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**AN INVESTIGATION OF
PORE WATER IN CHAMPLAIN SEA DEPOSITS
AT MER BLEUE
OTTAWA, CANADA**

by

Michael A. Woodley

A thesis submitted to
the faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Masters of Science

Department of Earth Sciences
Carleton University
Ottawa, Ontario
1996

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**AN INVESTIGATION OF
PORE WATER IN CHAMPLAIN SEA DEPOSITS
AT MER BLEUE
OTTAWA, CANADA**

submitted by Michael Woodley
in partial fulfillment of the requirements for
the degree of Master of Science

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ABSTRACT

Ion chemistry, ^{18}O and ^2H isotopes and geotechnical properties were analysed in an investigation of pore waters in core from borehole GSC-93-GM which intersected 54m of Champlain Sea sediments at the Mer Bleue bog east of Ottawa. The Mer Bleue sediments, including nearly 50m of marine clays, were deposited during the retreat of Wisconsinan ice beginning 12000 years B.P., when a marine embayment of the Atlantic Ocean occupied the Ottawa Valley for approximately 2000 years.

Pore water salinity grades from fresh to brackish to saline with depth in the sediment. Ionic character evolves downward in the sediments in a continuous series as follows:

reflecting a SO_4^{2-} reducing environment in the bulk of the marine clays at shallow and intermediate depths grading to a basal, near saline ($\text{TDS} \approx 10000\text{ppm}$), Na-Cl water with major ion proportions similar to seawater. The original seawater character of the pore water has been altered by dilution and the downward leaching of salts gradationally with depth by infiltrating modern meteoric water.

The sediments consist of clayey silt with clay increasing from 20 to 45% upward. Moisture ranges from 40 to 100%, declining with depth. Remoulded shear strengths range from 0.047 to 1.25t/m^2 and increase three-fold in the deepest most saline marine clay stratigraphic unit (III). A highly sensitive clay ($Tr=0.047\text{t/m}^2$) occurs at a depth of 27.6m in the zone of dilute brackish pore water ($\text{TDS} < 2600\text{ppm}$).

ACKNOWLEDGEMENTS

The author wishes to acknowledge his thanks and indebtedness to Drs. Fred Michel and Ken Terrance who suggested the project and who provided direction, assistance and guidance from beginning to end of this study. Their patience, discussion and careful review of the manuscript were key factors in bringing this study to a meaningful conclusion.

The author acknowledges the contribution of Drs. R. Burk, M. Robin and A. Donaldson who edited the manuscript, Dr. C. Gregoire (GSC), P. Lindsay (GSC), N. Morisset (U of O) and G. St-Jean (U of O) who provided laboratory analyses, Dr. T. Lawrence, M. Douma, M. Nixon, V. Allen and J. Mwenifumbo of the G.S.C. who provided background information and D. Allen and A. Briggs (of Carleton U.) who provided diagrams, references and moral support.

Finally, the author wishes to thank the GSC for providing the core material, without which this thesis would not have been possible.

TABLE OF CONTENTS

Acceptance Sheet.....	ii
ABSTRACT.....	iii
ACKNOWLEDGEMENTS.....	iv
TABLE OF CONTENTS.....	v
LIST OF TABLES.....	vii
LIST OF FIGURES.....	viii
 Chapter 1 INTRODUCTION.....	 1
1.1 Purpose.....	1
1.2 Location.....	1
1.3 Local climate.....	3
1.4 Previous work.....	3
 Chapter 2 GEOLOGICAL SETTING.....	 8
2.1 Bedrock geology.....	8
2.1.1 <i>Structure</i>	8
2.1.2 <i>Stratigraphy</i>	8
2.2 Quaternary geology.....	9
2.2.1 <i>Laurentide ice retreat</i>	9
2.2.2 <i>Quaternary stratigraphy</i>	17
2.2.3 <i>Mineralogy</i>	19
2.3 Hydrogeological properties of bedrock.....	22
2.4 Hydrogeological properties of Quaternary deposits.....	22
2.5 Geotechnical behaviour of Champlain Sea sediments.....	23
 Chapter 3 SOURCES of DATA.....	 25
3.1 Introduction.....	25
3.2 Sampling procedure.....	25
3.2.1 <i>Lithology</i>	25
3.2.2 <i>Geotechnical</i>	25
3.2.3 <i>Geochemical procedures</i>	26
3.2.3.1 <i>Isotope analysis</i>	26
3.2.3.2 <i>Ion chemical analysis</i>	27
 Chapter 4 PHYSICAL GEOLOGY AND GEOTECHNICAL RESULTS..	 28
4.1 Physical Geology.....	28
4.1.1 <i>Stratigraphy</i>	28
4.1.2 <i>Grain size</i>	30
4.1.3 <i>Correlation with geophysical logs and high resolution seismic</i>	30
4.2 Geotechnical.....	34
4.2.1 <i>Moisture</i>	34
4.2.2 <i>Shear strength</i>	34
4.2.3 <i>Sensitivity</i>	41

Chapter 5 GEOCHEMISTRY AND ISOTOPE RESULTS	43
5.1 Ion chemical results.....	43
5.1.1 <i>Characterisation of pore water ion chemistry</i>	43
5.1.1.1 <i>Salinity</i>	43
5.1.1.2 <i>Piper plots</i>	45
5.1.1.3 <i>Major ion proportions in seawater</i>	56
5.1.1.4 <i>Cation depth profiles</i>	57
5.1.2 <i>Elemental plots</i>	57
5.1.2.1 <i>Sodium</i>	60
5.1.2.2 <i>Potassium</i>	63
5.1.2.3 <i>Calcium</i>	66
5.1.2.4 <i>Magnesium</i>	66
5.1.2.5 <i>Strontium</i>	70
5.1.2.6 <i>Ca and Sr enrichment in till and varved sediments</i> ..	70
5.1.2.7 <i>Bicarbonate and sulphate</i>	73
5.1.2.8 <i>Br/Cl ratio</i>	76
5.1.3 <i>Saturation indices</i>	79
5.2 Isotope geochemistry.....	82
5.2.1 <i>Isotopes in Champlain Sea</i>	89
Chapter 6 DISCUSSION of RESULTS	91
6.1 Physical geology and geotechnical.....	91
6.1.1 <i>Physical geology</i>	91
6.1.2 <i>Geotechnical</i>	92
6.1.3 <i>Physical Hydrogeology</i>	93
6.2 Geochemistry and Isotopes.....	96
6.2.1 <i>Geochemistry</i>	96
6.2.2 <i>Isotope geochemistry</i>	100
6.3 Error due to evaporation in split-tube samples.....	101
Chapter 7 CONCLUSIONS and RECOMMENDATIONS	103
REFERENCES	106

LIST OF APPENDICES

Appendix 1 Lithological and Geotechnical Data	111
Table 1a. Lithological logs..	112
Table 1b. Geotechnical data.....	113
Appendix 2 Geochemical Data	114
Table 2a. Isotope data.....	115
Table 2b. Geochemical data.....	116
Appendix 3 Analytical Procedures	118
a. Ion chemical analysis and summary of detection limits.....	119
b. ¹⁸ O isotope analysis and ² H isotope analysis	122

LIST OF TABLES

TABLE

1. Chemical analyses (ppm) from shale bedrock groundwater at study site (after Briggs, 1995).....	7
2. Paleozoic stratigraphic nomenclature in Ottawa-St. Lawrence Lowland and Southwestern Ontario (after Briggs, 1995).....	10
3. General model for “quick clays” (after Torrance, 1983).....	24
4. Major ion proportions compared to seawater.....	56

LIST OF FIGURES

FIGURE

1	Location map of study site (after Douma and Nixon, 1993 and Iraynor, 1995).....	2
2	Salinity vs depth profiles in twenty Ottawa basin boreholes (after Torrance, 1988).....	5
3	Stratigraphic section of Palaeozoic rocks immediately underlying Mer Bleue	11
4	Geological map of study area (after Williams, 1984 and 1985 and Briggs, 1995).....	12
5	Resistant topographic features bordering Ottawa-St. Lawrence Lowland (after Gadd, 1988a).....	14
6	Four phases of deglaciation in Ottawa-St. Lawrence Lowland (after Gadd, 1988a).....	15
7	Extent of Champlain Sea in St. Lawrence Basin (after Prichonnet, 1988).....	16
8	Lithological description of Quaternary deposits at Mer Bleue (after Gadd, 1986).....	18
9	East-west and north-south cross-sections of Champlain Sea strata in Ottawa basin (after Gadd, 1986).....	20
10	Stratigraphic section borehole GSC-93-GM (after Douma and Nixon, 1993)	21
11	Stratigraphic section of observations in borehole GSC-93-GM.....	29
12	Grain size vs depth.....	31
13	Correlation of stratigraphy and geophysical record at borehole GSC-93-GM (modified after Douma and Nixon, 1993).....	32
14	Moisture content vs depth.....	35
15a	Undisturbed shear strength vs depth.....	36
15b	Remoulded shear strength vs depth.....	38
16	Shear strength and moisture vs depth... ..	39
17	Upper envelope of undisturbed shear strength (T_u) and remoulded shear strength (T_r) vs depth.....	40
18	Sensitivity (T_u/T_r) vs depth.....	42

19	Total dissolved solids (TDS) vs depth.....	44
20	TDS and pore water conductivity vs depth.....	46
21	Pore water conductivity and Geonix-39 conductivity vs depth (after Douma and Nixon, 1993).	47
22	Piper plot of thirty-two pore water samples.....	48
23a	Piper plot of fresh water samples.....	50
23b	Piper plot of brackish water samples.....	51
23c	Piper plot of saline water samples.....	52
24	Relative cations and anions vs depth.....	53
25	Cations (meq/l) vs depth.....	54
26	Anions (meq/l) vs depth.....	55
27a	Cation profiles - Group I (modified after Torrance, 1988).....	58
27b	Cation profiles - Group II (modified after Torrance, 1988).....	59
28	Na vs Cl.....	61
29	Na vs Cl of shield, basin and shale waters (after Briggs, 1995).....	62
30	K vs Cl.....	64
31	Ca + Mg vs $\text{HCO}_3 + \text{SO}_4$	65
32	Ca vs Cl.....	67
33	Mg vs Cl.....	68
34	Ca/Mg vs Cl.....	69
35	Sr vs Cl.....	71
36	Sr vs Cl in shield, basin and shale waters (after Briggs, 1995).....	72
37	HCO_3 vs Cl.....	74
38	SO_4 vs Cl.....	75
39	Br/Cl vs Cl.....	77
40	Br vs Cl.....	78
41	Br/Cl vs Cl in common shale waters (after Briggs, 1995).....	80

42	Saturation indices vs depth	81
43	Global meteoric water line and Ottawa meteoric water line (after Sager-Kinsman, 1995.....	84
44	$\delta^{18}\text{O}$ vs $\delta^2\text{H}$ in forty-five pore water samples.....	85
45	$\delta^{18}\text{O}$ vs depth.....	86
46	$\delta^{18}\text{O}$ vs Cl.....	87
47	$\delta^{18}\text{O}$ vs TDS.....	88
48	$\delta^{18}\text{O}$ vs TDS (Hillaire-Marcel meltwater - seawater mixing line).....	90
49	TDS and remoulded shear strength vs depth.....	94

Chapter 1 INTRODUCTION

In the Ottawa Valley, groundwater with high salinity is commonly encountered in domestic water wells. The salinity is generally considered to be residual from widely distributed marine clays deposited by the Champlain Sea during the retreat of the last ice sheet. Approximately 54m of core recovered from an Energy Mines and Resources borehole, which penetrated the marine clay sediments and underlying glacial sediments down to bedrock at Mer Bleue, has provided an opportunity to investigate many aspects of the geochemistry of pore water in the undisturbed clay.

1.1 Purpose

The purpose of this study is to characterise the pore water chemistry in Champlain Sea sediments and through a geochemical and isotopic characterisation, investigate influences which may have changed the sediments original seawater character of deposition. Finally, the relationship between pore water chemistry and geotechnical properties of Champlain Sea marine clays will be considered.

Salinity is the sum of the concentrations of dissolved solid species (TDS, total dissolved solids), and in groundwater may be derived from several sources. Among the possible sources of groundwater salinity are:

- connate seawater incorporated in the pores of the sediments at the time of deposition in a marine environment
- seawater which has migrated from another source
- the dissolution of evaporites in the bedrock
- ion exchange between the groundwater and the enclosing sediment or bedrock and
- the migration of deep-seated brines from the underlying Canadian Shield.

1.2 Location

The study area is located in the City of Gloucester, 12km due east of Ottawa city centre (Figure 1). The EMR borehole, GSC-93-GEOMAG (herein referred to as GSC-93-GM) is located near the centre of a ridge (elevation >75m a.s.l.) between two of the western arms of the Mer Bleue bog at the intersection of Anderson Road and the driveway to the GSC Geomagnetic Laboratory.

Generalized surficial geology of the Ottawa area showing the location of borehole GSC93-GEOMAG near Mer Bleu bog (modified from Fransham et al., 1976)

FIGURE 1 Location Map of Study Site (after Douma and Nixon, 1993 and Traynor, 1995)

Mer Bleue is situated on a lowland plain at a general elevation of 70m a.s.l., 7km south of the Ottawa River. The bog is approximately 40m higher than the Ottawa River and drains northward to the Ottawa via Green Creek and its small tributaries Ramsey and Borthwick Creeks. The ridge at the study site is part of a streamlined island formed in the proto-Ottawa River during the regression of the Champlain Sea.

Borehole GSC-93-GM was drilled to a depth of 62.5m in March 1993 by the Terrain Geophysics and Geothermal Section of the GSC for use as a geophysical logging test hole for training logging operators. The location of the borehole was chosen to coincide with a high resolution seismic reflection line shot over the area which shows a succession of glacial and postglacial strata overlying Paleozoic bedrock (Douma and Nixon, 1993).

1.3 Local Climate

The Ottawa area has a cool temperate continental climate with large annual temperature variation and moderate precipitation with low annual variation. Groundwater recharge is greatest during spring thaw run-off (Charron, 1978).

The Environment Canada temperature and precipitation statistics for Ottawa as of 1994 are as follows:

average annual temperature	5.9 °C	average annual precipitation	879.3 mm
coldest month - January av.	-10.9 °C	lowest precipitation-February	60.0 mm
warmest month - July av.	20.6 °C	highest precipitation-August	88.4 mm

1.4 Previous Work

Owen (1953) published a report on groundwater resources of Gloucester Township (now the City of Gloucester) in which he described the water-bearing units in the township and compiled an inventory of water wells. Owen characterised aquifers in Gloucester according to their groundwater chemistry and productivity.

In a preliminary report on the hydrogeology of Ottawa-Hull, Brandon (1960) noted that saline groundwater was found in wells drilled in thick marine clays thought to contain connate waters of Champlain Sea origin.

Charron (1978), in a report on the hydrochemistry of groundwater flow in the region between the Ottawa and St. Lawrence Rivers, used TDS as a measure of residence time. He concluded that water with a high chloride content was the result of long residence time, which facilitated the dissolution of salts in the aquifer. He noted that long residence times would be associated with areas of discharge. The Mer Bleue bog, and the Alfred bog to the east, were identified as discharge zones. Charron (1978) also concluded that bedrock surface topography is the major control on horizontal groundwater flow, since the contact zone between bedrock and overburden has been found to produce the largest volumes of groundwater.

The depositional history of glacial and post-glacial lithofacies in the Ottawa - St. Lawrence Lowland was outlined by Gadd (1980, 1986, 1988a and 1988b). The stratigraphy of the Mer Bleue bog was described by Gadd (1986) and Anderson (1988) using core retrieved from borehole CRF-21A drilled to a depth of 70m in 1969 at the GSC Geomagnetic Laboratory and located 250m east of the borehole currently studied, GSC-93-GM.

Gadd (1986) investigated Champlain Sea sediments using Shelby tube cores in 18 boreholes, including CRF-21A, which were drilled to refusal at both proximal and distal locations in the northwest arm of the sea which occupied the Ottawa Basin. Gadd correlated depositional units across a model 100x200km basin between Petawawa and Hawkesbury along the Ottawa Valley.

Gadd's basin study was followed up with an investigation of pore water chemistry, mineralogy and geotechnical behaviour of Champlain Sea sediments (Torrance, 1988). The major cations in pore waters squeezed from Champlain Sea sediments in 20 boreholes including most of Gadd's boreholes (between Petawawa and Hawkesbury) were reported by Torrance (1988) as salinity vs depth profiles as shown in Figure 2. Torrance concluded that sodium is the dominant pore water cation, that downward leaching had removed the salt in most sediments west of the South Nation River and that high residual salt content occurred where the sediments are thickest. Only one seawater salinity value (35ppt) was observed in the twenty boreholes. This occurred at 46m depth at Plaisance.

It was also noted by Quigley (1980) and Torrance (1983) that salt content may be an important factor influencing the geotechnical behaviour of the fine-grained marine sediments of the Champlain Sea deposits in the Ottawa Valley. Similar investigations of

Borehole sites and pore-water concentrations (expressed as normality in Champlain Sea sediments of the Ottawa valley)

FIGURE 2 Salinity vs depth profiles in twenty Ottawa basin boreholes (after Torrance, 1988)

pore water chemistry are reported from numerous sites in the St. Lawrence Lowland (Grondin 1978, Lebuis and Rissmann 1979), and these demonstrate that no broad spatial trends exist in the extent and pattern of salt removal.

Douma and Nixon (1993) described the sediments in borehole GSC-93-GM and correlated them with Gadd's major lithofacies units in CRF-21A and with Geonix-39 geophysical logs and a shallow seismic survey which intersects the borehole

A water well drilled to a depth of 106m, approximately 25m south of CRF-21A, predates Gadd's survey of boreholes.

It is generally assumed that in the Ottawa area, groundwater salinity originated from Champlain Sea water. Quigley (1980 and 1983) and Quigley *et al.* (1985) at Hawkesbury and Torrance (1988) in the Gadd study area have demonstrated the variable extent of current salt concentration in the Champlain Sea marine clays. Most recently Mitchell (1990) and Seguin (1995) both concluded a Champlain Sea origin for brackish groundwater in shallow Paleozoic aquifers west of Ottawa. In an investigation of brackish groundwater from wells and springs east of Ottawa, including groundwater from the bedrock in borehole GSC-93-GM, Briggs (1995) concluded that water-rock interaction was the controlling influence on groundwater salinity.

Briggs (1995) conducted geochemical analyses of well water from all three cased wells at the Mer Bleue GSC Geomagnetic Laboratory site as shown in Table 1. These samples are from the Carlsbad Shale bedrock underlying the Champlain Sea sediments at Mer Bleue. In addition, Briggs analysed S, Sr and C isotopes, concluding that the source of salinity in the shale was due to the leaching of solutes from the bedrock, and that the brackish groundwater in the shale is controlled by mineral dissolution-precipitation, solute adsorption-desorption and microbiological activity in an anaerobic shale environment.

