**A GEOCHEMICAL INVESTIGATION
INTO THE ORIGIN OF BRACKISH GROUNDWATER
FROM WELLS AND SPRINGS
EAST OF OTTAWA,
CANADA.**

by
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A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Master of Science

Department of Earth Sciences

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ABSTRACT

Brackish groundwater and associated gas from well sites in Gloucester, the springs at Carlsbad Springs, Caledonia Springs and Plantagenet Station were analyzed for their chemical composition and selected samples were analyzed for their isotopic composition (^{18}O , ^2H , ^{34}S , ^{13}C , $^{87}\text{Sr}/^{86}\text{Sr}$).

The groundwaters are Na-Cl water with 1 000-10 000 ppm TDS and they are hosted in the Carlsbad and, possibly, the Billings Formations. Their chemical composition shows similarities with groundwater from shale terrain in other locations, suggesting that the salinity is resulting from interaction with the shale bedrock. The ^{18}O and ^2H data show an unaltered meteoric isotope signature and indicates that they were recharged when it was warmer than today in the area. Isotopic composition of the methane gas and dissolved sulphate and carbonate in the groundwater indicate anaerobic bacteriological activity. The strontium isotope ratios show that the strontium has its origin in the shale bedrock. One ^{14}C analysis suggests groundwater recharge 4500-7800 years BP.

The brackish groundwaters are divided into two geochemical groups. The type A waters, which are the majority of the samples, contain very little to no dissolved sulphate and bicarbonate concentrations up to 1000 ppm, together indicating sulphate reduction. The three samples which are type B waters all come from the same fault block immediately east of the Gloucester Fault. They are characterized by very high sulphate levels combined with higher calcium and strontium content than the type A waters. Sulphur isotope data show that this is the result of gypsum dissolution and oxidation of pyrite in that part of the Carlsbad Formation.

Sources other than low temperature water-rock interaction examined as possible sources of the salinity are evaporite dissolution, leaking of saline groundwater and brines from the Canadian Shield, trapped Champlain Sea water and formation water. Evaporite dissolution, other than of gypsum in the type B waters, is eliminated due to lack of known major halite deposits in the area. On the basis of the chemical composition of the studied groundwaters, groundwater from the Canadian Shield can be excluded from further consideration. The fact that the ^{18}O and ^2H data plot on the local meteoric water line rules out the possibility that the groundwaters are of formation water origin. The mixing model for the Champlain Sea cannot completely account for the observed relationship between salinity and ^{18}O data. The chemical composition of the groundwaters show very little similarity to seawater. From the combined chemical and isotopic evidence, the Champlain Sea is a less likely source than interaction with the shale.

It may be possible that fresh groundwater exists below the shale in areas directly underlain by the Carlsbad Formation. Further study should include drilling and sampling of deep wells which penetrate through the shale and into the limestone below it.

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1 INTRODUCTION

In the area southeast of Ottawa, groundwater with high salinity is commonly encountered during the drilling of wells. Springs having a high content of dissolved solids are also well known in the region. A century ago some of these springs, such as Carlsbad Springs and Caledonia Springs, were highly regarded for their presumed therapeutic value by visitors to the resorts. Prior to their discovery by the settlers, they had been used by the indigenous people for medicinal purposes. Today the presence of salty tasting groundwater constitutes a nuisance to the rural residents, who continue to search for better quality sources. The source of these salts is not resolved, but many people believe it is related to the marine invasion by the Champlain Sea.

1.1 Purpose of present study.

The purpose of this thesis is to identify the source of the salinity in these groundwaters through a geochemical and isotopic characterization of the waters. The term salinity is a relatively loosely used term which primarily means NaCl content. However, since other salts also contribute to the total dissolved solids (TDS) load, for the purpose of this study salinity can be regarded as synonymous with high levels of dissolved solids.

Possible sources of the salinity are:

- Evaporites dissolved from the aquifer.
- Trapped seawater in pores of the aquifer material either of syngenetic (formation water) or epigenetic (Champlain Sea water) origin.
- Extensive water-rock interaction.
- Leakage of deep-seated Canadian Shield brines.

1.2 Location of the study area.

The study area is located to the south and east of Ottawa, as shown in Figure 1, and contains those parts of the City of Gloucester not serviced by the Regional Municipality of Ottawa-Carleton. Four of the springs at Carlsbad Springs in the eastern part of Gloucester (see Figure 3a) were located during this study. In addition, the springs at two other locations outside of Gloucester are included in the study. Caledonia Springs and Plantagenet Station are situated east of Gloucester, their respective distances being approximately 60 km and 45 km from the eastern edge of the city.

1.3 Local climate.

The average annual air temperature in Ottawa is 5.9 °C and the average annual precipitation is 879.3 mm. Temperature variations during the year are large, the coldest

Figure 1. Location of the study area: The City of Gloucester including Carlsbad Springs, and outside of Gloucester, the springs at Plantagenet Station and Caledonia Springs, all indicated in bold.

month on average being January (-10.9°C) and the warmest month being July ($+20.6^{\circ}\text{C}$). August has the highest precipitation (88.4 mm) while February is the driest month of the year (60.3 mm) (Environment Canada, 1992). Most groundwater recharge is considered to take place during spring thaw (Charron, 1978).

1.4 Previous work.

The springs at Caledonia Springs were mentioned in "Geology of Canada" by T.S. Hunt (1863), who presented chemical analyses of the spring water. In the same publication he also mentioned the occurrence of a mineralized spring in Gloucester called the Borthwick Spring. This spring has since ceased to exist and was not found during the present study. The occurrence of the spring sampled in this study at Plantagenet Station was also mentioned, together with the chemical analyses of two additional springs at Plantagenet. However, the spring at Plantagenet Station that was investigated for this study was not analyzed by Hunt.

In 1865, T.S. Hunt further described and presented analyses for water collected in 1847 and 1865 at Caledonia Springs. In Hunt's opinion, the salinity of the groundwater was the result of partial evaporation of sea water at the time of deposition of the host rock. The composition of the spring water would be a product of mixing between the saline end member and an alkaline type of water. As evidence for this he used the changing composition of the spring waters between 1847 and 1865.

Satterly and Elworthy (1917) and Elworthy (1918) described and presented analyses for springs across Canada. Included in their study were Caledonia Springs and Carlsbad Springs, and again the Plantagenet Station spring was mentioned. The purpose of their study was to provide an inventory of Canadian spring waters and their radioactivity, which was thought to be beneficial to human health at the time. No interpretation of the origin for the groundwater salinity was presented beyond that of Hunt (1865).

Owen (1953) published a report on the groundwater resources of Gloucester Township, now the city of Gloucester. He described the different water-bearing units in the township and provided a detailed inventory of the wells in Gloucester, area by area. He made a clear correlation between the aquifer material, and the quality and volume of groundwater found. He stated: "ground water from the Carlsbad Formation generally contains considerable quantities of dissolved mineral salts, chiefly in the form of sodium chloride". The well records he published have partially served as a base for the selection of sampling sites for the present study.

In 1960, L.V. Brandon produced a preliminary report on the hydrogeology of Ottawa-Hull. He concluded that groundwater with elevated levels of dissolved solids was found in the Carlsbad and Billings shales and in wells deeper than 30 m in the Ottawa limestone. Furthermore, saline groundwater was also found in wells where the thickness of marine clay is great. The latter was stated to be connate water of Champlain Sea origin.

Charron (1974) published a study of groundwater flow in Russell County, which borders Gloucester to the east. The conclusions from that study were incorporated into a report by Charron (1978), which consisted of a hydrochemical study of groundwater flow in the region between the Ottawa and St. Lawrence Rivers. The study area of Charron (1978) included Caledonia Springs and Plantagenet Station, but unfortunately Gloucester and Carlsbad Springs, located immediately to the west, were not covered. In his hydrochemical interpretation, Charron (1974 and 1978) used the TDS as a measure of residence time and as a tool to identify recharge and discharge areas. Waters with a high chloride content were identified as coming from a discharge area having had the longest time to dissolve salts in the aquifer. The Alfred bog and Mer Bleue bog were identified as discharge zones; Caledonia Springs and Carlsbad Springs are on the border of these respective bog areas. Charron (1978) implied that water-bedrock interaction was the major control on groundwater composition. He also stated that the bedrock surface topography is the major control on horizontal groundwater flow, since the contact zone between bedrock and overburden has been found to contain the largest volumes of groundwater.

Hydrogeological consultants in the Ottawa area generally consider the salinity in the groundwater to have originated from Champlain Sea water. However, no clearly documented evidence for this source has been reported by the consultants. A preliminary investigation of brackish groundwater in a shallow Palaeozoic aquifer west of Ottawa, conducted by Mitchell (1990) concluded that the salinity was of Champlain Sea origin, although he did not consider water-rock interaction other than evaporite dissolution.

2 GEOLOGICAL SETTING.

2.1 Bedrock geology.

The bedrock of the Ottawa area consists of Palaeozoic rocks, preserved in the Ottawa-St. Lawrence Lowland, overlying a Precambrian crystalline basement. These Precambrian rocks belong to the Grenville Province of the Canadian Shield and are exposed in the Gatineau Hills to the north of the Ottawa River. Palaeozoic rocks closely related to those in the Ottawa-St. Lawrence Lowland are found in south-central Ontario on the edge of the convergence between the Michigan and Appalachian Basins (King, 1969). The Ottawa-St. Lawrence Lowland is separated from the Palaeozoic terrain of south-central Ontario by the Frontenac Axis, which connects the Grenville Province in central Ontario with the Grenville Province in the Adirondacks.

The Palaeozoic sequence has been subject to erosion over millions of years, and today only the Cambrian and Ordovician sedimentary rocks remain. Extensive rifting and the possible initiation and migration of a hot-spot during the Cretaceous and early Tertiary caused heating of the rocks (Legall *et al.*, 1981). The rifting resulted in normal faulting, possibly along pre-existing zones of weakness. Associated with faults and particularly in or near fault junctions in the Ottawa-St. Lawrence Lowland are veins that contain minerals such as celestite and barite, sometimes together with calcite, fluorite, galena and sphalerite (Williams, 1991 and Carignan, 1989).

One of the major fault lines, the Gloucester Fault, runs through the city of Gloucester in a northwest-southeast direction and has a maximum vertical displacement of 554 m near Russell, immediately south of the study area. In the area immediately to the east of the fault, which is the downthrown block, the Palaeozoic sequence is the most complete in the area. Within the study area, a borehole (number DH-0-9 of Williams *et al.*, 1984) near site AB 93-20 in south Gloucester, has a measured Palaeozoic thickness of 537 m (Owen, 1953).

Table 1 shows the stratigraphy of the Palaeozoic rock units found in the Ottawa area. For a detailed description of each rock unit the reader is referred to Wilson (1946) or Williams (1991). As illustrated in Table 1, different researchers have used different classifications, the largest differences being for the Ottawa Group. The nomenclature of Wilson has been used for a long period of time by researchers in the Ottawa area and is, therefore, well established. However, the boundaries of her faunal zones were based on the occurrence of certain benthic fossils, providing biostratigraphic rather than chronostratigraphic units. Rocks corresponding to the Ottawa Group are found southwest of the Frontenac Axis under different names that were given to lithostratigraphic units by Liberty (1969). Therefore, Williams *et al.* (1984, 1985a and 1985b) and Williams (1991) have applied these names to the equivalent formations in the Ottawa-St. Lawrence Lowland. In the preparation of the individual parts of this study, the works upon which they are based have used different classifications. Therefore, different nomenclatures will be encountered in the present study. If this causes any confusion, the reader should

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	
Nepean	Nepean	Nepean	Mount Simon
	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			
Lowville	Gull River	Gull River	Gull River
Pamelia	Shadow Lake	Shadow Lake	Shadow Lake

Table 1. 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.

consult Table 1 for clarification.

2.1.1 Stratigraphy.

The Queenston Formation constitutes the top of the Palaeozoic sequence. In the Ottawa area it has a limited extent, and has not been encountered in the wells for this study. It consists of red oxidized shales, sandstone and conglomerates. The Carlsbad Formation is a grey shale which contains some impure limestone, dolomitic bands and more rarely sandy portions. The main non-clay mineral present in the rock is quartz, as reported for a sample collected in conc. 5 RF, lot 7 in Gloucester (Brady and Dean, 1966). Lesser amounts of plagioclase, calcite, dolomite, pyrite, anatase, potassium feldspar and organic material of unspecified nature are also present. The clay minerals in the <5 micron fraction are illite and chlorite.

The contact with the underlying Billings Formation is transitional and is often not easy to identify. The Billings Formation consists of thick beds of black, fissile shale. At the base of the formation there are a couple of metres of brown weathered shale. In a whole rock sample, the main mineral other than clay minerals present is quartz, with plagioclase, calcite and pyrite in lesser amounts. Organic material is also present in this sample, which comes from the east bank of the Rideau River at Smyth Road in Ottawa (Brady and Dean, 1966). The minerals in the <5 micron fraction are illite and chlorite.

Beneath the Billings Formation there is a thin transitional formation called the Eastview Formation, which consists of dark fine-grained limestone interbedded with shale. Due to its modest thickness it has not been reported in any of the well-logs investigated for this study. Williams (1991) included the Eastview in the underlying Lindsay Formation of the Ottawa Group, while Wilson (1946) and Williams *et al.* (1984, 1985a and 1985b) identified it as a separate formation.

The Ottawa Group, which is found below the Eastview Formation, is predominantly a dark fine-grained limestone. Dark grey, friable shale is found interbedded in the limestone, particularly towards the top. The group is divided into several formations with different composition in terms of calcite and clay content. Wilson (1946) divided the Ottawa Group into faunal zones, whereas Williams (1991) and Williams *et al.* (1984, 1985a and 1985b) divided it into formations, see Table 1. Hewitt (1960, 1972) has described sections of the Ottawa Group that are exposed at quarries in the Ottawa area.

The St. Martin Formation, below the Ottawa Group, is also a limestone with interbedded shaley or dolomitic members, which are more common toward its base. This formation has not been reported in the study area. Williams (1991) included this rock unit in the underlying Rockcliffe Formation. The latter is composed of predominantly light friable olive-grey shale with some pockets of iridescent shale. Within it, there are also some lenses of fine-grained grey silty sandstone. None of the wells investigated for this study draw their water from this formation.

The Oxford Formation underlies the Rockcliffe shales. It mainly consists of a thickly bedded, rusty weathering dolomite which changes laterally into limestone at some locations.

The March Formation, which underlies the Oxford Formation, consists of alternating grey sandstone, and sandy dolomite or blue-grey dolomite, all weathering rusty brown. Its upper boundary with the Oxford Formation is gradational.

At the base of the sequence, and grading into the March Formation, is the Nepean Formation. It is in general composed of a cream-coloured pure quartz sandstone, with some calcareous units, which weather grey and have irregular rust spots.

2.1.2 Bedrock distribution.

The distribution of the Palaeozoic rocks to the east of Ottawa is shown in Figure 2. In the western part of the study area, which lies west of the Gloucester Fault, rocks belonging to the March and Oxford Formations are found in outcrops and underlying the drift. In a small triangular area, which is too small to be distinguished in Figure 2, immediately west of the Gloucester Fault near South Gloucester, the Nepean sandstone exists at the surface.

Figure 2. Distribution of bedrock formations in the study area, from Wilson (1946).

A large area immediately east of the Gloucester Fault is directly underlain by shales of the Carlsbad and Billings Formations. This area extends to the east where its boundaries with other rock formations are defined by numerous faults. Travelling eastward to Plantagenet Station and Caledonia Springs, the Lindsay Formation becomes the dominant rock unit on the map sheet. However, according to Williams *et al.* (1985a and 1985b), the Carlsbad Formation is present south of Plantagenet Station (3 km) and Caledonia Springs (500 m). The locations of the faults that constitute the boundaries between the geological formations are not exactly known. Therefore, it is possible that the respective spring locations are situated within the boundaries for the Carlsbad Formation or on top of the faults. Even if the bedrock at Plantagenet Station and Caledonia Springs is the Lindsay Formation, the groundwater may be coming from the Carlsbad Formation and discharging through the Lindsay Formation.

2.2 Unconsolidated deposits.

The overburden found in the region today is mainly the result of the last glaciation, but a large portion is likely to have been repeatedly reworked from glaciation to glaciation. The sediments consist of till and glaciofluvial, glaciolacustrine and glaciomarine deposits. The Quaternary geology of the Ottawa area has been described by Fulton (1987) and Gadd (1986, 1988).

A typical cross-section of the drift cover reveals a layer of till, sometimes referred

to as hardpan, resting on top of bedrock. The till is mostly ground moraine less than 5 m thick (Kettles and Shilts 1987), but in the southwestern part of Gloucester, small drumlinoid structures have been reported at the surface (Owen 1953). Till thickness also increases significantly where it is found infilling pre-existing bedrock valleys (Wilson, 1990). The composition of the ground moraine reflects the nature of the rock on top of which it rests. Larger rock fragments originating from the crystalline bedrock of the Gatineau Hills can be found particularly in the northern portion of the study area.

Glaciofluvial deposits range from cross-bedded sand to coarse bouldery gravel. Locally "Black Gravel" has been encountered during well drilling, particularly near Ramsayville, Gloucester. It is so named because of its high content of shale from the Carlsbad and Billings Formations (Owen, 1953).

The most extensive surficial sediments are the massive clays deposited by the Champlain Sea. These are primarily composed of clay and silt-sized particles in thick beds. Mineralogically they are composed mainly of quartz, feldspar and amphibole, with illite and chlorite as the dominating clay minerals; illite being more abundant than chlorite (Torrance, 1988). The Champlain Sea deposits are found in flat plains in the Ottawa Valley, and are typically resting on top of varved fresh water clay. Associated with these deposits are near shore and beach deposits of sand. The greatest measured thickness of the Champlain Sea sediments is 100 m, at Treadwell 55 km downstream from Ottawa along the Ottawa River.

During and shortly after the last deglaciation, the changing course of the Ottawa River modified the Quaternary sediments and left behind remnants of river banks far from its present shores. Examples of such banks are found in the east-central portion of Gloucester beneath Dolman Ridge Road and Ridge Road.

The thickness of the drift cover varies greatly within the study area. This is partly due to the presence of bedrock valleys formed during some stage of erosion, and subsequent infilling by the overburden. In the area west of the Gloucester Fault, the bedrock is generally close to the surface, as deduced from the presence of outcrops, and from well-log records. The maximum depth to bedrock reported by Owen (1953) for that part of Gloucester is 32 m, in a location close to the Rideau River. East of the Gloucester Fault the depth to bedrock is generally greater, and several of the sampled wells in the central part of Gloucester have an overburden thickness near 60 m. The thickness of the overburden decreases to the north and towards the Gloucester Fault. At Carlsbad Springs it is approximately 16 m. The depth to bedrock is only 4 m at both Plantagenet Station and at Caledonia Springs (Elworthy, 1918).

2.3 General hydrogeologic properties of relevant bedrock units.

Water from the Carlsbad Formation commonly contains high levels of dissolved solids. Many of the investigated wells in Gloucester draw their water from the Carlsbad shale.

The Billings Formation usually produces water with a strong odour of hydrogen sulphide, and in some locations the groundwater is highly mineralized (Owen, 1953 and Brandon, 1960). Some of the wells, where the Carlsbad Formation has been indicated as the aquifer, may in fact be drawing their water from the Billings Formation. This is because the location of geological boundaries in relation to the wells is not exactly known, given the available data.

According to Owen (1953), shale beds within the Ottawa Formation can produce sufficient quantities of potable groundwater, while some limestone beds are quite massive and are not water-bearing. In wells that penetrate deeply into this rock unit it is possible to encounter mineralized water (Brandon, 1960). The saline springs at both Caledonia Springs and Plantagenet Station issue from the Lindsay Formation of the Ottawa Group (Hunt 1863, Elworthy 1918 and Williams *et al.*, 1985a and 1985b).

The March Formation is the best water-bearing formation in the area (Wilson, 1956) and the Oxford Formation is a fair to good source of groundwater (Owen, 1953 and Brandon, 1960). The Nepean sandstone provides good to excellent supplies of potable groundwater mainly from fractures (Owen, 1953 and Brandon, 1960). A few wells in this study are drilled into the Oxford to Nepean Formations.

2.4 General hydrogeologic properties of overburden.

Sand and gravel beds underlying marine clay and resting on top of bedrock are reported to yield the largest quantities of ground water. When the clay beds are more than 45 m thick, these aquifers tend to contain saline water. Occasional sand lenses within the clay may provide sufficient groundwater for domestic use, but they are local in occurrence and intersected by chance (Owen, 1953).

The clay and silt are not producing any significant amounts of groundwater. They may supply adequate amounts for domestic use, if the well has a large enough diameter. Most of the shallow wells in Gloucester draw their water from the clay or sandy horizons in the clay sequence. Sand overlying the clay may provide enough potable ground water if the thickness of the sand bed is more than 3.6 m (Owen 1953).

3 GEOCHEMISTRY.

Groundwater and associated gas were sampled during the period January to March of 1993 for selected wells in the main study area. The sample locations are also the three springs at Carlsbad Springs (Figure 3b) and the three springs at Caledonia Springs (Figure 3c). The spring at location Plantagenet Station (AB 93-34) included in this study is shown in Figures 1 and 2.

The selection of wells for sampling was based on well records from the Ontario Ministry of the Environment and the report on groundwater resources in Gloucester by Owen (1953). The well data are given in Appendix 1. The primary criterion was to select wells that were listed as containing saline and/or sulphurous water. For the purpose of comparison, some wells with relatively fresh water were also selected. In this group are included three analyses from the study by Sager-Kinsman (1995) on groundwater in the Manotick area.

3.1 Sampling procedure.

The springs and five of the wells were sampled directly through bailing, as they are not currently in use. The remaining well water samples were collected from wells that supply residences, public buildings, industries and barns. When domestic wells were being sampled, the water was usually collected from the kitchen sink tap, two

LEGEND

Sample location, type and number AB 93/94-:

- x Well finished in bedrock
- o Well in overburden
- s Spring
- r Outcrop

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

Figure 3a. Map showing the location of samples collected in Gloucester, with bedrock geology from Williams et al. (1984 and 1985a).

Figure 3b. Location of the springs in relation to each other at Carlsbad Springs.

Figure 3c. Location of the springs in relation to each other at Caledonia Springs.

of the samples come from bathroom taps and one from a tap in a basement. In all cases, any existing water-treatment system was by-passed. Industrial and barn wells were sampled from taps drawing water directly from the wells.

At each tap location, the water was allowed to run for 5-10 min. or longer if considered necessary, before sampling commenced, in order to make sure that the water was coming directly from the well. Temperature, conductivity and pH were measured on site. Alkalinity was measured using a HACH-kit titration, and the obtained value was converted to ppm HCO_3^- . Two 250 ml bottles were filled for geochemical analysis, one for anion composition and one for metals. Water for the latter was filtered and nitric acid was added as a preservative. The geochemistry sample bottles were sent to Bondar-Clegg for chemical analysis using ion chromatography and ICP (Appendix 2 and 3) within a couple of days. A 60 ml bottle of water was collected for strontium, oxygen and hydrogen isotope analyses. In a few selected locations, a one litre sample was taken for the purpose of ^{34}S and ^{13}C isotope analyses. Whenever it was necessary to store samples prior to analysis, an effort was made to ensure cold storage.

Gas samples were collected at eight locations using a glass bottle with an attached funnel. These were filled with sample water and then turned upside down in the water. As the gas bubbles rose through the water column, they displaced the water and were collected in the bottle. The funnel was removed, and the cap was replaced tightly while the bottle was still upside down in the water. The gas samples were analyzed on a gas

chromatograph (Appendix 4) in the chemistry department at Carleton University.

Chip samples from rocks representing the different aquifer units found in the study area were collected from core obtained during drilling on the Carleton campus (Wilson, 1990) and Algonquin College. Shale of the Carlsbad Formation was not present in these sections. However, it was possible to obtain a sample from the drilling of the hole from which groundwater sample AB 93-22 was collected. In addition outcrop samples of both Carlsbad and Billings shale were collected in the Ottawa area. Rock samples were analyzed for their chemical composition by means of X-ray fluorescence at the University of Ottawa, and the results are presented in Appendix 9.

3.2 Results and discussion.

Geochemical data for all groundwater samples are given in Appendix 4.

Groundwater can be classified according to its total dissolved solids (TDS) content as follows (Freeze and Cherry, 1979 p.84):

- <1 000 ppm = fresh,
- 1 000-10 000 ppm = brackish,
- 10 000-100 000 ppm = saline,
- >100 000 ppm = brine.

An examination of the chemical data in Appendix 4 shows that ground waters sampled for this study are either fresh or brackish. The most saline water samples have a TDS in the order of 10 000 ppm. The chemical data were analyzed using the following three methods.

The data were recalculated in milliequivalents (meq) and plotted in a Piper plot, which is a graphical illustration of the chemical character unrelated to TDS, of a group of water samples. The main purpose of the plot is to identify groups of water with similar chemical signatures and to delineate any mixing between water types.

A number of elemental plots were constructed in order to delineate the chemical character of the brackish waters. It was of particular interest to compare them to element ratios for seawater to determine whether or not they might be of seawater origin. A selection of those plots will be presented later in this chapter.

Finally, saturation indices were calculated using the computer program Wateq4F (Ball *et al.*, 1987). Saturation indices are discussed in conjunction with the element plots.

