The water chemistry of cruise 85-036 on Bras d'Or Lake, Cape Breton Island, Nova Scotia

Project 730072

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Mucci, A., and Pagé, P., The water chemistry of cruise 85-036 on Bras d'Or Lake, Cape Breton Island, Nova Scotia; in Current Research, Part A, Geological Survey of Canada, Paper 87-1A, p. 17-24, 1987.

Abstract

Bras d'Or Lake water samples were collected during the CSS Dawson 85-036 cruise in November 1985. Surface water samples were taken at various stations along the cruise track, while subsurface water samples were collected from selected deep basins. The salinity, temperature, total alkalinity, calcium concentration, pH and ^{18}O:^{16}O ratio were determined for each sample. The specific alkalinity and $\delta^{18}O$ measurements indicate that the lake waters are composed of a conservative mixture of seawater, typical of the Northwest Atlantic Ocean, and fresh water of mostly meteoric origin (direct precipitation). Groundwater from land drainage, whose composition should reflect the bedrock geology around the lake, is not an important component of the lake water mixture.

Résumé

Des échantillons d'eau du lac Bras d'Or ont été prélevés lors d'une mission (#85-036) à bord du CSS Dawson en novembre 1986. Des eaux de surface ont été échantillonnées en plusieurs points tout au long du parcours, tandis qu'un nombre d'échantillons ont été prélevés dans certains bassins profonds. La salinité, la température, l'alcalinité totale, la concentration en calcium, le pH et le rapport ^{18}O:^{16}O ont été déterminés pour chacun des échantillons. L'alcalinité specifique et le $\delta^{18}O$ indiquent que les eaux du lac sont composées d'un mélange raisonnable d'eau de mer typique du nord-ouest de l'ocean Atlantique et d'une eau douce d'origine principalement météorique (précipitation directe sur le bassin). L'eau souterraine provenant du lessivage des sols et dont la composition devrait refléter la géologie de la roche en place ne constitue pas une composante importante des eaux du lac.

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INTRODUCTION

Semi-enclosed bodies of seawater function as estuaries in which the flushing time is determined by the physical ability of outlets to drain the fresh water fraction. Bras d'Or Lake, on Cape Breton Island, is such a body of water and is partially isolated from the open ocean by long and narrow channels. The lake waters were sampled during the *CSS Dawson* 85-036 cruise, in November 1985, in order to assess, using chemical and isotopic tracers, the identity of the water mixture. Objectives were to determine the hydrological components of the lake waters with the help of conservative properties (alkalinity, isotope ratio) and examine the vertical structure of the water column over topographic troughs or basins in the deepest parts of the lake.

SAMPLING

Surface water was taken with a plastic bucket attached to a nylon rope over the side of the ship at various stations along the cruise track (Fig. 3.1). At selected stations, subsurface water samples were collected with 100/L Go-Flo bottles. Upon recovery, the temperature of the water was measured using a mercury thermometer. A 60 mL polypropylene bottle was promptly filled with the water and capped, leaving no headspace gas. This subsample was used to measure the pH of the water. Another 60 mL of water was filtered through a 0.45 μm Millipore filter and stored for later analysis of the calcium concentration and titration alkalinity.

Finally, for each station and depth, a 1 L plastic bottle was filled with water for $^{18}O:^{16}O$ and $^{2}H:^{1}H$ analyses, together with a 125 mL plastic bottle to which were added a few drops of $HgCl_2$, for later $^{13}C:^{12}C$ determinations.

ANALYSIS

The pH of the water samples was measured onboard at 25°C following thermal equilibration in a constant temperature bath. An Orion Research Ross combination electrode fitted with a piece of Tygon and Parafilm was inserted in the neck of the bottle, forming an airtight seal. This procedure was adopted to minimize CO_2 exchange with the atmosphere. The electrode was calibrated using NBS buffer solutions, before and after every 5 measurements. The precision of the pH measurements, once corrected for temperature (Harvey, 1963), was estimated to be better than ± 0.01 pH units.

The salinity of the water samples was determined from conductivity measurements using a Guildline 8400A salinometer. Calibration of the salinometer was done with IAPSO standard seawater. Total alkalinities, A_t, were determined by potentiometric titration with a dilute HC1 solution to the second equivalence point corresponding to the neutralization of bicarbonate ions using the method described by Mucci (in press). Reproducibility of these measurements was better than 0.4% using a Na_2CO_3 solution for standardization of the acid.

Calcium concentrations were determined potentiometrically with EGTA using the method described by Lebel and Poisson (1976). The titrant solution was standardized with IAPSO standard seawater. The precision of these measurements was better than 0.5%.