SAMPLE NO.	AB-93-16	AB-93-22	AB-93-30
(species)	(ppm)	(ppm)	(ppm)
Cl	5500	5200	1700
SO ₄	7.0	33	0
HCO ₃	933	1068	43
NO ₃	0	0	0
Br	22	19.5	16
Na	3700	3369	739
K	46	54	11
Ca	41	41	176
Mg	190	202	51
Sr	7.8	5.5	14
Ba	2.6	2.8	5.7
Fe	0.9	1.3	24
Mn	0.08	0.09	2.6
Cu	0	0	0
Zn	0	0	0
Pb	0.25	0.26	0
Cr	0	0	0
Mo	0	0	0
V	0	0	0
Al	0	0	0
Bi	0.21	0.25	0
Sb	0.28	0.33	
Te		0.27	
TDS	9977.1	9454.3	2761.7

pH	8.8	8.1	7.2
conductivity (uS/cm)	16000	16850	4860
alkalinity (ppm)	766	1050	35
temperature °C	7	9.5	11
HS (ppm)		75	

Table 1. Chemical analyses (ppm) from shale bedrock groundwater at study site (after Briggs, 1995).

Chapter 2 GEOLOGICAL SETTING

2.1 Bedrock Geology

The bedrock geology in most of Eastern Ontario consists of Precambrian crystalline basement overlain by flat lying Paleozoic sedimentary rocks of the Cambrian and Middle Ordovician (Wilson, 1946).

The Precambrian basement is part of the extensive Grenville Province of the Canadian Shield and these rocks are exposed as rugged highlands north of the Ottawa River in the Gatineau Hills, west of the Ottawa River and Rideau Lakes in the Madawaska and Frontenac Highlands and south of the St. Lawrence River in the Adirondack Mountains. The crystalline highlands form the raised margins of the Ottawa-St. Lawrence Lowlands, a Precambrian basin in which a Paleozoic marine succession of sandstones, dolostones, limestones and shales was deposited. The Paleozoic rocks at the Mer Bleue bog are overlain by more than 50m of Cenozoic marine and freshwater clays deposited on the Champlain Sea floor during the retreat of the Wisconsinan Laurentide ice sheet between approximately 12000 and 10,000 yr. B.P.(Rodrigues, 1988)

2.1.1 Structure

After Paleozoic deposition, and before the deposition of glacial materials, extensive rifting during the early Cretaceous and early Tertiary (Legall *et al.*, 1981) is thought to be coincident with the position of ancient crustal weaknesses. As a result, normal faults are abundant in the central and eastern part of the lowland, in particular in a triangular block between a fault zone trending east along the Ottawa River east of Ottawa and the Gloucester Fault zone trending southeast between Ottawa and the town of Russell. These fault zones intersect at Ottawa. A vertical displacement of more than 500m is known along the Gloucester Fault near Russell (Williams *et al.*, 1984).

2.1.2 Stratigraphy

Paleozoic strata in the Ottawa-St. Lawrence Lowland were deposited continuously and contemporaneously with thicker and more extensive marine deposits in the Michigan Basin of southwestern Ontario. The Frontenac Arch, a Precambrian ridge between the Adirondacks and the Madawaska Highlands, caused local thinning and draping of

Paleozoic deposits. Following erosion of Paleozoic rocks to form a Middle Ordovician peneplain in the Ottawa-St. Lawrence Lowland, the Arch was exposed (and became a barrier to east-west stratigraphic correlation). Table 2 (after Williams, 1991) shows the Paleozoic nomenclature developed locally by Wilson (1946) for the Ottawa-St. Lawrence Lowland based on faunal zones, and the probable correlative units with Paleozoic nomenclature west of the arch in the Michigan Basin.

A stratigraphic section typical of Paleozoic rocks immediately underlying the Mer Bleue bog is presented in Figure 3. The most recent geological map of the study area (Figure 4, after Williams *et al*, 1984 and 1985), indicates Billings Formation shale immediately underlies the Mer Bleue bog and that younger Carlsbad Formation shale to the south was likely intersected at the completion of borehole GSC-93-GM. The borehole is located at the western margin of the bog on the downthrown side of a normal south dipping fault trending subparallel to the Ottawa River and the Gloucester Fault. All three boreholes at the GSC Geomagnetic Laboratory (as noted in section 1.4 above) including GSC-93-GM are within 500m of the fault and the southern margin of Billings Shale. The abandoned water well at the site (Briggs borehole # AB-93-30) was drilled to a depth of 106m, and may have penetrated the Carlsbad Shale, Billings Shale and the underlying limestone of the Eastview or Lindsay Formations.

2.2 Quaternary Geology

After the erosion of Paleozoic rocks, several episodes of glaciation further eroded and reworked Precambrian and Paleozoic material to form till, fluvial, lacustrine and marine deposits. The last ice to occupy the Ottawa region was of Pleistocene Late Wisconsinan age. This ice retreated from the area 12,000 to 10,000 yrs. B.P. (Rodrigues, 1988). The Quaternary geology of the Ottawa-St. Lawrence Lowland has been described by Fulton (1987) and Gadd (1986, 1988a and 1988b).

2.2.1 Laurentide Ice Retreat

The source area for Wisconsinan ice was centered in north central Quebec. Through gravity flow, Wisconsinan ice would have radiated outward over the Precambrian Shield, flowing southward over the Ottawa-St. Lawrence Lowland. The southward flow would have been deflected by topographic highs and channeled by topographic lows into thicker

Wilson, 1946.	Williams <i>et al.</i> 1984, 1985a, 1985b.	Williams 1991.	Southcentral Ontario, Liberty 1969.
Queenston	Queenston	Queenston	Queenston
Russell	Carlsbad	Carlsbad	Georgian Bay
Carlsbad			
Billings	Billings	Billings	Blue Mountain
Eastview	Eastview	Ottawa Group. incl. Eastview (Divisions, see below)	Simcoe Group (Divisions, see below)
Ottawa Formation (Divisions, see below)	Ottawa Group (Divisions, see below)		
St. Martin	Rockcliffe	Rockcliffe	No equivalents
Rockcliffe			
Oxford	Oxford	Oxford	
March	March	March	Mount Simon
Nepean	Nepean	Nepean	
	Covey Hill	Covey Hill	Jacobsville

Divisions of the Ottawa (Simcoe) Group/Formation:

Wilson (Faunal zones)	Williams <i>et al.</i> (Formations)	Williams (Formations)	Liberty (Formations)
Cobourg	Lindsay	Lindsay	Lindsay
Sherman Fall	Verulam	Verulam	Verulam
Hull	Bobcaygeon	Bobcaygeon	Bobcaygeon
Rockland			
Leray	Gull River	Gull River	Gull River
Lowville			
Pamelia	Shadow Lake	Shadow Lake	Shadow Lake

Division of the Cambrian to Ordovician stratigraphic sequence in the Ottawa-St. Lawrence Lowland, showing terminology used by different authors for the respective formations (Groups where indicated). Disconformities according to Wilson (1946) are shown with double lines.

TABLE 2. Paleozoic Stratigraphic Nomenclature in Ottawa-St. Lawrence Lowland and Southwestern Ontario (after Briggs, 1995)

FIGURE 3 Stratigraphic section of Paleozoic rocks immediately underlying Mer Bleue

LEGEND

Sample location, type and number AB 93/94-

x Well finished in bedrock

Geological Formations

- ⑨ Queenston
- ⑧ Carlsbad
- ⑦ Billings
- ⑥ Eastview
- ⑤ Ottawa Group: L=Lindsay, V=Verulam,
B=Bobcaygeon, G=Gull River
- ④ Rockcliffe
- ③ Oxford
- ② March
- ① Nepean

—▼— Fault, with downthrown side indicated

..... Geological Boundary

—— Road

..... City/Township Boundary

500 m 2 km
0 1 km

FIGURE 4 Geological map of study area (after Williams et al., 1984 and 1985 and Briggs, 1995)

and faster moving lobes. Figure 5 shows the major topographic features bordering the Ottawa-St. Lawrence Lowland which would have defined the lobate ice flow (Gadd, 1988a). The direction of local ice flow in the Ottawa area would have been south along the Gatineau River and south and southeast across the Ottawa Valley.

The Quaternary record is represented mainly by materials deposited during the retreat of the Wisconsin ice sheet. In addition to glacial till and proglacial lacustrine, beach and fluvial deposits which are observed across Canada and the northern United States, the Ottawa-St. Lawrence Lowland was submerged by a marine transgression of the Atlantic Ocean. The Champlain Sea entered through the St. Lawrence channel and extended as far northwest as Pembroke on the Ottawa River (Barnett, 1988). As a result, the most extensive surficial sediments in the Ottawa-St. Lawrence Lowland are massive clays deposited by the Champlain Sea.

The Champlain Sea marine transgression occurred due to the weight of Laurentide ice prior to isostatic rebound. Figure 6 illustrates the development of the Champlain Sea inundation through four phases of deglaciation (Gadd, 1988a) in the Ottawa-St. Lawrence Lowland.

Following the merging of ice lobes to form a maximum ice advance in Phase 1, Phase 2 shows the retreat of the southern ice margin and the development of interlobate moraines north of Lake Ontario and in the St. Lawrence estuary where major ice lobes had stopped their advance and become stationary. Freshwater deposition of varved sediments in ponded meltwaters would have accompanied Phase 2. Phase 3 shows the transgression of the early Champlain Sea up the St. Lawrence Valley preceded and accompanied by ice drawdown and calving along the lowest course in its path (the former St. Lawrence and Ottawa Rivers) while the southern ice margin continued to retreat with interlobate moraines tracing the course of retreat toward the ice source as all major ice lobes retreated. Phase 4 shows the known extent of the Champlain Sea bounded by both land (Adirondacks) and remnant ice (Gadd, 1988a). Figure 7 shows the extent of the Champlain Sea relative to the Great Lakes (Prichonnet, 1988).

The final phase, before decantation of the Champlain Sea from the Ottawa-St. Lawrence Lowland, was its gradual dilution by the eastward drainage of freshwater from the vast glacial Lake Algonquin, which had been initially held back by ice dams. Extensive spillwaters from glacial lakes Algonquin and Agassiz from as far west as Manitoba and

Topography of the St. Lawrence Lowlands. Abbreviations: MAD, Madawaska Highland; LAUR, Laurentian Highland; ADIR, Adirondack Highland; GR-ND, Green-Notre-Dame mountains; D, Deschailons.

FIGURE 5 Resistant Topographic Features Bordering Ottawa-St. Lawrence Lowland.(after Gadd, 1988)

Phase 1

Phase 2

Phase 3

Phase 4

FIGURE 6 Four Phases of Deglaciation in Ottawa-St. Lawrence Lowland
(after Gadd, 1988a)

FIGURE 7 Extent of Champlain Sea in St. Lawrence Basin (after Prichonnet, 1988)

Saskatchewan, entered the marine embayment via the Fossmill and North Bay channels (French, 1975). This occurred between 11,500 and 11,000 yr. B.P. (Gadd, 1988a).

The Champlain Sea occupied the Ottawa-St. Lawrence Lowland for approximately 2000yr. between 11,500 and 9,200yr. B.P. ± 500 yrs. (Gadd, 1988a, Anderson, 1988 and Rodrigues, 1988), accounting for an extensive sequence of marine clay deposits commonly 20 to 60m thick (Belanger and Harrison, 1980) and up to 100m thick. With the onset of crustal rebound, the Champlain Sea began its retreat from the Ottawa area approximately 10,900yrs. B.P. (Anderson, 1988). The Sea gradually regressed, leaving remnant raised beaches more than 100m above the present day Ottawa River (French, 1975) and swampy marine ponds in topographic lows such as the Mer Bleue bog (Anderson, 1988), the Alfred bog and many other bogs in the Ottawa Valley. The thickest measured Champlain Sea deposits are 100m thick on the Ottawa River, at Treadwell, 55km east of Ottawa.

2.2.2 *Quaternary Stratigraphy*

It is generally accepted that a brief period of fresh glacial meltwater ponding immediately preceded the arrival of the Champlain Sea (Gadd 1986, 1988b, Hillaire-Marcel, 1988 and Rodrigues, 1988) resulting in the deposition of a thin sequence of rhythmically bedded varved clays (varved couplets ranging in thickness from <1 to 5cm), which serves as a widespread stratigraphic marker prior to the onset of marine deposition. These deposits range in thickness from 10m at the margins of the basin to less than 2m at its centre (Gadd, 1986). The varved clays may rest unconformably on Paleozoic rocks or may overlie a basal silty, sandy gravel till. The freshwater rhythmites grade upward into massive marine clay and silty clay which in turn grades upward into red grey banded clay and silty clay at the top of the sequence (Gadd, 1986 and Rodrigues, 1988). The red-grey-banded clay and silty clay can be found as shallow as 1m depth on uneroded sites north of Gatineau. A grey clay and overlying sand deposits of freshwater proto-Ottawa River fluvial origin are well preserved throughout the area of the proto-Ottawa River channel.

Based on texture, structure and colour banding, Gadd (1986) subdivided these sediments into five dynamic units (Figure 8) corresponding to transgressive and regressive environments of deposition as the sea invaded and retreated. The soft varved clay overlying till (unit I) was Gadd's glaciomarine rhythmite (unit II). The overlying stiff grey to olive-grey clays constitute marine prodelta (unit III), delta front (unit IV) and delta top (unit V)

Units A & B ABANDON CHANNEL	THICKNESS (in basin study)	CHAMPLAIN SEA - LITHOFACIES
Unit V SANDY EMERGENT DELTA	3 - 15m	<ul style="list-style-type: none"> - Cyclic sand/silt strata, clay/silt near base, similar to and may be continuous with Units IV and V. - Rhythmically laminated silt and clayey silt, clays light and dark grey to dark reddish brown, may be continuous with Units IV and V. <ul style="list-style-type: none"> - Horizontal beds or laminae of sand to silty clay, either fining upwards or as regular sand/silty clay bands, silty clay pink to red. Dominantly sandy texture, gradually increasing upward. May be continuous with Unit IV. Sedimentary structures as in Unit IV (truncation, cut-fill, distortion, convolutions, inclusions - mud balls, pebbles, "frozen" laminated sand, etc.) and additional current and wave action structures (cross laminations, ripple marks). No black banding. Magnetite, pyrite (& homblende) laminae. Fossils rare, fragmentary or absent.
Unit IV STRATIFIED DELTA FRONT	3 - 30m	<ul style="list-style-type: none"> - Light grey silt and clay (silt dominant), rhythmically or cyclically colour banded texture, similar to top of Unit III. Distinct cyclic thin bedded dark grey to red clayey sediment overlain by light grey silty clay and silt. Frequency and intensity of red coloured clay layers increasing upward. Fine grained sand partings increasing upward in frequency and thickness. Structure thin bedded and distinctly stratified (including tilting beds up to 30° unconformably within horizontal beds, channel cut-fill of coarser silt within otherwise regular and continuous strata, unsorted and distorted laminations (mud balls and clay lenses), black banding (1mm) and mottled (5cm) commonly cyclically coupled with a light (coarse) silt facies. Fossils present but not abundant.
Unit III MASSIVE PRODELTA	3 - 30m	<ul style="list-style-type: none"> - Light grey silt and silty clay, mainly massive and stiff (low clay content) Where thick grades upward to colour banded stratified silt/clay cycles with increased clay content. Clays red to dark grey. Most uniform texture of Leda Clay facies. Strata rare and related to increased clay content (colour bands) upward. Abundantly fossiliferous, mainly <u>Portlandia sp.</u> and microfossils - foraminifera and ostracoda. Free CO₃ (HCl test) and abundant fossil shells. Black unctuous bands (tubular patterns) give H₂S and SO₂ odour with HCl (test). Black oxidizes and disappears within 24hrs. Pyrite occurs as grains (1-3mm), tubules (1-6mm) and replacing microfossils.
Unit II SOFT VARVED CLAY	1.5 - 9m	<ul style="list-style-type: none"> - Grey coarse to fine silt and silty clay varves (diatactic), light (summer) to dark (winter) grey (red br. less common). Varve couplets 2mm to 5cm thick, fining upward. Free CO₃ variable, more in summer laminations. Minor <u>Portlandia sp.</u> near top. Where thick upper boundary gradational, varves less distinct, alternating varves and massive texture of Unit III.
Unit I TILL	0 - 5m	<ul style="list-style-type: none"> - Light to medium grey, compact basal (lodgment) till. Sandy to gravelly texture. Magnetite and pyrite common. Commonly permeable.

(after Gadd, 1986)

FIGURE 8 Stratigraphic Section of Quaternary Deposits at Mer Bleue

environments as the Ottawa basin gradually filled, with the site of deposition moving farther and farther into the centre of the basin as the sea retreated.

The uppermost clay and sand units (unit A and B) were interpreted as post Champlain Sea Holocene proto-Ottawa drainage abandoned channel and fluvial terrace deposits of reworked Champlain Sea material. These typically occur at the surface, but are commonly absent (eroded) at high elevation locations. At Mer Bleue this unit is represented as an east-west trending sandy ridge underlying the study site and capping the Champlain Sea marine succession. The ridge is part of a streamlined island formed in the proto-Ottawa River during the regression of the Champlain Sea, and was preserved when the river switched channels away from the Mer Bleue area 7650 years ago (Gadd, 1987). The ridge is thought to have preserved underlying Champlain Sea sediments (upper part of unit V) from erosion by the proto-Ottawa River, although some erosion may have occurred prior to sand deposition.

A correlation of these units in twenty boreholes is shown in cross-section, one parallel to and one across the trend of the northwest arm of the Champlain Sea between Petawawa and Hawkesbury in Figure 9. Generally, grain size coarsens upward within the Champlain Sea sediments and within each lithic unit and fines radially from the margin to the centre of the basin (Gadd 1986).

Figure 10 (after Douma and Nixon, 1993) illustrates the correlative stratigraphic sections through the Champlain Sea deposits at Mer Bleue bog in borehole GSC-93-GM and nearby borehole CRF-21A, which are separated by 250m. As illustrated, there is a close correlation of the stratigraphic record closely correlates in both boreholes with high-resolution seismic reflectors and down-hole geophysical log signatures.

2.2.3 Mineralogy

The Champlain Sea deposits are of mainly clay and silt size and are composed of 50% quartz and feldspar, less than 30% clay minerals (illite, chlorite, and traces of vermiculite and smectite), amphiboles and less than 2% oxide (dominantly crystalline) minerals (Torrance, 1990) and trace amounts of amorphous minerals (Torrance, 1995). They are derived mainly from glacially abraded Precambrian Shield rocks (Torrance, 1988). The carbonate content varies from 0 to 12% depending on their location and degree

Correlation chart for stratigraphic borings on a north-south axis of the Ottawa basin of the Champlain Sea; horizontal distances not to scale. Borings are identified by location and driller's record number (year-boring number).

Correlation chart for stratigraphic borings on an east-west axis of the Ottawa basin of the Champlain Sea; horizontal distances are not to scale. Borings are identified by locality and driller's record number year-boring number.