3.2.1 Piper plots.

3.2.1.1 Groundwater chemistry and aquifer types.

Figure 4 a-c show Piper plots for groundwater from the different aquifer types. The bedrock types present in the study area are the Carlsbad, Billings, Lindsay, Oxford, March and Nepean Formations. The Oxford, March and Nepean Formations effectively act as one aquifer in the Gloucester area (A. Sager-Kinsman, pers. comm.), and therefore will be referred to as Oxford in the following discussion. Wells AB 93-16 and 30 are located close to an inferred fault (see Figure 3a), and depending on their exact location with respect to the fault, they may be drawing their water from either the Carlsbad or Billings Formation. In the following discussion, these water samples are included in the group for which the Carlsbad Formation is considered to be the aquifer. It should also be kept in mind that in those locations where the Lindsay Formation is reported to be the aquifer, it may be that the water is actually coming from the Carlsbad Formation as discussed earlier.

A comparison of the diagrams reveals that groundwater samples from the Carlsbad and Lindsay Formations have the same chemical character, which is distinctively different from samples collected from the Oxford Formation.

Figure 4a. Piper plot of samples from Nepean-Oxford Formations (referred to in text as Oxford, samples AK are from Sager-Kinsman, 1995).

Figure 4c. Piper plot of groundwater from overburden.

The dominant cation in samples from the Oxford Formation is calcium with some magnesium (Figure 4a). By contrast, sodium is generally the dominant cation in the Lindsay and Carlsbad samples (Figure 4b). The dominant anion in the samples from the Oxford is bicarbonate, while in the Lindsay and Carlsbad samples it is chloride.

Overburden samples plot in a rather large area which partly overlaps that of the Nepean to Oxford samples (Figure 4c). Some of them are trending towards the sodium-chloride type waters found in the Carlsbad and Lindsay Formations.

3.2.1.2. Salinity.

As mentioned earlier, the groundwater samples in this study are fresh and brackish. In order to make the Piper plots easier to read, the brackish sample population was further subdivided into two arbitrary groups. Because there seemed to be a natural division at 5 000 ppm TDS, the following groups were defined:

Fresh water <1 000 ppm

Dilute brackish water 1 000-5 000 ppm

Brackish water >5 000 ppm

The compositions of the samples in each group are illustrated in Figure 5a-c. Table 2 is a summary of the main element composition of the different groundwater types discussed.

Figure 5b. Piper plot of brackish water, 5 000-10 000 ppm TDS.

Figure 5c. Piper plot of dilute brackish water, 1 000-5 000 ppm TDS.

Type	fresh	dilute brackish	type A	type B
No. of samples	18	9	10	3
Parameter	average (range)	average (range)	average (range)	average (range)
Cl (meq)	2.66 (0.05-7.4)	31 (11-60)	118 (84-155)	50.6 (7.8-80)
So ₄ (meq)	1.62 (0-4.8)	0.74 (0-5.2)	0.16 (0-0.69)	29 (15-39)
HCO ₃ (meq)	4.79 (1.1-10.4)	8.9 (0.70-16)	16 (11-22)	2.41 (2.0-3.2)
Na (meq)	3.05 (0.10-7.9)	33 (8.1-66)	120 (75-161)	50 (12-72)
K (meq)	0.17 (0.01-0.67)	0.31 (0.08-0.85)	1.03 (0.69-1.2)	0.42 (0.29-0.54)
Ca (meq)	3.39 (0.04-6.0)	3.3 (0.37-9.0)	1.28 (0.84-2.1)	21 (11-27)
Sr (meq)	0.04 (0-0.14)	0.06 (0.01-0.32)	0.11 (0.06-0.18)	0.27 (0.26-0.27)
Ba (meq)	0.001 (0-0.004)	0.02 (0-0.08)	0.06 (0.05-0.09)	0
Mg (meq)	1.86 (0.02-6.5)	2.8 (0.61-5.1)	11.5 (2.9-19)	5.5 (2.4-7.4)
pH	7.3 (6.5-8.8)	8.0 (7.2-8.3)	8.05 (7.7-8.8)	7.4 (6.8-7.9)
Conductivity (μ S/sec)	722 (280-1500)	3852 (2075-7270)	12398 (9240-16850)	6920 (3080-9450)

Table 2. Average and range of major ion content, pH and electrical conductivity for the different types of groundwater in this study.

The fresh waters are Ca,Mg-HCO₃ waters, as illustrated in Figure 5a, which is typical of groundwater in the limestone-dolomite terrain of the Nepean-Oxford Formations (samples AB 93-17,21,23, 24,26,27 and AK 93-43,44,48). This type of water is also found in overburden wells (AB 93-1,2,6,7,9a,14a,14b, and AB 93-9b,13 - possibly at contact with Oxford Fm.). Three of the fresh samples come from the Carlsbad Formation (AB 93-19,25,38). One of these samples, AB 93-38, is a Na-HCO₃ water, which is a product of ion exchange, where sodium from the shale aquifer replaces calcium and magnesium in the water.

The brackish water samples are plotted in Figure 5b. The dominant cation is Na, and Cl is the main anion. One of the brackish samples, AB 93-3, comes from overburden "black gravel", directly above the Carlsbad Formation. The aquifer material for the other samples in the group is Carlsbad Formation, except for the springs at Caledonia Springs and Plantagenet Station (AB 93-34 to 37), which are believed to issue from the Lindsay Formation. However, as mentioned earlier (page 13), there is a possibility that the aquifer material in these two locations also is the Carlsbad Formation. If this is the case, the occurrence of sodium chloride dominated brackish groundwater is strongly related to the Carlsbad Formation being the aquifer unit. Because there is a difference in chemical character between some of the brackish samples, they have been divided into two types of water. Type A is characterized by very low sulphate content, which in some samples equals zero. This type is defined by the following samples: AB 93-5,8,16,18,20,22,34-37.

Type B distinguish themselves from the type A group through the fact that although still Na-Cl water, they also contain Ca and SO_4 in significant amounts. This type group consists of the two samples AB 93-3 and 15.

The dilute brackish samples in Figure 5c plot in the area between the fresh Ca,Mg- HCO_3 and brackish Na-Cl waters. This indicates that they are mixtures between these two waters. The samples included in this group are AB 93-4,11,12,28,30,31,32,33,39 and 44. The aquifer material is Carlsbad Formation, except for sample AB 93-4 and 39 which come from overburden. Although its salinity is not as high as the two samples that define the type B group, sample AB 93-44 is also considered to be a type B water on account of its very high sulphate concentration. These three type B samples (AB 93-3,15 and 44) all come from the same fault block, which is bounded by the Gloucester Fault to the west.

3.2.1.3 Mixing between brackish and fresh water.

As shown by the dilute brackish waters, there is a mixing between the brackish water and the fresh water. Some of the fresh waters in Figure 5a also show a mixed signature, particularly those with a TDS nearing 1000 ppm (samples AB 93-25,26,23,24,2,7 and 13).

This mixing can be illustrated by historical data for the springs at Carlsbad Springs, whose relative positions are illustrated in Figure 3b. They have a chemical composition which is a product of mixing between type A or B water and water similar to freshwater

sample AB 93-38. A comparison with old chemical analyses (Elworthy, 1918 and Hunt, 1874) of the Carlsbad Springs reveals that the water from Magic Spring (AB 93-32) has changed dramatically. In 1874, the total mineral load of Magic Spring was in the order of 25 000 ppm and in 1917 it had declined to approximately 20 600 ppm. Today it has a TDS of approximately 1 600 ppm. The anion in the Magic water was more than 99% chloride in the previous analyses, while today Cl only accounts for approximately 60%, and 40% of the anion is bicarbonate. The cation composition has also changed from 75% Na, 17% Ca and 8% Mg to approximately 95% Na. The Lithia water has undergone a similar, although less dramatic, chemical change.

At the same time, the Gas Spring (AB 93-31) has maintained a relatively constant TDS and chemical composition. The explanation for this difference between the springs lies in the fact that the Magic water was rising from a 240 ft deep well (Elworthy 1918 p.35), which has since probably caved in and today the water is coming from a shallower depth. Unfortunately, there is no information as to what depth the Gas Spring may come from, but the Lithia water was said to come from a "vein" 60 ft deep, which according to records from nearby wells (MOE, 1976), places it in the clay or clay/gravel interface just above the bedrock surface. This illustrates the general impression in the area that the salinity of the groundwater increases with increasing depth.

3.2.1.4 Piper plots - discussion.

From the above, it is evident that the aquifer material has a strong influence on the chemical character of the groundwater. Sodium chloride groundwater with high TDS is never found in bedrock aquifers other than the Billings, Carlsbad and Lindsay Formations, and it is possible that these waters come from the Carlsbad Formation only (see previous discussion). On the other hand, the Oxford aquifer yields fresh groundwater with a calcium/magnesium bicarbonate chemical signature.

The strong relationship between groundwater chemistry and aquifer material is particularly evident in the area adjacent to the Gloucester Fault. In the area east of it, the Na-Cl brackish waters are found in or immediately above the Carlsbad Fm (samples AB 93-3,15 and 44). Immediately to the west, fresh water is found in the Oxford Formation and in the overburden on top of the Oxford Formation (samples AB 93-13,21 and 26).

3.2.2 Element plots and saturation indices.

In this section, the samples being discussed are the brackish and dilute brackish waters, unless otherwise stated, as they are the primary topic for this study. Seawater is often used as a reference in the plots because it has a relatively well defined average chemical composition. It is also of interest to compare the chemical composition of the groundwaters to that of seawater in order to evaluate whether the salinity is of Champlain

Sea origin.

In addition, the studied groundwaters are compared to analyses of typical shield brines (Frape and Fritz, 1987), sedimentary basin formation water (McNutt *et al.*, 1987 and Hitchon *et al.*, 1971) and groundwater occurring in sedimentary rocks where the salinity of the groundwater has been interpreted to be a product only of water-rock interaction (Von Damm, 1989 and Banner *et al.*, 1989). This water-rock interaction is primarily leaching of solutes from the host rock, but may also include ion exchange, mineral reactions and dissolution of evaporites.

Because formation waters often are found associated with petroleum in sedimentary basins, they are sometimes referred to as oil-field brines. Most of these groundwaters are considered to be of syngenetic origin, being seawater trapped in the pores of the rock at the time of deposition. At that point they may already be highly saline due to evaporation (Pauwels *et al.*, 1993). Subsequently, they have often undergone ultrafiltration (Graf, 1982), which concentrates the solutes, in addition to water-rock interaction (Hitchon *et al.*, 1971, Collins, 1975). Ultrafiltration is a process in which water is squeezed upward through a shale layer, while the solutes remain below the clay layer where they concentrate. If the original water is seawater trapped in the pores of the sediment, the resulting brine is far more concentrated than seawater. The water in such areas may also be produced by gypsum dehydration, or a mixture of the above, subsequently mixed with or even replaced by meteoric water falling as precipitation during more recent climatic

regimes (Hitchon and Friedman 1969, and McNutt *et al.* 1987).

3.2.2.1 Sodium.

Because the brackish groundwaters are of Na-Cl type, it seems quite likely that the relationship between sodium and chloride could aid in identifying the source of the salinity. In a plot of sodium against chloride (in meq), there is a linear correlation as illustrated in Figure 6. The samples show a closer fit to the halite dissolution line than to the seawater dilution line, especially for the higher TDS waters. This suggests that the salinity is not of seawater origin.

Data from previously cited literature are plotted in Figure 7. Unlike the brackish groundwaters in this study, shield brines (marked "M" in the plots) typically plot well below both the halite dissolution line and the seawater dilution line in Figure 7. This indicates that leakage of shield brines is not a likely source of the salinity.

Formation waters (indicated by "F") plot close to the 1:1 molar ratio line in Figure 7.

Although some water samples plot close to the seawater line, one of the few characteristics in common among groundwater from shale in different geographic areas is the Na/Cl ratio of one, as illustrated by the samples indicated by an "S" in Figure 7.

Figure 6. Plot of sodium versus chloride for all the brackish samples AB 93-.

Figure 7. Sodium plotted against chloride for different types of water where F=Formation Water, M=Canadian Shield Mine Water and S=Shale Water

Von Damm (1989) pointed to halite as being the control for this commonly observed 1:1 ratio of Na to Cl in shale groundwater throughout North America. This was concluded from the results of a three-pronged approach of data compilation (Von Damm, 1987), shale leaching experiments (Von Damm and Johnson, 1987) and reaction path modelling (Von Damm and VandenBrook 1988).

It cannot be ruled out that the brackish waters have a similar origin to a sedimentary basin formation water. However, given the evidence from Von Damm (1989), it is more likely that the ratios of Na to Cl of the groundwater in this study are products of interaction with the shale aquifer.

3.2.2.2 Potassium.

Potassium shows a linear correlation with chloride and a depletion relative to seawater as illustrated in Figure 8.

A comparison of the different types of saline groundwater indicate that most of them are depleted in potassium relative to seawater, with the exception of some formation water, as shown in Figure 9.

Potassium is the major ion most affected by cation exchange (Drever, 1988 p.240). It is both easily dissolved from rock-forming minerals during weathering and removed

Figure 8. Potassium plotted versus chloride for brackish samples AB 93-.

Figure 9. Plot of potassium versus chloride for different types of water where F=Formation Water, M=Canadian Shield Mine Water and S=Shale Water.

from solution to be included in secondary minerals such as phyllosilicates (Frape and Fritz, 1987). Because of the presence of clays and shales in the study area, cation exchange is likely to operate on the brackish waters.

In cation exchange calcium is most commonly adsorbed, and sodium and potassium are released. If calcium together with magnesium was originally balanced by bicarbonate and sulphate in a water, the cation exchange would result in a deficiency of calcium (and magnesium) relative to bicarbonate and sulphate. Therefore, a plot of the sum of calcium, strontium and magnesium against the sum of bicarbonate and sulphate may help identify cation exchange. Such a plot is presented in Figure 10 for the groundwater samples. It shows that indeed there is an excess of bicarbonate and sulphate in many of the groundwaters found in the Carlsbad and the Lindsay Formations. This agrees with the findings of Cerling *et al.* (1989), who used the same approach to identify cation exchange in streams draining shale terrain. By contrast, groundwaters from the Oxford Formation and overburden do not show such indications of cation exchange. Samples apparently most affected are relatively dilute brackish waters found in the Carlsbad Formation (AB 93-11,12,18,28,31-33). Cation exchange does not appear to play an important role in the waters with the highest chloride content, with the exception of AB 93-8. The depletion of potassium relative to seawater increases with increasing Cl content and is not more pronounced in AB 93-8 than in other brackish samples. Therefore, controls on the potassium content other than cation exchange must exist.

Figure 10. Plot of the sum of calcium, strontium and magnesium versus the sum of sulphate and bicarbonate for brackish and selected fresh water samples AB 93-.

3.2.2.3 Br/Cl ratio.

Special attention should be paid to the element Br. This is because, like Cl, it is a conservative element. If the waters are of seawater origin, although now diluted, they should have retained their Br/Cl (ppm/ppm) ratio characteristic of seawater, which is approximately 3.5×10^{-3} , as calculated from ocean water chemistry data given by Berner (1987), Hem (1985) and Pytkowicz (1983, p. 113). If the chloride and bromide come from halite dissolution, the Br/Cl ratio is in general lower than that of seawater, since Br tends to accumulate in a brine that is precipitating halite (Collins, 1975) rather than in the mineral. A Cl/Br value of 4000, corresponding to a Br/Cl ratio of 0.25×10^{-3} was used by Matray and Fontes (1990) for halite. Even though the Br/Cl ratio is considered to be conservative, there are processes that can alter it. Gerritse and George (1987) showed that leaching of decomposing soil organic matter can dramatically increase the Br/Cl ratio of groundwater.

The Br/Cl ratio is plotted against Cl (ppm) in Figure 11 for a selection of fresh to brackish groundwaters from the present study. Most of the brackish samples plot in an area slightly above the seawater line in Figure 11, with a few exceptions. Two samples, AB 93-30 and 32, have a Br/Cl ratio which is much higher than that of seawater, while sample AB 93-37 from the Gas Spring at Caledonia Springs plots well below the seawater line.

Figure 11. Plot of the Br/Cl ratio versus chloride for selected samples AB 93-. The horizontal line indicates the Br/Cl ratio for normal seawater.

Leaching of organic material present in the Carlsbad, Billings and Lindsay Formations could increase the Br/Cl ratio of seawater to produce the bromine enrichment observed for many of the brackish groundwater samples. The fact that the majority of the brackish samples plot in the vicinity of the seawater line may indicate that they are of this origin.

On the other hand, the Br/Cl ratio of sample AB 93-37 clearly contradicts seawater as the source of salinity in that sample. Instead, it could indicate halite as its source. Given its chemical similarity with the other brackish samples (see Figure 5b), there is no reason to believe that the source of salinity in sample AB 93-37 is different from that of the other samples. The anomaly of this sample could possibly be due to an analytical error, and no definite conclusions should be drawn on the basis of this sample alone.

The freshwater samples plot in a wide range of Br/Cl ratios from around 2×10^{-3} to 1×10^{-2} and one sample, AB 93-26, has a Br/Cl ratio identical to that of seawater. This means that a Br/Cl ratio around 3.5×10^{-3} is not exclusive to seawater, and is not uncommon in normal groundwater. Therefore, a Br/Cl ratio identical to that of seawater in a groundwater sample is not a conclusive piece of evidence for its seawater origin.

Shield brines usually have a higher Br/Cl ratio than that observed in the samples, as shown in Figure 12. Therefore, the Br/Cl ratios of the sampled groundwaters do not indicate leakage of a shield brine as responsible for their elevated salinities.

Figure 12. 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.

Formation waters tend to have a higher Br/Cl ratio than that of seawater, like the studied brackish waters. However, the range of Br/Cl ratios for formation waters is quite broad (Figure 12), and the fact that all of the waters in this study fall within it is not very indicative. The group of groundwaters which are considered to have acquired their salinity through interaction with shale bedrock alone tend to have Br/Cl ratios close to that of seawater (Figure 12). Like the brackish waters in this study, the range of Br/Cl ratios is relatively narrow. Given the evidence in this section, the observed Br/Cl ratio is most likely a product of interaction with the aquifer material. However, a seawater source cannot be dismissed.

3.2.2.4 Bicarbonate and sulphate.

As shown in Figure 13, bicarbonate is strongly enriched in the brackish waters with regard to seawater with comparable chloride concentrations. Bicarbonate shows a correlation with chloride in type A samples, which are the samples that contain no or very little sulphate, so sulphate in these samples is very depleted relative to seawater or non-existent (Figure 14). Samples that belong to group B, on the other hand, are rich in sulphate which show no correlation with chloride and are lower in bicarbonate compared to the type A group.

When looking at the characteristics of bicarbonate and sulphate concentrations in the groundwaters with regard to their origin, a simple comparison with the different categories

Figure 13. Plot of bicarbonate versus chloride for all brackish samples AB 93-.

Figure 14. Plot of sulphate versus chloride for all brackish samples AB 93-.

from the researched literature may not be indicative. This is because sulphate is controlled to a large extent by redox conditions that prevail in the aquifer. Under reducing conditions sulphate in groundwater is reduced to produce sulphide through oxidation of organic matter to CO_2 . Dissolution of CO_2 in turn produces dissolved carbonate species. Bicarbonate is therefore a product of sulphate reduction with the following stoichiometry:

At a pH above 7, $\text{HS}^- + \text{H}^+$ form rather than H_2S . If any reactive form of iron (Fe^{2+}) is present in the groundwater, iron sulphide will precipitate. The rate of reaction of the sulphate reduction process is very slow, unless mediated by bacteria. According to Collins (1975), the reduction may not take place at all if sulphate reducing bacteria are not present. Under oxidizing conditions sulphate is the stable form of sulphur. If any sulphides are present in the host rock, these may be oxidized to sulphate. Dissolution of gypsum may also add to the sulphate content.

The lack of sulphate in the type A samples, in combination with high bicarbonate values, indicates that sulphur reduction is an important process in the evolution of this water. The significantly higher sulphate concentration in the type B water (samples AB 93-3, 15 and 44) may be attributed to oxidizing conditions or lack of sulphur reducing bacteria in the part of the Carlsbad Formation immediately northeast of the Gloucester Fault.

3.2.2.5 Calcium.

Calcium shows a depletion relative to seawater only in the type A waters, as illustrated in Figure 15. Type B waters are enriched in calcium as compared to seawater with the same chloride content.

Shield groundwaters are also enriched in Ca relative to seawater (Figure 16), while the other two types of water plot in an area around the seawater mixing line. Therefore, a comparison based on the Ca versus Cl with these different types of water, does not add any new evidence for the origin of the brackish waters in this study.

The type B waters which come from an area immediately north-east of the Gloucester Fault, are distinctively different in their enrichment in calcium compared to the type A waters. They come from the Carlsbad Formation, like many of the type A waters. Therefore, there may exist a source of Ca unrelated to the aquifer type in this area of Gloucester. This will be discussed in section 3.2.2.7.

Figure 15. Plot of calcium versus chloride for all brackish samples AB 93-.

Figure 16. Plot of calcium versus chloride for different types of water where F=Formation Water, M=Canadian Shield Mine Water and S=Shale Water.

3.2.2.6 Strontium.

As illustrated by the plot of Sr against Cl (Figure 17), all of the brackish groundwater samples are enriched in Sr relative to seawater. However, the type B waters and sample AB 93-30 are enriched to a much larger extent than the type A waters. The stronger enrichment of Sr in the type B waters suggests that the source of Ca enrichment may also contain Sr, which is an element that frequently substitutes for calcium in calcium-bearing minerals. Enrichment of Sr is a feature that is shared with all the main groups of saline groundwater in Figure 18 and is attributable to water-rock interaction.

3.2.2.7 Source of Ca and Sr enrichment in type B waters.

The enrichment of Ca and Sr in the type B waters (samples AB 93-3, 15 and 44) is accompanied by elevated sulphate concentrations as illustrated by Figure 19. This may suggest that gypsum (and possibly celestite) dissolution is the source of the high Ca and Sr concentrations. Equilibration with gypsum and celestite is indicated by the fact that samples AB 93-3 and 44 are saturated with respect to both gypsum and celestite (Figure 20).

Literature on the Palaeozoic Formations found in the studied area does not mention the occurrence of gypsum in the Carlsbad Formation itself. However, Guillet (1964) reported the occurrence of a 1.5 m thick layer of gypsum in the Oxford Formation in the

Figure 17. Plot of strontium versus chloride for all brackish samples AB 93-.

Figure 18. Plot of strontium versus chloride for different types of water where F=Formation Water, S=Shale Water, M=Canadian Shield Mine Water.

Figure 19. Calcium and strontium plotted against sulphate for all brackish samples AB 93-.

Figure 20. Plot of saturation indices of celestite and gypsum for all brackish samples that contain sulphate.

Cornwall area. Thin gypsum layers have also been found in drillcore from the Geological Survey of Canada borehole at Lebreton St. in Ottawa (Michel, pers. comm.). It is possible that a similar situation occurs in the Oxford Formation close to the Gloucester Fault. Gypsum and anhydrite were also found in the Ottawa Valley by Sawford (1972). These minerals replace halite together with calcite in moulds contained in rocks belonging to the Pamelaia faunal zone of the Ottawa Formation. Celestite moulds in the same rock unit were also reported by Sawford (1972). Gypsum and celestite dissolved in the groundwater from either the Ottawa or Oxford Formation may be brought up along the Gloucester Fault and into the Carlsbad Formation.

Figure 19 also reveals that the type B samples (AB 93-3,15 and 44) are enriched in sulphate compared to the sulphate mineral dissolution line. Therefore, a source of sulphate other than gypsum also has to be considered. Oxidation of sulphide that is known to be present in the Carlsbad Formation is a very likely additional source of sulphate.

Another explanation for the $\text{Ca}+\text{Sr}/\text{SO}_4$ ratio not being equal to one, could be that Sr and Ca are not coming from the same mineral as SO_4 . Williams (1991) described occurrences of veins that contain celestite and barite, sometimes together with calcite, fluorite, galena and sphalerite. These are associated with faults, particularly in or near fault junctions in the Ottawa-St. Lawrence Lowland. According to Williams (1991) it is quite likely to find other such occurrences associated with faults and fault junctions in other locations in the lowlands. Calcium, strontium and sulphate in the groundwater could

be the product of interaction with such a vein associated with the Gloucester Fault. Dissolution of calcite, fluorite and celestite would result in elevated levels of calcium and strontium in the groundwater. At the same time oxidation of the sulphide minerals or dissolution of the sulphate minerals would be responsible for the dissolved sulphate. However, barite and celestite are not very soluble minerals, and these minerals would probably not account for any significant amounts of the sulphate in the water. Therefore, in such a situation most of the sulphate would come from the oxidation of sulphide minerals such as galena, sphalerite and pyrite. Lead, zinc and iron would then also be present in these groundwater samples, but neither lead nor zinc were reported in any of the type B groundwater analyses (see Appendix 4). These waters contain some iron, but since this can have other sources such as sedimentary pyrite in the shale, iron is not indicative on its own.

Given the above discussion, the elevated levels of calcium, strontium and sulphate, are most likely to originate from gypsum and celestite in the Palaeozoic rocks. This source is probably also responsible for the elevated Sr concentration noted earlier in sample AB 93-30.

In a later chapter (section 4.5.2 and 4.4.3.4) sulphur and strontium isotopic data will be discussed, and will provide additional information on the source of these constituents.

3.2.2.8 Magnesium.

Magnesium shows a linear correlation with chloride and a depletion relative to seawater as illustrated in Figure 21.

