12	3.65 3.90	0.23 0.24

Table 13. Major-element analyses (in wt%) of the clay and colloid-size fractions from the Goldthwait Sea deposits

Location	Depth in cms	size	v	Cr	Ni	Ba	Co	Си	РЬ	Zn	
87-3 # 2				_							
	03-08	2-1μm < 1μm	92 104	265 345	67 85	1038 817	27 50	108 182	19 27	102 137	
	13-18	2-1μm < 1μm	86 116	265 362	76 90	840 761	21 38	149 125	30 27	87 134	
	28-33	2-1μm < 1μm	92 118	291 376	75 90	856 812	22 41	108 156	31 35	79 135	
	48-53	2-1 μm < 1 μm	79 107	272 368	75 96	815 786	17 44	170 128	18 29	85 127	
	68-73	2-1 μm < 1 μm	91 116	335 351	85 99	837 824	31 51	138 123	18 33	93 134	
87-3 # 14	4										
	05-10	2-1μm < 1μm	98 116	133 154	58 66	554 553	51 69	10 21	30 34	111 143	
	30-35	2-1μm < 1μm	99 112	122 171	56 86	581 544	52 75	32 48	33 40	114 142	
	50-55	2-1μm < 1μm	97 114	121 182	62 66	573 540	56 82	18 14	52 30	119 147	
87-3 # 12	2										
	10-15	2-1μm < 1μm	95 122	195 285	73 91	965 771	58 78	23 31	25 32	104 139	
	40-45	2-1μm < 1μm	90 120	260 377	85 93	871 695	46 63	25 46	30 31	115 131	
	70-75	2-1μm < 1μm	92 124	240 379	74 99	722 642	33 49	22 41	27 42	110 132	

Table A-14. Minor-element analyses (in µg/g) of the clay and colloid-size fractions from Goldthwait Sea deposits

Sample number	SiO2	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe₂O₃	MnO	MgO	CaO	Na₂O	K <b>₂</b> O	P₂O₅
1	62.78	1.08	15.57	07.67	0.24	3.18	3.50	2.38	3.12	0.48
2	63.09	0.88	15.61	07.29	0.20	3.12	3.22	2.65	3.52	0.42
3	61.60	1.04	15.85	08.11	0.18	4.07	3.21	3.21	2.37	0.38
4	57.50	0.99	15.66	07.98	0.18	2.82	2.66	9.54	2.34	0.34
5	59.28	1.02	16.30	08.48	0.18	3.42	2.88	5.69	2.37	0.37
6	63.79	1.04	15.04	07.15	0.16	2.90	3.50	2.70	3.36	0.36
7	62.54	0.99	15.72	07.57	0.17	3.14	3.43	2.79	3.31	0.36
8	63.67	1.11	15.36	07.13	0.21	3.02	3.54	2.53	2.99	0.45
9	57.49	0.98	15.15	07.81	0.16	3.26	2.88	9.45	2.47	0.34
10	59.50	0.94	15.48	07.74	0.16	2.80	2.87	7.68	2.49	0.34
11	58.57	0.89	16.36	08.16	0.19	3.24	2.66	7.32	2.27	0.34
12	60.92	1.01	15.87	07.96	0.19	3.10	2.91	5.37	2.33	0.34
13	60.44	1.02	15.72	08.16	0.16	3.32	2.97	5.44	2.44	0.33
14	57.19	0.97	15.17	07.96	0.16	2.42	2.60	10.31	2.88	0.34

Table 15. Major-element analyses (in wt%) of the bulk lower St. Lawrence River and its estuarine suspended sediments

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Sample number	Co	Ni	Cu	Zn
1	18	61	28	131
2	21	54	36	148
3	15	40	34	143
4	16	70	29	146
5	14	38	52	231
6	13	33	44	210
7	15	38	52	240
8	17	46	49	240
9	15	38	38	190
10	14	39	41	194
11	18	44	34	202
12	14	36	38	173
13	15	39	40	190
14	14	39	77	188

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Table A-16. Minor-element analyses (in µg/g) of the bulk lower St. Lawrence River and its estuarine suspended sediments