FIGURE 9 West to East and North to South Cross-sections of Champlain Sea strata in Ottawa basin (after Gadd, 1986).

EM-39 borehole logs and high resolution seismic section at the Anderson Road borehole. Mist-ties between log depths and the calculated seismic section depth, particularly at shallow depths, are due to the 12 m offset between source and receiver. The lithofacies classification from a borehole CRF-21A is from Gadd (1986).

FIGURE 10 Stratigraphic section borehole GSC-93-GM (after Douma and Nixon, 1993)

of weathering (Torrance, 1988). Kettles and Shilts (1987) noted that carbonate content in tills increased to more than 10% where tills were underlain by Paleozoic carbonates.

2.3 Hydrogeological Properties of Bedrock

Water from the Carlsbad Formation commonly contains high levels of TDS, while water from the Billings Formation is known to have a strong H₂S odour, and in some locations may be highly mineralized (Owen, 1953 and Brandon, 1960). Shale beds in the Ottawa Formation can be aquifers producing potable water (Owen, 1953) whereas some limestones of the Ottawa Formation may be massive and not water-bearing. The Ottawa Formation may also produce mineralized water (Brandon, 1960). Fracturing within the bedrock can generally enhance the yields from the bedrock units (F. Michel, pers. comm.).

Water well AB-93-30 drilled to a depth of 106m at the GSC Geomagnetic Laboratory site, produced non-potable water from the shale bedrock. This well is located 250m east of borehole GSC-93-GM.

2.4 Hydrogeological Properties of Quaternary Sediments

The contact zone between the bedrock and the overburden (mainly Champlain Sea sediments) has been found to produce the largest volume of groundwater in the Ottawa-St. Lawrence Lowland on a regular basis (Charron, 1978). Owen (1953) reported that sand and gravel beds underlying marine clay and resting on bedrock yield the largest quantities of groundwater. These aquifers contain saline water when the overlying marine clays are more than 45m thick. Gadd (1986) noted that the basal till underlying the marine clays is commonly permeable.

Sandy lenses within the marine clays have been known to produce potable water. Most shallow domestic wells in Gloucester draw water from clays or sandy lenses in the glacial clay. Surficial fluvial sand and gravel more than 3.6m thick and overlying the clay is also a source of potable groundwater in the Ottawa Valley (Owen, 1953).

The magnetic susceptibility is reacting mainly to the presence of magnetite and less to hematite (magnetite has an average magnetic susceptibility approximately 500 times that of hematite) in the sediments (Telford *et al.*, 1976). Magnetite has been noted by Gadd to occur in his basal till unit I and sandy emergent delta unit V. However, magnetite has not been identified in the Ottawa Valley marine clays, but hematite has been (Torrance, 1986) at Casselman near the South Nation River. Most of the marine clay section has a constant value of approximately 5ppt above 40m depth where pink and red (iron oxide according to Gadd, 1986) and iron sulphide are seen as colour banding. Between 40m and 47m depth, susceptibility declines at a constant slope to zero. This zone is highlighted on the seismic section by an absence of stratification which suggests a good correlation with the massive prodelta facies in which sediments are stiff and unstratified. There is an absence of iron oxide and iron sulphide banding, in agreement with the decline in magnetic susceptibility.

Magnetic susceptibility spikes to a high of approximately 7ppt between 48 to 50m depth and declines to 2ppt in the varved clay. A large gradual increase in susceptibility from 2ppt in the varved clay to a maximum of 10ppt at 51.5 to 53m depth in the till probably reflects the primary mineralogy of the fresh till as described by Gadd (1986).

The electric conductivity gradually increases with depth at near constant slope to a maximum of nearly 400mS/m at 46m. Below this, conductivity remains at about 400mS/m. Conductivity trails off rapidly below the varved clay to less than 100mS/m in the till and lower (less than 50mS/m) in the bedrock.

Two zones of apparent cyclic skipping or large spikes in thin intervals (< 1m thick) occur on the conductivity and magnetic susceptibility logs at 10m and 15m depth. These correlate with discrete zones of no recovery in the drillers log and may indicate zones of either "quick clay" or sand lenses which could not be contained by the Shelby tube sampler and which may have been washed out before logging.

The peak values on the inductive conductivity log and the sustained levels on the magnetic susceptibility log in the marine clay section in borehole GSC-93-GM tracked at approximately twice the magnitude normally recorded in glacial overburden elsewhere in Eastern Canada (pers. comm. M. Douma).

The temperature log (recorded by the GSC in May 1995, Figure 13) indicates that water in the cased borehole was encountered at a depth of approximately 12m. This water

Factors producing a high undisturbed shear strength

Depositional	Post-depositional
Flocculation ^{1,2} salinity divalent cation adsorption high suspension concentration	Cementation bonds rapidly developed slowly developed Slow load increase time for cementation 'thixotropic' processes

Factors producing a low remoulded shear strength

Depositional	Post-depositional
Material properties low activity minerals dominate ^{1,2}	Minimal consolidation Leaching ¹ decrease in w > decrease in w Dispersants ² decrease in w > decrease in w

¹Essential in marine clays.²Essential in freshwater clays.

Table 3. General model for "quick clays" (after Torrance, 1983).

Chapter 3 DATA SOURCES AND ANALYSIS

3.1 Introduction

Data collection was based on the recovery of drill core samples contained in sealed Shelby tubes (measuring 0.60m X 0.05m diameter) from borehole GSC-93-GM. The sample material consisted mainly of soft clay. Tubes were selected to provide representative coverage of lithotypes and suspected lithological contacts down the borehole. In all, 41 Shelby tubes were investigated to a depth of 51.6m. In addition, three split tubes at 51.05m, 53.16m and 53.78m (measuring 0.60m X 0.04m) were also investigated.

3.2 Sampling Procedure

3.2.1 *Lithology*

The contents of 41 Shelby tubes were extruded, split along their length and sampled at regular intervals within their 0.60m length. Sampling was restricted to the inner portion of the core in order to minimize wall contamination and disturbance. Lithological descriptions from the drill site and the core sampling log are compiled in Appendix 1.

A sample for grain size was taken. Grain size analysis was conducted at the Mineral Tracing and Sedimentology Laboratory of the Geological Survey of Canada as reported by Traynor (1995). Grain size distribution in the <0.063mm fraction was determined using a Brinkman particle size analyser (as described by Syvitski, 1991) and results are tabulated in Appendix 1.

3.2.2 *Geotechnical*

Fall cone measurements for both undrained, undisturbed and remoulded shear strength were taken in the upper and lower parts of each tube, using 100g, 60g and 10g fall cones (Hansbo, 1957). Two samples from each tube, an upper and lower sample, were taken for immediate measurement of moisture content.

Geotechnical observations of fall cone penetration were converted to undisturbed shear strength ($T\mu$) and remoulded shear strength (Tr) and the sensitivity ($T\mu/Tr$) calculated using the conversion tables of Hansbo (1957), for each 0.60m core sample.

Water content was determined for both an upper and lower sample in each Shelby tube. The results of geotechnical measurements and water contents are tabulated in Appendix 1.

3.2.3 *Geochemical Procedures*

Samples were taken for pore water extraction using an air pressure activated pore water press powered by compressed nitrogen as described by Torrance (1976). The pore water extraction was conducted on sufficient sample to obtain approximately 10ml. of liquid extract from each sample for isotope and chemical analysis. The representative sample for grain size analysis (referred to in section 3.2.1 above) was taken immediately adjacent to the pore water samples.

The conductivity of each extract was measured using a Radiometer Copenhagen conductivity meter. The conductivities are listed in Appendix 2.

3.2.3.1 *Isotope Analysis*

Forty-five pore water extracts were analysed for oxygen-18 content using a gas source mass spectrometer with VG SIRA 12 triple collector at the University of Ottawa Stable Isotope Laboratory using a CO₂-water equilibration procedure at 25 °C as described in Appendix 3.

Twenty-two pore water extracts were further analysed for deuterium content using a gas source mass spectrometer and VG 602D double collector on hydrogen generated by the reduction of sample water on zinc at 430 °C, also at the University of Ottawa as described in Appendix 3.

Analytical precisions are ± 0.10 permil for oxygen and ± 1.5 permil for hydrogen respectively. The results of isotope analyses are reported in Appendix 2.

3.2.3.2 *Ion Chemical Analysis*

Thirty-two pore water extract samples were analysed for major ions at the Analytical Chemistry Laboratories of the Geological Survey of Canada. Cations were analysed by inductively coupled plasma and anions were analysed by ion chromatography, as outlined in Appendix 3. In addition to major anions, bromide was also measured by ion chromatography.

The results of chemical analyses are reported in Appendix 2.

Chapter 4 PHYSICAL GEOLOGY AND GEOTECHNICAL RESULTS

4.1 Physical Geology

4.1.1 Stratigraphy

A stratigraphic section is presented in Figure 12 based on the lithological description of core from borehole GSC-93-GM.

The bedrock occurs at a depth of 54m, where Carlsbad Shale was encountered. This is the depth of split-spoon refusal where core tube FM5378 was plugged with a shale clast. The marine clay/freshwater contact occurs at 50m depth. Above this contact the marine clam Portlandia sp. was found at a depth of 47m and several shell fragments were found at a depth of 48.2m. One shell fragment was found at a depth of 50.1m within the varves.

The exact position of the contact between the glacial till and the silt/clay varves is not known due to disturbance by the drill and poor recovery of sample. The contact lies between a depth of 51 and 53.8m. The varved zone is approximately 1.5m thick in nearby borehole CRF-21A (Gadd, 1986) . If the varved clay is the same thickness in borehole GSC-93-GM, its basal contact may be at a depth of 51.5m, resulting in a till thickness of approximately 2.5m. Below the marine clay/freshwater varved clay contact, approximately 38 varve years were counted over a thickness of 0.4m in sample FM4983. Thus approximately 140 varve years are represented by 1.5m of varved clays if deposited at a constant rate.

Colour banding (pink to reddish brown) is a distinctive feature in most of the marine clay above approximately 40m in depth. There is faint pink banding from 40 to 42.5m depth. The black bands indicate the presence of unoxidized iron sulphide compounds (and secondary pyrite mineralization) and the pink banding is attributed to iron oxides from hematite-rich feldspar mineralogy in local Precambrian granites (Gadd 1986). The black bands disappear after a few hours exposure to air (oxidation), which suggests that they have been preserved in a reducing environment in the marine clays. In addition, black sulphide specks were noted throughout the marine clay section.

FIGURE 11. Stratigraphic section of observations in borehole GSC-93-GM
(unit nomenclature after Gadd, 1986)

The base of the distinctive colour banding at approximately 40m likely marks the lower contact of Gadd's Stratified Delta Front (unit IV). Below this contact the clays are massive grey and very stiff with faint pink banding only in the upper 2m thus comprising Gadd's Massive Prodelta unit (unit III). The distinctive pink colour banding persists upward to a depth of approximately 4m in the borehole which may be interpreted as the maximum possible depth of erosion by the proto-Ottawa River (pers. comm. K.M. Torrance). Gadd's fluvial terrace freshwater lithofacies is likely above 4m depth. The lowermost sandy lens was found at 22m and may represent the basal contact of Gadd's Sandy Emergent Delta (unit V).

4.1.2 *Grain Size*

Although the bulk of the Champlain Sea sediment has the appearance and feel of clay, the grain size results indicate that the material is 55 to 80% silt as shown in Figure 12b. The grain size analyses (Traynor, 1995), were conducted on only the <60 μ m size fraction. Preliminary sieving revealed less than 5% by weight to be greater than 60 μ m. There may be a clay-rich zone with 50 to 55% clay at 9 to 11m depth and a possible silt lens with less than 20% clay at 46.5 to 48m depth. Generally, clay content increases slightly and gradually upward (Traynor, 1995) and although there are a number of coarsening upward sequences (e.g. 26 to 22m), the general coarsening upward trend reported in CRF-21A (Gadd 1986) is not seen in GSC-93-GM.

4.1.3 *Correlation with Geophysical Logs and High Resolution Seismic Section*

A distinct shift on the three Geonix-39 geophysical logs (as referred to above in section 1.4) and a strong seismic reflector correlate well with the lithological determination of the till/shale bedrock contact at 54m depth as shown in Figure 13. The natural gamma shifts from 200 cps in the shale to 100 cps above the contact and similarly the magnetic susceptibility maintains a constant 4.5ppt in the shale and increases dramatically above the contact. Inductive conductivity is low in the shale and increases 10-fold above the contact. In addition, the detailed temperature log registered a small change in slope at the till/bedrock contact. The uppermost zone in the shale is likely broken and fissured by ice movement and may include some till infilling. It is detected as a spiky transition on the gamma and magnetic susceptibility logs between 54 and 57.5m. The contacts between other lithological units are less distinct on the geophysical logs. The behaviour of all three Geonix logs at approximately 4m depth may be related to the base of the sandy fluvial terrace zone.

Percent Clay vs Depth

FIGURE 12 Grain size vs depth

EM-39 borehole logs and high resolution seismic section at the Anderson Road borehole. Mis-ties between log depths and the calculated seismic section depth, particularly at shallow depths, are due to the 12 m offset between source and receiver. The lithofacies classification from a borehole GSC-93-GM Gadd (1986).

FIGURE 13 Correlation of stratigraphy and geophysical record at borehole GSC-93-GM (modified from Douma and Nixon, 1993)

The magnetic susceptibility is reacting mainly to the presence of magnetite and less to hematite (magnetite has an average magnetic susceptibility approximately 500 times that of hematite) in the sediments (Telford *et al.*, 1976). Magnetite has been noted by Gadd to occur in his basal till unit I and sandy emergent delta unit V. However, magnetite has not been identified in the Ottawa Valley marine clays, but hematite has been (Torrance, 1986) at Casselman near the South Nation River. Most of the marine clay section has a constant value of approximately 5ppt above 40m depth where pink and red (iron oxide according to Gadd, 1986) and iron sulphide are seen as colour banding. Between 40m and 47m depth, susceptibility declines at a constant slope to zero. This zone is highlighted on the seismic section by an absence of stratification which suggests a good correlation with the massive prodelta facies in which sediments are stiff and unstratified. There is an absence of iron oxide and iron sulphide banding, in agreement with the decline in magnetic susceptibility.

Magnetic susceptibility spikes to a high of approximately 7ppt between 48 to 50m depth and declines to 2ppt in the varved clay. A large gradual increase in susceptibility from 2ppt in the varved clay to a maximum of 10ppt at 51.5 to 53m depth in the till probably reflects the primary mineralogy of the fresh till as described by Gadd (1986).

The electric conductivity gradually increases with depth at near constant slope to a maximum of nearly 400mS/m at 46m. Below this, conductivity remains at about 400mS/m. Conductivity trails off rapidly below the varved clay to less than 100mS/m in the till and lower (less than 50mS/m) in the bedrock.

Two zones of apparent cyclic skipping or large spikes in thin intervals (< 1m thick) occur on the conductivity and magnetic susceptibility logs at 10m and 15m depth. These correlate with discrete zones of no recovery in the drillers log and may indicate zones of either "quick clay" or sand lenses which could not be contained by the Shelby tube sampler and which may have been washed out before logging.

The peak values on the inductive conductivity log and the sustained levels on the magnetic susceptibility log in the marine clay section in borehole GSC-93-GM tracked at approximately twice the magnitude normally recorded in glacial overburden elsewhere in Eastern Canada (pers. comm. M. Douma).

The temperature log (recorded by the GSC in May 1995, Figure 13) indicates that water in the cased borehole was encountered at a depth of approximately 12m. This water

level indicates the hydraulic head in the shale bedrock at a depth of 58.5m where the casing is screened. Below 12m the borehole temperature declines gradually from 8.8 to 8.73°C at 28 to 30m. Below 30m the temperature increases gradually, returning to 8.8°C at 40m and reaching 9.1°C at 59m depth. There is a slight change in slope at the glacial till/bedrock contact at 54m.

4.2 Geotechnical

The results of geotechnical observations and analysis are tabulated in Appendix 1.

4.2.1 *Moisture*

The moisture content ranges between 40 and 100% by weight in the Mer Bleue Champlain Sea sediments (Figure 14). Variation within a Shelby tube is about the same as between adjacent Shelby tubes. Moisture determinations were not made for split-tube samples below the varved clay at 51m.

Generally, moisture content declines slightly with depth from 90% at 4m to 65% at approximately 40m, then declines more steeply below 40m to approximately 40% at 51m. This trend is interrupted at approximately 12m depth where moisture declines gradually to 60% then increases rapidly to 80% over a thickness of 4m. The more rapid decline in moisture below 40m correlates with observations of stiffer clays in the massive prodelta facies noted on the lithology log, and may correlate with a decline in clay content over the same zone as noted in the grain size results above.

4.2.2 *Shear Strength*

The undisturbed and remoulded shear strengths are listed in Appendix 1. The undisturbed shear strength (Figure 15a) of Champlain Sea sediments in borehole GSC-93-GM range from 0.66 to greater than 6.31/m² (the maximum reading for the 100g fall cone using conversion tables of Hansbo 1957). Thus, undisturbed shear strengths range from low to very high in the Champlain Sea sediments and are highly variable, even between adjacent samples. Low $T\mu$ values as measured in many samples may be a consequence of sample disturbance during field coring, core transport and the core sample extraction

FIGURE 14 Moisture content vs depth

FIGURE 15a Undisturbed shear strength vs depth

process. Undisturbed shear strengths at depth are generally two to three times higher than in shallow samples. This is the expected response to compaction.

Remoulded shear strengths (Figure 15b) range from 0.015 to 1.25t/m². They are highly variable and increase two to three fold at depths below 34m. The Tr for two samples (4374 and 4933) was greater than the maximum reading for the 60g fall cone conversion tables (after Hansbo, 1957).

There was generally close agreement between shear strength measurements at upper and lower positions in the same Shelby tube. However, the measurement of undisturbed shear strength was considered to be more reliable in the lower part of a core due to stress and minor disturbance to the top of each core during sample extrusion. Undisturbed shear strength could not be measured in five cores in which the material was observed to be disturbed throughout. In the case of a remoulded shear strength of clay-rich and silt-rich zones in sample FM2171, the clay-rich zone had the greater remoulded shear strength.

A plot of shear strength vs depth (Figures 15a and b), indicates that there is no consistent relationship between undisturbed and remoulded shear strength except that below 34m depth both tend to increase to two to three times higher than at shallower depths. This increase in strength correlates roughly with stiff clays and slightly lower moisture (greater compaction) in the massive prodelta facies below 40m. A comparison of shear strength and moisture content with depth (Figure 16), indicates that there is no direct (one to one) correlation in individual samples between undisturbed or remoulded shear strength and moisture.