Cited literature on other types of groundwater relates the Mg concentration to processes taking place in the aquifer, and the Mg content of the aquifer. In shield brines the relationship between magnesium and chloride does not show a consistent pattern for all locations. This can be seen by the scatter of data in Figure 22. Groundwater samples from any one mine site do show either a consistent enrichment or depletion in Mg compared to seawater. The magnesium content of the host rock is believed to be the main control on the magnesium content of the groundwater in the Canadian Shield (Frape and Fritz, 1987).

Most formation waters are depleted in magnesium with respect to seawater (Figure 22). The removal processes that have been identified are formation of chlorite from montmorillonite, and dolomitization (Hitchon *et al.*, 1971, and Collins, 1975). Groundwaters from shales are also depleted in Mg relative to seawater (Figure 22). Von Damm (1989) referred to carbonates as being one of the controlling factors on the chemistry of groundwater from shale.

Figure 21. Plot of magnesium versus chloride for all brackish samples AB 93-.

Figure 22. Magnesium plotted against chloride for different types of water where F=Formation Water, M=Canadian Shield Mine Water and S=Shale Water.

Since processes taking place in the aquifer seem to have such a strong control on the magnesium content of groundwater in this study, as well as in others, the Mg/Cl relationship does not offer any indication of the source of the salinity in the brackish groundwaters. However, the Ca/Mg ratio can give an indication of those processes that take place in the aquifer. As already mentioned, carbonate dissolution and precipitation may be significant and will be discussed below.

3.2.2.9 Ca/Mg ratio in type A waters.

Above a Cl concentration of approximately 1700 ppm (48 meq) a consistently low Ca/Mg ratio is observed in the type A waters and the dilute brackish samples AB 93-12 and 28. The Ca/Mg ratio has a value of 0.07-0.18 (Figure 23). The saturation indices of the same samples indicate supersaturation with respect to dolomite. They are, with the exception of samples AB 93-35 and 18, also supersaturated with respect to calcite, but to a lesser extent (Figure 24).

A mechanism that can explain the observed conditions is dissolution of dolomite and calcite with subsequent precipitation of calcite, after reaching supersaturation. At the same time magnesium remains in solution until supersaturation with respect to dolomite occurs. According to Hem (1985), dolomite dissolution is not readily reversible and dolomite does not tend to precipitate under conditions found in natural-water environments. In fact precipitate that forms from a solution that has attacked a magnesium limestone may be

Figure 23. Plot of the Ca/Mg molar ratio versus chloride for all brackish samples AB 93-.

Figure 24. Plot of the saturation index for dolomite and calcite in all brackish samples AB 93-.

nearly pure calcite. In such a system, the Ca/Mg ratio decreases as a product of long residence time and very low Ca/Mg ratios may be attained down a flow path (Hem, 1985).

Hem (1985) referred to sulphate reduction as a mechanism for replenishing CO₂. This may produce a system that resembles one that is open to CO₂, so that more carbonate is dissolved than expected in a system closed to the atmosphere. Plummer and Back (1980) described such a model for the Floridian aquifer. As indicated above, sulphate reduction is probably taking place in the brackish groundwaters in the present study. The addition of carbon dioxide through this reaction may be the driving force in the continuing dissolution of dolomite and calcite in the Carlsbad, Billings and Lindsay Formations.

Contrasting with the type A waters, the type B waters and AB 93-30 have a Ca/Mg greater than 1 and, except for AB 93-3, they are also undersaturated with respect to both calcite and dolomite. In the type B waters this is probably an effect of the high sulphate and calcium content, causing calcite to precipitate as a result of the common ion effect.

3.2.3 Gas samples.

Gas samples were collected at eight sites; wells AB 93-12,20,38 and springs AB 93-8,31,33,34 and 40. Samples AB 93-8,20 and 34 are associated with type A brackish water and samples AB 93-12,31 and 33 with dilute brackish waters. AB 93-38 is the only gas

sample occurring together with fresh water. AB 93-40 comes from White Sulphur Spring in Carlsbad Springs. This spring is now flooded by the meandering of Bear Brook. Therefore the gas sample was collected after its passage through the brook and no water sample accompanies it. The presence of gas was not detected in any of the three type B water sample locations.

The analyses obtained on the gas samples are presented in Table 3. These values are the mean of two runs (in some cases three runs). From the repeat runs, it is estimated that the results are reproducible within ± 1 percentage points for the major components and ± 0.1 percentage points for the minor constituents of the gas mixtures.

sample number, type of site	AB 93-8, flowing well	AB 93-12, tap in barn	AB 93-20, tap in barn	AB 93-31, spring
O ₂	0.4	8	18	0.5
N ₂	18	29	72	29
CO ₂	0.6	0.3	0.2	0.8
CH ₄	81	62	10	70
sample number, type of site	AB 93-33, spring	AB 93-34, spring	AB 93-38, tap in barn	AB 93-40, spring
O ₂	0.2	0.2	17	1.6
N ₂	20	31	69	21
CO ₂	0.2	1.0	0.0	0.6
CH ₄	79	67	14	77

Table 3. Composition of gas samples in percent.

The main constituents in all of the gas samples from the springs and the flowing well (AB 93-8) are methane and nitrogen (Table 3). The presence of methane is also indicated in the samples from taps, but these also contain varying proportions of oxygen. Because the spring samples are almost free of oxygen, it is suspected that the higher oxygen content in the well samples may be due to contamination from air entering the system between the well and the sampling point. The proportions of the gas constituents from the springs and the flowing well are approximately 70-80% methane and 20-30% nitrogen, with less than two percent each of oxygen and carbon dioxide.

Methane and nitrogen can be produced from the degradation of organic material in two different ways. First, there is the bacteriologically mediated decay of organic matter in an anaerobic environment at a low temperature. Secondly they can be produced through metamorphism of kerogen in the production of petroleum.

The reactions of interest for this study that are involved in the bacteriological decay of organic matter involve denitrification:

and fermentation:

In the absence of oxygen these reactions that oxidize organic carbon take place in a particular sequence which also contain sulphate reduction in accordance with progressively lower Eh. With decreasing Eh, denitrification is the first of the reactions to take place, followed by sulphate reduction which occurs at an Eh almost as low as fermentation. The sequence is generally strict, so that sulphate reduction does not occur until all nitrate has been used up, and neither does methanogenesis take place before all sulphate has been consumed. This decrease in Eh is coupled with the evolution of groundwater from recharge (Champ *et al.* 1978), and therefore residence time. Anaerobic bacteria that produce methane tend to be active at relatively shallow depths (Tiratsoo, 1979 p.34). In addition, biogenic production is more favoured in unconsolidated sediments, and is unlikely to take place in consolidated sediments. According to Kinghorn (1983 p.258), this is because the pore spaces in even poorly consolidated shales are too small to accommodate the methane producing bacteria. However, this is contradicted by the presence of bacteriologically produced methane in the Canadian and Fennoscandian Shield rocks, which was described by Lollar *et al.* (1993).

Methane can also be produced during late stage catagenesis and metagenesis of petroleum formation as illustrated in Figure 25. The late stage catagenesis produces wet gas, which is a mix of oil and gas. Metagenesis occurs at higher temperatures to produce hydrocarbons with a low carbon number, primarily methane, so called dry gas.

Temperature, degrees Celsius	Organic metamorphic facies	Associated hydrocarbons	CAI
60	Immature	Early dry gas, wet gas and oil	1.5
	Incipient maturation		
			2.0
90	Mature (Liquid window)	Heavy to light oil and wet gas	2.5
120			3.0
185	Supramature	Dry gas or barren	4.0

Figure 25. Stages in petroleum formation and correlation with approximate burial temperature and conodont alteration index, after Legall *et al.* (1981). The shaded area indicates conditions applicable to the study area.

Legall *et al.* (1981) used the conodont colour alteration index (CAI) to evaluate the degree to which Palaeozoic rocks in eastern Ontario have undergone petroleum forming metamorphism. They concluded that although the area has not been deeply buried, the CAI of 2.5 in the Ottawa-Hull area and 3.0 immediately to the east, indicate that the rocks have been heated to temperatures in the range of 85-120°C. This temperature corresponds to the production window for wet gas, and borders the region for dry gas production as shown in Figure 25 (Legall *et al.*, 1981). Small amounts of oil and gas have been encountered during test drilling in the study area (Petroleum Resources Centre, 1994).

Hydrogen sulphide was found to be associated with the brackish samples AB 93-22,35,36 using a HACH field measuring kit, and as noted in section 3.2.2.3. there is strong evidence of sulphate reduction in the type A waters. Despite this, none of the gas analyses indicated the presence of hydrogen sulphide, which is a gas commonly associated with both bacteriologically and thermogenically produced methane. Neither was any hydrogen sulphide odour detected at the particular gas sample sites. However, depending on the composition of the source material, the gas may lack hydrogen sulphide. If hydrogen sulphide is produced, it can also be removed either through sulphide precipitation or selective migration, or a combination of the two. Selective migration is a process through which only one gas in a gas mixture migrates away from the point of production. Hydrogen sulphide is an easily dissolved and transported gas with extremely high mobility (Pearson and Rightmire, 1980), while nitrogen is inert. Therefore, hydrogen

sulphide tends to migrate and nitrogen tends to stay where it is formed. Since the groundwater samples have pH values above 7, HS^- dissolved in the groundwater rather than H_2S gas would be expected to be present resulting from sulphate reduction. Therefore, sulphide thus produced is most likely to have precipitated as sulphide minerals. Fracture filling pyrite is commonly found in the shales in the study area as indication of this process.

The gas may on the other hand be abiotic and similar in origin to the gases found in the Canadian Shield. If this is the case, the gases could originate from the Canadian Shield rocks that underlie the Palaeozoic rocks of the Ottawa Valley. The gases would have ascended from great depths along faults. According to Williams *et al.* (1984), there is a fault at Carlsbad Springs in the vicinity of the springs. Like the gas samples in this study, abiogenic gases found in the Canadian Shield do not contain hydrogen sulphide, as indicated by analyses presented by Fritz *et al.* (1987a). Therefore, on the basis of the gas composition, this source cannot be ruled out.

Isotopic analysis of the carbon in the gas samples identifies their origin with greater certainty in section 4.7.

3.3 Geochemistry-discussion.

The Piper plots show that the brackish Na-Cl waters occur only in the Billings,

Carlsbad and, possibly, Lindsay Formations. By contrast, fresh groundwater with a Ca/Mg-HCO₃ chemical signature is found in the Nepean, March and Oxford Formations. This on its own suggests that the salinity is bedrock related.

Most of the brackish samples have very little to no sulphate and a low Ca/Mg molar ratio (<1), and have been labelled type A waters. The brackish groundwater samples have in general a 1:1 molar ratio of Na and Cl, which is consistent with the type of water commonly found in shales in North America. The water chemistry of groundwater migrating through shale is strongly influenced by halite, carbonate and reduced species such as pyrite and organic matter. They have a neutral to alkaline pH and HCO₃⁻ is the second most important anion (Von Damm, 1989). The chemistry of the brackish waters in this study are very similar to these shale-related groundwaters. This is, in addition to the Na/Cl molar ratio, also indicated by the Ca/Mg molar ratio and the presence of methane and nitrogen in associated gases being a product of the organically mediated reduction processes of fermentation and denitrification, together with the absence of sulphate in most of the waters (e.g. type A samples).

Some of the samples, although sharing their 1:1 molar ratio of Na to Cl with the type A waters, have elevated levels of calcium, strontium and sulphate and are denoted as type B waters. All of the type B samples come from the same fault block, immediately east of the Gloucester Fault, which suggests that there may be an additional source of calcium, strontium and sulphate associated with this part of the Carlsbad Formation. There is no

evidence of sulphate reduction in the form of hydrogen sulphide odour in the type B waters, although one would expect reducing conditions in a shale. The lack of hydrogen sulphide could be an indication of oxidizing conditions or it may be that sulphate reduction is not taking place in the type B waters because sulphate reducing bacteria are lacking in this part of the Carlsbad Formation. It is also possible that pyrite is formed rather than H_2S from the reduction process.

The above described chemical characteristics are also shared with formation waters found in sedimentary basins in North America. In areas such as the Western Canadian Sedimentary Basin, Illinois Basin and Michigan Basin, brines and saline water are found in sedimentary rocks associated with oil and gas accumulations. Because formation waters may also be found in shales, the interaction with the bedrock which controls the chemical character of the shale groundwater also influences the nature of the formation water. Other chemical characteristics of the brackish groundwater which are similar to both shale groundwater and formation water are the Br/Cl ratio and the depletion of potassium relative to seawater. Therefore, with respect to the chemical composition of the brackish groundwaters in this study, it may not be possible to discriminate between shale groundwater and formation water. However, because the interaction between groundwater and bedrock takes place at different temperatures for the two types and because ultrafiltration is an additional process affecting formation water but not shale groundwater, the two water types show isotopic differences, as is discussed in section 4.2.

The only source for the salinity in the brackish groundwaters that can be excluded at this point is a shield brine, primarily on account of its Br/Cl, Na/Cl and Ca/Cl ratios compared to most of the studied groundwaters.

Geochemical processes such as sulphate reduction and carbonate dissolution-precipitation control the composition of the groundwater. It is not possible to determine if the brackish groundwater is trapped Champlain Sea water since these processes would mask the original ionic proportions of sulphate, bicarbonate, calcium, strontium and magnesium. The observed 1:1 sodium to chloride molar ratio and the depletion of potassium relative to seawater are not consistent with a seawater source. Cation exchange would resolve these discrepancies, but was not indicated as an important process in the evolution of at least the most saline of the brackish groundwaters. However, there may be other processes not considered in this study that would modify a seawater signature to produce the observed relationship between sodium-potassium and chloride. The only geochemical evidence that is consistent with a seawater source is the Br/Cl ratio, but it is inconclusive.

Based on the geochemical evidence and the spatial correlation between brackish groundwater and shale bedrock, the most likely source for the salinity is water-rock interaction, either at low temperatures at the shallow depths where they are found today, or following the evolutionary path of formation water involving deeper burial.

4 ISOTOPE GEOCHEMISTRY.

4.1 Introduction.

Oxygen, hydrogen, strontium, sulphur and carbon isotopic compositions have been determined for selected samples in this study. The radioactive isotopes of hydrogen (^3H or tritium) and carbon (^{14}C) were also used to provide an age estimate of one of the samples in this study.

The stable isotopic signature of a given element in a sample is expressed as its delta value, which is the per mille deviation of the isotopic ratio of the sample (R_X) from that of a standard (R_{STD}):

$$\delta_X = [(R_X/R_{\text{STD}}) - 1] \times 10^3$$

The ratio R is: for oxygen $^{18}\text{O}/^{16}\text{O}$, for hydrogen $^2\text{H}/^1\text{H}$, for sulphur $^{34}\text{S}/^{32}\text{S}$, and for carbon $^{13}\text{C}/^{12}\text{C}$. The standard used depends on the element for which the isotopic ratio is analyzed. For the present study the standard used for oxygen and hydrogen is Standard Mean Ocean Water (SMOW), for carbon it is the Pee Dee Belemnite (PDB) and for sulphur it is Troilite from the Canyon Diablo iron meteorite (CDT). The routine precision (2σ) is ± 1.3 per mille for hydrogen, ± 0.10 per mille for oxygen, ± 0.20 per mille for sulphur and ± 0.10 per mille for carbon. Sample preparation and analytical procedures are

described in Appendix 5.

Unlike the stable isotope ratios described above, the strontium isotope composition is expressed as the ratio $^{87}\text{Sr}/^{86}\text{Sr}$. The routine precision (2σ) is ± 0.000025 .

The tritium content was measured as tritium units (T.U.), which is equal to an abundance of one atom of ^3H per 10^{18} atoms of hydrogen, with a precision of ± 8 T.U.

The radiocarbon content was measured as the percentage of modern carbon in the dissolved carbonate with a precision of $\pm 0.24\%$.

4.2 Oxygen and hydrogen isotopes.

The stable isotope composition of water is a product of the origin and mixing history of the water. Seawater has a $\delta^{18}\text{O}$ and $\delta^2\text{H}$ value close to 0 per mille by definition, since the isotopic ratios are measured relative to SMOW. Precipitation plots on a line, which has a slope and intercept dictated by local geographic and climatic conditions. Fritz *et al.* (1987b) defined this empirical relationship for the Ottawa Meteoric Water Line (OMWL) as $\delta^2\text{H} = 7.63\delta^{18}\text{O} + 6.53$. The Global Meteoric Water Line is an average of local meteoric water lines worldwide, and has been defined as $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$. It is used as a reference in areas where a local meteoric water line has not been defined, or for old groundwaters of unknown origin.

The $\delta^{18}\text{O}$ (and $\delta^2\text{H}$) relates to mean monthly surface temperature according to an empirical equation which is site specific. Dansgaard (1964) was the first to define this relationship, using data from North Atlantic coastal stations, as:

$$\delta^{18}\text{O} = 0.695T - 13.6, \text{ where } T = \text{mean annual air temperature in } ^\circ\text{C}$$

In general, precipitation falling during the winter is isotopically lighter than summer rains (Gat, 1980). The seasonal difference in oxygen isotope composition is smoothed out in the cumulative $\delta^{18}\text{O}$ for a year, yielding an average value which reflects the mean annual air temperature. This smoothing out of seasonal differences is also observed in groundwater where the water recharged at different temperatures and times of the year undergo mixing.

For the Ottawa area, Fritz *et al.* (1987b) presented the following formula relating oxygen isotope composition in precipitation to mean annual air temperature:

$$\delta^{18}\text{O} = (0.53 \pm 0.13)T - (14.44 \pm 0.86)$$

The general relationship between temperature, latitude and altitude is also reflected in the stable isotope composition of precipitation on a continental scale. The latitude effect in North America is approximately -0.5 per mille/degree latitude increase and the altitude gradient is -0.15 to -0.5 per mille/100 m elevation increase (Gat, 1980).

Different processes, such as evaporation, interaction with aquifer minerals or gases cause the isotopic signature of groundwater to deviate from its original composition. Figure 26 illustrates the effect of these processes on meteoric water. Ultrafiltration causes an enrichment of both ^2H and ^{18}O , the enrichment of ^{18}O being more pronounced and causing the stable isotope composition of originally meteoric water to plot to the right of the local meteoric water line. Interaction with carbonate minerals leads to an enrichment in ^{18}O , while formation of clay minerals causes a depletion of ^{18}O . Interaction and exchange with clay minerals also produces a depletion in ^2H (Kharaka and Carothers, 1986). The magnitude of all the alteration processes is dependent on several factors. These are the original isotopic compositions of the minerals and water, and temperature. In general, the higher the temperature, the larger the effect is on the stable isotope composition of the groundwater.

The evolution of sedimentary basin brines involves many of the above processes. These, in combination with the marine origin of most of the basin brines, produce the stable isotope composition observed in formation waters from the Illinois, Michigan and Western Canadian Sedimentary Basins and similar environments elsewhere in the world (Clayton *et al.*, 1966; Hitchon and Friedman, 1969; Graf, 1982; McNutt, 1987 and Pauwels *et al.*, 1993), as illustrated in Figure 27. The stable isotope composition of average seawater is also plotted in this figure.

Figure 26. Alteration processes which affect the stable isotope composition of meteoric water. After Welhan (1987).

Figure 27. Stable isotope composition of basin brines and formation water. After Longstaffe (1987), McNutt *et al.* (1987) and Clayton *et al.* (1966). Shown are also the Global Meteoric Water Line and the Ottawa Meteoric Water Line.

4.2.1 Results.

Twenty-seven samples were analyzed for their oxygen and hydrogen isotopic compositions using gas source mass spectrometers in the Department of Earth Sciences at the University of Ottawa: triple collector VG SIRA 12 for oxygen and double collector VG 602D for hydrogen. Most of these are brackish waters, but the fresh groundwater samples AB 93-13,17,21,26 and 38 were also included in the analysis for comparison purposes. The measured values are listed in Appendix 6.

Figure 28 shows the measured values plotted together with the Ottawa Meteoric Water Line (OMWL) as defined by Fritz *et al.* (1987b). The samples in this study fall on or near the OMWL and within the range of precipitation for Ottawa given by Fritz *et al.* (1987b), indicating that the water samples are of meteoric origin.

One of the samples, AB 93-30, has a much lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ value than the rest of the sample population. It has not been included in most of the data processing, because the reason for its significantly different stable isotope composition is not known. It may be caused by mixing with meltwater from the spring thaw, since the sampling of that particular well took place in early May. A mass balance calculation was carried out in order to evaluate the possibility that the $\delta^{18}\text{O}$ and salinity of sample AB 93-30 is a product of dilution of a more saline groundwater with meltwater. In the calculation, the $\delta^{18}\text{O}$ of winter precipitation and the sample were used to estimate the proportions of the

Figure 28. Plot of the hydrogen isotope composition against the oxygen isotope composition for all samples analyzed.

two components in such a mixing system, as described in Appendix 6. Depending on the $\delta^{18}\text{O}$ values assigned to the meltwater and the undiluted groundwater, it was found that the sample could contain 60-70% meltwater and 30-40% of a groundwater with a TDS of 6740-9200 ppm. This TDS value is consistent with the range observed for many of the samples in this study, indicating that the $\delta^{18}\text{O}$ of sample AB 93-30 is likely to be a result of mixing between groundwater and meltwater in the unused well.

4.2.2 Co-variance of TDS and $\delta^{18}\text{O}$.

An inspection of the plot of $\delta^{18}\text{O}$ versus TDS in Figure 29 (where the anomalous value of AB 93-30 has been excluded), reveals that there is a poor correlation between TDS and $\delta^{18}\text{O}$ ($r^2=0.30$). The correlation factor (r^2) is small, indicating that there are other factors also governing the stable isotope composition of the groundwater. A positive correlation between $\delta^{18}\text{O}$ and TDS is commonly found in saline groundwater where fresh groundwater mixes with a highly saline groundwater which has a stable isotope signature that is heavier than that of the fresh groundwater. Such a correlation would be observed both if the salinity is from a sedimentary basin brine or of Champlain Sea origin. Mixing models involving these two end members, and their validity will be discussed in the following sections.

Figure 29. Plot of TDS versus $\delta^{18}\text{O}$ ($r^2=0.30$ for regression line).

4.2.2.1 The Champlain Sea.

Since the groundwaters do not have a salinity equal to seawater, a dilution with fresh groundwater is indicated if trapped Champlain Sea water is the source for the salinity. Because seawater plots to the right of the meteoric water line, as illustrated in Figure 27, the mixing between these two waters would produce a small but consistent deviation from the OMWL. The brackish waters with the highest salinity would contain the largest proportion of the seawater component. The higher the salinity, the larger the deviation from the OMWL. This relationship does not prevail among the sample population. As Figure 30 shows, some of the most saline groundwaters, such as AB 93-8, 16 and 22 (with 7799, 9977 and 9454 ppm TDS respectively), do plot on the OMWL. However, as Figure 30 also illustrates, the difference in stable isotope composition for the range concerned between meteoric groundwater and dilute seawater is not large enough to distinguish with certainty between the two.

Several authors have investigated the oxygen isotope composition of biogenic carbonates deposited in the Champlain Sea, and the paleo-salinity of the sea (Hillaire-Marcel, 1988; Wassenaar *et al.*, 1988 and Rodrigues, 1992). Their general conclusion is that the water in the Champlain Sea varied in salinity due to dilution with glacial continental run-off which had a light oxygen isotope composition. The inferred $\delta^{18}\text{O}$ of the seawater component in the mixing system is close to 0 per mille. The $\delta^{18}\text{O}$ value for the glacial meltwater varies within a relatively wide range from -45 to -25 per mille

Figure 30. Plot showing the stable isotope composition of the brackish groundwaters. Shown are also the OMWL and a line illustrating mixing between seawater and average local meteoric groundwater.

according to Wassenaar *et al.*(1988) or from less than -30 to -16 per mille (Hillaire-Marcel, 1988). With an average $\delta^{18}\text{O}$ value for lakes and rivers of -8 to -16 per mille, continental run-off that discharged into the Champlain Sea had, during most of the sea's existence, a $\delta^{18}\text{O}$ of -16 per mille. The mixing line by Hillaire-Marcel (1988) for the two end members contributing to the Champlain Sea is shown together with data from this study in Figure 31. It shows that the data points all plot below the Champlain Sea mixing line. If the salinity in the groundwater is of Champlain Sea origin, mixing with a third low TDS component is necessary to explain this dilution. This component would most likely be modern fresh groundwater (recent precipitation).

If the regression line in Figure 29 is regarded as a mixing line for modern groundwater, it should intersect the Champlain Sea mixing line at some point in order for this three component mixing model to be valid. When the regression line is extrapolated to a $\delta^{18}\text{O}$ which corresponds to that of seawater (0 per mille) it is found that the two lines never intersect, as shown in Figure 31. The TDS corresponding to the seawater $\delta^{18}\text{O}$ is only 30 000 ppm for the extrapolated regression line. This does not support the Champlain Sea as the source for the salinity in the groundwaters in this study.