Isotope measurements ($^{18}O:^{16}O$) were performed at the GEOTOP laboratory using the standard equilibration method, on a triple collector VG Micromass spectrometer. Results are given in δ notation with respect to SMOW, with a precision of ± 0.2‰.

RESULTS

Results of the analyses described above are presented in Table 3.1, along with the position and depth at which each sample was collected.

The specific alkalinity, A_t/Cl‰, and $[Ca^{2+}]$/Cl‰ ratio were calculated for each sample in order to verify if the various bodies of water sampled were subjected to compositional variations other than conservation mixing between continental freshwater and seawater. Chlorinity was calculated from the salinity according to the following relationship (UNESCO, 1966):

$$\text{Cl‰} = \text{S‰} / 1.80655 \tag{1}$$

Results of these calculations are presented in Table 3.2.

The $[Ca^{2+}][CO_3^{2-}]$ ion concentration product of the water samples was calculated to determine their saturation

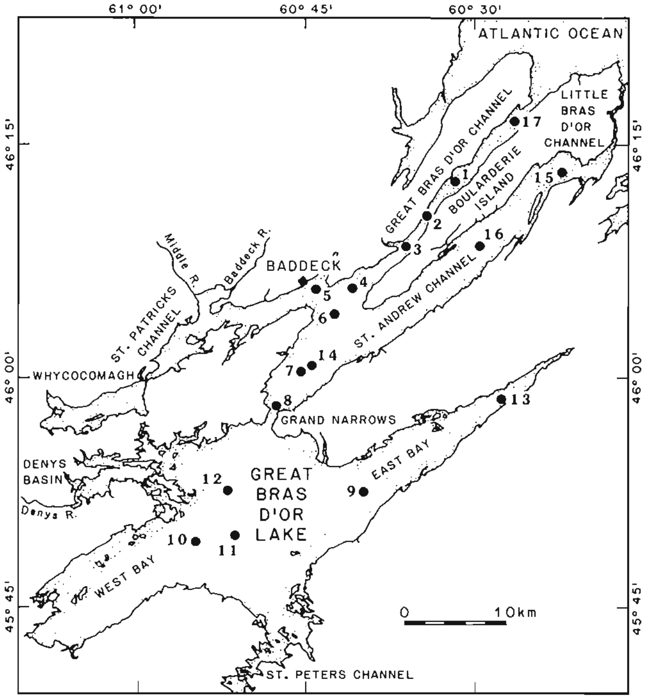

Figure 3.1. Location of water stations in Bras d'Or Lake.

Table 3.1 Measured physical and chemical parameters of water samples collected from Bras d'Or Lake in November 1985

Station	Position		Depth	Temp.	S	pH 25°C	$[Ca^{2+}]$	A_t	^{18}O δ_{smow}
	Lat°N	Long°W	(m)	(°C)	($^0/_{00}$)		(m mole kg^{-1})	(meq kg^{-1})	(‰)
1.1	461219	603238	0	9	26.596	7.956	7.18	1.736	−2.53
2.1	461039	603436	0	9.5	26.537	7.949	7.13	1.746	−3.16
3.1	460843	603610	0	9.5	26.537	7.951	7.15	1.730	−2.68
4.1	460673	603871	0	9	26.518	7.959	7.10	1.736	−3.37
5.1	460580	604400	0	9	26.544	7.963	7.12	1.751	−3.00
6.1	460400	604242	0	9	26.254	7.955	7.00	1.709	−3.14
7.1	460082	604525	0	9	25.797	7.938	6.70	1.680	−2.78
8.1	455752	604790	0	9	25.226	7.918	6.82	1.653	−2.83
9.1	455218	604004	0	9	24.870	7.944	6.62	1.639	−2.99
10.1	454885	605520	0	9	25.174	7.908	6.68	1.643	−3.43
11.1	454919	605111	145	5	25.782	7.664	6.84	1.652	−3.39
11.2	454919	605111	90	6	25.782	7.725	6.82	1.662	−3.26
11.3	454919	605111	20	9	25.174	7.894	6.70	1.637	−2.85
11.4	454919	605111	0	9	25.174	7.907	6.64	1.636	−3.45
12.1	455203	605211	0	9	25.266	7.898	6.67	1.640	−3.38
13.1			0	9	24.563	7.852	6.46	1.617	−3.06
14.1	460120	604463	200	2	28.170	7.731	7.68	1.831	−2.77
14.2	460120	604463	100	4	27.875	7.764	7.55	1.823	−2.96
14.3	460120	604463	50	8.5	27.875	7.923	7.39	1.800	−2.31
14.4	460120	604463	0	9	25.782	7.913	6.86	1.686	−3.38
15.1	461334	602212	0	9	26.685	7.933	7.17	1.745	−3.12
16.1	460863	603008	255	0.8	27.875	7.663	7.57	1.809	−2.92
16.2	460863	603008	150	1.0	27.580	7.669	7.48	1.806	−2.97
16.3	460863	603008	75	3.5	27.579	7.720	7.51	1.813	−2.30
16.4	460863	603008	25	9	26.685	7.912	7.19	1.763	−3.03
16.5	460863	603008	0	9	26.685	7.941	7.10	1.746	−3.25
17.1	461663	602640	0	9	28.758	—	7.92	1.885	−2.84