In a broad sense there is a correlation of the highest values (upper envelope of values) of undisturbed shear strength ($T\mu$) with depth (Figure 15a) if the lower values are ignored due to the effects of disturbance. The disturbance of material during the drilling operation and during extrusion from the Shelby tubes, noted above, may have precluded obtaining a reliable determination of undisturbed shear strength. Disturbance during various stages of sample recovery would generally tend to reduce $T\mu$. Low $T\mu$ values when they occur adjacent to much higher $T\mu$ values may be assumed, therefore, to be a result of disturbance. An estimate of true $T\mu$ can be made by extrapolating $T\mu$ values from the upper envelope of $T\mu$ values. Figure 17 shows the plot of the upper envelope of $T\mu$ values in comparison with the measured Tr values. The trend of the upper envelope of $T\mu$ values fits the expected response to compaction of the sediments with depth. The estimated $T\mu$ values are generally an order of magnitude greater than Tr values at the same depth.

Tr vs Depth

FIGURE 15b Remoulded shear strength vs depth

Moisture, shear strength vs depth

FIGURE 16 Shear strength and moisture vs depth

Shear strength vs Depth

FIGURE 17 Upper envelope of undisturbed shear strength (T_u) and remoulded shear strength (T_r) vs depth

4.2.3 Sensitivity

The ratio of undisturbed to remoulded shear strength yields sensitivity, a standard geotechnical measure of the degree to which clay can be transformed by remoulding into a viscous slurry (Terzaghi, 1944).

In the Champlain Sea marine clay section in borehole GSC-93-GM, remoulded shear strengths are at least an order of magnitude lower than the undisturbed shear strengths. Using the upper envelope of $T\mu$ values, sensitivity vs depth is plotted in Figure 18. Sensitivity generally ranges between 10 and 50. In addition, there are a few sharp peaks of 55 to 80 in individual samples occurring at intermittent depths between 12 to 14m and at 30m, 42m and 46m. An exceptionally higher sensitivity of 145 occurs in one sample at a depth of 27.6m. This range of sensitivities is similar to that in other Champlain Sea marine clays.

The observed large peaks in sensitivity appear to be independent of other observed or measured factors and it may not be possible to further analyse sensitivity without more detailed and controlled data measurement. The periodic sensitivity peaks "are related to the interaction of changes in a number of factors" with depth (pers. comm. J.K. Torrance).

Sensitivity vs Depth

FIGURE 18 Sensitivity (T_{μ}/T_r) vs depth

Chapter 5 GEOCHEMISTRY AND ISOTOPE RESULTS

5.1 Ion Geochemical Results

The geochemical data for borehole GSC-93-GM is summarised in table form in Appendix 2. Due to the small volume of pore water extract available for analysis, bicarbonate species concentration could not be measured using conventional laboratory methods. Instead, bicarbonate was assumed to account for the total negative ion concentration required to achieve a charge balance in each sample. Bicarbonate was therefore calculated using the following charge balance relationship:

$$\sum z m_c - \sum z m_a = z m_b$$

where z is ionic valence, m_c is molality of cation species, m_a is molality of anion species and m_b is molality of bicarbonate species. For samples 4785, 5316a and 5378 there was an excess of anion species and bicarbonate was given a value of zero.

5.1.1 Characterisation of Pore Water Ion Chemistry

5.1.1.1 Salinity

The pore water from borehole GSC-93-GM may be classified according to its total dissolved solids (TDS) content (Freeze and Cherry 1979) as follows:

<1000 ppm	= fresh
1000-10000 ppm	= brackish
10000-100000 ppm	= saline
>100000 ppm	= brine

According to this classification, the pore waters are fresh above approximately 10m, brackish between 10m and 50m and saline below 50m, as shown in a plot of TDS vs depth in Figure 19. The brackish and saline zones correlate generally with the marine clays, and the underlying varved clays and till respectively.

The depth of the freshwater zone may indicate the depth to which meteoric water is infiltrating downward from the surface and therefore the low TDS observed in pore waters

TDS vs Depth

FIGURE 19 Total dissolved solids (TDS) vs depth

is a function of short residence time. Below 10m, TDS increases gradually with depth at nearly constant slope to approximately 5500 ppm at 40m depth, the dilute brackish zone. Between 40m and the base of the marine clay section at 50m, the concentrated brackish zone, there is a sharp increase in TDS to a range of 8000 to 10000 ppm. Below 50m, TDS sharply increases to saline concentrations, reaching a maximum of 20000ppm at the base of the till at 54m depth.

A plot of TDS and pore water conductivity vs depth (Figure 20) indicates a very close correlation of conductivity with TDS over the entire depth range. A minor divergence in the two curves in Figure 20 is likely due to an increased concentration in divalent ions which is discussed below.

A comparison between the pore water conductivity curve and the Geonix down hole conductivity log by the GSC, shown in Figure 21, indicates a close correlation in the general shape of the curves over the same depth range. However, the pore water log is truncated at the base of the till at 54m, whereas the GSC log measures the decline in conductivity in the shale below 54m. The dramatic peak in conductivity below 50m depth is not detailed on the borehole log, and the maximum reading of approximately 400mS/m at 46m correlates with a pore water conductivity of approximately 1200mS/m.

5.1.1.2 *Piper Plots*

The Piper plot is a graphical representation of chemical character based on the relative abundance in milliequivalents (meq) of the major ions. The purpose of the plots is to identify groups of pore water samples with similar chemical character and to illustrate mixing between water types. Using the ion chemistry data set from 32 samples converted to milliequivalents (meq) Piper plots were constructed.

As shown in the Piper plot of all 32 samples in Figure 22, Na is the dominant cation, and anion character appears to follow a trend between end members HCO_3 to Cl and then Cl to SO_4 , with the bulk of samples dominated by Cl. The diamond field which accounts for both cations and anions in the middle of Figure 22 portrays the evolution in pore water character as shown by arrows. Beginning with sample 1, at the top of the borehole, the pore water evolves downward as follows:

TDS, Conductivity vs Depth

FIGURE 20 TDS and pore water conductivity vs depth

FIGURE 21 Pore water conductivity and Geonix-39 conductivity vs depth

FIGURE 22 Piper plot of thirty-two pore water samples

The bulk of the samples fall within the NaCl region of the Piper plot.

Piper plots of fresh, brackish and saline pore waters are plotted in Figures 23a,b and c respectively. The fresh pore waters have a Na-Ca-Mg-HCO₃ character. The brackish waters are mainly Na-HCO₃ and Na-Cl in character. The saline waters are Na-Cl and Na-Mg-SO₄-Cl in character. The character of the fresh and brackish waters is the same as that found by Briggs (1995) in a study of groundwater from wells and springs east of Ottawa.

Given that increasing sample number (in Figure 22) corresponds to increasing depth (as listed with ion chemistry results in Appendix 2), then the evolution of water type may be followed downhole. In the fresh water zone at the top of the borehole, pore water grades from a Na-Ca-Mg-HCO₃ water at approximately 4m to a Na-HCO₃ water at 10m. In the brackish zone, pore water evolves gradually from a Na-HCO₃ character at approximately 11m to equal parts Na-Cl and Na-HCO₃ at 24m to a predominantly Na-Cl water at the base of the marine clay at 50m depth. The Na-Cl character persists in the underlying saline varved clay zone to a depth of approximately 51m, but below 51m changes rapidly to a character dominated by SO₄, resulting in a mix of Ca-Mg-SO₄ and Na-Cl type water at 54m at the base of the Champlain Sea sediments.

The gradual evolution of dominant cations and anions with depth is illustrated in Figure 24. The evolving water types are correlated with the Champlain Sea stratigraphy in borehole GSC-93-GM.

The trend toward decreasing relative HCO₃ with depth reaches a minimum at the base of the marine clay. The zone of relative abundance of HCO₃ ion (4 to 46m) correlates roughly with the zone of black FeS₂ specks and banding within the marine clays which suggests a reducing environment in this zone. It should be noted here, however, that it may be misleading to draw conclusions based on the relative abundance of cation and anion species where TDS is very low in the near-surface fresh water zone.

The trend toward increasing relative SO₄ begins in the marine clay at 36m (#19 on the Piper plot) but accelerates rapidly in the coarser varved clay/silt and till to a maximum at the till/shale bedrock contact.

Figures 25 and 26 indicate that Na and Cl account for most of the TDS within the marine clay section, and Na and Cl with additional minor Mg and Ca and significant SO₄

FIGURE 23a Piper plot of fresh water samples

FIGURE 23b Piper plot of brackish water samples

FIGURE 23c Piper plot of saline water samples

Cations vs Depth

FIGURE 25 Cations (meq/l) vs depth.

Anions vs Depth

FIGURE 26 Anions (mcq/l) vs depth

concentration account for the chemistry of pore water underlying the marine clay section. Thus the NaCl character described in relative abundance Piper plots is confirmed by absolute concentrations of major ions in the marine clay pore waters at Mer Bleue.

5.1.1.3 Major Ion Proportions in Seawater

A comparison of major ion proportions in seawater and the concentrated brackish and saline zones in borehole GSC-93-GM is presented in Table 4. In addition, ion proportions in the upper metre of the varved clay zone (Shelby tube samples at 50 to 51m depth) and the zone of Ca-Mg-SO₄ type waters (below 51m depth) are presented in comparison to various known water types.

Table 4. Major Ion Proportions Compared to Seawater

Water Type	HCO ₃ ⁻ %	SO ₄ ⁻ %	Cl ⁻ %	Na ⁺ %	Mg ⁺⁺ %	Ca ⁺⁺ %	K ⁺ %
Seawater	0.2	4.7	45	39	8.9	1.7	0.9
Conc. Brackish water	5.8	3.0	41.6	42.5	5.23	1.32	0.97
Varved Clay	6.0	2.8	41.1	42.2	6.0	0.93	0.9
Saline water	1.5	19.97	28.59	36.42	9.07	3.46	1.03
Ca-Mg-SO ₄ type water		28.54	22.34	33.53	10.6	4.72	1.1
Underlying Carlsbad Shale (Briggs, 1995)	4.7	0.5	49.5	43.9	5.1	0.6	0.4
Michigan Basin (Frape and Fritz, 1982)	0.01	0.1	49.9	40.2	2.2	7.2	0.37
Shield Brine, NW Ont. (Frape and Fritz, 1982)	0.5	0.05	49.4	21.7	4.2	23.9	0.25

The fresh and dilute brackish waters are not represented in the above comparison due to their large HCO₃ content which distorts their SO₄ and Cl proportions. The concentrated brackish waters closely resemble seawater in ion proportions. The varved clay waters are similar to the concentrated brackish waters of unit III. Both the saline and Ca-Mg-SO₄ waters are similar to seawater except for excess Ca cation and excess SO₄ replacing Cl as the dominant anion. The underlying Carlsbad Shale also has seawater proportions except for low SO₄ which appears to be replaced by HCO₃. The contrasting

proportions of the sedimentary basin brines and Shield brines highlight the similarity between the other water types.

5.1.1.4 Cation Depth Profiles

The depth profile of the sum of cations curve is compared in Figures 27a and 27b with those in twenty boreholes in the Champlain Sea sediments taken between Pembroke and Hawkesbury (Gadd, 1986 and Torrance, 1988). As noted previously, with the exception of Bourget, profiles upstream of the junction of the South Nation and Ottawa Rivers, Group I, are dilute at shallow depths, reach peak concentrations generally below 15-20m and have peak concentrations <100meq/l. Below the South Nation River and at Bourget near the South Nation River, Group II profiles reach 200meq/l within 10 to 15m of surface, are convex to a peak between 200 to 400meq/l and, where thick enough (>20m), trail off in concentration toward the base of the profile.

The Mer Bleue depth profile is similar to Group I in location and shape except for a higher peak concentration of 175meq in the marine clays. A concentration of 300meq is reached in the underlying till and varved clay, although this lower zone is not represented in the other profiles.

As at Mer Bleue, the dominant cation in most profiles is Na (Torrance, 1988), with variable Ca and minor Mg and K in both thick and thinner sequences. There are six exceptions, all in Group I, where Ca and Mg are more abundant than Na through most of the marine clay section: Chapeau, Wakefield, Westmeath, Beachburg and in the upper 11 to 12m of Quyon (1) and Angers.

5.1.2 Elemental Plots

Elemental plots are a graphical representation of element concentrations in ppm or meq, as ratios or as combinations in order to demonstrate and define chemical character. They are particularly useful for the comparison of sample data with known element ratios in seawater (and other marine clays). The composition of seawater is used as a reference because the average composition of seawater has remained relatively well defined and stable with time and its graphical presentation facilitates the comparison of current pore water salinity with original Champlain Sea water.

FIGURE 27a Cation profiles - Group I (modified after Torrance, 1988)

FIGURE 27b Cation profiles - Group II (modified after Torrance, 1988)

As shown in Figures 25 and 26, the concentration of most cation and anion species increases with depth such that trends in most major ion species concentration correlates directly with depth. Therefore, in the following discussion of individual element concentrations, it is convenient to note that sample points in the graphical representation of increasing concentration for most species is synonymous with points of increasing depth.

Cl is a relatively conservative ion and therefore is used as a reference in the comparison between ion species in this section. However, it is possible that Cl depletion or enrichment could account for the ion ratios referred to below. Therefore, the depletion or enrichment of Cl should be considered for all elemental comparison diagrams below.

5.1.2.1 *Sodium*

The Mer Bleue pore waters are characterised as NaCl type, therefore the relationship between sodium and chloride may be important in identifying the source of salinity in Champlain Sea sediments. A plot of Na vs Cl, as presented in Figure 28, indicates a linear correlation and a closer fit with the halite dissolution line than with the sea water mixing line.

Most samples are enriched in Na and plot above the halite line and well above the seawater line. Two exceptions are samples FM4663 and FM4785, near the base of the marine clay section, which plot near the seawater line and occur in a silt lens with less than 20% clay content. In a leaching process with freshwater displacement (downward) of saltwater, the Na concentration should be reduced more slowly than the Cl. This would displace the line upward and to the left of the seawater line.

Samples from the varved clay and till below the marine clay, where SO_4 anion becomes more dominant than Cl, are relatively depleted in Cl and form a separate group well above the linear trend of the other samples. Two samples from the top of the varved clay unit, 4983 and 5044, plot on the halite dissolution line. Briggs (1995) sample AB-93-22, from the shale groundwater at 58.5m depth in borehole GSC-93-GM, plots on the halite dissolution line in Figure 28.

A plot in Figure 29 of Na vs Cl in a compilation of shield brines (Frape and Fritz, 1987), sedimentary basin formation waters (McNutt *et al.*, 1987 and Hitchon *et al.*, 1971) and shale waters (Von Damm, 1989), indicates that shield brines are depleted in Na, shale

Na vs Cl

FIGURE 28 Na vs Cl

Sodium plotted against chloride for different types of water where
 F=Formation Water, M=Canadian Shield Mine Water and S=Shale Water
 FIGURE 29 Na vs Cl of shield, basin and shale waters (after Briggs, 1995)

waters plot along the seawater line and basin formation waters may be enriched in Na relative to seawater. It is therefore likely that pore waters in varved clay and till beneath the marine clay are influenced by the proximity of a shale aquifer (underlying Carlsbad Formation) and other Paleozoic sedimentary basin formation waters and are influenced least by Shield brines. The 1:1 Na to Cl ratio common in North American shale groundwater is a result of halite control (Von Damm, 1989). This could also be a consequence of leaching and ion exchange effects from downward displaced Champlain Seawater at the study site.

5.1.2.2 *Potassium*

A plot of K vs Cl in Figure 30 indicates a close linear correlation uniformly enriched in K relative to seawater and even greater enrichment for the three most basal samples underlying the marine clay.

Among the major ions, K is most affected by cation exchange (Drever, 1988). It is normally removed from rock-forming minerals and then precipitated in secondary minerals such as phyllosilicates (Frape and Fritz, 1987). In cation exchange Na and K are released to solution and Ca is adsorbed in their place. The enrichment of Na and K noted above may indicate that cation exchange in Champlain Sea sediments has influenced pore water chemistry.

If cation exchange has occurred with Na and K being released to solution and Ca being adsorbed by minerals, then the original pore water balance between the other major cations, Ca and Mg, and the anions HCO_3 and SO_4 would have changed such that $\text{Ca} + \text{Mg}$ are deficient relative to $\text{HCO}_3 + \text{SO}_4$. As shown in Figure 31, cations are depleted in all but two adjacent marine clay samples, 4663 and 4785. As in other plots the basal saline samples underlying the marine clay (5105-5378) form a separate group with excessive depletion of divalent cations. Generally, there is a depletion of divalent cations relative to HCO_3 and SO_4 , which further suggests that cation exchange has influenced pore water chemistry. Samples 4663 and 4785 occur at depths of 46.63m and 47.85m respectively which correspond to a silt zone with low clay content. The low clay content and therefore lower surface area in this zone may have slowed the cation exchange process.

K vs Cl

FIGURE 30 K vs Cl

Ca + Mg vs HCO₃ + SO₄

FIGURE 31 Ca + Mg vs HCO₃ + SO₄

5.1.2.3 *Calcium*

A plot of Ca vs Cl in Figure 32 indicates a linear trend from slightly enriched in near surface samples to slightly depleted Ca at greater sample depth in the marine clay section with respect to seawater. Samples from the varved clay and till form a separate group that is highly enriched in Ca with respect to seawater and all other samples. An exception is sample 4663 from a zone of low clay content.

The graph therefore may not provide evidence for original seawater in the marine clays, but does highlight an excess of Ca in the near surface fresh pore waters and a distinct contrast in pore water chemistry between the marine clays and the till and varved clay lithofacies.

5.1.2.4 *Magnesium*

A plot of Mg vs Cl shown in Figure 33 indicates a linear correlation, with Mg depleted relative to seawater in the marine clay sediments. The basal till and varved clays form a separate group enriched in Mg relative to seawater.

Most formation waters and groundwater from shales are depleted in Mg with respect to seawater (Briggs, 1995). The formation of chlorite from montmorillonite and the formation of dolomite are processes which may remove Mg from solution (Hitchon *et al.*, 1971, Collins, 1975). In shale groundwater, carbonates are a controlling factor (Von Damm, 1989).

Since Mg and Ca are divalent cations which can substitute for one another in mineral forming and dissolution reactions, it may be useful to consider the Ca/Mg ratio. As shown in Figure 34, a plot of Ca/Mg vs Cl gives a scatter which is roughly linear indicating a gradual decline of Ca relative to Mg with increasing Cl and depth. The till and varved clays form a parallel trend, slightly enriched in Ca.

As noted above, both Ca and Mg are depleted in the marine clay pore waters. The decline with depth in Ca relative to Mg may be a direct response to the decline in HCO_3^- with depth to negligible below 40m, and the gradual increase in SO_4 with depth beginning at 36m. In addition, CO_2 produced by SO_4 reduction tends to prevent dissolution of carbonates (Hem, 1985). The saturation indices (section 5.1.3) may indicate saturation

Ca vs Cl

FIGURE 32 Ca vs Cl

Mg vs Cl

FIGURE 33 Mg vs Cl

Ca/Mg vs Cl

FIGURE 34 Ca/Mg vs Cl

with respect to calcite and dolomite in the marine clays, especially at intermediate and greater depths where the pH is likely to be greater than in the near surface. Hence, there may be a tendency toward precipitation of calcite and dolomite with depth in the marine clays. However, the dissolution of dolomite is not reversible in natural water environments (Hem, 1985). Thus, once dissolved, dolomite will not be precipitated even in a saturated solution. Instead, calcite will be precipitated leaving an excess of Mg in solution.