It may be argued that the regression line does not describe the mixing between modern fresh groundwater and Champlain Sea water because there is a wide range of $\delta^{18}\text{O}$ and TDS values along the Champlain Sea line, and therefore there are an infinite number of Champlain Sea end members. This would explain the scatter of data points and

Figure 31. Plot showing the mixing line for the Champlain Sea (after Hillaire-Marcel, 1987) and the regression line for the brackish groundwaters.

the poor correlation ($r^2=0.30$ for the regression line in Figure 29) between the two variables. Although it is true that the Champlain Sea did vary in salinity and oxygen isotope composition within the basin, the variation within any geographically restricted area within the basin was much more limited and did not cover the complete range of values. Furthermore, the Champlain Sea had a distinct density and salinity stratification, so that light continental run-off with a low salinity and light oxygen isotope composition existed at the surface. The salinity increased towards the bottom, where a wedge of high salinity seawater extended from the present mouth of the St. Lawrence River well into the Champlain Sea basin. Since it would be mainly the saline bottom water that infiltrated into the underlying sediments and bedrock, this puts a further constraint on the TDS and $\delta^{18}\text{O}$ of the Champlain Sea component in the study area. The salinities that Wasenaar *et al.* (1988) inferred from deep water invertebrate macrofossils for the bottom water fall in the range 25 to 35 per mille (approximately equivalent to ppm). A value of 27 per mille was given by Hillaire-Marcel (1988) for the Ottawa region throughout the Champlain Sea phase. Most of the data from this study plot between the limiting mixing lines defined by this TDS value for the Champlain Sea and local meteoric groundwater with a $\delta^{18}\text{O}$ from -12 to -10.5 per mille (Sager-Kinsman, 1995) as shown in Figure 32. However, some of the samples are not enclosed by this envelope, and therefore this Champlain Sea mixing model does not offer a completely satisfactory explanation for the observed relationship between $\delta^{18}\text{O}$ and TDS among the samples.

Figure 32. Plot showing the mixing line for the Champlain Sea (after Hillaire-Marcel, 1987) and the lines that define local mixing between fresh groundwater and Champlain Sea bottom water with a 27 000 ppm TDS.

4.2.2.2 Formation water.

As has previously been mentioned, less saline formation waters are usually mixtures between basin brines and more recent meteoric water. Oil-field basin brines are encountered in the Michigan sedimentary basin in southwestern Ontario in the same (Upper Ottawa Group) rock units that are found to contain brackish water in the Ottawa area (McNutt *et al.*, 1989). Therefore, it is quite possible that the brackish waters in this study originated in this way.

In Figure 33, a line illustrating the mixing between average meteoric groundwater and mean formation water from the Michigan basin in Ontario, as calculated using data from McNutt *et al.* (1989) is shown. As illustrated in Figure 33, this mixing produces a significant deviation from the OMWL which is not observed in this study. Therefore, it is concluded that the salinity of the groundwater is not of formation water origin.

4.2.3 Comparison between brackish and fresh groundwater.

In Figure 34, samples from the Manotick area (Sager-Kinsman, 1995), which are unnumbered, are plotted together with data for this study. The aquifers in Manotick are the Oxford, March and Nepean Formations. These groundwaters also fall on or close to the OMWL and have tritium values that indicate recharge since 1952 (Sager-Kinsman, pers. comm.). The fresh groundwaters of Sager-Kinsman, together with the fresh water

Figure 33. Plot showing the stable isotope composition of the brackish groundwaters. Shown are also the OMWL and a line illustrating mixing mean local meteoric groundwater and an average basin brine with $\delta^{18}\text{O} = -2.2$ per mille, $\delta^2\text{H} = -29.4$ per mille and TDS = 228 128 ppm as calculated using data for formation water from McNutt *et al.* (1989).

Figure 34. Stable isotope composition of the samples in this study, and that of Sager-Kinsman (1995) as indicated by squares.

samples from the Oxford Formation in this study, define a range of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values which are slightly lower than that of the brackish groundwaters in this study (with the exception of sample AB 93-30).

The $\delta^{18}\text{O}$ data of Sager-Kinsman fall within the range of -10.5 to -12 per mille. This range coincides with that of precipitation in the Ottawa area (Fritz *et al.*, 1987b), while many of the brackish groundwaters in this study fall outside of that range and are isotopically heavier (-9 to -10.5 per mille). It is unlikely that these heavier $\delta^{18}\text{O}$ values can be attributed to lower latitude or altitude at recharge. The latitude effect would put the point of recharge south of Lake Ontario. Lower altitude at the point of recharge is not possible since the Ottawa-St. Lawrence Lowland is surrounded on all sides by higher elevation terrains. Therefore, the $\delta^{18}\text{O}$ values indicate that most of the brackish water was recharged at a time when the climate was warmer in the Ottawa area than it has been during the last 50 years.

$\delta^{18}\text{O}$ values of fresh groundwater from the Nepean-Oxford Formations in this study and of Sager-Kinsman (1995) were inserted into the ^{18}O -temperature equation of Fritz *et al.* (1987b). The calculated mean annual air temperature values of 4.8 to 7.4°C correspond well with the mean annual air temperatures (between 4.8° and 7.1°C with an average of 5.9°C) recorded during the period 1972-1992, which confirms the validity of the equation for the data set. Inserting $\delta^{18}\text{O}$ data for the brackish groundwaters into the same equation gives mean annual air temperatures of 7.3 to 10.2°C. This leads to a search in the climatic

records for periods when temperatures were warmer than today. The average annual air temperature has increased by 0.7°C during the last hundred years. Furthermore, it has not been at least as warm as it is today in the St. Lawrence Lowland since the warming period of 950-1250 AD, the so called Medieval High. An earlier warming period peaked around 6 000 years ago (Gullett and Skinner, 1992). Therefore, an age of at least 750 years would be implied for the brackish groundwaters.

4.2.3.1 Water-rock interaction.

In the preceding chapter on geochemistry, groundwater subject to interaction with shale and other sedimentary rocks defined one groundwater type. Unlike formation waters, this type of groundwater is meteoric in origin, and it has not been subject to evaporation or ultrafiltration. Banner *et al.* (1988) presented data for saline groundwater in central Missouri which acquired significant amounts of solutes (up to 36 000 mg/l TDS) through water-rock interaction while retaining its meteoric stable isotope composition. A similar evolution of the brackish waters in this study is possible. Any water-rock interaction would have to have taken place at sufficiently low temperatures as to not affect the stable isotope composition of the groundwater. As indicated above, the brackish groundwaters could have been recharged several hundred years ago, which would provide a long time for the groundwater to interact with the bedrock.

The correlation between TDS and $\delta^{18}\text{O}$ (Figure 29) could be explained by residence

time. If the mean annual air temperature peaked at a certain time, the meteoric water that infiltrated into the bedrock since then would have a progressively lower $\delta^{18}\text{O}$ value as the mean annual air temperature decreased. The salinity, as a result of water-rock interaction, would be expected to be higher the longer the time allowed for the interaction processes. Therefore, the longer the residence time, the higher the TDS and $\delta^{18}\text{O}$ value. This is only applicable if the mean annual air temperature over the time period has consistently fallen. This is not the case if the brackish groundwaters are 6 000 years old, because of the Medieval High 950-1250 AD. Alternatively, if all the groundwater with elevated TDS was recharged at the same time when the climate was milder, then the lower salinity together with a lower $\delta^{18}\text{O}$ value is the result of mixing. In this scenario, the larger the proportion of fresh recent water is, the lower the TDS and $\delta^{18}\text{O}$.

4.2.4 Oxygen and hydrogen isotopes-summary.

In the above it has been outlined how the brackish waters could have acquired their solute load. Two mixing models were presented. One of them is a three component model where the end members are Champlain Sea water, glacial meltwater and local meteoric groundwater. An examination of the TDS and stable isotope composition as compared to that of the Champlain Sea does not offer conclusive evidence, although it cannot be discounted. In the other model, a basin brine is mixed with local meteoric water. This would produce a small but consistent deviation from the OMWL, which has not been observed. Although the Champlain Sea cannot be ruled out, it is more likely that the

groundwaters are of meteoric origin and their TDS is a product of water-rock interaction during a prolonged residence time. The stable isotope data suggest recharge during a period of warmer climatic conditions at least 750 years ago.

4.3 Tritium.

Tritium is a naturally occurring radioactive isotope of hydrogen which can serve as a tool for dating groundwater. As an addition to the natural abundance of tritium, nuclear weapons testing during the period 1952-1962 contributed to abnormally high levels of tritium in the atmosphere and, therefore, in groundwater recharge during that period of time. Since the end of that period, the concentration of tritium in precipitation has declined steadily towards the natural background level of 4-25 T.U. that prevailed prior to 1952 in the northern hemisphere (Gat, 1980). In the Ottawa area tritium concentrations have stabilized around 50 T.U (Michel, pers. comm.).

Due to the short half-life of only 12.26 years (Faure, 1986), this method is only useful for water that was recharged later than 1952, which was the year when the nuclear weapons testing commenced. Because of indications that the groundwaters in this study were older than 1952, the tritium concentration was measured only for sample AB 93-15 to confirm the pre-1952 age of the groundwater and as a complement to the radiocarbon dating carried out on that sample.

4.3.1 Result.

The tritium analysis carried out on brackish sample AB 93-15 gave a result of $<6 \pm 8$ T.U., indicating that the sample was recharged before 1952. This is in contrast to fresh water samples from the Oxford Formation, which were recharged since 1952 (A. Sager-Kinsman pers. comm.). If the sample contains any proportion of modern groundwater as a result of mixing, the proportion of fresh water is so small that the tritium concentration of the groundwater is below the detection limit.

4.4 Strontium isotopes.

The isotopic composition of strontium in groundwater depends on the strontium isotope ratio of the strontium source. Therefore, the strontium isotope ratio may be a useful indicator of the origin and history of the strontium in a groundwater sample.

4.4.1 Background.

Strontium 87 is the radiogenic product formed from the decay of rubidium 87 by emission of a negative beta particle. Initially a sample contains a certain amount of naturally occurring common strontium 87. As radioactive decay of rubidium proceeds, the strontium 87 content in a sample which contains both elements will increase with time. Strontium 86 is a stable isotope, and the strontium isotope composition is expressed as

the atomic ratio $^{87}\text{Sr}/^{86}\text{Sr}$.

Rubidium does not form a mineral of its own, but substitutes for potassium in mica, potassium feldspar, certain clay minerals, and in evaporite minerals such as sylvite and carnallite. Strontium substitutes for calcium in minerals such as plagioclase, apatite and calcium carbonate. In addition, it can also substitute for potassium in potassium feldspar if this is coupled with replacement of Si^{4+} by Al^{3+} . Strontium may form its own minerals strontianite (SrCO_3) and celestite (SrSO_4), which can occur in carbonate and certain hydrothermal rocks.

Most rock types contain both rubidium and strontium. Due to radioactive decay of ^{87}Rb , the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a rock increases with time. The ^{87}Sr is concentrated in rubidium-bearing minerals such as potassium feldspar and mica. Crystalline rocks and terrestrial sedimentary rocks, such as shales and sandstones, which are rich in these minerals, may have a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a function of time. Due to its fine grain size, a shale is normally well mixed, and could locally have a fairly uniform strontium isotope composition. However, influence from local sources could cause a variation on a regional scale. Following deposition of the clay in the ocean, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is affected quite significantly by the decay of rubidium which increases the ratio and by diagenesis which can either increase or decrease the ratio. Because rubidium-bearing minerals are more resistant to weathering compared to strontium-bearing minerals, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is further increased in a shale of some age which is subjected to interaction with

groundwater, while the groundwater attains a slightly lower isotopic ratio. The overall result is that a shale tends to have a low strontium content, and a high and variable strontium isotope ratio.

On the other hand, carbonate rocks normally contain strontium in abundance, while they have low concentrations of rubidium. Therefore, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a carbonate changes very slowly with time. Unless alterations during diagenesis take place, which are usually less significant than in shales, the strontium isotope composition of the carbonate remains close to that of the seawater in which it precipitated. The strontium isotope composition in the ocean is in turn a reflection of the relative contributions of Sr from mid-ocean ridge, terrestrial and carbonate sources. Because this relationship has changed throughout geologic time, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater has fluctuated within the range 0.7066-0.7092 during the Phanerozoic. A curve for the $^{87}\text{Sr}/^{86}\text{Sr}$ variation in seawater during the Phanerozoic has been established from strontium isotope analysis of carbonates of different ages (Burke *et al.*, 1982; Elderfield, 1985; Hodell *et al.*, 1990).

Due to their mineralogical differences, a carbonate is richer in strontium and usually has a lower and more distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than a shale of the same age. The strontium isotope ratio of the carbonate has only slightly increased compared to that of the ocean at the time of deposition, while that of the shale has increased significantly since sediment deposition due to the decay of rubidium. These differences between carbonates and shales are reflected by the groundwaters which come into contact with them.

Similarly, the geology of a drainage basin also controls the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a surface water body. Because of this, it is uncertain whether the strontium isotope composition of the groundwaters in this study can be expected to answer the question of whether they are of Champlain Sea origin. As has been mentioned earlier, the Champlain Sea comprised a mixture of marine water and glacial meltwater from the Laurentide ice-sheet, which by itself may have produced a strontium isotope composition different from that of the contemporaneous ocean. The strontium concentration and isotopic composition of the glacial meltwater is not known, but its $^{87}\text{Sr}/^{86}\text{Sr}$ can be assumed to be quite high because most of the area that it drained consisted of Canadian Shield rocks. However, the concentration of strontium in average seawater is usually several times that of fresh water bodies. Therefore, the strontium in the Champlain Sea would not have changed its isotopic composition away from that of the sea until the ratio of freshwater to seawater was quite high.

Even if the strontium isotope composition of the surface water was not significantly different from that of the ocean, interaction with sediments deposited in the Champlain Sea could have changed the original $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the seawater. Large amounts of mechanically weathered bedrock material from the surrounding shield area as well as from the Ottawa-St. Lawrence Lowland were deposited in this restricted arm of the ocean. Chemical weathering of the sediments that accumulated on the bottom of the Champlain Sea would alter the strontium content and isotopic composition of any sea water trapped in the pores to reflect that of the sediments.

4.4.2 Sampling and analysis of strontium isotope composition.

Twenty four groundwater samples and seventeen rock samples were selected for Sr isotope analysis. The majority of the waters are brackish water, but some fresh waters from overburden and bedrock sources are included for comparison purposes. Chip samples from rocks representing the different aquifer units found in the study area were collected from samples obtained during drilling on the Carleton University campus (Wilson, 1990) and at Algonquin College. Carlsbad shale was not present in these sections. However, it was possible to obtain a core sample from the drilling of the hole from which groundwater sample AB 93-22 was collected. In addition, samples of both Carlsbad and Billings Formations were collected from outcrops in the Ottawa area. Because Wilson (1990) used the terminology of Wilson (1946), it will be used in this section (please refer to Table 1).

The samples were analyzed on a MAT 261 solid source thermal ionization mass spectrometer in the Department of Earth Sciences at Carleton University; sample preparation is described in Appendix 7 and analytical procedure is given in Appendix 8. Runs of the NIST SRM 987 and Eimer and Amend SrCO_3 standards gave 0.710284 ± 0.000030 ($n=3$) and 0.708017 ± 0.000018 ($n=1$) respectively. Averages of previously obtained results in the laboratory are 0.710257 ± 0.000022 for NIST SRM 987 during the period 1991-95 and 0.708030 ± 0.000020 ($n=6$) for Eimer and Amend. The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for NIST SRM quoted in the literature is 0.71025 (Cousens, pers. comm.).

4.4.3 Results.

Table 4 and 5 list the Sr content and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the water and rock samples studied. The routine precision (2σ) is ± 0.000025 . The initial ratios in Table 5 were calculated from the measured rubidium and strontium contents and the age ($t=450 \times 10^6$ years) of the rock and the decay constant, λ for the radioactive decay of ^{87}Rb , using the following relationships:

$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{INT.}} = (^{87}\text{Sr}/^{86}\text{Sr})_{\text{M}} - (^{87}\text{Rb}/^{86}\text{Sr})_{\text{CALC.}}(e^{\lambda t} - 1)$ (Faure, 1986 p.119), where $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{INT.}}$ = initial ratio, $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{M}}$ = measured ratio, $(^{87}\text{Rb}/^{86}\text{Sr})_{\text{CALC.}} = 2.892(\text{Rb}/\text{Sr})$ (Blenkinsop, pers. comm.) and the decay constant, $\lambda = 1.42 \times 10^{-11} \text{ y}^{-1}$.

On the basis of the strontium isotope ratios obtained for the groundwaters, and the ratios obtained for their respective bedrock aquifers, the groundwater samples can be divided into three categories. First, there are the samples found in the Oxford, March and Nepean Formations. Secondly, there are the waters that are found in the shale of the Carlsbad Formation and, possibly, the Billings Formation. The third category includes groundwater samples that are presumed to come from the Cobourg faunal zone of the upper Ottawa Formation. The strontium isotope ratios for these groundwaters as compared to that of the bedrock is illustrated in Figure 35.

Groundwater samples.			
sample #	Aquifer	Sr-ratio	Sr (ppm)
AB 93-3	Overburden	0.71036	11.98
AB 93-4	Overburden	0.71063	0.688
AB 93-5	Carlsbad	0.71104	3.245
AB 93-8	Carlsbad	0.71111	3.087
AB 93-11	Carlsbad	0.71106	1.42
AB 93-12	Carlsbad	0.71185	2.221
AB 93-13	Overburden	0.70996	5.551
AB 93-15	Carlsbad	0.71076	11.67
AB 93-16	Carlsbad	0.71129	7.835
AB 93-17	Oxford	0.70953	1.699
AB 93-18	Carlsbad	0.71074	2.609
AB 93-20	Carlsbad	0.71143	3.15
AB 93-21	Oxford	0.71004	4.48
AB 93-22	Carlsbad	0.71075	5.505
AB 93-24	Nepean-Oxford	0.70979	1.67
AB 93-25	Carlsbad	0.71182	0.495
AB 93-26	Oxford	0.71007	5.894
AB 93-28	Carlsbad	0.71161	1.482
AB 93-30	Carlsbad	0.71193	13.82
AB 93-32	Carlsbad	0.71178	1.083
AB 93-34	Cobourg	0.71103	4.195
AB 93-35	Cobourg	0.71049	5.928
AB 93-36	Cobourg	0.71079	6.039
AB 93-39	Overburden	0.70958	2.185

Table 4. Strontium isotope ratios and strontium content of groundwater samples.

Rock samples					
Sample #	Formation	Sr ratio	initial ratio	Sr (ppm)	Rb (ppm)
AB 93-58	Carlsbad	0.71521	0.69200	131	164
AB 93-65	Carlsbad	0.71008	0.69950	192	109
AB 93-67	Carlsbad	0.70862	0.70586	364	64
AB 93-57	Billings	0.70927	0.70517	409	92
AB 93-66	Billings	0.71393	0.69778	176	167
AB 93-51	Cobourg	0.70834	N/A	N/A	N/A
AB 93-52	Cobourg	0.70833	0.70686	396	32
AB 93-53	Hull	0.70810	0.70791	479	7
AB 93-54	Sherman Fall	0.70836	0.70689	462	39
AB 93-56	Rockland	0.70815	0.70757	652	20
AB 93-60	Rockcliffe	0.72101	0.71229	340	160
AB 93-55	Oxford	0.70908	0.70652	242	35
AB 93-61	Oxford calcite	0.70951	0.70932	683	8
AB 93-62	Oxford	0.70996	0.70182	109	48
AB 93-59	March	0.71029	0.70215	43	19
AB 93-63	March	0.70902	0.70402	95	26
AB 93-64	Nepean	0.70889	0.70459	70	16

Table 5. Measured and initial strontium isotope ratios and strontium and rubidium content of rock samples.

Figure 35. Comparison of strontium isotope ratios for groundwater with strontium isotope ratios for bedrock. In all groups of groundwater, the symbol $\times$ indicates fresh water, other symbols identify brackish or dilute brackish water.

No strontium data are available on the overburden itself, but water from wells in clay/sand overburden in Gloucester has been analyzed (Table 4). These samples (AB 93-3,4,13 and 39) show a small variability in the Sr isotopic ratio (0.70958-0.71063) and a large variation in Sr content (0.688-11.98 ppm). The overburden itself is a product of erosion of Precambrian and Palaeozoic rocks which vary widely in their strontium isotopic composition. The material from these sources may occur in different proportions in the sediments depending on the location within the basin thereby giving rise to differences in strontium contents and isotope ratios. At any location, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the groundwater could be considered to be an averaging of the strontium isotopic ratios of the more easily weathered minerals in the overburden with which the groundwater has interacted.

4.4.3.1 Groundwater from the Oxford, March and Nepean Formations.

The water samples from the Oxford, March and Nepean Formations have strontium isotope ratios (0.70953-0.71007) very close to that of the bedrock (0.70889-0.71029) as shown in Figure 35, and the ratios do not change with the strontium concentration in the water. This indicates that the isotopic signature of the groundwater is acquired primarily through carbonate dissolution and strontium isotope equilibration with the aquifer. No major mixing has taken place with water from other sources. The groundwater samples that come from the Oxford to Nepean Formations are all fresh and relatively recent.

4.4.3.2 Brackish groundwater from the Carlsbad and possibly Billings Formation.

The groundwaters that are found in these shales have a relatively wide range of strontium isotope ratios (0.71074-0.71193). At the same time, the bedrock of the Carlsbad Formation displays an even wider range (0.70862-0.71521), which encompasses that of the groundwaters (see Figure 35). The two analyses of the samples of the Billings Formation indicate that there is a spread in strontium isotopic ratios also for this bedrock unit. The variation in strontium isotopic ratio may be a product of several factors as outlined above and could include mineral transformations during diagenesis, subsequent interaction with groundwater and a difference in initial $^{87}\text{Sr}/^{86}\text{Sr}$. The latter could be a function of vertical variations in lithology. Although shales can be assumed to be laterally homogeneous, the Billings and, in particular, the Carlsbad Formations contain carbonate layers (see section 2.1.1). This may have an effect on the strontium isotopic composition. As mentioned earlier, carbonates do not significantly change their strontium isotope ratio due to their low rubidium content. This is in contrast to rocks that are composed of predominantly Rb-bearing minerals, which can normally be found in shales. Therefore, it would be logical that a carbonate horizon in a shale has a lower isotopic ratio than the rest of the rock. For the five shale samples (AB 93-57,58,65,66 and 67) there is a relationship between a high CaO content and a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, as shown in Figure 36.

Figure 36. Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ against CaO content for rock samples from the Billings and Carlsbad Formations.

Calculated initial isotope ratios are, as shown in Table 5 varied, which could mean the shales were not homogeneous at the time of deposition. Furthermore, the low initial ratios indicate a lack of closed system conditions with regard to strontium. Therefore, post-depositional alterations due to diagenetic effects are also indicated by these rocks. These factors together have produced the observed variation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the shales, which in turn is reflected by the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of groundwater interacting with the shales. A smoothing out effect is observed as the water circulates between horizons of different isotopic and chemical composition, thereby giving the groundwaters a narrower range of isotopic ratios. The fact that the analysis of the shales were carried out on a leachate rather than the dissolved rock may also explain the initial ratios observed, because leaching does only extract the most mobile strontium. It does also simulate what the groundwaters interact with better than whole-rock dissolution.

Although the actual $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of each individual groundwater sample from the Carlsbad Formation seems to be random, there are three samples which have very similar values. These are AB 93-5, 8 and 11, which come from the same fault block at similar levels in the Carlsbad Formation. Since the groundwater flow in the bedrock can be assumed to be fracture controlled, the similar strontium isotopic ratios may indicate that the three samples have had a relatively common flow path history in terms of the rock units encountered.

4.4.3.3 Groundwater from the Cobourg faunal zone.

The limestone of the Cobourg faunal zone has an isotopic ratio (0.70833-0.70834) that reflects the Ordovician ocean at the time of limestone deposition. The isotope ratio obtained on water samples from the Cobourg faunal zone fall in a range of 0.71049-0.71103, which is significantly above that of the aquifer, as seen in Figure 35. A very similar relationship between strontium isotope composition in the Ottawa Group and in the groundwater contained therein, was observed by McNutt *et al.* (1987) in the Michigan Basin of SW Ontario. They interpreted it to be a product of extensive fluid migration. In their study, McNutt *et al.* (1987) did not identify a source rock for the radiogenic Sr. McKenna *et al.* (1992) noted that in the Michigan-Appalachian basin the Sr isotopic ratios are more radiogenic towards the edges of the basin. This was interpreted as being due to an increased influence from the crystalline basement bedrock surrounding the basin. Such an interpretation does not necessarily mean that there is large scale fluid migration connecting the Precambrian and the sedimentary basin. Rather, sediments found close to the edge of the basin contain a larger proportion of basement material than do sediments found in the centre of the basin. Steuber *et al.* (1987) concluded that radiogenic Sr in brines found in the same aquifers in the Illinois Basin have their origin in clay minerals in shales and sandstone.

A similar situation may explain the observed strontium isotope ratio observed in the groundwaters (sample 93-34, 35 and 36) issuing from the Cobourg faunal zone. At

Caledonia Springs and Plantagenet Station, the Cobourg faunal zone constitutes the uppermost bedrock formation. However, as previously mentioned (see page 10), fault-bounded contacts with the Carlsbad Formation exist close to the springs in both locations. It is likely that the groundwater is coming from the Carlsbad Formation, with which it has equilibrated isotopically, and is discharging through the Cobourg faunal zone. The discharge may take place along the faults or the location of the faults are in reality such that the bedrock underlying Caledonia Springs and Plantagenet Station is the Carlsbad Formation rather than the Cobourg faunal zone. In either case, the strontium isotopic signature of these spring waters is more consistent with that of the Carlsbad Formation itself and the groundwater samples that come from it than with the isotopic composition of the Cobourg faunal zone.