Location	Depth	Q	PF	KF	A	I	С	Q	PF	KF	Α	I	С
	in cms			2-	·1 μm	****t		•••		< 1	µm		
Saint Cé	saire			_									
	70-75	07	35	14	12	27	05	06	16	07	09	52	10
	105-110	08	33	13	11	29	06	07	15	07	09	53	09
	150-155	09	34	13	11	26	07	06	14	06	11	53	10
	180-185	08	35	14	10.	28	05	07	14	06	10	55	08
	210-215	11	31	10	08	31	09	06	15	07	07	56	09
	235-240	12	30	09	09	30	10	07	14	06	08	56	09
	270-275	12	28	09	11	29	11	08	13	05	09	54	11
	325-330	09	32	10	13	30	06	07	13	07	09	54	10
	335-340	08	34	11	12	28	07	08	13	05	08	57	09
	375-380	09	38	12	08	26	07	06	11	04	05	64	10
	395-400	08	39	16	07	24	06	06	10	03	05	66	10
Sparrowt	nowk Point	t											
	10-15	16	33	14	12	20	05	10	17	08	11	47	07
	45-50	15	33	13	11	22	06	09	17	08	10	49	07
	75-80	15	33	12	11	23	06	09	14	07	10	51	09
	145-150	14	34	12	10	23	07	08	16	08	09	51	08
	255-260	16	33	13	10	22	06	09	14	06	09	53	09
	355-360	13	33	12	11	24	07	08	13	06	09	55	09
	425-430	12	34	13	10	24	07	08	13	05	08	56	10
	465-470	13	33	12	10	25	07	07	14	06	08	56	09
	485-490	14	32	13	11	24	06	07	13	04	09	57	10
	515-520	12	34	15	09	25	05	08	15	04	07	56	10
	545-550	14	33	14	08	25	06	07	14	05	06	59	09
	575-580	12	33	14	08	26	07	06	13	04	06	60	11
Casselm	an												
	15-20	15	28	10	13	27	07	09	19	06	10	47	09
	45-50	17	28	09	12	28	06	07	18	07	11	49	08
	90-95	14	26	08	12	33	07	08	20	08	11	45	08
	115-120	13	25	09	11	37	05	08	17	07	09	52	07
	145-150	14	27	08	10	34	07	07	15	07	10	53	08
	190-195	15	25	10	10	34	06	08	17	08	12	46	09
	240-245	14	26	09	11	33	07	07	19	09	11	45	09
	310-315	13	26	09	09	37	06	06	18	09	11	48	08
	355-360	15	27	08	10	35	05	06	21	07	10	49	07

Table A-17. Semi-quantitative mineralogy of marine clay and colloid-size fractions from the Champlain Sea deposits

Q-quartz; PF-plagioclase feldspar; KF-potassium feldspar; A-amphibole; I-Illite; C-chlorite.

core	Depth	Q	PF	KF	Α	I	С	Q	PF	KF	Α	I	С
	in cms				1μm					< 1	µm		
87-3 #	2												
	03-08	07	32	09	10	31	11	05	21	08	11	42	13
	13-18	08	32	10	11	26	13	04	21	07	17	43	08
	28-33	08	31	09	12	28	12	05	21	08	11	40	15
	48-53	07	31	08	16	26	12	05	23	06	11	40	15
	68-73	06	36	07	10	28	13	04	24	06	12	43	11
87-3 #	14												
	00-05	09	30	10	11	30	10	07	20	09	10	42	12
	06-10	80	29	11	12	29	11	07	19	08	11	43	12
	16-20	08	30	09	13	29	11	06	21	09	12	41	11
	21-25	07	30	10	12	28	13	05	20	08	11	42	14
	26-30	07	28	12	14	27	12	05	19	09	13	41	13
	31-35	07	29	12	13	28	11	06	20	10	10	42	12
	36-40	08	28	11	14	26	13	06	17	10	12	41	14
	41-45	07	31	09	15	28	10	06	20	09	11	42	12
	46-50	07	34	08	13	29	09	05	19	10	11	44	11
	51-55	06	35	08	12	28	11	05	22	08	10	42	13
87-3 #	12												
	00-05	15	37	11	11	17	09	09	24	10	12	32	13
	10-15	14	32	09	13	24	08	08	23	09	08	40	12
	20-25	10	31	10	10	30	09	06	19	10	09	42	14
	30-35	09	32	10	08	34	07	06	20	08	11	43	12
	40-45	09	29	08	12	34	08	07	19	07	13	41	13
	50-55	10	27	07	09	38	09	08	18	09	09	43	13
	60-65	11	29	08	10	32	10	09	17	09	14	39	12
	70-75	09	28	07	10	38	08	06	18	08	09	49	10
	75-83	11	26	06	09	39	09	05	16	06	09	51	13

Table A-18. Semi-quantitative mineralogy of marine clay and colloid-size fractions from the Goldthwait Sea deposits

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Q-quartz; PF-plagioclase feldspar; KF-potassium feldspar; A-amphibole; I-Illite; C-chlorite.