state with respect to calcite. Carbonate ion concentrations were calculated from the in situ pH and carbonate alkalinity of the sample, A_c, according to the following equation:

$$[CO_3^{2-}] = \frac{Ac}{2 + (10^{-pH}/K'_2)} \qquad (2)$$

where K'_2 is the second apparent dissociation constant of carbonic acid in seawater. Values determined by Mehrbach et al. (1973) as refitted by Millero (1979) were used in this study. The carbonate alkalinity was calculated from the total alkalinity according to:

$$A_c = A_t - [B(OH)_4^-] \qquad (3)$$

where $[B(OH)_4^-]$ is the product of the first dissociation of boric acid. The boric acid contribution to the total alkalinity was estimated from the total boric acid content of the sample ($\Sigma B = 1.17 \times 10^{-5} \times S‰$) and the following relationship.

$$[B(OH)_4^-] = \frac{K'_B \times \Sigma B}{(K'_B \times 10^{-pH})} \qquad (4)$$

where K'_B is the first apparent dissociation constant of boric acid. The apparent dissociation constants determined by Lyman (1957) were used for this calculation.

The saturation state or omega of the water samples with respect to calcite was calculated from the $[Ca^{2+}]\,[CO_3^{2-}]$ ion concentration product of the sample and the stoichiometric solubility of calcite, K^*_c, at the appropriate temperature and salinity (Mucci, 1983) according to the following equation:

$$\Omega = \frac{[Ca^{2+}]\,[CO_3^{2-}]}{K^*_c} \qquad (5)$$

Results of these calculations are presented in Table 3.2.

The CO_2 partial pressure, P_{CO_2}, in equilibrium with the water was also calculated from the in situ pH and carbonate alkalinity using the first and second apparent dissociation constants of carbonic acid determined by Merhbach et al. (1973) as refitted by Millero (1979) and the solubility constants of CO_2 in seawater determined from the equation of Weiss (1974) which is based on the measurements of Murray and Riley (1971). Calculated P_{CO_2}'s are presented in Table 3.2 and Figures 3.2C, 3.3C and 3.4C.

Isotope ratios given in Table 3.1 were corrected in Figure 3.5 for nonlinerarity with respect to salinity, owing to the definition itself of this parameter. In fact, there is (1 – S) kg of pure water (solvent) in 1 kg of seawater (solution); the solvent being characterized by a given isoptope concentration. Thus, the notation Δ is used in Figure 3.5, and defined following the theoretical considerations of Paren and Potter (1984) as:

$$\Delta = (1 - S)\ \delta^{18}O \qquad (6)$$

In Figure 3.5, linearity between Δ and S is indicative of the conservative mixing behaviour of two end-member components.