The basal till and varved sediments both were enriched in Ca and Mg relative to seawater and have slightly higher Ca/Mg ratios. Their Ca and Mg pore water concentration is likely influenced by other factors such as calcite and dolomite dissolution along a flow path of circulating meteoric waters.

5.1.2.5 *Strontium*

Although Sr concentration may be relatively insignificant above 35m depth in the borehole, a plot of Sr vs Cl in Figure 35 indicates a linear trend along the seawater mixing line in the marine clays below 27m depth. This suggests a chemical imprint of original seawater in unit III and unit IV pore waters. Samples 4663, 4785 and 4983 are exceptions, having Sr concentrations of zero. The samples from the till and varved clay lithofacies again form a distinct group which is highly enriched in Sr relative to seawater except for till sample 5316A which has no Sr. This may indicate that the source of Ca enrichment may also contain Sr, which commonly substitutes for Ca in Ca-bearing minerals. Sample 3607 is an exception, with excess Sr in the marine clay group.

Enrichment of Sr is common to Shield brines, formation waters and shale water (Figure 36) and is normally attributed to water-rock interaction. Briggs found that sample AB-93-22 from the underlying Carlsbad Shale was enriched in Sr relative to seawater and therefore typical of shales.

5.1.2.6 *Ca and Sr Enrichment in Till and Varved Sediments*

The enrichment of Ca and Sr in till and varved sediments underlying the marine clays is also accompanied by elevated SO_4 concentration as noted on the Piper plots. Therefore gypsum and celestite dissolution may be a source of excess Ca and Sr.

Sr vs Cl

FIGURE 35 Sr vs Cl

FIGURE 36 Sr vs Cl in shield, basin and shale waters (after Briggs, 1995)

A plot of saturation indices of celestite and gypsum (section 5.1.3) indicates that the till pore waters are saturated with respect to celestite and gypsum, whereas the pore waters associated with the overlying Champlain Sea sediments are undersaturated.

5.1.2.7 Bicarbonate and Sulphate

As shown in Figures 37 and 38 (and as discussed under Piper plots above, section 5.1.1.2), pore waters in the marine clays in borehole GSC-93-GM are excessively enriched in HCO_3^- and generally depleted in SO_4 relative to Cl in comparison to seawater. CaCO_3 shells were noted in Unit III of the Champlain Sea marine clays, and CO_3 effervescence with HCl was noted in most strata. Although Torrance (1988) found <1% opaque iron sulphides, black FeS_2 specks, were noted throughout the marine clays in the study section. According to Gadd (1986) there may also be sulphide mineral (pyrite) replacement of CaCO_3 shells but this was not observed in borehole GSC-93-GM. (As previously noted, the HCO_3^- concentration was not measured, but is assumed to account for the anions required to complete the charge balance in each sample).

In both figures, the pore water samples from the till and varved clay underlying the marine clay section plot as exceptions, with relatively excess SO_4 and depleted HCO_3^- relative to seawater. CO_3 shells were observed in only trace abundance in the till and varved clays. The nearby Billings Shale, however, is noted for pyrite mineralization and strong H_2S odour.

Two other exceptions occur at 47.85m depth which has very low HCO_3^- relative to Cl, and at 49.33m, which has a SO_4 concentration slightly higher than common seawater.

Sulphate is controlled to a large extent by the redox conditions in the aquifer. In a reducing environment SO_4 is reduced to sulphide through the oxidation of organic matter. Hillaire-Marcel (1988) has noted evidence of significant CO_2 produced by the decay of marine organic matter in Champlain Sea sediments. There may be as much as 1% organic matter in Champlain Sea sediments (J.K. Torrance pers. comm.). Thus, organic carbon is oxidized to carbon dioxide in the presence of sulphur-reducing bacteria (Collins, 1975). The dissolution of the CO_2 produces dissolved CO_2 species, and thus HCO_3^- is a byproduct of SO_4 reduction as summarised below:

HCO₃ vs Cl

FIGURE 37 HCO₃ vs Cl

SO₄ vs Cl

FIGURE 38 SO₄ vs Cl

The marine clays therefore have preserved a reducing environment, and HCO_3^- and sulphide are present in excess as a byproduct of sulphate reduction. At a pH above 7, $\text{HS}^- + \text{H}^+$ form rather than H_2S . The pH is assumed to be above 7 in the marine clays at Mer Bleue (see section 5.1.3). As noted above (section 4.1.1), black iron sulphide specks were observed in most of the marine clay section.

In an oxidizing environment, sulphate is the stable form of sulphur. Hence oxidizing conditions may predominate in the basal till and varved clays where sulphate is the dominant anion, and HCO_3^- is absent. However, reducing conditions are expected in shales such as the underlying Carlsbad Shale, and the till and varved clay pore waters and the shale are likely well connected by good permeability. Oxidizing conditions in the till and varved clays could be a result of deep-seated meteoric waters circulating along the bedrock surface, or the excess SO_4 may be due to a lack of sulphur-reducing bacteria in this zone. The dissolution of gypsum, if initially present, may be another source of SO_4 contributing to a high sulphate content in the basal till and varved clays.

5.1.2.8 *Br/Cl Ratio*

The original seawater Br/Cl ratio can be preserved independent of dilution and cation activity since both Br and Cl are very conservative elements. In seawater the Br/Cl ratio is approximately 3.5×10^{-3} (Berner, 1987, Hem, 1985, Pytkowicz, 1983).

A plot of the Br/Cl ratio vs Cl as presented in Figure 39 indicates that brackish water samples plot in two clusters above the seawater line corresponding roughly to the dilute brackish water of unit IV and the concentrated brackish waters of unit III. The samples from unit IV plot on or just above the 3.5×10^{-3} line for the seawater Br/Cl ratio, particularly between 24 and 38m depth. The samples from unit III and the top of the varved clay at 50.4m, plot as a broader ranging group, well above the seawater line.

The saline varved clay below 51m and the till samples plot on a separate trend straddling the seawater line which intersects the seawater line at sample 5378, the base of the till. The fresh water and dilute brackish samples down to 14m depth form a separate low concentration group, with negative slope trending away from the seawater line. A plot of Br vs Cl (Figure 40) further illustrates that a linear relationship in the 24 to 38m depth range is disrupted elsewhere.

Br/Cl vs Cl

FIGURE 39 Br/Cl vs Cl

Br vs Cl

FIGURE 40 Br vs Cl.

The dilute brackish pore waters in unit IV in the 24 to 38m depth zone may have retained a Br/Cl imprint of the original Champlain Sea water. The concentrated brackish pore waters in unit III may have been influenced by leaching of decomposing soil organic matter (Gerritse and George, 1987), which tends to increase the Br/Cl ratio. Hilliare-Marcel (1988) has noted evidence of the decay of organic matter in Champlain Sea sediments.

The basal till and varved clay samples were thought to have been deposited in a freshwater environment which preceded marine conditions, and therefore are not expected to retain a seawater Br/Cl ratio. The low Br/Cl ratio in two of these samples, 5316A and 5316B, may suggest that these pore waters are influenced by halite dissolution ($\text{Br/Cl} \approx 0.25 \times 10^{-3}$ for halite, Collins, 1975) either in the underlying Carlsbad Shale or in other laterally connected Paleozoic rocks. The basal samples plot in a zone similar to that of common shale water as shown in Figure 41 after Briggs (1995). Briggs' sample AB-93-22, from the shale at 58.5m in borehole GSC-93-GM, plots near the seawater line along the same trend with the till pore waters (Figure 39).

Dissolution of road salt and downward infiltration of surface water may have influenced the shallow pore waters down to 14m depth. However, halite dissolution apparently has least affected the shallowest samples and most affected the deeper samples in this group and therefore is unlikely to have been the main source of the low Br/Cl ratio. It is possible that evidence of original seawater may have been retained in the sediments at 24 to 38m depth but has been removed elsewhere.

5.1.3 Saturation Indices

Saturation indices for each water sample were calculated using the standard computer programs Wateq4F (Ball *et al.*, 1987) and Solmineq 88 (Kharaka *et al.*, 1988). The pH of pore waters was estimated to range from 7.2 at shallow depths to 8 at depth. A water sample from the underlying shale had a pH of 8.1 (Briggs, 1995) according to an on site portable meter. Séguin (1995) reported an average pH of more than 7.5 for fresh and brackish waters in a study of shallow well water west of Ottawa. Figure 40 summarizes pore water saturation indices over the Champlain Sea sediment section. The sediments are generally saturated with respect to dolomite and calcite down to the varved clays. The till is saturated with respect to celestite and gypsum.

Br/Cl ratio plotted versus Cl (ppm) for different types of water where F=Formation Water, M=Canadian Shield Mine Water and S=Shale Water.

FIGURE 41 Br/Cl vs Cl in common shale waters (after Briggs, 1995)

LOG (AP/KT) at pH 7-8

FIGURE 42 Saturation indices vs depth

5.2 Isotope Geochemistry

The results of 45 oxygen and 20 hydrogen isotope analyses are listed in Appendix 2. The results are expressed as the per mille (‰) deviation of the heavy to light stable isotopic ratio, R_x , from that in a standard, R_{std} , such that

$$\delta_x = [R_x/R_{std} - 1] \times 1000$$

For oxygen the ratio is $^{18}\text{O}/^{16}\text{O}$ and for hydrogen the ratio is $^2\text{H}/^1\text{H}$. The standard is Standard Mean Ocean Water (SMOW) for both oxygen and hydrogen, since precipitation that recharges groundwater originates primarily from the evaporation of ocean water.

The isotopic composition of water is a function of the origin of the water and of the subsequent mixing history of the water. Most water on the continents originates as precipitation from clouds formed over the oceans. The precipitation subsequently mixes with surface water and/or groundwater. Since $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ are measured relative to SMOW, seawater therefore has $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values close to 0‰. However, the isotopic composition of rain or snow in most areas is not the same as that of ocean water. As precipitation moves away from the equator toward higher latitudes, heavier isotopes are preferentially lost from the vapour to precipitation in a temperature-controlled process of fractionation. In North America, the effect of latitude on $\delta^{18}\text{O}$ is approximately -0.5‰/degree latitude and for altitude is -0.15 to -0.5‰/100m elevation (Gat, 1980).

The global meteoric relationship between ^{18}O and ^2H in samples of precipitation from sites around the globe is described by the Global Meteoric Water Line as defined by Craig (1961) in the following relationship:

$$\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$$

The isotopic $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of local Ottawa precipitation plots on the Ottawa Meteoric Water Line (OMWL) with a unique slope and intercept as a function of local variations in precipitation caused by isolated evaporation effects and the seasonal effect of local geography and climate. Two equations of the OMWL have been developed by Fritz *et al.* (1987) as follows:

$$\delta^2\text{H} = 7.63 \delta^{18}\text{O} + 6.53 \quad \text{based on data from 1975 to 1982,}$$

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and $\delta^2\text{H} = (7.68 \pm 0.12)\delta^{18}\text{O} + (9.50 \pm 1.48)$ based on data from 1970 to 1978.

The OMWL and the GMWL are plotted in Figure 43.

The oxygen-18 and deuterium isotope data for borehole GSC-93-GM are plotted in Figure 44, with the OMWL for comparison. The samples from the marine clay section plot in a tight cluster around the OMWL, with $\delta^{18}\text{O}$ ranging generally from -10 to -8‰, indicating that the marine clay pore waters are strongly influenced by local precipitation infiltrating from the surface. The till and varved clay sediments plot as a separate group diverging to the right of the OMWL toward increasing $\delta^{18}\text{O}$ from -6.2 to -2‰ over a relatively narrow variation in deuterium (-58 to -48‰) with increasing depth. One exception plots between these two groups, with a $\delta^{18}\text{O}$ of -7.1‰ at a depth of 11.28m. This was a small sample and therefore is assumed to have been affected (enriched in $\delta^{18}\text{O}$) by head-space evaporation.

A plot of $\delta^{18}\text{O}$ vs depth in Figure 45 highlights the dramatic increase in $\delta^{18}\text{O}$ below 50m. It is noted that this shift occurs in samples taken from split tubes which are vulnerable to evaporation, rather than sealed Shelby tubes. A plot of $\delta^{18}\text{O}$ vs Cl concentration in Figure 46, indicates that Cl in the split tube sample is apparently not over concentrated by evaporation relative to the other samples. In a plot of $\delta^{18}\text{O}$ vs TDS (Figure 47), the increased SO_4 relative to Cl is taken into account in the varved clays and till underlying the marine clays. In this plot the split tube samples stand out as hyperconcentrated in TDS relative to the marine clay group of samples taken from Shelby tubes. Hyperconcentration due to evaporation would likely produce a uniform increase in TDS, whereas the measured TDS in the split-tube samples plot not in a uniform cluster, but as a trend with TDS increasing over a range between 10000 and 20000ppm.

The split-tube samples, which were removed from the split-tubes at the drill site and stored in plastic for more than six months before sampling, were susceptible to drainage, evaporation and potential oxidation depending on how well they were sealed. Their pore waters were extracted using a mechanical hydraulic press method due to their sandy silt grain size. Hence, evaporation that took place between the coring operation at the drill site and pore water sampling, may be a factor in the isotopic composition of the split-tube samples.

FIGURE 43 Global meteoric water line and Ottawa meteoric water line
(after Sager-Kinsman, 1995)

$\delta^{18}\text{O}$ vs $\delta^2\text{H}$

FIGURE 44 $\delta^{18}\text{O}$ vs $\delta^2\text{H}$ in forty-five pore water samples

FIGURE 45 $\delta^{18}\text{O}$ vs depth

FIGURE 46 $\delta^{18}\text{O}$ vs Cl

$\delta^{18}\text{O}$ vs TDS (ppm)

5.2.1 Isotopes in Champlain Sea

Many natural processes such as changes of state of water in the atmosphere and chemical interaction of water and minerals in groundwater can cause fractionation of heavy and light isotopes of oxygen and hydrogen. Among the most common and excessive fractionation occurs with the precipitation of snow at low temperature and humidity in a central continental location such as at Ottawa and formerly in the area of accumulation of the Laurentide ice mass. The result of Wisconsinan ice formation was the accumulation of a vast reservoir of water depleted in $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

As outlined under Champlain Sea stratigraphy (section 2.2.2), till and varved clays were likely deposited in a fresh isotopically light meltwater environment which preceded the gradual transgression of the marine sea (Gadd, 1988a). The transition to marine clay deposition, marked the beginning of approximately 2000 yrs. of marine conditions with $\delta^{18}\text{O}$ close to 0‰. The Champlain Sea likely coexisted in close proximity, for a period with the melting ice sheet contributing clastic sediments and isotopically light run-off. The gradual dilution of the sea through mixing with local run-off was hastened by mixing with fresh isotopically light surficial meltwaters derived from proglacial lakes as far west as Saskatchewan.

The $\delta^{18}\text{O}$ of Laurentide glacial run-off from melting ice has been estimated by Wassenaar(*et al.*, 1988) to range between -45 and -25‰ and by Hillaire-Marcel (1988) at a more conservative range of -30 to -16‰. The wide range accounts for basal subglacial meltwater (lightest) and surficial glaciofluvial and glaciolacustrine meltwater influenced more by atmospheric conditions during melting and run-off. The findings of Hillaire-Marcel are based on of Champlain Sea carbonates mollusc shells from which he developed a correlation between paleosalinity and $\delta^{18}\text{O}$ of Laurentide ice meltwater.

The borehole samples are plotted in Figure 48 along with Hillaire-Marcel's simple two-component mixing line between a glacial meltwater with $\delta^{18}\text{O}$ of -16‰ and a seawater with $\delta^{18}\text{O}$ of 0‰ (salinity of 35ppt) where TDS is assumed to approximate salinity. The current borehole data plot well below the mixing line, indicating that a third source of water would have to have contributed to the seawater-meltwater mix. In the Mer Bleue Champlain Sea sediments, the most obvious source of other water is modern meteoric water, most likely as downward infiltrating precipitation and as slightly older circulating meteoric water following a longer flow path along the weathered bedrock-till interface.

$\delta^{18}\text{O}$ vs TDS

FIGURE 48 $\delta^{18}\text{O}$ vs TDS with (Hillaire-Marcel meltwater - seawater mixing line)

Chapter 6 DISCUSSION OF RESULTS

6.1 Physical Geology and Geotechnical

6.1.1 *Physical Geology*

The lithological observations in borehole GSC-93-GM indicate that the stratigraphy are conformable in most respects to observations made by Gadd (1986) in his type section for Champlain Sea sediments in borehole CRF-21A located 250m east. Based on the close correlation of the lithology and the geophysical logs, Gadd's five depositional facies were delineated and found to have approximately the same thicknesses as in borehole CRF-21A.

The grain size analysis indicates that the marine clays are composed mainly of silt and 20 to 45% clay. The low proportion of clay is a function of the immaturity of the glacial debris, which has not been subjected to extensive winnowing during long fluvial transport as with common clays. Grain size was found generally to fine upward in the study section, whereas Gadd observed a general coarsening upward in his basin study. This may suggest a central basin location for these Champlain Sea deposits.

Although magnetite is referred to by Gadd (1986) as occurring in unit V and the basal till (unit I) the magnetic susceptibility log (GSC Geonix-39 log, Figure 13) is generally high within units V, IV and parts of unit III and exceptionally high in the top part of unit I, accounting for the bulk of the Champlain Sea sediments. Gadd did not likely use Mössbauer spectroscopy to supplement his mineral identification. Among minerals with high magnetic susceptibility Torrance (1986) has reported the only confirmation by Mössbauer spectroscopy of hematite in the Ottawa Valley Champlain Sea sediments occurring at Lemieux near the South Nation River.

For hematite to produce the same magnetic susceptibility log anomaly, it would need to be present in 100 to 1000 times greater abundance than magnetite, based on their relative average magnetic susceptibilities (Telford *et al.*, 1976). Such abundance of hematite would likely have been recognized by the naked eye, but is not reported in the literature. It is possible therefore that magnetite is present as colloid size crystalline mineral grains or as concentrations in the minor (<1%) amorphous material in Champlain Sea sediments (Torrance, 1995), but will require detailed Mössbauer analysis for identification. The presence of magnetite may vary with location and may depend mainly on the local

provenance of the sediment. The noted magnetic anomaly does appear to correlate closely with the red oxide colour banding noted in units III, IV and V in borehole GSC-93-GM.

The marine clays are characterised by a reducing environment. The readily oxidized black (FeS_2) sulphide banding which occurs throughout Units IV and V and in the upper 2m of Unit III, has been preserved in a reducing environment in the marine clays.