Location	Depth in cm	Mineral 2-1µm	Maturity (M <sub>M</sub> ) <1µm
Saint Césaire			
Sum Cosuro	70-75	0.52	1.94
	105-110	0.61	2.00
	150-155	0.57	2.03
	180-185	0.56	2.10
	210-215	0.82	2.24
	235-240	0.83	2.32
	270-275	0.83	2.41
	325-330	0.65	2.21
	335-340	0.61	2.54
	375-380	0.57	3.70
	395-400	0.48	4.22
Sparrowhowk Point			
•	10-15	0.42	1.50
	45-50	0.49	1.60
	75-80	0.52	1.94
	145-150	0.54	1.79
	255-260	0.50	2.14
	355-360	0.55	2.29
	425-430	0.54	2.54
	465-470	0.58	2.32
	485-490	0.54	2.58
	515-520	0.52	2.54
	545-550	0.56	2.72
	575-580	0.60	3.09
Casselman			
	15-20	0.67	1.60
	45-50	0.69	1.58
	90-95	0.87	1.36
	115-120	0.93	1.79
	145-150	0.91	1.91
	190-195	0.89	1.49
	240-245	0.87	1.38
	310-315	0.98	1.47
	355-360	0.89	1.47

 $\bigcirc$ 

Table A-19. Mineral maturity in marine clay and colloid-size fractions from the Champlain Sea deposits

Соге	Depth	Mineral	Maturity M
	in cm	2-1µm	<1µm
37-3 # 2			
	03-08	0.82	1.38
	13-18	0.74	1.13
	28-33	0.77	1.38
	48-53	0.69	1.38
	68-73	0.77	1.29
7-3 # 14			
	00-05	0.78	1.38
	06-10	0.77	1.45
	16-20	0.77	1.24
	21-25	0.79	1.44
	26-30	0.72	1.32
	31-35	0.72	1.35
	36-40	0.74	1.41
	41-45	0.69	1.35
	46-50	0.69	1.38
	51-55	0.71	1.38
37-3 # 12			
	00-05	0.44	0.98
	10-15	0.59	1.30
	20-25	0.76	1.47
	30-35	0.82	1.41
	40-45	0.86	1.38
	50-55	1.09	1.56
	60-65	0.89	1.28
	70-75	1.02	1.69
	75-83	1.17	2.06

C

Table A-20. Mineral maturity in marine clay and colloid-size fractions from the Goldthwait Sea deposits

Location	Depth in cm	Chemica 2-1µm	l Maturity (Ch <sub>M</sub> ) <1μm
Saint Césaire			
	70-75	1.98	2.24
	210-215	2.40	2.60
	325-330	2.33	2.79
	375-380	2.28	2.81
Sparrowhowk Point			
-	10-15	2.02	2.26
	75-80	2.13	2.52
	255-260	2.16	2.55
	465-470	2.32	2.58
	575-580	2.27	2.74
Casselman			
	45-50	2.17	2.54
	145-150	1.76	1.96
	310-315	2.35	2.86

Table A-21. Chemical maturity in marine clay and colloid-size fractions from the Champlain Sea deposits

Core	Depth in cm	Chemical Maturity Ch <sub>м</sub> 2-1µm <1µm		
87-3 # 2				
	03-08	1.48	1.86	
	13-18	1.27	1.73	
	28-33	1.18	1.58	
	48-53	1.16	1.52	
	68-73	1.41	1.74	
87-3 # 14				
	05-10	1.39	1.69	
	30-35	1.46	1.78	
	50-55	1.51	1.75	
87-3 # 12				
	10-15	1.41	1.70	
	40-45	1.51	1.74	
	70-75	1.51	1.76	
	70-75	1.51	1.76	

C

Table A-22. Chemical maturity in marine clay and colloid-size fractions from the Goldthwait Sea deposits

Figure B-1. Scanning electron photomicrograph of the St. Lawrence estuarine suspended particulate matter showing the presence of diatoms (for details, refer to text, page-97)