Another source to consider for the radiogenic strontium is the overburden, which at Caledonia Springs and Plantagenet Station consists of marine clay. A comparison between the strontium isotope ratios in the overburden wells and the spring waters from Caledonia Springs and Plantagenet Station show that the overburden well waters have ratios similar to or lower than the spring waters (see Figure 35). However, with the exception of AB 93-3, the strontium content in the well water is less than half of that of the spring waters. This means that in order to attain the same strontium concentration as found in the spring water, water coming from the overburden would have to dissolve additional amounts of strontium in the bedrock. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the underlying bedrock is less than 0.7084 if it is the Cobourg faunal zone, which would lower the strontium isotope ratio of the

overburden water to levels below that of the spring waters. Therefore, it is unlikely that the overburden material can produce the observed radiogenic strontium isotope ratios without significant input from the Carlsbad Formation shales.

4.4.3.4 Strontium isotope ratios of the type B waters.

As was mentioned in section 3.2.2.6, the groundwater samples that are denoted type B (AB 93-3,15 and 44) and sample AB 93-30 were found to have elevated Sr contents compared to the rest of the brackish samples. However, they do not have different strontium isotopic ratios from the other brackish groundwater samples. As mentioned before, the possibility exists that there are hydrothermal veins containing celestite associated with the Gloucester Fault and the fault at the location of AB 93-30. According to the model of Carignan (1989), the water that deposited such veins was of meteoric origin. This water would have interacted with and acquired its solutes from the Ordovician sedimentary rocks. Therefore, the Sr isotopic ratio of water found in the sedimentary rock today and that of the hydrothermal veins would be expected to be very similar. Therefore, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is not a useful tool in identifying the source of strontium and calcium in the type B waters.

4.4.4 Summary-strontium isotopes.

The similarity between the strontium isotope ratios of the recent fresh water found

in the Oxford, March and Nepean Formations and that of the aquifer, shows that isotopic equilibration has taken place between the water and rock. The water has probably not interacted with any other rock type, and the strontium in the water is largely the result of dissolution of minerals in the aquifer.

The strontium isotope ratio of the groundwater from the Carlsbad Formation falls within the range for the bedrock, which indicates isotopic equilibration with the aquifer. On the other hand, the strontium isotope ratio of the groundwater issuing from the Cobourg faunal zone does not reflect that of the bedrock. The more radiogenic strontium may have its source in the clay overburden, but is more likely to originate from the shales of the Carlsbad Formation.

4.5 Isotopic composition of dissolved sulphate.

The isotopic composition of sulphur in sulphide and of oxygen and sulphur in sulphate provide information on the origin of these constituents in groundwater. In this study, the purpose of the isotopic analyses was to identify the source of the dissolved sulphate in the groundwater.

4.5.1 Background.

Possible sources of sulphate in groundwater include dissolution of evaporite minerals,

such as gypsum and anhydrite, which can produce a sulphate concentration of up to 2000 mg/l. Sulphate and sulphide minerals in volcanic and hydrothermal deposits may also contribute to sulphate dissolved in groundwater. Another important source of sulphate, depending on the local redox conditions, may be the oxidation of sulphide in sedimentary rocks, such as shale. A few milligrams per litre can also come from modern atmospheric precipitation (Pearson and Rightmire, 1980).

4.5.1.1 ^{34}S .

The sulphur isotope ratios ($^{34}\text{S}/^{32}\text{S}$) of evaporite minerals reflect that of the sulphate in the sea water from which they precipitated. Through geologic time this ratio has varied between +10 and +35 per mille. The $\delta^{34}\text{S}$ of sulphate in the ocean today is slightly above +20 per mille, and the corresponding value for the Ordovician sea was +27 to +29 per mille (Faure, 1986 p.532).

Primary sulphides in deep seated igneous rocks have a $\delta^{34}\text{S}$ close to that of the standard troilite (CDT), which by definition is 0 per mille. The sulphur isotope value of sulphur compounds in volcanic fluids and rocks show a wider range due to isotope exchange processes and contamination from sources other than primary sulphur. Therefore, the range of $\delta^{34}\text{S}$ in sulphate is approximately +10 to +30 per mille and in sulphide 0 to -12 per mille (Figure. 11-1, Krouse, 1980) in volcanic deposits.

Reduction of sulphate is an important process in many groundwaters, in which hydrogen sulphide or sulphide minerals are produced from the reduction of sulphate according to the reaction on page 46. The fractionation factor associated with the reaction is typically large; a value in the order of -40 per mille is not unusual, leading to a depletion in ^{34}S of the produced sulphide compound, and an enrichment in the remaining sulphate. In systems found in nature, spontaneous sulphate reduction in response to lowered Eh is slow, but the process is usually mediated by anaerobic bacteria, which speed it up considerably. The degree of isotope fractionation is inversely proportional to the rate of sulphate reduction, which is in turn controlled by temperature and/or sulphate concentration (Faure, 1986 p.524). As a result of the variability of naturally occurring conditions, sulphide produced by sulphate reduction has a broad range of $\delta^{34}\text{S}$. However, its value is typically negative, which makes it possible to distinguish between sedimentary and unaltered igneous sulphide deposits through sulphur isotope analysis.

Oxidation of sulphide leads to depletion in the produced sulphate by -3 to -17 per mille ^{34}S relative to the sulphide, as observed under laboratory conditions (Nakai and Jensen, 1964). Although a depletion of -14 per mille has been observed in gypsum relative to pyrite (Pearson and Rightmire, 1980), in natural systems, the fractionation factors usually belong in the conservative end of that range, as exemplified by negligible fractionation found at Yellowstone (Krouse, 1980). Nevertheless, if the source of sulphate in groundwater is the oxidation of sedimentary sulphide, the initial negative $\delta^{34}\text{S}$ of the reacting sulphide can lead to a larger negative value for the produced sulphate.

4.5.1.2 ^{18}O .

The oxygen isotope composition of evaporite minerals reflects that of the sulphate in the sea water from which they precipitated and oceanic sulphate today has an oxygen isotope ratio of +9.6 per mille (Pearson and Rightmire, 1980). Through geologic time it has varied between +17 and +10 per mille and the $\delta^{18}\text{O}$ of sulphate in the Ordovician ocean fluctuated only slightly around +14 per mille (Faure, 1986 p.532).

The oxygen isotope composition of hydrothermal and volcanic sulphate minerals is dependent on the temperature of formation because of its effect on the fractionation factor between fluid and mineral phases and the origin of the fluid. Typically the $\delta^{18}\text{O}$ values of rocks and minerals are enriched relative to SMOW (Faure, 1986 p.460).

Reduction of sulphate enriches the residual sulphate in ^{18}O by 4.5 per mille, and the reverse, where sulphate is produced by sulphide oxidation leads to the enrichment of the sulphate by 4.6 per mille relative to the water (Pearson and Rightmire, 1980).

The oxygen isotope equilibrium fractionation factor between water and dissolved sulphate is temperature dependent. From the relationship given by Kyser (1987), it has a value of approximately +32 per mille at the temperatures encountered in this study. The equilibrium fractionation factor between solid gypsum and water is around +25 per mille at the same temperatures (Kyser, 1987). However, 10^3 - 10^5 years are required to attain

isotope equilibrium between sulphate and water in subsurface conditions (Faure, 1986); too slow for equilibrium to be attained in recent non-thermal groundwaters.

4.5.2 Results.

Eight water samples were analyzed with respect to the sulphur isotope signature of their dissolved sulphate. The selection of samples for sulphur isotope analysis was restricted by the fact that most type A samples, which are the majority of the brackish waters, were found to contain little or no sulphate. Therefore, only one type A brackish sample (AB 93-22) was included in the analysis. The isotopic composition of hydrogen sulphide associated in abundance with AB 93-22 was also analyzed. Samples AB 93-3, 15 and 44 constitute the type B group of groundwater, and while they are brackish waters they also have a high sulphate content making them interesting for sulphur isotope analysis. For comparison purposes, a few fresh water samples were also included in the analysis. The results of the sulphur isotope analysis are presented in Table 6.

It was also of interest to evaluate whether the sulphate in the type B waters is at present undergoing reduction to produce H_2S , and therefore an attempt to sample sulphide in AB 93-15 was made. However, the presence of sulphide was not indicated by testing using a HACH field measuring kit. Therefore, if sulphate is at present being reduced, the sulphide would be precipitating as pyrite rather than forming H_2S .

One gypsum sample from the Gull River Formation, approximately 430 ft. below the surface in the GSC borehole at Lebreton St. mentioned in section 3.2.2.7 and five samples of pyrite from the Billings Formation (supplied by Dr. Michel) were submitted for sulphur isotope analysis to determine the isotopic composition of potential sources of sulphate in the Ordovician rocks.

sample #, type	date	sulphur compound	Conc., ppm	$\delta^{34}\text{S}$, per mille
AB 93-3, B	94-11-03	SO_4	1880	+10.0
AB 93-4, dilute brackish	93-07-08	SO_4	248	+6.9
AB 93-13, fresh	93-07-08	SO_4	111	+12.1
AB 93-15, B	93-07-08	SO_4	740	+9.5
AB 93-17, fresh	93-07-08	SO_4	24	+15.7
AB 93-22, A	93-07-08	SO_4	33	+71.3
AB 93-22-2, A	93-12-16	SO_4	33	+84.1
AB 93-25, fresh	93-07-08	SO_4	83	+9.0
AB 93-44, B	94-03-11	SO_4	1510	+8.8
AB 93-22-2, A	93-12-16	$\text{H}_2\text{S-1}$	75	+90.9
AB 93-22-2,A	93-12-16	$\text{H}_2\text{S-2}$	75	+83.1

Table 6. Results of sulphur isotope analyses of dissolved sulphate in groundwater samples.

The gypsum sample together with groundwater samples AB 93-15 and 44 were also subjected to oxygen isotope analysis of sulphate to further constrain the conditions of sulphate formation in the groundwater. The sulphur isotope analyses of the pyrite were

carried out at the University of Ottawa while the oxygen isotope analysis and the sulphur isotope analysis of the gypsum sample were conducted at the University of Waterloo. The results are given in Table 7.

Type of sample	$\delta^{34}\text{S}$, per mille
Sedimentary pyrite Billings Fm.	-4.4
Sedimentary pyrite Billings Fm.	-5.3
Pyrite fossil Billings Fm.	+24.4
Pyrite "blebs" Billings Fm.	+36.7
Secondary pyrite in fracture Billings Fm.	-16.3
Gypsum Ottawa Group	+28.6
sample	$\delta^{18}\text{O}$, per mille
Gypsum Ottawa Group	+17.5
AB 93-15	+11.9
AB 93-44	+10.9

Table 7. Results of sulphur and oxygen isotope analysis of some sulphur minerals and oxygen isotope analysis of sulphate in two type B water samples.

From Table 6 it can be seen that with the exception of one sample, AB 93-22 which will be discussed below, the obtained $\delta^{34}\text{S}$ of dissolved sulphate falls within the range +6.9 to +15.7 per mille. There is no correlation between isotopic composition and sulphate content. The type B samples show a distinct and narrow $\delta^{34}\text{S}$ range from +8.8 to +10.0 indicating that the sulphate in these samples share the same origin. Because samples AB 93-4, 13, 17 and 25 differ by a maximum of 5.7 per mille from the type B

waters, it is believed that the source of sulphate in these samples is similar to that of the type B waters with some local modifications.

With the exception of AB 93-22, the $\delta^{34}\text{S}$ of the groundwater samples are too low to be originating solely from the dissolution of evaporite minerals in the bedrock which, as indicated by the gypsum sample in Table 7, have a $\delta^{34}\text{S}$ close to the predicted value for the Ordovician. Oxidation of pyrite in the sedimentary rocks alone would, based on the available pyrite analyses in Table 7, either produce a negative sulphur isotope signature or a value well above that of the analyzed dissolved sulphate. The fact that the obtained $\delta^{34}\text{S}$ values of the sulphate in the groundwaters do not match the sulphur isotope composition of any single potential source of sulphate indicates that they are most likely the product of a combination of at least two processes. As shown in the following, by using the $\delta^{34}\text{S}$ and, where applicable, the $\delta^{18}\text{O}$ of the possible source minerals and of samples AB 93-15 and 44, it is possible to further constrain the sources of sulphate in the type B samples and presumably in all of the samples except AB 93-22.

The first case to consider is one where the sulphate comes entirely from the oxidation of pyrite, which would have to be a mixture of at least two of the different types in Table 7 in order to produce the observed sulphur isotope composition in the dissolved sulphate. Because there are different pathways through which pyrite can be oxidized, the interpretation of the oxygen isotope composition of the sulphate has to be carefully undertaken. The different pathways and their relative proportions of oxygen from

atmospheric ($\delta^{18}\text{O}=+23.8$ per mille) and groundwater sources were discussed by van Everdingen *et al.* (1985). Following the first pathway, 100% of the oxygen comes from the water:

where the availability of Fe^{3+} is determined by the rate-limiting reaction:

while in the second pathway, the oxidation of pyrite involves free oxygen:

The relative contribution of the two pathways can vary, and the resulting oxygen isotope composition of the sulphate is a function of this, as well as of the $\delta^{18}\text{O}$ of the water and of the oxygen isotope fractionation between the reactants and the produced sulphate, as illustrated in Figure 37. In constructing this diagram van Everdingen *et al.*, 1985 used the values -11.2 per mille for atmospheric oxygen and +2.6 per mille for water oxygen to quantify the oxygen isotope shift due to kinetic isotope effects during their incorporation into the sulphate ion. By using Figure 37 (from van Everdingen *et al.*, 1985), it can be seen that at the oxygen isotope compositions measured for the dissolved sulphate and for the groundwater ($\delta^{18}\text{O}_\text{S}=+11.9$ and +10.9, $\delta^{18}\text{O}_\text{W}=-10.2$ and -9.2 per mille for AB 93-15 and 44), fall outside the range of possible combinations of atmospheric oxygen to water oxygen. This means that the oxidation of sulphide alone cannot account for the observed isotopic composition of the dissolved sulphate and the high concentration of sulphate in

Figure 37. Relationship between $\delta^{18}\text{O}_s$ (oxygen isotope ratio of dissolved sulphate) and $\delta^{18}\text{O}_w$ (oxygen isotope ratio of water) in the oxidation of sulphide. Straight lines indicate the expected $\delta^{18}\text{O}_s$ versus $\delta^{18}\text{O}_w$ relations for increasing contributions of oxygen (0-100%) from atmospheric oxygen. From van Everdingen *et al.* (1985).

the groundwater. It also confirms that the elevated levels of Ca, Sr and SO_4 could not have their source in any epithermal vein associated with the Gloucester Fault. If this was the case most of the sulphate would originate from oxidation of the sulphide minerals contained therein, as discussed in section 3.2.2.7, which is not possible given the oxygen isotope data.

As has already been established on the basis of the sulphur isotope composition of the dissolved sulphate as compared to that of gypsum in the bedrock, the sulphate in the groundwater could not be originating from dissolution of gypsum alone. Therefore, the last possibility to evaluate is that the dissolved sulphate comes from the dissolution of gypsum in combination with oxidation of pyrite in the bedrock. Due to their high $\delta^{34}\text{S}$ compared to the dissolved sulphate, the pyrite fossil and bleb were discarded as possible sources of sulphur. The remaining three pyrite samples in Table 7 were used in a mass balance calculation as described in Appendix 10. By using the $\delta^{34}\text{S}$ of the dissolved sulphate, gypsum and pyrite, it was found that depending on the $\delta^{34}\text{S}$ of the pyrite, 45-70% of the sulphate is dissolved gypsum. If 100% of the oxygen came from the water itself, the resulting $\delta^{18}\text{O}$ of the dissolved sulphate is in the range +5.3 (45% gypsum) to +10.4 (70% gypsum) per mille.

The calculated oxygen isotope values are a few per mille lower than those measured on the dissolved sulphate. There are several likely explanations for this discrepancy. It may be that the $\delta^{34}\text{S}$ of the pyrite being oxidized is lower than any of the sedimentary

pyrite values in Table 7. This would require a larger proportion of gypsum in the mass balance, thereby increasing the $\delta^{18}\text{O}$ of the dissolved sulphate further. Another possibility is that if the groundwaters are of considerable age, the long residence time is allowing the system to move toward isotopic equilibrium between water and sulphate. Dissolved sulphate in equilibrium with water where the $\delta^{18}\text{O}$ is -9 would have a $\delta^{18}\text{O}$ of approximately +23 per mille. Thirdly, some of the oxygen in the portion which comes from pyrite oxidation may be dissolved free oxygen of atmospheric origin having a $\delta^{18}\text{O}=+23.8$ per mille (Horibe *et al.*, 1973). This is the most likely explanation, because at a neutral pH Fe^{3+} is not the stable form of dissolved iron. Because of this, the portion of sulphate which originates from pyrite oxidation is mainly the result of reaction (B), which does not involve Fe^{3+} but utilizes atmospheric oxygen, rather than of reaction (A), where oxygen from the water is the reactant.

Earlier in this section, the possibility of pyrite precipitating as the result of sulphate reduction in AB 93-15 was mentioned. Reduction of sulphate produces a larger enrichment of the sulphur than of the oxygen in the residual sulphate. The observed oxygen isotope ratios of both AB 93-15 and 44, are more positive than the observed sulphur isotope ratios. It is possible to produce this relationship if most or all of the sulphate in the groundwater was originally the product of sulphide oxidation followed by reduction. By using the isotope data of the dissolved sulphate and the groundwater it was possible to establish boundary conditions for this scenario. The pyrite originally oxidized would have a $\delta^{34}\text{S}$ of -38 or less if it assumed that 70 % of the sulphate thus produced

was reduced. If only 25% or less of the sulphate was reduced, then the $\delta^{34}\text{S}$ of the sulphide originally oxidized could be as high as 0 per mille. The latter scenario is a more likely one considering that sample AB 93-15 still has a relatively high sulphate content (748 ppm). For example, the values $\delta^{34}\text{S}=-7.7$ per mille (could result from 3 per mille fractionation associated with the oxidation of sedimentary pyrite in Table 7) and $\delta^{18}\text{O}=+10$ per mille (the value resulting from 100% oxygen coming from the atmosphere-see Figure 37) were inserted into a spreadsheet to calculate the amount of sulphate reduction required to attain an isotopic composition of the residual sulphate similar to the measured values. Assuming isotope fractionation factors of +40 per mille for the sulphate and +4.5 per mille for the oxygen in the reduction process, it was found that reduction of approximately 35% of the dissolved sulphate would produce such an isotopic composition of the residual sulphate. Therefore, partial sulphate reduction cannot be ruled out with certainty. However, since this process requires most or all of the sulphate to be the result of sulphide oxidation, rather than a combination with gypsum dissolution, this scenario does not account for the elevated levels of calcium and strontium noted in sections 3.2.2.5 to 3.2.2.7.

Based on the isotopic analyses of the sulphate, a two component mixture of dissolved gypsum and oxidized pyrite is the most likely source of sulphate in the type B waters. It is also probable that a similar scenario is applicable to the remaining samples, with the exception of AB 93-22. The somewhat depleted $\delta^{34}\text{S}$ of sample AB 93-4 may be attributable to a larger proportion of the sulphate being due to sulphide oxidation. Since

this well is shallow and in overburden, the source of the sulphide could be unstable sulphide compounds in the clay deposited by the Champlain Sea, as described by Gadd (1986). The odour of hydrogen sulphide was experienced at this site during sampling, which may indicate the presence of these sulphide compounds dissolved in the water. At the sampling site of AB 93-17, the odour of hydrogen sulphide was also detected. The enriched sulphur isotope signature of sulphate in this sample compared to the other samples may be a product of sulphate reduction.

As mentioned earlier, the sulphate in AB 93-22 has a significantly different sulphur isotope composition. The sulphate concentration in the sample is only 33 ppm, which can be considered low compared to the high chloride content (5200 ppm). The reason for this is sulphate reduction, based on the unpleasant rotten egg odour emitted by the water. On a repeat visit to the well, the sulphide content was measured using a HACH field test kit, and found to be approximately 75 ppm. During this second visit, both sulphide and sulphate were collected for sulphur isotope analysis. The results (Table 6) show that the isotopic signatures for sulphate and sulphide were very similar. This is not to be expected if the sulphate is residual after partial reduction, because sulphate reduction causes a large fractionation. Therefore, it is suspected that the enriched sulphur isotope signature of the H_2S in this sample is the result of the reduction of the last portion of highly enriched residual sulphate. The sulphate in the sample was then produced by partial re-oxidation of the H_2S at the time of sampling, which was accompanied by a small depletion of ^{34}S in the produced sulphate.

4.6 Isotopic composition of dissolved carbonate.

^{13}C analysis has been used in this study to identify the source of dissolved inorganic carbon in the groundwater samples. In particular it is useful for distinguishing between organic and inorganic sources of carbon.

4.6.1 Background.

Organic carbon in soils and the CO_2 produced by their degradation have $\delta^{13}\text{C}$ values in the range of -20 to -30 per mille (Deines, 1980). As a consequence, kerogen, which is organic material preserved in recent sediments, has the same range of carbon isotope composition. Kerogen in older sediments and metasediments is commonly slightly lighter, with a $\delta^{13}\text{C}$ value around -28 to -30 per mille (Deines, 1980). By contrast, methane which is the product of the bacteriological or thermal degradation of kerogen has a broad range of $\delta^{13}\text{C}$ values from -21 to -90 per mille.

The $\delta^{13}\text{C}$ of carbonate precipitated in the oceans from the Cambrian to the Tertiary has remained close to zero per mille with a slight decrease as age increases, as described by Veizer and Hoefs (1976). Precambrian carbonates have an approximately 3 per mille heavier $\delta^{13}\text{C}$ value. Freshwater carbonates are depleted in ^{13}C with respect to marine carbonate, having an average value of -4.93 ± 2.75 per mille (Keith and Weber, 1964).

Atmospheric CO_2 has a $\delta^{13}\text{C}$ value of -7.0 per mille and any dissolved carbonate species in precipitation will have the same carbon isotope composition.

The following is a summary of the different processes that can affect the carbon isotope composition during the development of a groundwater starting at the point of recharge, as described by Mook (1980):

1) When water infiltrates through a soil, it dissolves CO_2 in the soil, which has a $\delta^{13}\text{C}$ of approximately -25 per mille. Because the proportion of soil CO_2 to atmospheric CO_2 usually is large, the resulting $\delta^{13}\text{C}$ of the dissolved CO_2 is close to -25 per mille. The carbon dioxide in the water forms carbonic acid (H_2CO_3) and dissolves any carbonate mineral present in the soil or bedrock. Often these minerals have a value close to that of marine carbonates (approximately 0 per mille):

The resulting bicarbonate in solution contains carbon which is a mixture of equal proportions of C_{SOIL} and C_{CARB} , resulting in a $\delta^{13}\text{C}$ close to -12 per mille.

2) In areas with peat bogs, part of the soil CO_2 may originate from dissolution of soil carbonates by humic acids, which results in $\delta^{13}\text{C}=0$, equal to that of the soil carbonate.

3) In regions where the soil or bedrock is free of carbonate, the soil CO_2 may instead contribute to erosion of silicate rocks:

This reaction retains the original carbon isotope composition of the soil carbon, which is approximately -25 per mille.

4) During the evolution of the groundwater, additional carbon may be added through the oxidation of organic material with subsequent dissolution of carbonate:

If $m=6n$, the resulting $\delta^{13}\text{C}$ is approximately -12 per mille.

5) The process of sulphate reduction through oxidation of organic carbon in the rock or of methane,

gives a depleted carbon isotope composition of -25 per mille, or lower if the carbon

species is methane.

6) Other processes that can affect the isotopic composition of the dissolved carbon are cation exchange (eg. calcium-sodium), where additional carbonate may be dissolved to maintain saturation with calcite, and dissolution-precipitation.

4.6.2 Results.

Eight groundwater samples were selected for ^{13}C isotope analysis. The results are presented in Table 8.

Some of the samples were re-analyzed after collecting a new sample in 1994. This was done because the $\delta^{13}\text{C}$ originally obtained for AB 93-15 (AB 93-15-1a) was very different from a value later obtained on a sample from the same site submitted for ^{14}C analysis (AB 93-15-2). The repeat analysis of the original sample (AB 93-15-1b), which gave a value more consistent with AB 93-15-2, indicates that the analysis of AB 93-15-1a was erroneous due to sample mix-up in the field or in the laboratory. Therefore, it was desirable to check the validity of the analyses of the remaining samples. Although some variations were observed between samples collected in 1993 and 1994, none of the differences were as large as between sample AB 93-15-1a and AB 93-15-2.

Sample number	Sampling date	Analysis date	Prep.	$\delta^{13}\text{C}$ (per mille)	HCO_3 (ppm)
AB 93-4-1a	93-02-03	93-07-08	BaCO_3	-14.2	475
AB 93-4-1b	93-02-03	94-03-28	DIC	-12.8	475
AB 94-4	94-03-12	94-03-28	DIC	-15.8	618
AB 93-12	93-01-29	94-04-07	DIC	-14.6	959
AB 93-13	93-01-30	93-07-08	BaCO_3	-12.1	290
AB 93-13	94-03-12	94-03-28	DIC	-13.4	296
AB 93-15-1a	93-02-03	93-07-08	BaCO_3	-10.3	124
AB 93-15-1b	93-02-03	94-02-15	DIC	-21.6	124
AB 93-15-2	93-08-25	94-02-01	DIC	-22.7	116
AB 94-15	94-03-12	94-03-28	DIC	-24.1	117
AB 93-17	93-02-03	93-07-08	BaCO_3	-13.2	252
AB 93-22-1	93-03-25	93-07-08	BaCO_3	-23.8	1280
AB 93-22-2	93-10-01	94-04-07	DIC	-24.7	783
AB 93-25-1a	93-01-29	93-07-08	BaCO_3	-16.4	632
AB 93-25-1b	93-01-29	94-04-07	DIC	-15.4	632
AB 93-35-1a	93-02-10	93-07-08	BaCO_3	-15.1	750
AB 93-35-1b	93-02-10	94-03-28	DIC	-15.1	750
AB 94-35	94-03-13	94-03-28	DIC	-13.9	874

Table 8. Results of carbon isotope analysis of dissolved bicarbonate. DIC indicate samples prepared by direct production of CO_2 through reaction with phosphoric acid. BaCO_3 identifies samples from which BaCO_3 was precipitated by adding BaCl_2 to the water sample at $\text{pH} > 11.0$ with subsequent reaction with phosphoric acid to produce CO_2 for analysis.