The Champlain Sea sediments are characterised by excess carbonate content. In the study section, very few fossil shells were observed except at the base of unit III whereas Gadd observed shell fragments in units III, IV and V; however, the sediments in this study tested positively for CO_3 content throughout the section.

6.1.2 *Geotechnical*

The moisture content of the marine clays is very high. By comparison, silt may have a porosity of 35 to 50% and a common clay is expected to have a porosity of 40 to 70% (Freeze and Cherry, 1979). If the clay size material has a density of approximately 2.65 and the density of water is one, moisture contents by weight basis in the 40 to 100% range may indicate that the marine clays are 35 to 75% water by volume. These water contents equate to porosities which are normal in clays but high for silts. However, these moistures are not excessive for Champlain Sea marine clays and they are likely the result of the flocculated clay structure due to deposition in a highly saline environment as referred to above (section 2.5) in a model for "quick clays" (Torrance, 1983). Based on the very high moisture content, it may be predicted that the marine clays are likely to be unstable when subjected to a load (stress) (Torrance, 1988). The high moisture content at the top of the marine clay strata suggests a flocculated clay structure due to significant seawater salinity, even in the latter stages of Champlain Sea deposition.

Finally, there is a general decline in moisture content with depth which is the expected response to the weight of greater overburden with depth, but may in addition be associated with a general decline in clay content (and hence particle surface area) with depth.

The three-fold increase in both undisturbed and remoulded shear strength, beginning below 34m depth in the borehole, correlates roughly with stiff clays and slightly lower moisture (compaction) in the massive prodelta facies below 40m. The massive

prodelta facies (unit III) between 40 to 50m depth also was found to have elevated brackish salinity (TDS of 5500 to 10000ppm), the maximum electrical conductivity and a conspicuous decline in magnetic susceptibility.

The observed large peaks in sensitivity (six values of $T\mu/Tr > 60$ between 10 and 48m depth) appear to be independent of other observed or measured factors and it may not be possible to further analyse sensitivity without more detailed and controlled data measurement. The periodic sensitivity peaks are a common feature in the marine clays and "are related to the interaction of changes in a number of factors" with depth (pers. comm. J.K. Torrance). However, it has been determined that a highly sensitive clay occurs at a depth of 27.6m in the borehole. Its remoulded shear strength, 0.047 t/m^2 , is nearly an order of magnitude lower than in adjacent samples. Its moisture content, approximately 73 to 80%, and silt content, 67%, are similar to adjacent samples.

A large variation in remoulded shear strength is commonly a controlling factor affecting sensitivity in "quick clays". Given that the upper envelope of $T\mu$ values based on the least disturbed samples is a reliable estimate of $T\mu$ (Crawford and Eden, 1965 and Lefevbre, 1981), then variation in Tr appears to be the controlling factor in estimating sensitivities in the Champlain Sea sediments in borehole GSC-93-GM.

Tr closely correlates with TDS (Figure 49) to a depth of approximately 35m and the major increase in Tr below 35m depth correlates with the increase in TDS up to the concentrated brackish levels in unit III. However, the low Tr of the sensitive clay at 27.6m appears to be independent of the trend of TDS which suggests that other factors are also influencing Tr .

6.1.3 Physical Hydrogeology

Modern surface drainage at Mer Bleue is handled by Green Creek and its narrow meandering tributaries with a hydrostatic potential of approximately 40m above the Ottawa River over a distance of approximately 10km. The permeable till/shale contact (Charron, 1978) is the likely flow path for downward displaced pore water and occurs at approximately the same elevation as the Ottawa River in both GSC boreholes at the study site. Displaced pore water at the till/shale contact may have a hydrostatic potential of approximately 10m above the bed of the Ottawa River, 7km away. Although surface topography does not necessarily mimic bedrock topography, the location of the Ottawa

TDS & Remoulded Strength vs Depth

FIGURE 49 TDS and remoulded shear strength vs depth

River as a regional drainage system predates Wisconsinan time. There is a high probability, therefore, that the bedrock topography over the short distance between Mer Bleue and the Ottawa River slopes toward the Ottawa River.

The high proportion of silt size material in the Champlain Sea sediments may result in a significant hydraulic conductivity (K) for these sediments. Unweathered marine clay may have K ranging from 10^{-10} to 10^{-4} cm/s, whereas silt may range from 10^{-7} to 10^{-3} cm/s (Freeze & Cherry, 1979). Since these glacial sediments are poorly sorted and may contain 20 to 45% clay, they may have a K value in the lower end of the range for clayey silt of 10^{-7} cm/s.

The near-surface marine clay sediments may be assumed to be saturated and therefore below the watertable where measured moisture contents are greater than 95% at a depth of 3 to 4m in the borehole. The hydraulic head for a point at 3 to 4m depth therefore, is well above the piezometric surface noted at 12m depth (in section 4.3 above) for a point at 58.5m depth in the shale bedrock. Therefore, at the location of borehole GSC-93-GM there is a downward gradient based on hydraulic head, and it may be speculated that Mer Bleue is currently an area of recharge. Thus, pore water migration may currently be downward toward and below the bedrock surface.

Assuming an average hydraulic conductivity of 10^{-7} cm/s, an average porosity (n) of 0.5 for the Champlain Sea sediments and a hydraulic gradient (i) of 0.16 (determined from borehole water level for 58m depth and the water table), then using the relationship for velocity (v) where $v = Ki/n$ gives $v = 3.2 \times 10^{-10}$ m/s. Thus, in one year pore fluids could move approximately 0.01m. In 7000 years, since the retreat of the Champlain Sea and the last stages of proto-Ottawa River drainage, pore fluids could have moved 70m.

There is, therefore, the potential for downward migration and drainage of original pore water from the entire thickness of the Champlain Sea section at Mer Bleue. The extent of potential pore water migration or drainage will be a function mainly of the history and duration of recharge and discharge conditions at the Mer Bleue site. It may be inferred, however, that the depth of fresh water infiltration to 10m depth and the apparent dilution of original seawater salinity in the dilute brackish zone to 40m depth are indicators of the minimum extent of pore water displacement in the same order of magnitude as calculated. The likely back diffusion of salts due to the salinity gradient would suggest that even greater pore water displacement has occurred.

If Mer Bleue is a recharge area, there is a potential for downward migration of infiltrating meteoric water. Because the underlying till/weathered shale horizon is at approximately the same elevation as the Ottawa River and likely has good permeability (Charron, 1978), there is potential for downward pore water displacement and drainage of the entire thickness of Champlain Sea sediments at Mer Bleue.

Although Carlsbad Shale is assumed to underlie the study site, the influence of the Billings Shale as a geochemical influence should not be ignored. Due to the close proximity of a fault, the Billings Shale could be between 50 and 500m to the north. This location, however, would likely be downstream on a flow path between borehole GSC-93-GM and the Ottawa River. Due to faulting, the Billings Shale also occurs 6km to the south, potentially upstream of the borehole in the vicinity of the upper reaches of Ramsey Creek.

6.2 Geochemistry and Isotopes

6.2.1 *Geochemistry*

The classification of pore water salinity in the Champlain Sea sediments in borehole GSC-93-GM is apparently strata-dependent. The varved clays and till contain saline water, the massive pro delta facies (unit III) contains concentrated brackish water and units IV and V contain dilute brackish pore water. The depth of the freshwater zone from 0 to 10m may indicate the depth to which meteoric water is infiltrating downward from the surface and therefore the low TDS observed in pore waters is a function of short residence time.

The down-hole shift from low to high concentration brackish pore water below 40m depth is also coincident with a decrease in magnetic susceptibility, a decrease in moisture content, a slight decrease in clay content, and an apparent increase in both undisturbed and remoulded shear strengths.

The maximum TDS in the borehole is much less than that predicted by Rodrigues (1988) from marine foraminifera which required a 30 to 34ppt saline environment and have been documented in the Ottawa Basin near Mer Bleue. In addition, part of the maximum TDS zone includes the varved clay and till strata which were deposited in a freshwater environment. This suggests that saline and brackish pore waters have migrated into these strata.

The close correlation between TDS and pore water conductivity suggests that a reliable estimate of TDS can be determined from quick and simple pore water conductivity measurements in the Champlain Sea sediments.

A comparison between pore water conductivity and borehole log conductivity indicates that a reasonable estimate of salinity in the marine clay sediments appears possible using the Geonix conductivity log. Scale settings, the large 3m source receiver spacing and the fact that the Geonix instrument measures the bulk conductivity of both sediment and pore water account for differences in detail and magnitude between the two conductivities.

The pore water is characterised as evolving continuously in ionic character from the near surface to the base of the Champlain Sea sediments as follows:

The Piper plots indicate that the pore water in Champlain Sea sediments in borehole GSC-93-GM can be generally characterised as a NaCl type water. The Na-Ca-Mg-HCO₃ character of the fresh water zone and the Na-HCO₃ and Na-Cl character of the dilute brackish water zone was also observed by Briggs (1995) in an investigation of brackish groundwaters in Paleozoic rocks (Carlsbad and Lindsay Formations) east of Ottawa.

The relationship between HCO₃ and SO₄ anions is a function of the reducing environment in the marine clays such that SO₄ is reduced to form sulphides, with HCO₃ being given off as a reaction byproduct. As noted above, black sulphide specks were observed in most marine clay samples. Hence the zone of high HCO₃ down to more than 40m depth is a zone in which SO₄ is being reduced. Below 36m depth, the rate of SO₄ reduction gradually decreases and the production of HCO₃ correspondingly declines to zero at 46m depth, while SO₄ gradually increases in concentration.

SO₄ increases gradually below 36m depth and is the dominant anion in the till unit. The source of SO₄ could be from original seawater or could be due to a reversal of the redox reaction where sulphide is oxidized to SO₄ and HCO₃ is used up (reduced), as indicated by declining HCO₃ below 40m depth. The excess SO₄ in the till may be a result of the dissolution of gypsum in underlying Paleozoic rocks.

The best preserved remnants of original Champlain Sea waters would most likely be found in the deepest undisturbed marine clays. The Piper plots and relative abundance diagrams confirm that a NaCl pore water character is dominant at the base of the marine clay section. Above this the NaCl character is diluted by mixing with Ca-Mg-HCO₃ dominated surface water which has migrated (infiltrated) downward. Beneath the clay, the varved clay down to 51m depth also has a NaCl character suggesting that the NaCl waters in unit III have been displaced downward. The saline pore waters are dominated by SO₄ resulting in a mix of Ca-Mg-SO₄ and Na-Cl type waters circulating through coarser grained material at the till/shale bedrock contact.

The comparison with major ion proportions in seawater further indicates that remnant Champlain Sea water may be preserved in the concentrated brackish zone associated with unit III at the base of the marine clay section and in the underlying varved clays. This further suggests that the pore waters have been displaced downward from unit III to unit II. The saline waters and the Ca-Mg-SO₄ type waters underlying the marine clay have ion proportions which approximate seawater proportions except for the addition of SO₄. The Sr/Cl ratio confirms evidence of original seawater over most of the marine clay section.

Contrary to this, the Br/Cl ratio suggests evidence of original seawater preserved in unit IV but not in unit III. It is suggested that Br/Cl in unit III may have been altered upward by a process of leaching of decomposing organic matter. However, decomposing organic matter has been cited as a component of SO₄ reduction occurring in unit IV, which suggests that the Br/Cl ratio should be altered upward in unit IV as in unit III. Thus, the Br/Cl ratio as a diagnostic indicator for seawater is apparently inconsistent, possibly as a result of a partitioning of Br and Cl in other environmental chemical activity in the marine clays.

A comparison with cation profiles in other Ottawa basin marine clays indicates that high elevation sites are depleted in total salt content and most markedly at shallow depth. It has been suggested that a flattened curve depleted in cations at the top of the profile may be a response to downward infiltration of meteoric water and dilution of original seawater in the pores of the marine clays (Torrance, 1988). It is noted that Group I boreholes are generally at higher elevations than Group II boreholes, and therefore based on elevation alone, may be more susceptible to drainage and flushing by infiltrating meteoric waters. Mer Bleue is located in the lower range of elevation in Group I, but the basal Champlain

Sea sediment/bedrock contact is above the current Ottawa River, and so the potential for drainage facilitated by the overburden/bedrock aquifer as referred to by Charron (1978) and Owen (1953) is significant.

Elevation may also have influenced the concentration of original seawater salinity due to stratification of salinity within the Champlain Sea. Group II at a lower elevation would have been deposited in a deeper, heavier, more saline sea than Group I. Group I would have been deposited at the same time but in an upper diluted salinity strata influenced more by mixing with meltwaters. It is possible therefore that even thick sections such as Venosta and Touraine have not retained seawater salt concentrations due both to low original seawater salinity (< 35ppt) and subsequent significant leaching.

Six of the 20 Ottawa basin marine clay sections had Mg-Ca cation-dominated pore waters in contrast to mainly Na dominance at Mer Bleue. The dominance of Ca and Mg would suggest the presence of abundant carbonate material (possibly marine shells) and/or carbonate minerals in close proximity. Up to 12% glacial limestone and dolomite detritus in the marine clays was noted by Torrance (1988). Shield marbles and possible remnant Paleozoic outliers predating Wisconsinan ice may be the source of carbonate detrital. Kettles and Shilts (1987) found >10% carbonate detritus in till underlain by limestone and dolomite bedrock. The influence of adjacent or underlying limestone and dolomite on pore water chemistry would be enhanced by the process of infiltrating surface waters, and as noted above, Ca and Mg dominance occurs only in the Group I boreholes where infiltration and leaching is suspected.

The elevated Na/Cl and K/Cl ratios (with respect to halite and seawater) and the slightly depleted Ca/Cl and Mg/Cl ratios (with respect to seawater) in the marine clays at Mer Bleue suggests that an ionic process involving cation exchange has influenced the pore water chemistry. In this process, monovalent cations (Na and K) are stripped from the sediment into solution and divalent cations (Ca and Mg) are adsorbed to satisfy the cation exchange capacity of the minerals. The charge balance on the particles, therefore, is satisfied by the uptake of divalent cations, mainly Ca and Mg, available from infiltrating surface water. The occurrence of moderate concentrations of Ca and Mg in the near surface fresh water zone suggests that infiltrating surface waters are continuously replenishing Ca and Mg downward thus enhancing the cation exchange process.

The cation exchange process is likely induced by leaching due to the infiltration of fresh meteoric waters which have decreased the salinity and upset the adsorbed/solution cation balance. Leaching, as referred to above for Group I sites, has apparently influenced most of the marine clay section at Mer Bleue.

Further evidence of leaching is seen in the slightly depleted Cl proportions for pore waters in unit III and unit II compared to seawater (Table 4). Cl depletion will also affect the interpretation of the cation ratios, although, the effect on monovalent cation ratios due to Cl depletion is exactly offset by the opposite effect on divalent cation ratios. That is, if Cl depletion has occurred, then monovalent cations (interpreted as enriched, above) will be interpreted as originally less enriched, and divalent cations (which are interpreted as depleted, above) will be interpreted as originally more depleted. Thus, the balance of cations, involved in the cation exchange process, is unaffected.

The influence of halite dissolution is suggested by Na/Cl and K/Cl ratios for pore waters in the varved clays between 50 and 51m depth. The source of halite is not in the varved clay but could be in the underlying bedrock along a flow path. The strong Na-Cl character of the pore water in unit II and unit III may suggest that dilute remnant seawater is present.

The saturation indices confirm the possibility that dissolution of SO_4 minerals, gypsum and celestite, may be a source of SO_4 contributing to the Mg-Ca- SO_4 character of pore water in the till and lower varved clays. The saturation indices may also suggest that the marine clay pore waters are saturated with respect to calcite and dolomite and thus confirms the presence of carbonate minerals in the marine clay section as noted by Gadd (1986) and Torrance (1988). However, because the pH in this zone was estimated, further sampling will be required to confirm these results.

6.2.2 *Isotope Geochemistry*

In the interpretation of isotope results, four samples from below 51m depth and one sample at 11.3m depth must be ignored due to error (see section 6.2.2.1).

The isotopic compositions of the marine clay and varved clay pore waters suggest that they consist mainly of meteoric waters, which have likely infiltrated downwards from the surface. In the plot of $\delta^{18}\text{O}$ vs depth (Figure 45), there is apparently a very slight trend

toward seawater $\delta^{18}\text{O}$ with depth within the unit III marine clays and unit II varved clays, however the shift is too small to account for the apparent seawater ion proportions noted for these zones.

The $\delta^{18}\text{O}$ data of Séguin (1995), for brackish groundwaters east of Ottawa, plot in a similar area on the $\delta^{18}\text{O}$ vs TDS plot (Figure 48), but are distributed over a broader range of $\delta^{18}\text{O}$ ranging from -16 to -9‰ and a smaller TDS range of up to 6000ppm. Séguin has interpreted the data as indicative of mixing between dilute seawater and meteoric water. In contrast, the narrow range of $\delta^{18}\text{O}$ values between -9.5 and -8.5‰ in the Mer Bleue sediments over a larger range of TDS suggests very little change in $\delta^{18}\text{O}$ with increasing TDS and, therefore, no apparent mixing trend between meteoric water and dilute seawater. An exception occurs in the upper 5m of the sediment where the uppermost three samples represent depleted and inhomogeneous late fall and winter recharge.

If the $\delta^{18}\text{O}$ values (ignoring the split-tube samples) represent original seawater, then it may be speculated that salinity did not change throughout the history of the Champlain Sea. This is unlikely given the dynamic stratigraphy documented at many sites in the basin. If the $\delta^{18}\text{O}$ values are representative of original seawater over the entire history of the Champlain Sea (Figure 45), then the changing $\delta^{18}\text{O}$ of a sea undergoing early concentration and then gradual dilution of salinity would need to be exactly offset by the $\delta^{18}\text{O}$ of mixing between seawater and meltwater. This is unlikely. Similarly, the effect on $\delta^{18}\text{O}$ of mixing with modern meteoric water would produce a greater change in the upper part of the sediments, nearer the source of infiltrating waters than at depth. This is not observed, except in the upper 5m of the borehole.

It is suggested, therefore, that the mixing with or replacement by meteoric waters is complete from top to bottom of the sediments and, although a small proportion of original seawater may be reflected in the $\delta^{18}\text{O}$ values, the dilution and displacement of original pore water appears to be uniform over the entire record of Champlain Sea deposits.

6.3 Error Due to Evaporation in Split-tube Samples

The trend toward seawater $\delta^{18}\text{O}$ in the till (unit I) is difficult to explain in a natural water mixing model and correlates best with the likely effects of evaporation and oxidation due to the split-tube sampling method used in the till. Most outstanding is the SO_4 anomaly

in the till. SO_4 is at approximately seawater proportions in unit III, the lowermost zone of the marine clays, and in the lowermost Shelby tube samples in the underlying varved clays (SO_4 ranges between 5 to 14 meq/l over these two zones). In the underlying split-tube samples, which include the till (unit I) and the lower part of the varved clay (sample 5105), SO_4 increases more than ten-fold (ranging between 90 and 200 meq/l). The underlying shale has a low SO_4 concentration of less than 1.5 meq/l at a depth of 58.5m (Briggs, 1995). It is difficult to explain a till and varved clay layer approximately 3m thick with such high SO_4 concentration between strata with well documented low SO_4 concentrations. The high SO_4 therefore is assumed to be the result of oxidation of sulphide minerals in the sediment (mainly pyrite) and hyperconcentration of the pore water due to evaporation while the split-tube samples were exposed to air before pore water sampling was undertaken.

Evaporation would explain the hyperconcentration of Na, K, Ca, Mg and SO_4 illustrated in the elemental plots. Similarly, evaporation and pyrite oxidation would account for the difference between the Geonix-39 conductivity log and the pore water conductivity below 51m depth. The sample at 11.28m is also suspected of having excess $\delta^{18}\text{O}$ ($\delta^{18}\text{O} = -7.13\text{‰}$) due to head-space evaporation.

Since the increase in TDS below 51m is due mainly to artificially increased SO_4 due to evaporation, it is assumed that the true TDS in the till and varved clay is similar to the TDS in the deepest Shelby tube sample at 50.4m, approximately 10000ppm. A TDS of approximately 10000ppm is in close agreement with the TDS observed in the underlying Carlsbad Shale (Briggs, 1995).

Chapter 7 CONCLUSIONS AND RECOMMENDATIONS

An uninterrupted record of Champlain Sea deposits was encountered in borehole GSC-93-GM. The major stratigraphic units (Gadd, 1986) of marine clays were observed as follows: unit V; 3.6 to 22m depth, unit IV; 22 to 40m depth and unit III; 40 to 50m depth. The underlying varved clay (unit II) and till (unit I) freshwater deposits occur between 50 and 54m depth and are underlain by Paleozoic shale.

Pore waters are fresh from 0 to 10m, dilute brackish in unit IV and the remainder of unit V (up to TDS = 5500ppm) and concentrated brackish in unit III, unit II and unit I (up to a TDS of approximately 10000ppm). The estimate of TDS in the basal Champlain Sea sediments is in close agreement with TDS in the underlying Carlsbad Shale.

Infiltrating meteoric water has acquired from the sediments an ionic character which evolves in a continuous series as a function of residence time and depth from surface to basal glacial strata as follows:

The ionic character of the pore water reflects a SO_4 reducing environment at shallow and intermediate depths in unit V and unit IV of the marine clays and a NaCl pore water with seawater ion proportions at the base in unit III and unit II. The pore water character in the basal till (unit I) is assumed to be similar to that in unit II.

The acquired seawater character has been modified by infiltrating meteoric water from the surface down to the basal units of the Champlain Sea sediments. Although the pore waters are diluted and leached, evidence of a seawater origin for the dissolved ions is retained in the pore waters of units III and II which have a NaCl character and seawater ion species proportions.

Evidence for dilution of the entire column of Champlain Sea sediment pore waters includes:

- fresh and brackish pore waters occupy the marine clays where moisture contents (ranging from 45 to 100%) are indicative of clays with flocculated structure deposited in a saline seawater environment.

- maximum TDS ($\approx 10000\text{ppm}$) is one third of the fossil biogenic determination of Champlain Sea salinity in the Mer Bleue area.
- $\delta^{18}\text{O}$ values fall within a narrow range consistent with local meteoric waters from surface to basal units of the Champlain Sea sediments.
- $\delta^{18}\text{O}$ values vary over a narrow range (-9.5 to -8.5‰) whereas TDS increases from fresh to approximately 10000ppm over the entire depth range of the sediments.

Evidence in the pore water chemistry for leaching includes:

- reduced Cl proportions compared to seawater.
- elevated monovalent/divalent cation proportions due to cation exchange induced by leaching.

Through a process of cation exchange enhanced by leaching and the influx of divalent cations (Ca and Mg) from infiltrating surface water, Na and K salts are being removed downward. Evidence of downward displacement of pore water includes:

- a hydraulic gradient such that the site is currently a recharge area.
- $\delta^{18}\text{O}$ values of the entire column of pore waters are interpreted to be primarily meteoric.
- salinity changes gradationally and continuously from fresh near the surface to a maximum at the base of the sediment.
- Varved clays (originally freshwater deposits) have the same salinity, NaCl character and seawater ionic proportions as the overlying marine clays (unit III).
- ionic ratios are consistent with a leaching process operating in conjunction with cation exchange.
- excess Ca and Mg in the near surface is consistent with the weathering of carbonates by infiltrating surface waters.

The silty texture of the sediments and the hydraulic gradient at the study site has resulted in the migration downward of original pore waters and has facilitated the downward leaching and flushing of salts gradationally with depth in the marine clays by modern meteoric water.

A highly sensitive clay occurs in the deeper part of the zone of dilute brackish pore waters (depth = 27.6m, TDS $\approx$ 2600ppm, moisture content $\approx$ 80%) and has a remoulded shear strength of 0.047t/m².

Remoulded shear strengths generally increase three-fold in the deepest marine clay stratigraphic unit (massive prodelta unit III). This zone is characterised by a concentrated brackish pore water salinity (>5500ppm), a more silty texture, declining moisture (<60%) and has likely undergone more compaction due to its greater depth in the marine clays.

At Mer Bleue, it was demonstrated that the borehole geophysical electrical conductivity log provided a good estimate of salinity. The electrical conductivity log and pore water conductivity measurements support the chemical analysis of salinity.

Finally, relatively high magnetic susceptibilities were encountered in units IV and V of the marine clays at Mer Bleue.

It is recommended that further work on the Champlain Sea sediments in borehole GSC-93-GM may be possible since (at time of writing) a plastic wrapped split of most cores remains in cold storage. A study of the biological assemblage of ostracods and foraminifera (as in Rodrigues, 1988) may yield a salinity of deposition profile for the Champlain Sea at Mer Bleue.

It is recommended that special sampling techniques may be considered for sampling tills in order to avoid oxidation and evaporation effects so that their true pore water chemistry may be investigated. It is anticipated that evidence of original seawater will more likely be found at low-lying sites with low potential for drainage.

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Appendix 1 Lithological and Geotechnical Data.**Table 1a. Lithological Logs.****Table 1b. Geotechnical Data.**

Table 1a

DEPTH m	LITHOLOGY description	SAMPLING LOG description	DRILL SITE LOG description	DEPTH m
3.66 Clay, grey	with distinct pink band at 37 cm	Grey silty clay, top 6cm br. clay silty clay, rootlets, pink 4-10.3m	Clay, grey	3.66 61 cm
4.27 Clay, grey, stiff	base pink band one third from top	Grey clay, pinkish bands 20-24cm, fairly massive	Clay, grey	4.27 59 cm
4.84 Clay, grey, stiff	water sample 26-58cm from top	Grey clay, stiff, uniform	Clay, grey	4.84 61 cm
7.31 Clay, grey		Grey silty clay, uniform, moderate stiff, no bit or pink	Clay, grey	7.31 57.5 cm
7.92 Clay, grey	some sulphide	Grey silty clay, massive, bit S specks, minor sand & kg near top	Clay, grey	7.92 57 cm
8.53 Clay, blue-grey	silphur small	Grey massive clay, 2cm br gy pool 30-42cm, minor bit S	Clay, grey	8.53 52 cm
10.67 Clay, grey	uniform, sulphide, water from 25cm+	Grey clay, uniform, sulphide	Clay, grey	10.67 46 cm
11.28 Clay, grey	silphide	Grey silty clay, uniform	Clay, grey	11.28 35 cm
11.69 Clay, grey	v. faint pink, sulphide near bottom, w50+	Grey clay, very faint pink, sulphide near bottom	Clay, grey	11.69 81.5 cm
12.5 Clay, grey	silphide specks, softer in top half, w5+	Grey silty clay, massive, bit S specks, other streaks in top half	Clay, grey	12.5 80 cm
13.72 Clay, grey	silphide	Grey silty clay, bit S (top med) soft dist except base, void 5cm	Clay, grey	13.72 59.5 cm
14.39 Clay, grey	silphide, faint pink at base	Grey silty clay, bit S (top med) soft dist except base, void 5cm	Clay, grey	14.39 58 cm
18.39 Clay, grey	narrow pink bands dip (10-20, 252 zones)	Grey clay uniform, bit specks, not bit S band 10-18cm top 13cm dist	Clay, grey	18.39 50.5 cm
20.62 Clay, grey	28cm sand disturbed/11cm clay, at 5 and	Grey/pink banded clay, Scumle bands dip 13-15cm pink between	Clay, grey	20.62 47 cm
21.71 Sand, silty/clay	2cm sandy soil band at 15cm, bit S46cm+	Grey, 0-31 cm silty, v. gritty, silty, 31-41cm firm clay	Silt-clay, grey	21.71 41 cm
22.25 Clay, lt br grey	minor pink and faint bit bands (1 cm)	Grey clay, bit S below 23.8cm, 22.37cm sandy dist west bank	Silt-clay, grey	22.25 48 cm
22.89 Clay, lt br grey	med deformed pink bands, fracture top	Grey clay, bit S below 23.8cm, 22.37cm sandy dist west bank	Silt-clay, grey	22.89 27 cm
24.31 Clay, grey	2cm pink bands 0-54cm	Grey clay, v. soft, dist, uniform, middle pink band deformed, vertical	Grey, fine	24.31 43 cm
25.91 Clay, lt grey	soft, v. conformed pink bands	Grey clay, v. soft, dist, uniform, middle pink band deformed, vertical	Grey, fine	25.91 54 cm
26.52 Clay, grey	very soft	Grey clay v. soft, highly deformed, distributed	Grey, fine	26.52 53 cm
27.58 Clay, grey	silphide	Grey clay, silphide	Grey, fine	27.58 50 cm
28.12 Clay, grey	banding, top 8cm soft, stiff below	Grey silty clay, 21cm pink 16-30cm, minor bit specks, top 8cm stiff	Clay, grey	28.12 17 cm
29.25 Clay, pink-grey	pink grey bands bottom 30cm, stiff base	Grey silty clay, 21cm pink 16-30cm, minor bit specks, top 8cm stiff	Clay, grey	29.25 43 cm
30.33 Clay, lt grey	11cm, 1cm bit sulphide & pink banding	Grey silty clay, faint pink med, bit S patches, top 1/3 liquidy	Clay, grey	30.33 12.5 cm
31.35 Clay, grey	silphide, very disturbed	Grey clay, bit specks, disturbed, pink med, top 1cm blocky chunks	Clay, grey	31.35 31 cm
31.87 Clay, grey & pink	irregular, minor FeS2 @ bottom	Grey & pink, marbled more on top	Clay, grey	31.87 29.5 cm
32.91 Clay, pink/grey	cone shaped banding, with silphide	Grey clay, massive pinkish mottled streaks throughout	Clay, grey	32.91 53 cm
34.24 Clay, pink/grey	firm pink	Med pink gy bit clay, deformed throughout, firm, but 5cm stiffest	Clay, grey	34.24 15 cm
34.88 Clay, grey	banding, dipping 0-30, silphide banding	Grey clay, strong pink top pink bands (up to 2cm) top 5cm dist bit S	Silt, clay	34.88 48 cm
35.46 Clay, pink/grey	prominent silphide bands, small for bit	Grey silty clay, stiff, strong pink bands 2cm med/gy, bit S 35.81c	Clay, grey	35.46 56 cm
36.07 Clay, grey	bit FeS zones, pink/gy bands, stiff base	Br gy clay, top 18cm dist ht pink, strong bit S bands below, blotch ab	Clay, grey	36.07 60 cm
37.75 Clay, blue-grey	top half (recovered soft, silphide)	Grey clay, deformed pink-br bands, 40-50cm dist, firm	Clay, grey	37.75 60 cm
39.42 Clay, grey	firm banding	Grey clay, strong mottled bit S bands, 0-2cm other more deform	Clay, grey	39.42 61 cm
41.84 Clay, grey	firm banding, very stiff	Grey clay, v. stiff, faint pink bands throughout, bit S top midbase	Clay, grey	41.84 58 cm
43.74 Clay	stiff, minor faint bit, Portland 46.95	Br gy clay, v. stiff, faint pink bands throughout, bit S top midbase	Clay, grey	43.74 61 cm
46.65 Clay, grey	stiff, minor faint bit, Portland 46.95	Grey clay, dry stiff, bit med, shell frag 46.95cm, 5mm pebbles 47.15c	Clay, grey	46.65 55.5 cm
47.85 Clay, grey	stiff, minor fine sand, br FeS, shells bot	Grey silty clay, stiff dry, shell esp below 48.78cm, top 7cm br dist	Clay, grey	47.85 58 cm
49.35 Clay, grey	stiff below 25cm, soft above	Grey clay, stiff, bit specks, break 49.35cm, moist br gy above	Clay, grey	49.35 55.5 cm
49.83 Clay, grey	shell 25cm, med/fine contact 49.95m	Massive clay, pale, bit organic/49.95cm, irregular (30) pebbles	Clay, grey	49.83 54 cm
50.44 Clay, grey	bit below 50.7m, distal above 120cm	Lu di br v. med, top 5cm dist, 5-19cm firm-structure, 19cm bands	Clay, grey	50.44 54 cm
51.05		fine material	Clay, grey	51.05
53.16		fine material	Clay, grey	53.16
53.165		fine material	Clay, grey	53.165
53.78		fine material	Clay, grey	53.78

Table 1b Geotechnical Data

Table 1b

SAMPLE NO.	DEPTH m	Undist. sh str T_{μ} (t/m^2)	Remould sh str T_r (t/m^2)	Sensitivity T_{μ}/T_r	Moisture top (%)	Moisture bottom (%)	DEPTH m	LITHOLOGY description	comments
FM 366	3.66	2.4	0.2	12.6	69.9	76.5	3.66	Clay, grey	with distinct pink band at 37 cm
FM 427	4.27	1.5	0.1	27.5	92.8	89.3	4.27	Clay, grey	faint pink banded one third from top
FM 488	4.88	2.5	0.1	32.9	91.3	88.1	4.88	Clay, grey	water sample 28-38cm from top
FM 731	7.31	2.6	0.2	13.7	62.7	69.4	7.31	Clay, grey	
FM 792	7.92	6.0	0.2	26.1	63.7	65.1	7.92	Clay, grey	some sulphide
FM 853	8.53	4.0	0.1	33.3	65.6	65.7	8.53	Clay, blue-grey	sulphur smell
FM 1067	10.67	6.0	0.1	60.0	59.9	59.4	10.67	Clay, grey	uniform, sulphide, water from 25cm+
FM 1128	11.28	4.2	0.2	26.3	59.3		11.28	Clay, grey	sulphide
FM 1189	11.89	6.3	0.1	88.7	62.6	69.8	11.89	Clay, grey	v. faint pink, sulphide near bottom, w30+
FM 1250	12.5	3.2	0.1	53.3	57.0	61.0	12.5	Clay, grey	sulphide specks, softer in top half, w25+
FM 1372	13.72	3.0	0.1	49.2	63.4	61.9	13.72	Clay, grey	
FM 1433	14.33		0.092/0.015		64.1	66.0	14.33	Clay, grey	sulphide
FM 1859	18.59	3.7	0.2	19.5	59.7	78.1	18.59	Clay, grey	sulphide, faint pink at base
FM 2062	20.62	4.6	0.2	27.1	83.0	68.0	20.62	Clay, grey	narrow pink bands dip 10-20, 252 zones
FM 2171	21.71		0.19/0.018		82.1	74.6	21.71	Sand, silty/Clay	29cm sand disturbed/11cm clay, silty sml
FM 2225	22.25	1.8	0.2	10.6		77.8	22.25	Clay, lt br grey	2cm sandy wet band at 13cm, blk S36cm+
FM 2289	22.89	5.0	0.2	25.0			22.89	Clay, lt gm grey	minor pink and faint blk bands (1cm)
FM 2431	24.31	1.8	0.2	10.6	74.7	70.7	24.31	Clay, grey	mid deformed pink bands, fracture @ top
FM 2591	25.91	0.9	0.2	5.1		69.8	25.91	Clay, lt. grey	2cm pink bands @ 54cm
FM 2652	26.52	0.7	0.1	6.0	77.3	76.1	26.52	Clay, grey	soft, v. conformed pink bands
FM 2758	27.58		0.0		78.4	73.0	27.58	Clay, grey	very soft
FM 2812	28.12		0.1		70.9	0.0	28.12	Clay, grey	sulphide
FM 2925	29.25	7.2	0.3	26.7	72.5	65.6	29.25	Clay, pink-grey	banded, top 8cm soft, stiff below
FM 2979	29.79	6.0	0.1	54.5	85.2	71.9	29.79	Clay, grey	pink-grey bands bottom 30cm, stiff @ base
FM 3033	30.33	1.6	0.3	5.4	68.4		30.33	Clay, lt. grey	11cm, 1cm blk sulphide & pink banding
FM 3133	31.33		0.11/0.14		69.1		31.33	Clay, grey	sulphides, very disturbed
FM 3187	31.87	1.3	0.2	8.0	72.5		31.87	Clay, grey & pink	marbled (mottled) more @ top
FM 3293	32.93	2.0	0.3	7.7	67.1	70.0	32.93	Clay, pink/grey	irregular, minor FeS2 @ bottom
FM 3424	34.24	1.5	0.3	5.2	65.9		34.24	Clay, pink/grey	cone shaped banding, with sulphides
FM 3488	34.88	8.5	0.5	17.7	66.5	65.8	34.88	Clay, grey	some pink
FM 3546	35.46	6.9	0.5	13.0	62.4	66.7	35.46	Clay, pink/grey	banded, dipping @ top, sulphide banding
FM 3607	36.07	3.2	0.2	18.8	113.1	69.4	36.07	Clay, grey	prominent sulphide bands, smpl for Elz
FM 3775	37.75	5.0	0.4	12.5	72.8	66.5	37.75	Clay, blue-grey	blk FeS zones, pink/grey bands, stiff base
FM 3942	39.42	3.1	0.6	5.4	85.4	60.1	39.42	Clay, grey	top half disturbed soft, sulphides
FM 4184	41.84	7.5	0.1	57.7	62.5	62.6	41.84	Clay, grey	faint banding
FM 4374	43.74	7.5	1.1	6.6	64.9	60.5	43.74	Clay	faint banding, very stiff
FM 4663	46.63	9.2	0.1	76.7	61.4	53.2	46.63	Clay, grey	stiff, minor faint blk, Portland @ 46.95
FM 4785	47.85	10.5	0.9	11.3	52.0	38.1	47.85	Clay, grey	stiff, minor fine sand, tr FeS, shells bot
FM 4933	49.33	8.2	1.3	6.6	50.2	51.6	49.33	Clay, grey	stiff below 23cm, soft above
FM 4983	49.83	2.3	0.7	3.2	43.9	41.8	49.83	Clay, grey	shells 25cm, salt/fresh contact @ 49.95m
FM 5044	50.44	7.5	0.4	18.3	38.0	40.1	50.44	Clay, varved	flat below 50.7m, distorted above, L2Xsec
FM 5105	51.05						51.05		
FM 5316A	53.16						53.16		
FM 5316B	53.165						53.165		
FM 5378	53.78						53.78		