With the exception of two samples (AB 93-15 and 22), the $\delta^{13}\text{C}$ values fall in the range of -12.1 to -16.4 per mille, which is close to that of groundwater that has attained

its dissolved carbon through the normal carbon evolution of process 1) in the above background section.

The remaining two samples, have a $\delta^{13}\text{C}$ of around -24 per mille, which is a biogenic isotope signature. From the presence of hydrogen sulphide gas dissolved in brackish type A sample AB 93-22, there is little doubt that sulphate reduction is responsible for the biogenic carbon isotope signature of the dissolved bicarbonate in this sample (-24.7 per mille). The Sulphur Spring at Caledonia Springs (type A brackish sample AB 93-35) was named from the hydrogen sulphide associated with it. Here too sulphate reduction is taking place, as it probably did in type A sample AB 93-12, which today completely lacks SO_4^{2-} . However, these two waters do not have the depleted $\delta^{13}\text{C}$ of AB 93-22. A portion of the dissolved carbonate can probably be attributed to dissolution of carbonate from the bedrock, thereby balancing the organic isotope signature resulting from sulphate reduction. It was indicated in a previous section, that dissolution of carbonate minerals has taken place along the flow path of the type A groundwater. Unlike samples AB 93-35 and 12, there may be very little carbonate dissolution taking place in the part of the Carlsbad Formation from which AB 93-22 originates, presumably because of its low carbonate content. The rock sample (sample AB 93-58) which comes from the same borehole as the water sample contains only 1.4% CaO, contrasting with an outcrop sample of the Carlsbad Formation (AB 93-67) collected elsewhere in Gloucester (see Figure 3a) which has a CaO content of 17.51%.

Type B sample AB 93-15 was chosen for ^{14}C dating and therefore, it is important to understand the processes that control the dissolved carbonate content and its carbon isotope composition. It has a $\delta^{13}\text{C}$ value of -24.1 per mille indicating a biogenic source which, as in sample AB 93-22, could have been oxidized through the reduction of sulphate or another oxidant. The high bicarbonate concentration which would result from oxidation of organic material via sulphate reduction or any other oxidation process has not been observed in AB 93-15, which contradicts the sulphate reduction theory. This would be eliminated if some of the bicarbonate had precipitated as carbonate as a result of the common-ion effect. However, as mentioned in section 4.5.2, this source for the sulphate would not explain the high calcium and strontium content in sample AB 93-15.

In order to explain the isotopic composition of this sample, as well as its low bicarbonate content, it is here proposed that AB 93-15 (and the other two type B samples) is the result of mixing between a type A brackish groundwater containing no sulphate, and a groundwater low in Na-Cl but with a high sulphate content, as described in the following: Oxidation of organic material through sulphate reduction did in the past eliminate the sulphate from a brackish groundwater. The produced sulphide was removed from the water either through pyrite precipitation or migration of the gas phase. This created a type A water chemically similar to AB 93-12, which today neither has any dissolved sulphate nor sulphide, but is high in bicarbonate. Subsequently, mixing with a modern and relatively fresh groundwater which contained high levels of sulphate took place. That groundwater originated from the Oxford Formation, where a portion of the

high sulphate content was acquired through dissolution of gypsum in the aquifer (see section 3.2.2.7). A certain amount of pyrite oxidation in the shale also contributed to its sulphate content after migration across the Gloucester Fault into the Carlsbad Formation. This is consistent with the findings in section 4.6, where the sulphate isotope composition indicates that AB 93-15 acquired its high sulphate content in part through gypsum dissolution and partially from the oxidation of pyrite. As a result of mixing with the high calcium-sulphate groundwater, the bicarbonate from the type A groundwater was precipitated as calcite, or consumed in the neutralization of H^+ from the oxidation of the sulphide.

The above mixing theory complicates the interpretation of the obtained ^{14}C content of AB 93-15. However, with the present knowledge a simpler hypothesis that would satisfactorily explain all the observed data including bicarbonate, calcium, strontium and sulphate concentrations as well as sulphur and carbon isotope ratios, could not be identified. In section 4.8 an analysis of the reliability of the ^{14}C data will be presented.

4.7 Carbon isotope composition of methane.

As was mentioned in the section on the gas sample composition, the carbon isotope composition of the methane may provide insight into how the gas was formed.

4.7.1 Background.

As was mentioned in section 4.6.1, methane of organic origin has a carbon isotope signature in the wide range of -21 to -90 per mille. Although there can be some overlap and local variations, in general it is possible to distinguish between bacteriologically produced methane and methane produced from the thermal degradation of kerogen. According to Tiratsoo (1979 p.46), methane produced through bacteriological decomposition at temperatures below 75°C has $\delta^{13}\text{C}$ values in the light range of -90 to -50 per mille. Most catagenically produced gas falls in the range -50 to -40 per mille, while dry post-mature gas is heavier and has $\delta^{13}\text{C}$ values ranging from -40 to -25 per mille. In addition, the bacterial methane can be subdivided into acetate fermentation and carbon dioxide reduction pathways. The ranges with respect to the $\delta^{13}\text{C}$ are <-70 to -60 per mille for the CO_2 reduction and <-70 to -43 per mille for acetate formation (Sherwood Lollar *et al.*, 1993).

4.7.2 Results.

Eight gas samples were analyzed for their carbon isotope composition and the results are presented in Table 9. The obtained carbon isotope ratios of the eight samples fall in the range -56.5 to -64.7 per mille which, given the above background, indicates anaerobic bacteriological degradation of organic material following the acetate fermentation pathway as the source of the gas.

sample number, type of site	AB 93-8, flowing well	AB 93-12, tap in barn	AB 93-20, tap in barn	AB 93-31, spring
$\delta^{13}\text{C-CH}_4$ (per mille)	-59.4	-56.3	-60.4	-57.8
sample number, type of site	AB 93-33, spring	AB 93-34, spring	AB 93-38, tap in barn	AB 93-40, spring
$\delta^{13}\text{C-CH}_4$ (per mille)	-57.4	-64.7	-57.1	-56.5

Table 9. Results of carbon isotope analysis of methane.

As pointed out above, there is overlap between the different types of methane and the obtained data are only slightly depleted with respect to the catagenically produced methane, which may lead to the speculation that the gas in this study is of thermogenic origin. Jenden *et al.* (1993) discussed isotopic data obtained on catagenically produced methane from the Queenston Formation and the lower Ottawa Group of the Appalachian basin in western and central New York State. The rocks have a CAI of 2.5-3 (Jenden *et al.*, 1993), which is the same as for the rocks in this study. The methane in their study have carbon isotope ratios of -30.9 and -30.7 per mille (Jenden *et al.*, 1993), which is significantly heavier than the methane samples in this study. This indicates that the gas in this study does not share the thermogenic origin with the methane from New York.

4.8 ^{14}C dating.

The concentration of the radioactive isotope of carbon in the dissolved carbonate

species may be useful in estimating the age of a groundwater. However, as will be discussed below, the dating of groundwater is more complicated than the dating of organic remains and archaeological specimens, and therefore subject to many assumptions.

4.8.1 Background.

^{14}C is the product of a variety of nuclear reactions in the atmosphere through the interaction between cosmic-ray produced neutrons and the stable isotopes of nitrogen, oxygen and carbon. As these reactions are continuously taking place, the natural concentration of radioactive carbon can be considered to be constant. As long as a living organism or a volume of water is exchanging with the atmosphere it contains 100% modern carbon. After the interaction with the atmosphere ceases, the concentration of radioactive carbon starts to decrease due to the radioactive decay of ^{14}C . The carbon-14 age of a substance can be obtained from its ^{14}C content using the following equation:

$$T = -(t_{1/2} / \ln 2) \ln(A_M / A_0) \text{ years,}$$

where A_0 =initial ^{14}C activity before radioactive decay in pmC (percent modern carbon), A_M =measured activity, $t_{1/2}$ =the half-life of the radioactive carbon, 5730 ± 40 years.

The value of A_0 can in other types of samples be assumed to be 100%, but it is subject to a great deal of uncertainty in groundwater dating. This is because there are

several processes that may alter the carbon isotope composition during the evolution of a groundwater, as described in section 4.6.1. Dissolution of soil carbonates, oxidation of organic carbon, dissolution of carbonate rock and sulphate reduction through oxidation of organic material in the aquifer may all introduce dead carbon, which produces an apparent age which is higher than the real age of the groundwater. Because the magnitude of fractionation for ^{14}C is twice as large as for ^{13}C due to the above processes (Mook, 1980) the $\delta^{13}\text{C}$ of a sample to be carbon-14 dated is obtained in order to estimate the nature and extent of the fractionating processes.

The above processes dilute the original ^{14}C content of a sample by a factor q so that $A_0 = q \cdot A$, where $A = 100 \text{ pmC}$. A calculation of q can be made for each reaction from the general mass balance equation:

$$q = (\delta^{13}\text{C}_{\text{FINAL}} - \delta^{13}\text{C}_{\text{REACT}}) / (\delta^{13}\text{C}_{\text{INITIAL}} - \delta^{13}\text{C}_{\text{REACT}})$$

For example, in process 1) described in section 4.6.1 $\delta^{13}\text{C}_{\text{REACT}}$ (carbon isotope ratio of reactant) is equal to the carbon isotope signature in the soil carbonate, $\delta^{13}\text{C}_{\text{INITIAL}}$ is equal to that of the soil CO_2 , and $\delta^{13}\text{C}_{\text{FINAL}}$ is that measured on a groundwater sample following the dissolution of the carbonate. If $\delta^{13}\text{C}_{\text{INITIAL}} = -26$ per mille, $\delta^{13}\text{C}_{\text{REACT}} = 0$ per mille, and $\delta^{13}\text{C}_{\text{MEASURED}} = -13$, then $q = 0.5$ meaning that 50% of the carbon is dead carbon from the aquifer and 50% is carbon dioxide from the decomposition of contemporaneous organic material in the soil. If carbon from other sources is added throughout the evolution of the

groundwater, a q factor has to be calculated for each process. The $\delta^{13}\text{C}_{\text{INITIAL}}$ in each calculation of q is that which was the $\delta^{13}\text{C}_{\text{FINAL}}$ from the previous reaction. As a result, q for all the reactions will be the product of the q s for each reaction: $q=q_1*q_2*q_3*..q_n$.

4.8.2 Analysis and results.

The ^{14}C concentration in sample AB 93-15 was measured by IsoTrace Radiocarbon Laboratory at the University of Toronto. The analysis gave 16.35 ± 0.24 pmC, translating into an apparent age of 14550 ± 120 years BP.

It is highly unlikely that the obtained apparent age is the real age of the groundwater because 14550 years ago the study area was covered by the Laurentide ice-sheet, and groundwater recharge did not take place.

As mentioned previously, sample AB 93-15 is interpreted as being a mixture between a type A groundwater and a modern high sulphate groundwater. The interpretation of the ^{14}C analysis of the mixing system described is very complex and subject to many uncertainties. The carbon isotope composition and the q factor for the modern portion of the mixture may be estimated on the basis of carbon isotope analyses obtained on fresh water from the Oxford Formation, such as AB 93-17 ($\delta^{13}\text{C}=-13.2$ per mille). However, the $\delta^{13}\text{C}$ of the type A groundwater prior to mixing is not known. In order to attain the observed carbon isotope ratio of -24.1 per mille after mixing, it must have had a depleted

signature of <-24.1 per mille. However, in order to calculate q for the sulphate reduction, the $\delta^{13}\text{C}$ of the organic material that was oxidized in this process also has to be a known factor. The organic material may be either residual kerogen in the shale with a $\delta^{13}\text{C}$ value of -28 to -30 per mille (Deines, 1980) or methane which has a $\delta^{13}\text{C}$ value close to -60 per mille as given in section 4.7. The relative proportions of the two components in the mixture may be estimated by using the chloride content of some samples in this study which can be assumed to represent the end members.

4.8.2.1 Calculation of the age of the brackish type A component.

In the following, some calculations are presented to illustrate the different possible scenarios and the ages they give rise to. Some assumptions are:

- The relative proportions of the modern and the type A water are nearly equal. This is calculated from the chloride content of samples AB 93-22 and 26 (remains unchanged after gypsum dissolution), which serve as the hypothetical components in the mixture. AB 93-26 was chosen as the freshwater end member because it comes from a well in the Oxford Formation immediately west of the Gloucester Fault. AB 93-22 was selected as the brackish type A end member since it is one of the most saline groundwaters in this study and has a similar carbon isotope composition to AB 93-15.

Cl (ppm) AB 93-22: $5200 (*0.52) + \text{AB 93-26: } 263 (*0.48) = 2830$,

which is the same as the analytical value of AB 93-15.

- No fractionation took place during subsequent processes so that the carbon isotope ratio is retained in the remaining bicarbonate. This is only done in order to simplify the calculations.

Additional assumptions are presented for each scenario below.

Scenario I:

- With this mixture the contributions of dissolved carbonate from the two samples are:

HCO_3 from AB 93-22: $0.52 \times 1068 = 555.4$ ppm

93-26: $0.48 \times 282 = 135.4$ ppm

gives total HCO_3 : 691 ppm

- From the proportions of the bicarbonate contributed by the fresh water sample we get $(0.48 \times 282) / 691 = 0.196$, which means that approximately 20% of the bicarbonate originates from the modern sample. From the relationship $0.2 \times (-13.2) + 0.8 \times X = -24.1$ this gives a $\delta^{13}\text{C}$ of the type A water of -26.8 per mille.

- q in the modern sample is calculated using the carbon isotope composition of the only

sample from the Oxford Fm. that was analyzed, AB 93-17. The $\delta^{13}\text{C} = -13.2$ per mille, which indicates that if the soil CO_2 during infiltration had the commonly occurring value of $\delta^{13}\text{C} = -26$ per mille (Deines, 1980), and that of the carbonate subsequently dissolved was 0 per mille, then $q = (-13.2 - 0) / (-26 - 0) = 0.5$ and therefore, $A_0 = 50$ pmC.

- If 20% of the total bicarbonate comes from the modern groundwater, where 50% of the bicarbonate is modern, then 10% of the total is modern. This leaves $16.35(\text{measured}) - 10 = 6.35$ pmC which is due to decay of old carbon in the type A water. If this constitutes 80% of the total bicarbonate in the type A end member, then this carbon activity should be multiplied by $100/80 = 1.25$, which gives 7.94 pmC in the type A water.

- From the above deductions that the $\delta^{13}\text{C}$ of the type A water is -26.8 per mille, and the $\delta^{13}\text{C}$ before sulphate reduction is -13 per mille with $q_1 = 0.5$, the following age calculations can be made:

1) - If the $\delta^{13}\text{C}$ of the organic material is that of kerogen = -29 per mille, then:

for the sulphate reduction process $q_2 = (-26.8 - (-29)) / (-13 - (-29)) = 0.14$, and for the final product $q = q_1 * q_2 = 0.5 * 0.14 = 0.07$, $A_0 = 7$ which is less than 7.94 and therefore not valid.

2) - If the $\delta^{13}\text{C}$ of the organic material is that of methane = -59 per mille (average of samples in section 4.7), then:

$$q_2 = (-26.8 - (-59)) / (-13 - (-59)) = 0.7$$

$q=0.5*0.7=0.35$ giving $A_0=35$ and $T=12\,268$ years BP.

Scenario II.

- Most of the fresh water bicarbonate was consumed through carbonate precipitation due to the common-ion effect before mixing with the brackish water. The analytical value of 16.35 pmC is accounted for solely by the brackish type A water, where the original carbon isotope signature is undiluted by the fresh water. Therefore, the $\delta^{13}\text{C}$ value of the type A end member is the same as that of AB 93-15 (-24.1 per mille). These age calculations are also applicable if sulphate reduction resulting in pyrite precipitation is taking place at present.

3) - If the $\delta^{13}\text{C}$ of the organic material is that of kerogen=-29 per mille, then:

$$q_2=(-24.1-(-29))/(-13-(-29))=0.31$$

$q=q_1*q_2=0.5*0.31=0.16$, which gives $A_0=16$ being smaller than A (16.35) and therefore not valid.

4) - If the $\delta^{13}\text{C}$ of the organic material is that of methane=-59 per mille (average of samples in section 4.7), then:

$$q_2=(-24.1-(-59))/(-13-(-59))=0.76$$

$q=0.5*0.76=0.38$ giving $A_0=38$ and

$T=6\,974$ years.

Given the fractionation factor of -2 per mille between bicarbonate and calcite at 10°C (Kyser, 1987), the carbon isotope ratios attained prior to calcite precipitation may have been somewhat higher than those used in the calculations. Using a less depleted $\delta^{13}\text{C}_{\text{INITIAL}}$ value may give valid ages from case 1) and 3) and somewhat higher ages in 2) and 4). The estimation of the original $\delta^{13}\text{C}$ before calcite precipitation is subject to many estimations, such as the proportion of the dissolved carbonate species remaining in solution and the fractionation factor between aqueous and solid phases as well as between aqueous phases, the exact values of the fractionation factors being temperature dependent. Such estimation is, if at all possible, not necessary for the purpose of the thesis. Therefore, the above calculations were redone assuming that the $\delta^{13}\text{C}$ of the bicarbonate prior to calcite precipitation was an arbitrarily chosen -20 per mille. In case 1) and 2) this gives a $\delta^{13}\text{C}$ of the type A water of -21.7 per mille (from the relationship $0.2*(-13.2)+0.8*X=20$). The value of -20 per mille is used in cases 3) and 4). In Table 10 it is shown how this affects the calculated ages.

Case #	T (years), no fractionation	T (years), fractionation
1)	invalid	8 725
2)	12 268	13 479
3)	invalid	4 484
4)	6 974	7 876

Table 10. Groundwater ages obtained as a function of whether fractionation during calcite precipitation is taken into account in the age calculations. In the case of fractionation, the $\delta^{13}\text{C}$ prior to calcite precipitation is -20 per mille.

4.8.2.2 Discussion of the age determinations.

Fractionation of the dissolved carbonate species is likely to have taken place during calcite precipitation. Therefore, this discussion will focus on the data set in the right hand column of Table 10.

Case 2) gives an age of 13 479 years, which is before the existence of the Champlain Sea, and would mean recharge during the pre-Champlain Sea fresh water phase. Recharge during this period of time would give depleted oxygen isotope ratios due to the presence of large amounts of meltwater rather than the somewhat enriched oxygen isotope ratios displayed by the studied groundwaters. The remaining three calculations give post-Champlain Sea ages.

It is most likely that some calcite precipitation took place in the fresh groundwater, thereby removing at least a portion of the bicarbonate from that end member prior to mixing, as illustrated by scenario II. At least half of the dissolved sulphate in AB 93-15 is believed to originate from gypsum dissolution which took place prior to mixing. This would create supersaturation of calcite through the common ion effect in the fresh water, and calcite precipitation. Therefore, scenario II is probably closer to the real situation than scenario I.

It is probable that the organic material utilized in the sulphate reduction process was

kerogen as in case 3), rather than methane. This is because the degradation of organic material takes place in a strict order, as mentioned in section 3.2.3. Methane producing fermentation does not occur until all sulphate has been consumed in the oxidation of organic material. Therefore, methane produced from the type A water through fermentation could not be present before all sulphate was consumed through sulphate reduction. However, case 4) can not be definitely rejected because methane could have been produced elsewhere and through migration become associated with the type A water. It has been shown that methane has been found associated with brackish groundwater elsewhere in the study area. The source of the organic carbon could also be a mixture between kerogen and methane creating a scenario intermediate between 3) and 4). The source of the organic carbon cannot be resolved with the present state of knowledge.

From the above discussion case 3) most closely reflects the actual conditions under which the dissolved carbonate species in AB 93-15 developed, giving an age of approximately 4 500 years BP. If some of the organic carbon in the sulphate reduction process was methane, the age could be somewhat higher. This gives a groundwater age in the range 4 500 to 7 900 years, which encompasses the peak of the climatic warming 6 000 years ago, a result that supports the interpretation of the stable isotope composition in section 4.2.3. Although a scenario which has been described as less likely, if sulphate reduction does take place at present, then the age calculations for case 3) and 4) are applicable. This means that it does not matter for the purpose of carbon dating whether sulphate reduction takes place in the past or present.

Although the age range obtained from calculations 3) and 4) is a probable one, it is based only on the interpretation of chemical and isotopic data. A more detailed hydrogeological investigation of the Gloucester area could, together with the geochemical data from this study, serve as background for a more reliable carbon isotope dating of a sample more suitable than AB 93-15.

5 DISCUSSION.

As stated in the introductory chapter, possible sources for the salinity of the groundwaters in this study are:

- Evaporites dissolved from the aquifer.
- Trapped seawater in pores of the aquifer material either of syngenetic (formation water) or epigenetic (Champlain Sea water) origin.
- Leakage of deep-seated Canadian Shield brines.
- Extensive water-rock interaction.

5.1 Evaporite dissolution.

In chapter 3 it was shown that the molar ratio of sodium and chloride, which constitute the bulk of the salinity in most of the brackish groundwater samples, is equimolar. This could indicate that simple dissolution of halite is the source of salinity in these groundwaters. However, since there have been no reports of evaporites occurring in the Carlsbad Formation, which is the host for the brackish groundwater, evaporite dissolution is not the most likely origin for the dissolved solids. An exception to this is demonstrated by a few samples which have been denoted type B water. They contain a significant proportion of sulphate and calcium in addition to the sodium and chloride. It was found through isotopic analysis of the dissolved sulphate that dissolution of gypsum

is contributing to the salinity in these samples.

A source for the gypsum can be theorized to be the Oxford Formation as follows. The occurrence of type B waters is restricted to one fault block in the Carlsbad Formation immediately east of the Gloucester Fault Zone. In this part of the study area, the fault constitutes the geological boundary with what is indicated by Williams *et al.* (1984) as the Nepean Formation to the west. However, the well information available for the two bedrock wells in that location, AB 93-21 and 26, lists the aquifer material to be limestone, which would be the Oxford Formation rather than the Nepean Formation.

The Oxford Formation is reported to contain calcite filled vugs, which originally were gypsum nodules. It is possible that some of the gypsum has not been completely replaced. Massive gypsum has also been reported in the Oxford Formation elsewhere in the St. Lawrence Lowland. Therefore, there may be gypsum available in the Oxford Formation that is locally responsible for high levels of sulphate in groundwater. Groundwater with high levels of dissolved gypsum migrating from the Oxford Formation across the fault to mix with the sodium-chloride brackish groundwater in the Carlsbad Formation is in agreement with the groundwater flow direction in this part of the Oxford Formation (A. Sager-Kinsman, pers. comm.). Although none of the fresh groundwater in this study or that of Sager-Kinsman (1995) have elevated levels of sulphate comparable to the type B waters, it is possible that such groundwater could occur locally in horizons where gypsum is present in the bedrock of the Oxford Formation.

From the combined sample location and geological map of Figure 3a it is seen that samples AB 93-3,15 and 44, which constitute the type B group come from locations relatively distant from the supposed position of the Gloucester Fault zone indicated by Williams *et al.* (1984). However, since this position is approximate, and there are no outcrops in the area, it is quite likely that the real position of the fault is further to the east in this part of the study area. The presence of limestone rather than shale in well AB 93-26, which in Figure 3a actually is situated in the Carlsbad Formation east of the fault, also supports this hypothesis.

In summary, evaporite dissolution is not believed to be responsible for the salinity of the brackish groundwater in this study, except for the samples with high levels of sulphate where gypsum dissolution has taken place.

5.2 Formation water.

The element plots in chapter 3 show that the brackish groundwaters in this study are geochemically similar to formation waters. Formation water is typically associated with petroleum and natural gas occurrences in sedimentary basins. Given that methane gas was found in conjunction with the brackish groundwater, and that formation water occurs together with petroleum and gas in equivalent bedrock units in SW Ontario, this possible origin is relevant to explore.

If, as the term formation water implies, a portion of the groundwater has been present in the bedrock since the Ordovician, then it has also undergone burial and heating which corresponds to petroleum forming temperatures. These conditions are indicated by the alteration of conodonts found in the bedrock. As a response to increased temperature and pressure, ultrafiltration will take place through a shale layer, which further concentrates the solutes in the groundwater in the lower portion of the shale unit. This could explain why the brackish groundwater only occurs in shale, as was noted in chapter 3. However, water-rock interaction including mineral reactions at temperatures exceeding 50°C results in isotopic exchanges between water and mineral phases leading to the enrichment of ^{18}O in formation water. Such enrichment was not observed in the brackish groundwaters in this study, which were found to be of meteoric origin. Due to the possibility of creating a water far exceeding the salinity of seawater through the above processes, it is evident that if the salinity in this study is of formation water origin, the levels of salinity in the brackish waters indicate extensive dilution. Therefore, it could be argued that in order to attain the relatively low TDS observed in this study, such a high proportion of meteoric water would be required, that the resulting dilute formation water would plot close to the local meteoric water line. In this scenario, the groundwater would still retain a small but consistent deviation from the local meteoric water line, which was not observed. The oxygen and hydrogen isotope composition of the brackish groundwaters proves that they could not be derived from syngenetic formation water.