Appendix 2 Geochemical Data**Table 2a. Isotope Data****Table 2b. Geochemical Data**

Table 2a Isotope Data

Table 2a

SAMPLE NO.	DEPTH m	LAB RUN	$\delta^{18}O$ ‰	$\delta^{2}H$ ‰
FM 366	3.66	2	-10.31	-71.1
FM 427	4.27	2	-9.94	
FM 488	4.88	2	-9.91	-64.7
FM 731	7.31	2	-9.51	-64.8
FM 792	7.92	2	-9.17	
FM 853	8.53	2	-9.11	-63
FM 1067	10.67	2	-9.27	
FM 1128	11.28	2	-7.13	-56
FM 1189	11.89	2	-9.25	
FM 1250	12.5	2	-9.56	-63.1
FM 1372	13.72	2	-9.05	
FM 1433	14.33	2	-8.41	-59.7
FM 1859	18.59	2	-8.91	-62.5
FM 2062	20.62	2	-8.88	-62.5
FM 2171	21.71	3	-9.55	-68.3
FM 2225	22.25	3	-9.25	
FM 2289	22.89	3	-9.06	
FM 2431	24.31	3	-9.31	
FM 2591	25.91	3	-8.97	
FM 2652	26.52	3	-9.1	
FM 2758	27.58	3	-9.14	
FM 2812	28.12	3	-8.87	
FM 2925	29.25	2	-8.95	
FM 2979	29.79	2	-8.94	
FM 3033	30.33	3	-9.01	-65.4
FM 3133	31.33	3	-9.5	
FM 3187	31.87	3	-8.59	
FM 3293	32.93	3	-8.98	
FM 3424	34.24	2	-9.09	-60.8
FM 3488	34.88	2	-8.9	
FM 3546	35.46	2	-8.52	-56.3
FM 3607	36.07	1	-9.08	
FM 3775	37.75	1	-9.15	-54.9
FM 3942	39.42	1	-9	
FM 4184	41.84	1	-8.7	
FM 4374	43.74	1	-8.97	-61.9
FM 4663	46.63	1	-8.93	-59.5
FM 4785	47.85	1	-8.49	
FM 4933	49.33	1	-8.72	-63.4
FM 4983	49.83	1	-8.88	
FM 5044	50.44	1	-8.68	-58.9
FM 5105	51.05	1	-5.32	-51.9
FM 5316A	53.16	1	-6.11	-60.3
FM 5316B	53.165		-3.89	-49.8
FM 5378	53.78		-1.94	-47.2

Cation Data

Table 2b

SAMPLE NO.	DEPTH m	Piper plot serial no.	Na+ mg/l	Na+ meq/l	Mg++ mg/l	Mg++ meq/l	Ca++ mg/l	Ca++ meq/l	K+ mg/l	K+ meq/l	Sr++ mg/l	Sr++ meq/l	Sum Cations meq/l	TDS ppm
FM 366	3.66	1	59.0	2.6	16.4	1.4	35.7	1.8	9.2	0.2	0.62	0.01	6.0	444.0
FM 427	4.27													
FM 488	4.88	2	81.0	3.5	13.4	1.1	31.2	1.6	11.9	0.3	0.41	0.01	6.5	522.6
FM 731	7.31	3	133.0	5.8	14.5	1.2	30.0	1.5	20.7	0.5			9.1	722.1
FM 792	7.92					0.0		0.0						
FM 853	8.53	4	191.0	8.3	8.6	0.7	14.2	0.7	18.0	0.5	0.40	0.01	10.2	808.7
FM 1067	10.67	5	267.0	11.6	8.7	0.7	12.8	0.6	20.2	0.5	0.50	0.01	13.5	1069.6
FM 1128	11.28													
FM 1189	11.89													
FM 1250	12.5	6	336.0	14.6	7.5	0.6	17.1	0.9	20.4	0.5	0.39	0.01	16.6	1311.9
FM 1372	13.72	7	346.0	15.1	5.9	0.5	5.7	0.3	16.8	0.4	0.75	0.02	16.3	1266.1
FM 1433	14.33													
FM 1859	18.59	8	592.0	25.8	17.6	1.5	19.7	1.0	30.5	0.8	0.61	0.01	29.0	2135.7
FM 2062	20.62	9	633.0	27.5	11.9	1.0	25.1	1.3	28.9	0.7	0.90	0.02	30.6	2246.6
FM 2171	21.71													
FM 2225	22.25	10	603.0	26.2	10.4	0.9	14.5	0.7	26.9	0.7	1.00	0.02	28.6	2125.5
FM 2289	22.89													
FM 2431	24.31	11	713.0	31.0	19.6	1.7	25.2	1.3	36.6	0.9	0.92	0.02	34.9	2431.4
FM 2591	25.91	12	773.0	33.6	14.4	1.2	15.5	0.8	35.4	0.9	1.33	0.03	36.6	2533.2
FM 2652	26.52													
FM 2758	27.58	13	784.0	34.1	18.4	1.6	17.5	0.9	35.1	0.9	0.49	0.01	37.5	2587.0
FM 2812	28.12													
FM 2925	29.25	14	1063.0	46.2	27.6	2.4	22.7	1.1	49.3	1.3	0.50	0.01	51.0	3398.8
FM 2979	29.79													
FM 3033	30.33	15	944.0	41.1	51.6	4.4	16.5	0.8	50.2	1.3	0.49	0.01	47.6	3272.0
FM 3133	31.33													
FM 3187	31.87	16	1215.0	52.8	34.0	2.9	23.6	1.2	48.3	1.2	0.57	0.01	58.2	3878.2
FM 3293	32.93	17	1249.5	54.4	32.1	2.8	29.6	1.5	45.9	1.2	0.46	0.01	59.8	3951.7
FM 3424	34.24	18	1360.7	59.2	41.4	3.6	26.4	1.3	54.0	1.4	0.64	0.01	65.5	4366.8
FM 3488	34.88													
FM 3546	35.46													
FM 3607	36.07	19	1750.0	76.1	61.5	5.3	32.8	1.6	62.3	1.6	3.63	0.08	84.7	5521.7
FM 3775	37.75	20	1663.0	72.3	73.1	6.3	46.5	2.3	63.4	1.6	1.24	0.03	82.6	5315.9
FM 3942	39.42	21	1634.0	71.1	53.4	4.6	39.1	2.0	58.3	1.5	0.73	0.02	79.1	5123.7
FM 4184	41.84	22	2518.0	109.5	122.1	10.5	57.7	2.9	91.3	2.3	1.64	0.04	125.3	7907.8
FM 4374	43.74	23	2779.0	120.9	140.5	12.1	68.6	3.4	97.5	2.5	1.74	0.04	138.9	8657.9
FM 4663	46.63	24	3053.0	132.8	297.0	25.5	131.8	6.6	130.4	3.3		0.00	168.2	9963.0
FM 4785	47.85	25	2645.0	115.1	215.8	18.5	87.6	4.4	128.2	3.3		0.00	141.2	8459.9
FM 4933	49.33	26	3081.0	134.0	121.0	10.4	41.6	2.1	103.6	2.6	1.59	0.04	149.2	9509.0
FM 4983	49.83	27	3233.0	140.6	261.2	22.4	79.8	4.0	122.0	3.1		0.00	170.1	10415.3
FM 5044	50.44	28	3269.0	142.2	207.2	17.8	46.1	2.3	109.3	2.8	2.16	0.05	165.1	10095.2
FM 5105	51.05	29	4490.0	195.3	485.6	41.7	272.2	13.6	190.8	4.9	6.58	0.15	255.6	15724.6
FM 5316A	53.16	30	2507.6	109.1	472.4	40.5	467.7	23.3	166.0	4.2		0.00	177.2	11368.8
FM 5316B	53.165	31	4328.0	188.3	773.0	66.3	550.2	27.5	249.9	6.4	14.85	0.34	288.8	19371.2
FM 5378	53.78	32	4670.0	203.1	827.0	71.0	610.6	30.5	280.9	7.2	12.58	0.29	312.0	19688.1

Table 2b

SAMPLE NO.	DEPTH m	Piper plot serial no.	Br - ppm	Br - meq/l	SO4 -- ppm	SO4 -- meq/l	Cl - ppm	Cl - meq/l	HCO3 - ppm	HCO3 - meq/l	TDS ppm	Conductivity mS/cm
FM 366	3.66	1	0.05	0.00	39.2	0.8	45.4	1.3	238.4	3.9	444.0	0.37
FM 427	4.27											0.36
FM 488	4.88	2	0.05	0.00	6.7	0.1	17.8	0.5	360.1	5.9	522.6	0.42
FM 731	7.31	3	0.05	0.00	10.4	0.2	35.9	1.0	477.5	7.8	722.1	0.62
FM 792	7.92											0.60
FM 853	8.53	4	0.05	0.00	4.5	0.1	64.0	1.8	508.0	8.3	808.7	0.65
FM 1067	10.67	5	0.05	0.00	18.4	0.4	83.2	2.3	658.8	10.8	1069.6	0.82
FM 1128	11.28											1.11
FM 1189	11.89											0.95
FM 1250	12.5	6	0.05	0.00	42.2	0.9	102.0	2.9	786.3	12.9	1311.9	1.15
FM 1372	13.72	7	0.05	0.00	4.4	0.1	141.0	4.0	745.5	12.2	1266.1	1.19
FM 1433	14.33											1.62
FM 1859	18.59	8	1.87	0.02	4.8	0.1	410.0	11.6	1058.7	17.4	2135.7	2.04
FM 2062	20.62	9	2.11	0.03	3.1	0.1	441.0	12.4	1100.7	18.0	2246.6	2.16
FM 2171	21.71											1.50
FM 2225	22.25	10	1.75	0.02	2.0	0.0	378.0	10.7	1088.0	17.8	2125.5	2.01
FM 2289	22.89											2.79
FM 2431	24.31	11	2.51	0.03	2.7	0.1	685.0	19.3	945.9	15.5	2431.4	2.67
FM 2591	25.91	12	3.14	0.04	1.9	0.0	746.0	21.0	942.6	15.4	2533.2	2.78
FM 2652	26.52											2.92
FM 2758	27.58	13	3.40	0.04	0.1	0.0	770.0	21.7	958.0	15.7	2587.0	2.75
FM 2812	28.12											3.22
FM 2925	29.25	14	4.70	0.06	7.0	0.1	1215.0	34.3	1009.0	16.5	3398.8	3.96
FM 2979	29.79											4.17
FM 3033	30.33	15	3.37	0.04	5.4	0.1	964.0	27.2	1236.4	20.3	3272.0	3.46
FM 3133	31.33											3.72
FM 3187	31.87	16	4.92	0.06	8.6	0.2	1377.0	38.8	1166.2	19.1	3878.2	4.47
FM 3293	32.93	17	5.16	0.06	3.6	0.1	1460.0	41.2	1125.5	18.4	3951.7	4.51
FM 3424	34.24	18	5.63	0.07	22.3	0.5	1533.0	43.2	1322.7	21.7	4366.8	5.11
FM 3488	34.88											6.14
FM 3546	35.46											6.81
FM 3607	36.07	19	8.03	0.10	67.8	1.4	2137.0	60.3	1398.7	22.9	5521.7	6.08
FM 3775	37.75	20	8.02	0.10	54.3	1.1	2160.0	60.9	1246.3	20.4	5315.9	6.49
FM 3942	39.42	21	14.40	0.18	85.8	1.8	2038.0	57.5	1199.9	19.7	5123.7	6.87
FM 4184	41.84	22	21.40	0.27	253.0	5.3	3415.0	96.3	1427.6	23.4	7907.8	9.32
FM 4374	43.74	23	22.30	0.28	331.0	6.9	3911.0	110.3	1306.3	21.4	8657.9	9.80
FM 4663	46.63	24	29.00	0.36	416.0	8.7	5279.0	148.9	626.8	10.3	9963.0	11.71
FM 4785	47.85	25	28.30	0.35	424.0	8.8	4931.0	139.1	0.0	0.0	8459.9	11.80
FM 4933	49.33	26	21.70	0.27	667.0	13.9	3836.0	108.2	1635.5	26.8	9509.0	11.10
FM 4983	49.83	27	23.40	0.29	431.0	9.0	4925.0	138.9	1339.9	22.0	10415.3	12.06
FM 5044	50.44	28	28.10	0.35	477.0	9.9	4842.0	136.6	1114.3	18.3	10095.2	12.54
FM 5105	51.05	29	22.00	0.28	4369.0	91.0	5741.0	161.9	147.4	2.4	15724.6	15.25
FM 5316A	53.16	30	6.03	0.08	5459.0	113.7	2290.0	64.6	0.0	0.0	11368.8	9.86
FM 5316B	53.165	31	12.20	0.15	9657.0	201.1	3786.0	106.8	0.0	0.0	19371.2	14.74
FM 5378	53.78	32	16.00	0.20	8836.0	184.0	4635.0	130.7	0.0	0.0	19888.1	20.70

Appendix 3 Analytical Procedures

- a. Ion chemical analysis and summary of detection limits**
- b. ^{18}O isotope analysis and ^2H isotope analysis**

a. Ion chemical analysis and summary of detection limits

August 22, 1995

Attached is the procedure for the dissolution of rocks for analysis by ICP-ES and ICP-MS. One thing to note that the final solution for ICP-ES containing 1 g per 100 mL is further diluted by a factor of 10 for ICP-MS determination. During this dissolution step, internal standard (Re) is added.

The ICP emission spectrometer is a Perkin-Elmer Optima 3000 and the ICP mass spectrometer is a Perkin-Elmer Sciex ELAN 5000. Both are equipped with autosamplers and the MS is equipped with a flow injection system for on-line dilution ($\times 10$) and addition of internal standards. The precision of both instruments is about 2% and the accuracy based on the analysis of standard reference materials such as BCR-1 and AGV-1 is better than 5%.

Limits of detection of ICP-MS is about 20 ppb (in the sample) for most elements of the periodic table. As part of our quality control system, 5% of our samples are randomly duplicated (blind) from beginning to end of the analytical process. All results are blank corrected. During each analytical run, control samples and standard reference materials are analyzed.

For trace metals, accuracy is better than 5% with an equivalent precision at ten times above the limit of detection.

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Determinations of anions by ion chromatography:

Anions are determined on a Dionex Series 4500i Ion Chromatograph (Sunnyvale, CA, U.S.A.) fitted with an IonPac AS4A-SC (4 mm) column. Five mL of sample solution are chromatographed and concentrations of individual anions determined by peak-profile areas. The Ion Chromatograph is fitted with a conductivity detector. The limit of detection for each anion (listed below) is 50 ppb in solution.

Anions Determined:

Nitrate
Nitrite
Fluoride
Phosphate
Sulphate
Chloride
Bromide

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June, 1995

REPORT OF DIONEX ANALYSIS

DATE: 04/20/94

REPORT NO.: 4-94

SUBMITTED BY: F. MICHAL

PROJECT NO.: 380077

METHOD: DIONEX ION CHROMATOGRAPHY ANALYSER.

ELEMENT	ESTIMATE OF ERROR (ABSOLUTE + RELATIVE %)	DETERMINATION LIMIT (PPB)
BR	5	50
CL	5	100
SO4	5	50

ANALYST:.....*R.V.*..... SUPERVISOR:.....*C. Henry*.....

STABLE ISOTOPE TECHNIQUES OTTAWA-CARLETON GEOSCIENCE CENTRE STABLE ISOTOPE FACILITY

Carbonates

The carbon and oxygen isotopic composition of carbonates is determined by the analysis of CO_2 generated by the reaction with 100% phosphoric acid (McCrea, 1950). The ^{18}O fractionation factors used for the carbonate- H_3PO_4 reactions are:

calcite, 25°C	$\alpha=1.01025$	(Friedman & O'Neil 1977, Sharma & Clayton 1965)
dolomite, 50°C	$\alpha=1.01065$	(Rosenbaum & Sheppard 1986)
ankerite, 50°C	$\alpha=1.010603$	(Rosenbaum & Sheppard 1986)
siderite, 50°C	$\alpha=1.010454$	(Rosenbaum & Sheppard 1986)
magnesite, 50°C	$\alpha=1.01160$	(Perry & Tan 1972)
rhodochrosite, 25°C	$\alpha=1.0101203$	(Friedman & O'Neil 1977)
witherrite, 25°C	$\alpha=1.0109697$	(Friedman & O'Neil 1977)

The CO_2 is analysed on a triple collector VG SIRA 12 mass spectrometer. The routine precision (2σ) on a pure carbonate analysis is 0.10‰.

Organic carbon

The isotopic composition of organic carbon is determined by the analysis of CO_2 produced by combustion with copper oxide at 800°C. The CO_2 is analysed on a triple collector VG SIRA 12 mass spectrometer. The routine precision (2σ) on the analyses is 0.20‰.

Water

The deuterium-hydrogen ratio in water is determined by the analysis of H_2 generated via zinc reduction at 500°C. The H_2 gas is analyzed on an automated double collector VG 602D mass spectrometer. The results are normalized to SMOW. The routine precision (2σ) on the analyses is 1.5‰.

The oxygen isotopic composition of water is determined by CO_2 -water equilibration at 25°C using an automated system. The CO_2 is analyzed on a triple collector VG SIRA 12 mass spectrometer. The CO_2 -water fractionation factor used at 25°C is 1.0412 (Friedman & O'Neil 1977). The routine precision (2σ) on the analyses is 0.10‰.

The isotopic composition of dissolved inorganic carbon (DIC) in water is determined by the analysis of CO_2 generated by reaction with phosphoric acid. The CO_2 is analyzed on a triple collector VG SIRA 12 mass spectrometer. The routine precision (2σ) on the analyses is 0.10‰.

Sulphides and sulphates

The sulphur isotopic composition of sulphates is determined by the analysis of SO_2 produced by combustion with copper oxide at 1100°C. The SO_2 is analyzed on a triple collector VG SIRA 12 mass spectrometer. The routine precision (2σ) on the analyses is 0.20‰.

The sulphur isotopic composition of sulphides is determined by the analysis of SO_2 produced by combustion with copper oxide at 1050°C. The SO_2 is analyzed on a triple collector VG SIRA 12 mass spectrometer. The routine precision (2σ) on the analyses is 0.20‰.

Disseminated sulphides and sulphates are chemically extracted using the Kiba method (Ueda & Sakai, 1983), which consists of heating the sample with dehydrated phosphoric acid containing stannous ions as a reducing agent. The resulting H_2S is precipitated as Ag_2S , which is then converted to SO_2 as outlined above.

END

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