5.3 The Champlain Sea.

Some infiltration and entrapment of Champlain Sea water probably took place at the end of the last glaciation. The salinity of the most saline groundwaters in this study compares approximately to a threefold dilution of seawater, which may have taken place both before and after infiltration into the subsurface. As previously shown, the brackish groundwater occurs only in the shale of the Carlsbad Formation. This preferential distribution could be a function of the low hydraulic conductivity of the shale, so that the seawater was preserved only in this rock type. The hydraulic conductivity of the Nepean, March and Oxford Formations, which have been found to contain fresh groundwater, are higher than that of the Carlsbad Formation. Therefore, the sea water could have been flushed out of these aquifer units more easily, while being retained in the shale.

The only geochemical evidence from chapter 3 that suggests a seawater origin is the Br/Cl ratio. However, the observed Br/Cl ratio is not exclusive to seawater, and therefore not conclusive without other supporting evidence.

The bedrock in which the brackish groundwater occurs has a very strong influence on the chemical character of the brackish groundwaters. For example, the activity of anaerobic bacteria in the reducing conditions of the shale has eliminated sulphate from most of the groundwater samples (type A waters) through sulphate reduction, thereby also raising the bicarbonate concentration well above that of seawater with the same TDS. In

other groundwaters denoted as type B, dissolution of sulphur bearing minerals are the source for the dissolved sulphate. The strontium in the groundwater was shown to originate from the shale bedrock, see section 4.4.3. Dissolution and precipitation of carbonate minerals were discussed in section 3.2.2.9. All of these processes would help to obliterate the original relative proportions of the solutes in the seawater that existed 10 000 years ago. They also contribute solutes to the groundwater, so that at least a portion of the salinity is in fact due to interaction with the bedrock environment.

The obtained groundwater age of 4 500 to 7 900 years BP does not indicate a Champlain Sea origin of the salinity. The hypothetical range of oxygen isotope ratios and TDS defined by the Champlain Sea water mixing model in section 4.2.2.1 does not satisfactorily describe all the sample compositions with respect to oxygen isotope composition and TDS.

5.4 Canadian Shield brines.

Potential conduits for deep-seated brines and saline groundwaters from the Canadian Shield are not difficult to find, given the abundance of faults in the area which are believed to continue into the Canadian Shield. However, these are not restricted to the Carlsbad Formation, so there is no logical reason why the brackish groundwater would occur only in the shales in the study area.

The elimination of brines from the Canadian Shield as a possible source of the salinity in the brackish groundwater is further substantiated by geochemical evidence. These include the higher sodium to chloride ratio and lower Br/Cl and Ca/Cl ratios of the studied waters as compared to shield brines. Furthermore, the stable isotope composition of the water indicates a meteoric origin.

5.5 Water-rock interaction.

The occurrence of the brackish groundwater is spatially related to the Carlsbad Formation, which could indicate that interaction with the shale is the source of the salinity. The element plots for the brackish groundwater in chapter 3 show a chemical similarity to groundwater found in shale elsewhere. In particular, the 1:1 Na:Cl ratio, also observed in this study, was pointed out by Von Damm (1987) as the common denominator among groundwaters in shale terrains. Her observation was independent of geographical location and whether or not halite was present in the bedrock.

As indicated by the stable isotope signature of the water, any water-rock interaction took place at low temperatures and thus did not alter the ^2H and ^{18}O ratios of the meteoric water. The nature of this interaction is envisioned to be primarily leaching of solutes from the minerals in the shale. As discussed by Charron (1974 and 1978), chloride content resulting from interaction with the bedrock can be considered to be a measure of residence time of a groundwater. It is possible that a portion of the solute load, primarily

cations, originates from the evaporite minerals originally precipitated in the hypersaline depositional environment of the bedrock. These have been dissolved by groundwater and do not exist at present. However, some of the cations may have been adsorbed onto clay minerals contained in the shale. The ensuing leaching by groundwater of meteoric origin could contribute to the elevated TDS observed in the groundwater at present. The strontium isotope data indicates that at least this element does have its source in the shale bedrock.

The obtained ^{14}C age of the dissolved bicarbonate is, according to one of the scenarios in section 4.8, in the range 4 500 to 7 900 years. This is in agreement with the oxygen isotope composition, which indicates that the groundwater was recharged at a time when the climate was milder than today in the study area. According to the climatic records, the area experienced a warming period that peaked at approximately 6000 years ago.

The brackish groundwater is concluded to be the result of interaction between meteoric groundwater and the shale of the Carlsbad Formation, primarily slow leaching of solutes.

Brackish groundwater is also encountered in some overburden wells, as shown by samples AB 93-3, 4 and 39. Samples AB 93-4 and 39 are dilute brackish waters which come from locations where deeper wells were wells penetrating the underlying Carlsbad

shale yield more saline waters. These deeper wells (AB 93-15 at AB 93-4 and AB 93-18 at AB 93-39) have static water levels (for AB 93-15 it is 78.0 m and AB 93-18 64.0 m) close to the elevation of the well bottoms of AB 93-4 and 39 (78.3 and 70.1); see Appendix 1. It is therefore likely that the salinity in the shallow wells are the result of seepage of the more saline groundwater from below. Well AB 93-3 is much deeper than AB 93-4 and 39, with its bottom at 50.3 m.a.s.l., which is 5.5 m above the bedrock surface and well below the static water level of AB 93-15, being the closes well to AB 93-3 in the Carlsbad shale. The salinity is higher than in the other two overburden wells, which due to the proximity to the bedrock is very likely to be resulting from leakage from the Carlsbad shale. It can also be the result from interaction with black gravel which constitutes the overburden at that location.

As shown by samples AB 93-19, 25 and 38, it is possible to extract fresh groundwater from the Carlsbad Formation. The actual location of the Gloucester Fault may be further east than indicated by Williams *et al.* (1984) as was discussed in chapter 5, and therefore it is possible that AB 93-19 in reality is not a sample from the Carlsbad Formation. However, such an explanation is not applicable for AB 93-25 and 38, which come from wells located well within the geological boundaries of the Carlsbad Formation (see Figure 3a). The presence of brackish groundwater may be limited to certain horizons in the bedrock or the distribution of fresh and brackish groundwater may be related to recharge and discharge areas, as suggested by Charron (1978).

6 CONCLUSIONS.

The chemistry of the brackish groundwater is controlled by mineral dissolution-precipitation, solute adsorption-desorption and by microbiological activity in the anaerobic environment of the shale. This is shown by geochemical evidence and by the strontium, sulphur and carbon isotopic data of dissolved species. The source for the salinity is interaction with the bedrock, primarily by leaching of solutes from the bedrock. Some of these solutes, primarily cations, may have originally come from the dissolution of evaporite minerals deposited in the hypersaline environment in which sedimentation of the shale took place. Properties that are unique to the shale bedrock, such as the low hydraulic conductivity, which leads to long residence times, and retention of solutes on clay minerals, cause the preferential occurrence of the brackish groundwater in shale only.

Dissolution of sulphate minerals from the Oxford Formation in combination with sulphide oxidation is the source of the elevated sulphate and calcium levels in some brackish waters in the south end of Gloucester immediately east of the Gloucester Fault. This was indicated by the chemical data and confirmed by isotopic analysis of the sulphate.

The oxygen and hydrogen isotope composition of the groundwater show a meteoric origin, which contradicts the existence of both formation water and remnant Champlain Sea water trapped in the shale. These data also indicate that the groundwater was

recharged at a time when the climate was milder in the study area than it is today, either at 950-1250 AD or around 6 000 years BP.

An attempt to date one of the brackish groundwater samples through tritium analysis shows that it is not recent. An interpretation of the result from the ^{14}C analysis gives a time of recharge of approximately 4 500 to 7 900 years ago, which is supported by the oxygen and hydrogen isotope data. However, this ^{14}C estimation was subject to many assumptions, and the only certain conclusion with regard to its age is that the brackish groundwater is older than 1952.

The carbon isotope composition of associated methane gas indicates that they are the product of bacteriological fermentation.

Since the brackish groundwaters are spatially related with the shale, it is implied that in areas where the Carlsbad Formation constitutes the top of the bedrock column, drilling below that level may yield groundwater with lower salinity. However, it is highly likely that little or no sulphate is present in the groundwater, due to sulphate reduction. This leads to two potential problems, one being the existence of hydrogen sulphide gas. The other is the presence of barium dissolved in the water, because the presence or absence of sulphate has a strong influence on the levels of barium in the groundwaters, due to the low solubility of barite. This mechanism is well illustrated by the levels of barium which exceed the drinking water standard of 1.0 ppm in most of the sulphate free type A

brackish groundwaters on one hand and the type B waters on the other hand which are high in sulphate but contain no barium (see Appendix 3). There are no wells in this study which are drilled through the shale bedrock and into the underlying limestone, with the possible exception of AB 93-30. Since this well is situated very close to a fault, its exact location with respect to the fault, and therefore the stratigraphy at the site, is not known.

The dilute brackish groundwater present in wells drawing water from overburden which rests on top of the Carlsbad Formation is interpreted to be the result of upward leaking of brackish groundwater from the shale.

It is possible to extract fresh groundwater from the Carlsbad Formation. However, it is not clear whether the occurrence of brackish groundwater is limited to certain horizons in the bedrock or is related to recharge and discharge areas.

A more systematic hydrogeological survey of that part of the City of Gloucester which is underlain by the Carlsbad Formation is necessary for a better understanding of the controls of groundwater quality in the shale. This would also form the basis for a more meaningful interpretation of ^{14}C data obtained on sample AB 93-15 or any sample obtained at that time. Such a survey would by necessity involve the establishment of new observation points because there are few wells that contain brackish groundwater which have not been included in this study.

The reason why there are so few existing wells beyond those sampled in this study which contain brackish groundwater is the poor water quality. Many wells that were listed by Owen (1953) have since been filled in and overburden wells containing water with a lower TDS have replaced them. The overburden consists to a large extent of clays, which may not yield sufficient quantities of groundwater and it was shown that such wells may still produce relatively saline water. Therefore, further work in the area should include sampling of any existing wells which may penetrate below the shales or the drilling of such a well.

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APPENDICES.

APPENDIX 1. Depth and aquifer data for sampled wells and springs.

Well depth data originate from the Ontario Ministry of the Environment and the report on groundwater resources in Gloucester by Owen (1953).

Explanation of aquifer terms:

Ca = Carlsbad Formation

Bi = Billings Formation

Li = Lindsay Formation

Ox = Oxford Formation

Ma = March Formation

obdn. = overburden, unspecified. Where the nature of the overburden is known the terms sand and clay are used as applicable.

In accordance with the well data published by the Ontario Ministry of the Environment, the term "Water found" is used to indicate the depth(s) at which water was encountered during drilling of a well.

Sample # AB 93/94-	1	2	3	4	5
Ground surface (m.a.s.l.)	85.4	77.7	77.7	81.7	77.7
Depth to bedrock (m)	N/A	25.9	32.9	21.3	0.0
Water found (m)	16.8	N/A	N/A	N/A	51.8
Depth to water (m)	1.2	N/A	N/A	N/A	N/A
Well depth (m)	18.3	4.3	27.4	3.4	56.7
Bedrock surface (m.a.s.l.)	N/A	51.8	44.8	60.4	N/A
Water found (m.a.s.l.)	68.6	N/A	N/A	N/A	25.9
Static level (m.a.s.l.)	84.1	N/A	N/A	N/A	N/A
Well bottom (m.a.s.l.)	67.1	73.5	50.3	78.3	21.0
Aquifer	obdn.	sand	obdn.	sand	Ca
Sample # AB 93-	6	7	8	9a	9b
Ground surface (m.a.s.l.)	92.7	79.2	67.1	57.9	57.9
Depth to bedrock (m)	7.0	60.0	34.4	2.4	2.4
Water found (m)	N/A	N/A	39.6 46.3	N/A	N/A
Depth to water (m)	3.7	N/A	0	N/A	N/A
Well depth (m)	10.7	7.6	47.2	N/A	2.4
Bedrock surface (m.a.s.l.)	85.6	19.2	32.6	55.5	55.5
Water found (m.a.s.l.)	N/A	N/A	27.4 20.7	N/A	N/A
Static level (m.a.s.l.)	89.0	N/A	67.1	N/A	N/A
Well bottom (m.a.s.l.)	82.0	71.6	19.8	N/A	55.5
Aquifer	sand	obdn.	Ca	clay	obdn.

Sample # AB 93-	11	12	13	14a	14b
Ground surface (ma.s.l.)	78.0	78.6	79.9	76.2	76.2
Depth to bedrock (m)	29.6	42.1	26.5	54.9	54.9
Water found (m)	37.2 44.2 51.2	N/A	26.2	N/A	N/A
Depth to water (m)	13.7	2.1	1.2	N/A	N/A
Well depth (m)	64.6	54.3	26.2	15.2	N/A
Bedrock surface (m.a.s.l.)	48.5	36.6	53.3	21.3	21.3
Water found (m.a.s.l.)	40.8 33.8 26.8	N/A	53.6	N/A	N/A
Static level (m.a.s.l.)	64.3	76.5	78.6	N/A	N/A
Well bottom (m.a.s.l.)	13.4	24.4	53.6	61.0	N/A
Aquifer	Ca	Ca	obdn.	obdn.	obdn.
Sample # AB 93-	15	16	17	18	19
Ground surface (m.a.s.l.)	81.7	76.5	88.1	74.7	103.6
Depth to bedrock (m)	21.3	64.0	N/A	25.9	4.9
Water found (m)	N/A	64.0 70.1	N/A	N/A	48.8
Depth to water (m)	3.7	12.5	4.0	10.7	18.3
Well depth (m)	59.7	70.1	21.3	29.0	72.8
Bedrock surface (m.a.s.l.)	60.4	12.5	N/A	48.8	98.8
Water found (m.a.s.l.)	N/A	12.5 6.4	N/A	N/A	54.9
Static level (m.a.s.l.)	78.0	64.0	84.1	64.0	85.4
Well bottom (m.a.s.l.)	22.0	6.4	66.8	45.7	30.8
Aquifer	Ca	Ca or Bi	Ma or Ox	Ca	Ca

Sample # AB 93-	20	21	22	23	24
Ground surface (m.a.s.l.)	79.2	79.9	76.2	117.3	117.0
Depth to bedrock (m)	60.0	24.4	61.0	0.0	2.1
Water found (m)	4.9 50.6 65.2	32.3	N/A	11.3 32.9 53.0	19.8 36.3 57.3
Depth to water (m)	2.7	0.3	11.6	7.3	22.2
Well depth (m)	67.7	32.9	62.2	76.2	70.1
Bedrock surface (m.a.s.l.)	19.2	55.5	15.2	117.4	114.9
Water found (m.a.s.l.)	74.4 28.6 14.0	47.6	N/A	106.1 84.4 64.3	97.2 80.8 59.7
Static level (m.a.s.l.)	76.5	79.6	64.6	110.0	94.8
Well bottom (m.a.s.l.)	11.6	46.9	14.0	41.2	46.9
Aquifer	Ca	Ox	Ca	Ox+Ma+Ne	Ox+Ma+Ne
Sample # AB 93-	25	26	27	28	30
Ground surface (m.a.s.l.)	83.8	82.3	88.4	79.2	76.5
Depth to bedrock (m)	47.2	27.7	15.2	48.8	61.0
Water found (m)	48.8	32.6	16.8	54.9	N/A
Depth to water (m)	16.8	0.0	4.6	3.0	10.1
Well depth (m)	50.3	33.2	17.4	56.1	106.7
Bedrock surface (m.a.s.l.)	36.6	54.6	73.2	30.5	15.5
Water found (m.a.s.l.)	35.0	49.7	71.6	24.4	N/A
Static level (m.a.s.l.)	67.1	82.3	83.8	76.2	66.4
Well bottom (m.a.s.l.)	33.5	49.1	71.0	23.2	-30.2
Aquifer	Ca	Ox	Ox	Ca	Ca or Bi

Sample # AB 93/94-	31	32	33	34	35
Ground surface (m.a.s.l.)	70.1	68.6	68.6	52.0	50.9
Depth to bedrock (m)	16.8	16.8	16.8	4.3	4.3
Water found (m)	N/A	N/A	N/A	N/A	N/A
Depth to water (m)	0.0	N/A	0.0	0.0	0.0
Well depth (m)	spring	73.2	spring	spring	spring
Bedrock surface (m.a.s.l.)	53.3	51.8	51.8	64.3	46.6
Water found (m.a.s.l.)	N/A	64.0	N/A	N/A	N/A
Static level (m.a.s.l.)	70.1	N/A	68.6	68.6	50.9
Well bottom (m.a.s.l.)	spring	-4.6	spring	spring	spring
Aquifer	Ca	Ca	Ca	Li	Li
Sample # AB 93-	36	37	38	39	44
Ground surface (m.a.s.l.)	50.9	50.9	85.4	74.7	79.2
Depth to bedrock (m)	4.3	4.3	25.0	25.9	25.9
Depth to water (m)	0.0	0.0	3.7	N/A	N/A
Well depth (m)	spring	spring	32.0	4.6	29.6
Bedrock surface (m.a.s.l.)	46.6	46.6	60.4	48.8	53.3
Static level (m.a.s.l.)	50.9	50.9	81.7	N/A	N/A
Well bottom (m.a.s.l.)	spring	spring	53.3	70.1	49.7
Aquifer	Li	Li	Ca	obdn.	Ca

APPENDIX 2. Chemical analyses, detection limits.

Element	Lower detection limit	Method
Cl	0.10 ppm	Ion chromatography
NO ₃	0.10 ppm	Ion chromatography
SO ₄	0.01 ppm	Ion chromatography
Br	0.4 ppm	Ion chromatography
Ag	10 ppb	ICP
Al	0.2 ppm	ICP
Fe	0.2 ppm	ICP
Mn	0.02 ppm	ICP
Mg	0.2 ppm	ICP
Ca	0.2 ppm	ICP
Na	0.2 ppm	ICP
K	0.5 ppm	ICP
Cu	5 ppb	ICP
Pb	100 ppb	ICP
Zn	20 ppb	ICP
Mo	50 ppb	ICP
Cr	20 ppb	ICP
V	20 ppb	ICP
As	200 ppb	ICP
Bi	200 ppb	ICP
Te	200 ppb	ICP
Ba	40 ppb	ICP
Sb	200 ppb	ICP
Sn	200 ppb	ICP
Sr	20 ppb	ICP
W	200 ppb	ICP

Chemical analyses are estimated to be reproducible within 10% of the obtained analytical values.

APPENDIX 3. Chemical analyses (in ppm) of the groundwater and field measurements.

sample #	AB 93-1	AB 93-2	AB 93-3	AB 93-4	AB 93-5
Cl	1.9	166	2280	374	2995
SO ₄	37	89	1880	248	0
HCO ₃	180	350	120	475	682
NO ₃	0	14	0.10	0	3.7
Br	n/a	n/a	8.6	0.84	13
Na	2.6	81	1540	186	1742
K	1.7	6.5	16	6.5	29
Ca	44	120	469	180	17
Sr	0.49	0.35	12.0	0.69	3.2
Ba	0.1	0.21	0	0.09	3.5
Mg	18	15	90	48	86
Fe	0.5	0.2	1.8	0.8	0
Mn	0	0.92	0.41	0.14	0
Cu	0	0.06	0	0	0
Zn	0	0	0	0	0
Pb	0	0	0	0	0
Cr	0	0	0.02	0	0
Mo	0	0	0	0	0
V	0	0	0	0	0
Al	0	0	0.2	0	0
Sb	0	0	0	0	0
TDS	193.7	664.6	6344.0	1279.2	5203.8
Field measurements					
pH	7.8	6.5	7.9	7.2	8.2
cond.	330	1220	8230	2075	9240
alk. CaCO ₃	153	286	98	389	560
temp.	9	10	8	11	10

sample #	AB 93-6	AB 93-7	AB 93-8	AB 93-9a	AB 93-9b
Cl	10	152	4075	44	90
SO ₄	27	94	32	56	108
HCO ₃	70	315	1342	332	405
NO ₃	0.56	1.6	0	5.4	0
Br	n/a	n/a	15	n/a	n/a
Na	7	125	2877	43	82
K	15	3.2	41	4.7	0
Ca	23	62	13	52	100
Sr	0.08	0.28	3.1	1.3	2.6
Ba	0	0	2.5	0	0.22
Mg	1.7	15	110	23	14
Fe	0.2	0	0	0	0
Mn	0.02	0.07	0	0	0
Cu	0.01	0.03	0	0.02	0.01
Zn	0.23	0	0.08	0.27	0.12
Pb	0	0	0.12	0	0
Cr	0	0	0	0	0
Mo	0	0	0	0	0
V	0	0	0	0	0
Al	0	0	0	0	0
Sb	0	0	0.22	0	0
Sn	0	0	0.21	0	0
TDS	119.4	608.9	7799.1	393.1	597.2
Field measurements					
pH	7.2	7.1	8.3	7.3	7.1
cond.	200	1080	11430	710	1030
alkalinity	57	269	1100	272	332
temp.	7	9	7	9	9

sample #	AB 93-11	AB 93-12	AB 93-13	AB 93-14a	AB 93-14b
Cl	1520	2120	152	88	14
SO ₄	0	0	111	84	42
HCO ₃	549	959	290	245	134
CO ₃		13			
NO ₃	0	1.1	0.1	10	2.9
Br	5.3	9.6	0.75	0.4	n/a
Na	972	1510	104	34	11
K	16	33	6.2	26	4.1
Ca	46	20	63	114	42
Sr	1.4	2.2	5.6	0.36	0.29
Ba	1.5	1.9	0.05	0.08	0.06
Mg	30	62	32	13	5.2
Fe	0	0	1.1	0.2	0
Mn	0	0	0.05	0.35	0.37
Cu	0	0	0	0.01	0.03
Zn	0	0	0	0.61	0.04
Pb	0	0	0	0	0
Cr	0	0	0	0	0
Mo	0	0	0	0	0
V	0	0	0	0	0
Al	0	0	0	0	0
Sb	0	0.22	0	0	0
Sn	0	0.22	0	0	0
TDS	2861.6	4244.4	604.3	491.9	188.3
Field measurements					
pH	8.3	8.3	7.8	6.8	6.5
cond.	4410	7270	280	760	330
alkalinity	450	900	238	426	110
temp.	10	9	15	4	7

sample #	AB 93-15	AB 93-16	AB 93-17	AB 93-18	AB 93-19
Cl	2830	5500	36	3000	127
SO ₄	740	7.0	24	0	66
HCO ₃	124	933	252	919	177
NO ₃	2.8	0	0.3	3.8	4.7
Br	12.7	22	n/a	13	n/a
Na	1661	3700	25	1998	58
K	21	46	6.1	27	5.7
Ca	225	41	47	7.9	63
Sr	12	7.8	1.7	2.61	0.23
Ba	0	2.6	0.27	3.4	0.15
Mg	81	190	27	35	12
Fe	1.3	0.9	0.7	0	0.3
Mn	0.21	0.08	0.03	0	0
Cu	0	0	0	0	0.05
Zn	0	0	0	0	0.03
Pb	0	0.23	0	0	0
Cr	0	0	0	0	0
Mo	0	0	0	0	0
V	0	0	0	0	0
Al	0	0	0	0	0
Bi	0	0.21	0	0	0
Sb	0	0.28	0	0	0
TDS	5631.2	9977.1	292.0	5542.9	424.0
Field measurements					
pH	7.4	8.8	7.9	8.0	6.7
cond.	9450	16000	480	9940	830
alkalinity	102	766	207	754	145
temp.	10	7	9	10	9

sample #	AB 93-20	AB 93-21	AB 93-22	AB 93-23	AB 93-24
Cl	4070	77	5200	92	130
SO ₄	0	85	33	228	154
HCO ₃	901	288	1068	420	311
NO ₃	3.8	0	0	0.1	1.2
Br	15.6	n/a	19.5	0.2	n/a
Na	2750	80	3369	43	90
K	46	5.7	54	5.8	7.4
Ca	20	59	41	120	85
Sr	3.2	4.48	5.5	1.6	1.7
Ba	4.9	0.06	2.8	0.06	0.07
Mg	150	16	202	79	37
Fe	0.8	0.9	1.3	1.0	0.3
Mn	0	0.06	0.09	0.06	0.11
Cu	0	0.01	0	0	0.07
Zn	0	0.03	0	0	0.03
Pb	0.19	0	0.26	0	0
Cr	0	0	0	0	0
Mo	0	0	0	0	9.16
V	0	0	0	0	0.17
Al	0	0	0	0	0
Bi	0	0	0.25	0	0
Sb	0	0	0.33	0	0
Te	0	0	0.27	0	0
TDS	7507.4	468.9	9454.3	777.8	668.1
Field measurements					
pH	8.1	7.4	8.1	6.8	6.9
cond.	11855	830	16850	1200	1050
alkalinity	738	236	1050	344	255
temp.	8	8	9.5	11	11
H ₂ S (ppm)			75		

sample #	AB 93-25	AB 93-26	AB 93-27	AB 93-28	AB 93-30
Cl	220	263	3.5	1900	1700
SO ₄	82	80	34	0	0
HCO ₃	632	282	195	770	43
NO ₃	1.0	0	0	1.3	0
Br	n/a	0.90	n/a	7.4	16
Na	182	144	4.4	1340	739
K	9.6	9.2	2.2	14	11
Ca	106	69	52	8.6	176
Sr	0.50	5.9	0.59	1.5	14
Ba	0.06	0.05	0.10	1.8	5.7
Mg	51	30	19	42	51
Fe	0.2	0.7	0.4	0	24
Mn	0.07	0.07	0	0	2.6
Cu	0	0	0	0.01	0
Zn	1.1	0	0	0	0
Pb	0	0	0	0	0
Cr	0	0	0	0	0
Mo	0.06	0	0	0	0
V	0	0	0	0	0
Al	0	0	0	0	0
Sb	0	0	0	0	0
TDS	964.5	741.7	212.0	3694.8	2761.7
Field measurements					
pH	7.4	7.9	7.6	8.3	7.2
cond.	1500	1240	360	6010	4860
alkalinity	518	231	160	644	35
temp.	7	9	12	11	11

sample #	AB 93-31	AB 93-32	AB 93-33	AB 93-34	AB 93-35
Cl	555	581	598	5470	3330
SO ₄	0	0	0	1.0	3.1
HCO ₃	606	536	647	1158	750
CO ₃		71			
NO ₃	1.0	0	0.8	8.9	4.0
Br	n/a	4.8	n/a	18	12
Na	530	613	632	3700	1958
K	10	11	5.5	47	32
Ca	7.7	20	7.4	32	28
Sr	0.63	1.1	1.2	4.2	5.9
Ba	0.32	0.65	0.82	5.2	4.1
Mg	5.0	7.4	7.4	236	93
Fe	0	0	0	0.8	0
Mn	0	0.02	0	0.06	0
Cu	0	0	0	0	0
Zn	0	0	0	0	0
Pb	0	0	0	0.29	0
Cr	0	0	0	0	0
Mo	0	0	0	0	0
V	0	0	0	0	0
Al	0	0	0	0	0
Bi	0	0	0	0.26	0
Sb	0	0	0	0.36	0
TDS	1407.8	1574.2	1566.6	10094.2	5839.5
Field measurements					
pH	8.5	8.3	8.3	7.8	7.7
cond.	2230	2710	2680	14430	10020
alkalinity	497	566	550	1010	616
temp.	5	8	8	2	8
H ₂ S (ppm)					2

sample #	AB 93-36	AB 93-37	AB 93-38	AB 93-39	AB 93-44
Cl	4160	4150	27	658	275
SO ₄	0.78	0	0	72	1510
HCO ₃	958	851	390	304	196
NO ₃	3.8	3.9	0	0	0.39
Br	15.2	3.1	0.4	n/a	n/a
Na	2900	2700	146	245	280
K	40	40	0.5	3.3	11
Ca	29	28	0.8	134	541
Sr	6.0	5.8	0.06	2.18	11
Ba	6.5	5.1	0.04	0.10	0
Mg	152	145	0.3	50	30
Fe	0.7	0.6	0	0.6	3.5
Mn	0	0	0	0.05	0.18
Cu	0	0	0	0.02	0
Zn	0	0	0	0	0
Pb	0.21	0.20	0	0	0
Cr	0	0	0	0	0.21
Mo	0	0	0	0	0
V	0	0	0	0	0
Al	0	0	0	0	0
Sb	0.26	0.28	0	0	0
TDS	7785.4	7500.1	367.2	1315.0	2759.0
Field measurements					
pH	7.8	7.8	8.8	7.4	6.8
cond.	12130	12080	640	2420	3080
alkalinity	786	698	320	249	161
temp.	8	7.5	10	8	12.5
H ₂ S (ppm)	0.6				

APPENDIX 4. Gas chromatography analyses.

List of samples:

Sample number	Location
AB 93-8	Unused flowing artesian well, Russell Road, Carlsbad Springs
AB 93-12	Tap in barn, Baseline Rd., Ramsayville
AB 93-20	Tap in barn, Leitrim Rd., Ramsayville
AB 93-31	Soda Spring, Carlsbad Springs
AB 93-33	Magic Spring, Carlsbad Springs
AB 93-34	Plantagenet Station Spring
AB 93-38	Tap in barn, Hawthorne Rd., Ramsayville
AB 93-40	White Sulphur Spring, Carlsbad Springs

Detector: Varian thermal conductivity detector type ABCD (10 V)

Resin: HaySepD polymer, mesh size 100/120

Run time: 10 min.

Carrier Gas: He

Run temperature: 40°C, isothermal

Sample rate: 10.00 Hz

APPENDIX 5. Sample preparation and analysis of stable isotopes.

Oxygen and hydrogen.

Determination of the $^2\text{H}/^1\text{H}$ ratio of the sample was carried out on hydrogen gas produced by the reduction of water with zinc at 430°C . The gas was analyzed on an automated double collector VG 602D mass spectrometer. The routine precision (2σ) is ± 1.3 per mille.

The $^{18}\text{O}/^{16}\text{O}$ ratio was determined by CO_2 equilibration at 25°C using an automated system. Analysis of the CO_2 was carried out on a triple collector VG SIRA 12 mass spectrometer. The CO_2 -water fractionation factor used is 1.0412 (Friedman and O'Neil, 1977). The routine precision (2σ) is ± 0.10 per mille.

Sulphur.

Preparation of samples for sulphur isotope composition analysis started with the precipitation of BaSO_4 by adding BaCl to the water sample. The produced powder was treated with 10% HCl to remove any BaCO_3 that may have co-precipitated. The BaSO_4 was then combusted with copper oxide at 1000°C to produce SO_2 for analysis.

Water samples that were to be analyzed for sulphide sulphur isotope composition were precipitated with a metal acetate. This was done in the field due to the volatility of H_2S . For this study two different acetates were used in order to compare their suitability in terms of yield and precision. Zinc acetate and cadmium acetate were added to two respective sample splits, all from the same location. In the laboratory the zinc and cadmium sulphides were converted to silver sulphide in a silver nitrate solution. The silver sulphide was combusted with copper oxide at 1050°C to produce SO_2 for analysis.

The SO_2 produced by either of the methods described was analyzed on a triple collector VG SIRA 12 mass spectrometer, and the routine precision (2σ) in the analyses is ± 0.20 per mille.

Carbon.

Two different methods were used in the production of the CO_2 gas to be analyzed. The first method involves the precipitation of BaCO_3 by adding an appropriate amount of BaCl to the water sample. The BaCO_3 was subsequently reacted with phosphoric acid to produce CO_2 .

The second method is a direct reaction of the water with phosphoric acid thus producing CO_2 for analysis. The latter method referred to as DIC constitutes one step only in a closed system and therefore decreases the risk of contamination. A sample produced through BaCO_3 precipitation is a fine powder which usually also contains BaSO_4 . This often leads to difficulties in homogenizing the sample. For these reasons DIC is a preferable method for producing CO_2 .

The CO_2 produced by either method was analyzed on a triple collector VG SIRA 12 mass spectrometer. The routine precision (2σ) in the DIC analyses is ± 0.10 per mille.

APPENDIX 6. Oxygen and hydrogen isotopic data.

sample AB 93-	3	4	5	8	11
$\delta^{18}\text{O}$	-10.9	-11.3	-9.8	-9.3	-10.5
$\delta^2\text{H}$	-77	-76	-68	-64	-72
sample AB 93-	12	13	15	15b	16
$\delta^{18}\text{O}$	-10.2	-11.6	-10.3	-10.1	-9.4
$\delta^2\text{H}$	-72	-81	-74	-74	-64
sample AB 93-	17	18	20	21	22
$\delta^{18}\text{O}$	-11.1	-9.5	-9.6	-11.5	-9.0
$\delta^2\text{H}$	-81	-64	-68	-81	-62
sample 93-	25	26	28	30	31
$\delta^{18}\text{O}$	-9.6	-11.6	-10.1	-15.7	-10.6
$\delta^2\text{H}$	-67	-82	-72	-116	-75
sample AB 93-	33	34	35	36	38
$\delta^{18}\text{O}$	-10.5	-10.6	-9.5	-9.4	-10.9
$\delta^2\text{H}$	-70	-77	-70	-68	-74
sample AB 93-	39	44			
$\delta^{18}\text{O}$	-10.8	-9.2			
$\delta^2\text{H}$	-75	-65			

CALCULATION OF THE PROPORTIONS OF THE COMPONENTS IN A MIXTURE BETWEEN WINTER PRECIPITATION AND BRACKISH GROUNDWATER.

The $\delta^{18}\text{O}$ of winter precipitation was calculated using average air temperatures for a winter (December to March) and the equation of Fritz *et al.* (1987) given on page 41. The average winter air temperature was obtained by calculating an average of the mean monthly air temperature for December to March as given by Environment Canada (1993). The obtained value was inserted as T in the equation of Fritz *et al.* (1987), to calculate a $\delta^{18}\text{O}$ value for the winter precipitation for the mass balance equation. The proportions of meltwater and brackish groundwater components in sample AB 93-30 is estimated from a mass balance calculation using the $\delta^{18}\text{O}$ values for sample AB 93-30 and winter precipitation together with the upper and lower $\delta^{18}\text{O}$ values measured for the brackish groundwater in this study which have a TDS exceeding that of AB 93-30 (-10.9 for AB 93-3 and -9 per mille for AB 93-22).

Mean monthly temperatures (in °C):

December	-7.7
January	-10.9
February	-9.5
March	-3.0

Average	-7.8,

inserted into the equation $\delta^{18}\text{O} = (0.53 \pm 0.13)T - (14.44 \pm 0.86)$, gives $\delta^{18}\text{O}_{\text{WINTER PRECIP.}} = -18.5$ per mille. Chloride concentration of precipitation is assumed to be 0, as indicated by Charron (1978).

Proportion of brackish groundwater (X) in the mixture is calculated using the $\delta^{18}\text{O}$ of the end members and sample AB 93-30:

$$X \cdot \delta^{18}\text{O}_{\text{WINTER PRECIP.}} + (1-X) \cdot \delta^{18}\text{O}_{\text{GROUNDWATER}} = \delta^{18}\text{O}_{\text{SAMPLE}} ; \text{TDS}_{\text{GROUNDWATER}} = \frac{\text{TDS}_{\text{SAMPLE}}}{(1-X)}$$

$\delta^{18}\text{O}_{\text{SAMPLE}} = -15.7$ per mille for AB 93-30, $\delta^{18}\text{O}_{\text{WINTER PRECIP.}} = -18.5$ per mille and the range for $\delta^{18}\text{O}_{\text{GROUNDWATER}}$ is -11 to -9 per mille as defined by the measured values for brackish groundwater in this study.

for $X \cdot \delta^{18}\text{O}_{\text{GROUNDWATER}} = -9$ per mille $X=0.70$, $\text{TDS}_{\text{GROUNDWATER}} = 9207$ ppm;
for $X \cdot \delta^{18}\text{O}_{\text{GROUNDWATER}} = -11$ per mille $X=0.63$, $\text{TDS}_{\text{GROUNDWATER}} = 7465$ ppm.

Alternatively the mean winter temperature for the interstream area between the Ottawa and St. Lawrence Rivers of -9°C (Charron, 1978) can be used, giving the following results:

$\delta^{18}\text{O}_{\text{WINTER PRECIP.}} = -19$ per mille,

for $\delta^{18}\text{O}_{\text{GROUNDWATER}} = -9$ per mille $X=0.67$, $\text{TDS}_{\text{GROUNDWATER}} = 8369$ ppm;
for $\delta^{18}\text{O}_{\text{GROUNDWATER}} = -11$ per mille $X=0.59$, $\text{TDS}_{\text{GROUNDWATER}} = 6736$ ppm.

APPENDIX 7. Sample preparation for strontium isotope analysis.

Approximately one gram of water was evaporated and 1-2 ml of 2.5 N HCl was added prior to separation as described below.

Approximately 0.1 g of powdered rock sample was required for analysis. The carbonate rock samples were dissolved in 2.5 N HCl before Sr separation. The Rockcliffe shale sample was dissolved in 1 ml HF and left for 24 hours at 100°C. After drying, 1 ml of HNO₃ was added, and the sample was again dried. Then 1 ml of 2.5 N HCl was added and the lid was left on for approximately 1 hour after drying, and the sample was finally dissolved in 2 ml 2.5 N HCl overnight at 100°C. The same procedure was tried but was not successful for the Carlsbad and Billings shale samples. Instead, these were leached using 2 ml 2.5 N HCl for 24 hours at 100°C. Samples containing any visible solid residue were centrifuged before separation.

The strontium was separated by means of cation exchange by HCl elution through 20 cm columns of 0.7 cm internal diameter filled with 3 ml of Bio-Rad AG50W-X8 cation exchange resin (200-400 mesh).

Elution procedure:

1. Load sample, which is in 2.5 N HCl.
2. Wash with 1 ml 2.5 N HCl.
3. Wash with 10 ml 2.5 N HCl.
4. Wash with 7 ml 2.5 N HCl.
5. Add 6 ml 2.5 N HCl and collect Sr fraction.
6. Wash with 2 aliquots of 10 ml 6.5 N HCl to clean the column.
7. Wash with 4 ml 2.5 N HCl.
8. Wash with 10 ml 2.5 N HCl to recondition the column.
9. Add approximately 2 ml 2.5 N HCl and cap the column.

The above procedure was repeated for all the rock samples except those of the Carlsbad and Billings Formations, in order to ensure a complete elimination of other cations from the samples.

Samples of the Carlsbad and Billings Formations were put through the above procedure only once. Following this, they were subject to a second separation by cation exchange by HCl elution through 10 ml polypropylene chromatography columns containing 1 ml teflon powder coated with di(2-ethylhexyl) orthophosphoric acid (HDEHP).

Elution procedure:

1. Load sample in 250 μ l 0.01 N HCl.
2. Wash with 1 ml 0.01 N HCl.
3. Add 3 ml 0.01 N HCl and collect Sr fraction.
4. Wash with 2 aliquots of 12 ml 6 N HCl to clean the column.
5. Wash with 12 ml 0.01 N HCl to recondition the column.
6. Add 4 ml 0.01 N HCl and cap the column.

APPENDIX 8. Thermal ionization mass spectrometry.

Strontium isotope ratios for both groundwater and aquifer material were analyzed using a Finnigan-MAT 261 multi-collector solid source mass spectrometer. The machine is a 90 degree deflection, magnetic sector instrument in an effective radius of curvature of 64 cm. A Hewlett-Packard series 9000 computer controls the operation of the instrument.

The sample was loaded onto a single tantalum filament with 4 μ l phosphoric acid. The filament was heated at 1.2 A electrical current and the sample allowed to dry. The sample was then taken to glowing (approx. 2 A) for a fraction of a second.

Run temperature: 1440-1600°C

Number of blocks: 10 (or until $2\sigma_{\text{MEAN}} < \pm 0.000025$)

Runs per block: 10

APPENDIX 9. XRF, sample preparation and analysis.

X-ray fluorescence analyses were carried out on a Phillips PW 2400 XRF machine of fused pellets produced from the following mixture: 1.3 g rock powder, 0.433 g Li_3CO_3 , 3.9 g $\text{Li}_2\text{B}_4\text{O}_7$.

Loss on ignition (LOI) was calculated from the difference in sample weight before and after firing at 1050°C. The fired powders from the shale samples were used in the production of the pellets for this type of rock, and a couple of duplicate fired and unfired samples of carbonate rocks were also used.

List of rock samples:

Sample number	Rock type/formation	Location
AB 93-51	Cobourg	ELBA2: 30.5 m, 32.0 m
AB 93-52	Cobourg	ELBA2: 47.2-48.1 m
AB 93-53	Hull	ELBA2: 100.6-101.5 m
AB 93-54	Sherman Fall	ELBA2: 70.1-71.0 m
AB 93-55	Oxford	M1: 123.4-125.0 m, 140.2 m, 149.5 m
AB 93-56	Rockland	P3: 114.3 m, 125.0 m
AB 93-57	Billings	ELBA2: 18.0 m
AB 93-58	Carlsbad	EMR borehole at Anderson Rd.: 61 m
AB 93-59	March	Coxall, well AK 93-42 of Sager-Kinsman (1995)
AB 93-60	Rockcliffe	AC2: 36.0 m
AB 93-61	Calcite vug in Oxford	AC2: 95.4 m
AB 93-62	Oxford	AC2: 84.7 m
AB 93-63	March	AC2: 116.7 m
AB 93-64	Nepean	AC2: 147.2 m
AB 93-65	Carlsbad	outcrop, Hwy. 417/ Cyrville Rd.
AB 93-66	Billings	outcrop, Green's Creek/ Innes Rd.
AB 93-67	Carlsbad	outcrop, Belgreen Rd.

Explanations:

ELBA2, M1, P3 - boreholes at Carleton University campus (Wilson, 1990).

AC2 - borehole at Algonquin College, Woodroffe campus, Ottawa.

F - sample fired before XRF analysis, D - duplicate sample

Results of XRF analyses:

Analysis, %	AB 93-58F	AB 93-65F	AB 93-67	AB 93-57F	AB 93-66
SiO ₂	55.71	55.61	47.37	43.02	56.47
Al ₂ O ₃	16.48	12.83	8.12	10.69	15.77
Fe ₂ O ₃	6.9	5.66	3.86	3.25	6.54
MgO	3.16	2.67	1.92	2.66	3.36
CaO	1.4	7.36	17.51	13.83	2.58
Na ₂ O	0.88	1.23	1.40	0.82	0.68
K ₂ O	4	2.63	1.39	2.35	3.80
TiO ₂	0.79	0.73	0.49	0.54	0.73
P ₂ O ₅	0.12	0.16	0.15	0.2	0.12
MnO	0.07	0.16	0.29	0.05	0.07
S	0	0	0	0	0
Sub-total (%)	89.51	89.04	82.65	77.41	90.31
Analysis, ppm					
Ba	356	336	171	272	266
Nb	15	15	6.4	10	9.9
Zr	133	191	164	188	123
Y	23	30	31	24	21
Sr	131	192	364	409	176
Rb	164	109	53	92	153
Zn	66	69	44	49	184
Ni	48	37	33	54	81
Cr	94	66	38	70	95
V	139	97	56	78	122
Total (ppm)	1169	1142	961	1246	1230
LOI (%)	6.75	9.16	16.4	19.92	8.4
Total (%)	96.38	98.31	99.00	97.45	98.65

Analysis, %	AB 93-52	AB 93-52D	AB 93-53	AB 93-53D	AB 93-54
SiO ₂	10.19	10.18	0.05	0.04	9.23
Al ₂ O ₃	2.49	2.48	0.1	0.09	2.89
Fe ₂ O ₃	1.05	1.09	0.15	0.17	1.04
MgO	1.22	1.23	0.4	0.4	1.09
CaO	45.04	45.03	54.85	54.91	45.51
Na ₂ O	0.11	0.1	0.09	0.06	0.09
K ₂ O	0.68	0.68	0.01	0	0.84
TiO ₂	0.11	0.11	0.01	0.01	0.12
P ₂ O ₅	0.055	0.054	0.177	0.174	0.14
MnO	0.031	0.031	0.1	0.1	0.03
S				0	
Sub-total (%)	60.976	60.985	55.937	55.954	60.980
Analysis, ppm					
Ba	49	44	0	8	4
Nb	3	4	2	1	3
Zr	43	43	8	7	38
Y	4	5	1	1	3
Sr	396	395	478	480	462
Rb	32	32	7	8	39
Zn	2	3	0	0	8
Ni	1	39	9	0	12
Cr	33	31	12	11	24
V	11	10	0	0	18
Total (ppm)	574	606	517	516	611
LOI (%)	36.61	36.61	43.46	43.46	36.82
Total (%)	97.64	97.66	99.45	99.47	97.86

Analysis, %	AB 93-54F	AB 93-56	AB 93-60	AB 93-55	AB 93-61
SiO ₂	10.98	4.91	51.15	15.68	0
Al ₂ O ₃	3.38	1.33	13.87	3.32	0.01
Fe ₂ O ₃	1.14	0.47	4.94	1.49	0.74
MgO	1.22	0.91	3.83	6.73	0.27
CaO	49.56	49.91	6.96	34.38	54.61
Na ₂ O	0.12	0.08	0.53	0.19	0.04
K ₂ O	0.62	0.36	5.46	1.48	0
TiO ₂	0.14	0.05	0.69	0.13	0.01
P ₂ O ₅	0.15	0.117	0.77	0.088	0.006
MnO	0.03	0.04	0.103	0.207	0.22
S	0	0			
Sub-total (%)	67.34	58.177	88.303	63.695	55.906
Analysis, ppm					
Ba	26	11	445	317	0
Nb	4	2	11	3	1
Zr	41	16	176	53	10
Y	5	1	41	16	37
Sr	491	652	340	242	683
Rb	27	20	160	35	8
Zn	12	3	37	12	0
Ni	119	270	57	2	27
Cr	27	20	96	28	13
V	12	11	84	21	9
Total (ppm)	764	1006	1447	729	788
LOI (%)	36.82	40.46	9.96	34.57	41.71
Total (%)	104.24	98.74	98.41	98.34	97.69

Analysis, %	AB 93-62	AB 93-59	AB 93-63	AB 93-63F	AB 93-64
SiO ₂	18.67	69.01	11.72	11.26	76.23
Al ₂ O ₃	4.58	1.54	2.31	2.19	1.1
Fe ₂ O ₃	1.99	0.2	0.92	0.8	1.01
MgO	14.54	4.11	16.26	15.43	1.62
CaO	21.58	10	26.6	24.71	8.4
Na ₂ O	0.1	0.06	0.06	0.1	0.06
K ₂ O	2.46	0.83	1.54	1.21	0.57
TiO ₂	0.2	0.06	0.13	0.11	0.06
P ₂ O ₅	0.056	0.092	0.086	0.08	0.047
MnO	0.077	0.062	0.135	0.12	0.062
S			0	0	
Sub-total	64.253	85.964	59.761	56.01	89.159
Analysis, ppm					
Ba	101	63	103	87	74
Nb	4	1	3	3	0
Zr	51	47	115	105	166
Y	7	5	8	6	6
Sr	109	43	95	86	70
Rb	48	19	26	21	16
Zn	3	7	0	2	0
Ni	17	3	20	9	11
Cr	40	23	23	15	23
V	37	13	19	22	8
Total ppm	417	224	412	356	374
LOI (%)	33.35	12.61	38.52	38.52	7.8
Total (%)	97.64	98.6	98.32	94.57	97

APPENDIX 10. Mass balance calculation of the resulting isotopic composition of dissolved sulphate, using a combination of sources of sulphate.

Isotope data used in the calculations:

sample	$\delta^{34}\text{S}$	$\delta^{18}\text{O}_\text{s}$	$\delta^{18}\text{O}_\text{w}$
AB 93-15	+9.5	+11.9	-10.1
AB 93-44	+8.8	+10.9	-9.2
gypsum	+28.6	+17.5	
sed. pyrite 1	-4.4		
oxidized sed. pyrite 1	-21.4 to -7.4*		
sed. pyrite 2	-5.3		
oxidized pyrite 2	-22.3 to -8.3		
fracture pyrite	-16.3		
oxidized fracture pyrite	-33.3 to -19.3		

* = as calculated using fractionation factors from Nakai and Jensen (1964) and Krouse (1980).

Proportion of the sulphate from oxidation of sulphide=X=

$$\delta^{34}\text{S}_\text{s} - \delta^{34}\text{S}_\text{GYPSUM} / \delta^{34}\text{S}_\text{OX.PYRITE} - \delta^{34}\text{S}_\text{GYPSUM}$$

Proportion of the sulphate from gypsum=1-X.

Calculated oxygen isotope ratio of dissolved sulphate= $\delta^{18}\text{O}_\text{s}$ =

$$X * (\delta^{18}\text{O}_\text{w} + 4.5) + (1-X) * 17.5.$$

The range of values $\delta^{34}\text{S}_\text{OX.PYRITE}$ values is from the table above; -33.3 to -7.4 per mille. The maximum and minimum values of X and $\delta^{18}\text{O}_\text{s}$ that these values yield will be calculated for each sample.

Sample AB 93-15:

Minimum proportion of sulphide sulphur in the dissolved sulphate, and the resulting $\delta^{18}\text{O}_\text{s}$:
 $\delta^{34}\text{S}_\text{OX.PYRITE}$ of -33.3 gives X=0.308 and $\delta^{18}\text{O}_\text{s}$ = +10.40

Maximum proportion of sulphide sulphur in the dissolved sulphate, and the resulting $\delta^{18}\text{O}_\text{s}$:
 $\delta^{34}\text{S}_\text{OX.PYRITE}$ of -7.4 gives X=0.530 and $\delta^{18}\text{O}_\text{s}$ = +5.29,
 to be compared with measured $\delta^{18}\text{O}_\text{s}$ value of +11.9.

Sample AB 93-44:

Minimum proportion of sulphide sulphur in the dissolved sulphate, and the resulting $\delta^{18}\text{O}_s$:
 $\delta^{34}\text{S}_{\text{OX.PYRITE}}$ of -33.3 gives $X=0.320$ and $\delta^{18}\text{O}_s = +10.43$

Maximum proportion of sulphide sulphur in the dissolved sulphate, and the resulting $\delta^{18}\text{O}_s$:
 $\delta^{34}\text{S}_{\text{OX.PYRITE}}$ of -7.4 gives $X=0.550$ and $\delta^{18}\text{O}_s = +5.34$,
to be compared with measured $\delta^{18}\text{O}_s$ value of +10.9.

SEE P. 20

IN POCKET