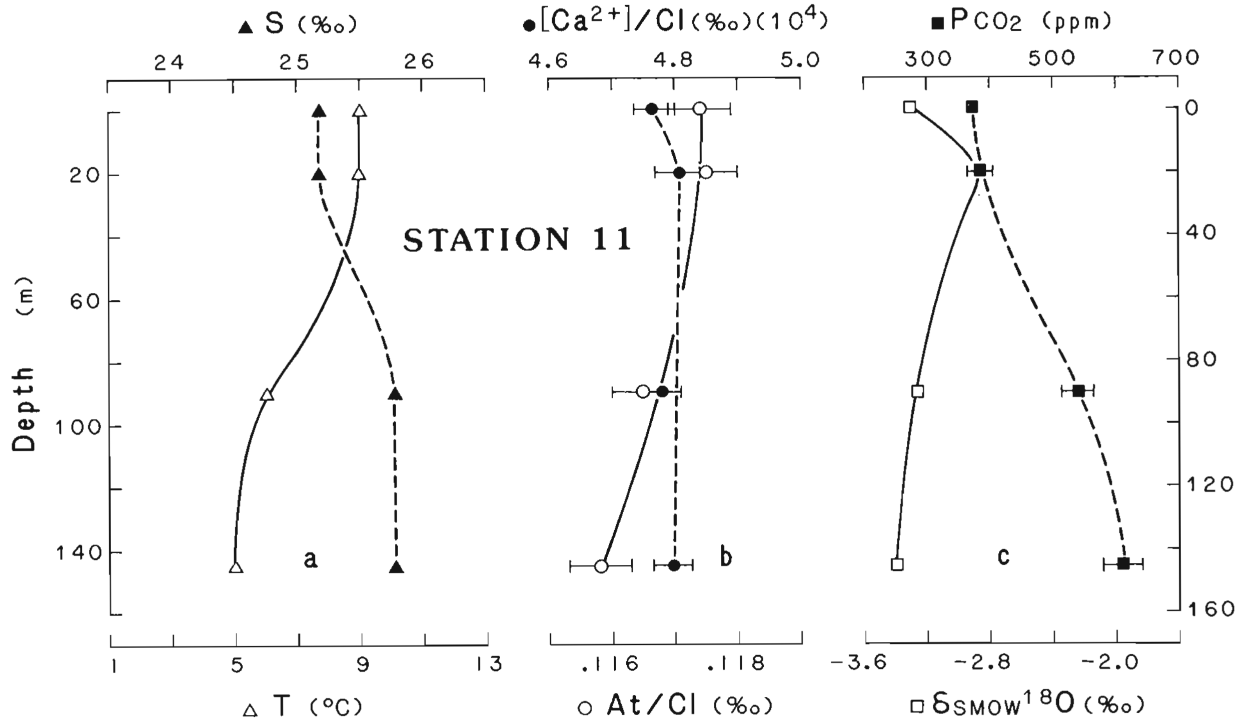

Figure 3.2. Depth profiles at station 11

Table 3.2 Results of chlorinity calculated from the salinity, the saturation state of the water samples with respect to calcite, and calculated P_{CO_2}.

Station	Cl (‰)	$[Ca^{2+}]$Cl‰ (10^4) ±0.25	At/Cl‰ ± .0005	$pH^{in\text{-}situ}$ ±0.01	A_c (meq kg^{-1})	$[Ca^{2+}]$ $[CO_3^{2-}]$ ($mole^2$ $kg^{-2} \times 10^7$)	Ω_C	PCO2 (ppm) ±3%
1.1	14.722	4.877	.1179	8.134	1.691	7.18	1.81	338
2.1	14.689	4.854	.1189	8.121	1.702	7.13	1.79	353
3.1	14.689	4.867	.1178	8.123	1.686	7.15	1.79	348
4.1	14.679	4.840	.1183	8.137	1.691	7.10	1.81	335
5.1	14.693	4.846	.1192	8.141	1.706	7.12	1.84	335
6.1	14.533	4.820	.1176	8.133	1.665	7.00	1.74	335
7.1	14.280	4.692	.1176	8.116	1.639	6.70	1.59	345
8.1	13.964	4.884	.1184	8.096	1.615	6.82	1.55	360
9.1	13.767	4.809	.1191	8.122	1.600	6.62	1.58	336
10.1	13.935	4.794	.1179	8.097	1.606	6.68	1.46	374
11.1	14.271	4.793	.1158	7.864	1.629	6.84	0.82	611
11.2	14.271	4.779	.1165	7.923	1.635	6.82	0.97	538
11.3	13.935	4.808	.1175	8.067	1.601	6.70	1.42	384
11.4	13.935	4.765	.1174	8.080	1.599	6.64	1.44	371
12.1	13.986	4.769	.1173	8.071	1.603	6.67	1.42	380
13.1	13.597	4.751	.1190	8.025	1.585	6.46	1.25	424
14.1	15.593	4.925	.1174	7.966	1.800	3.67	1.10	501
14.2	15.430	4.893	.1181	7.982	1.791	3.98	1.20	490
14.3	15.430	4.789	.1166	8.105	1.755	5.81	1.76	370
14.4	14.271	4.807	.1181	8.089	1.647	4.69	1.55	371
15.1	14.771	4.854	.1181	8.109	1.702	5.42	1.72	362
16.1	15.430	4.906	.1172	7.913	1.783	3.02	0.91	559
16.2	15.267	4.900	.1183	7.914	1.780	2.99	0.91	559
16.3	15.266	4.919	.1188	7.939	1.784	3.50	1.07	541
16.4	14.771	4.868	.1194	8.088	1.722	5.27	1.67	386
16.5	14.771	4.868	.1194	8.088	1.702	5.46	1.73	354
17.1	15.919	4.975	.1184	—	—	—	—	—

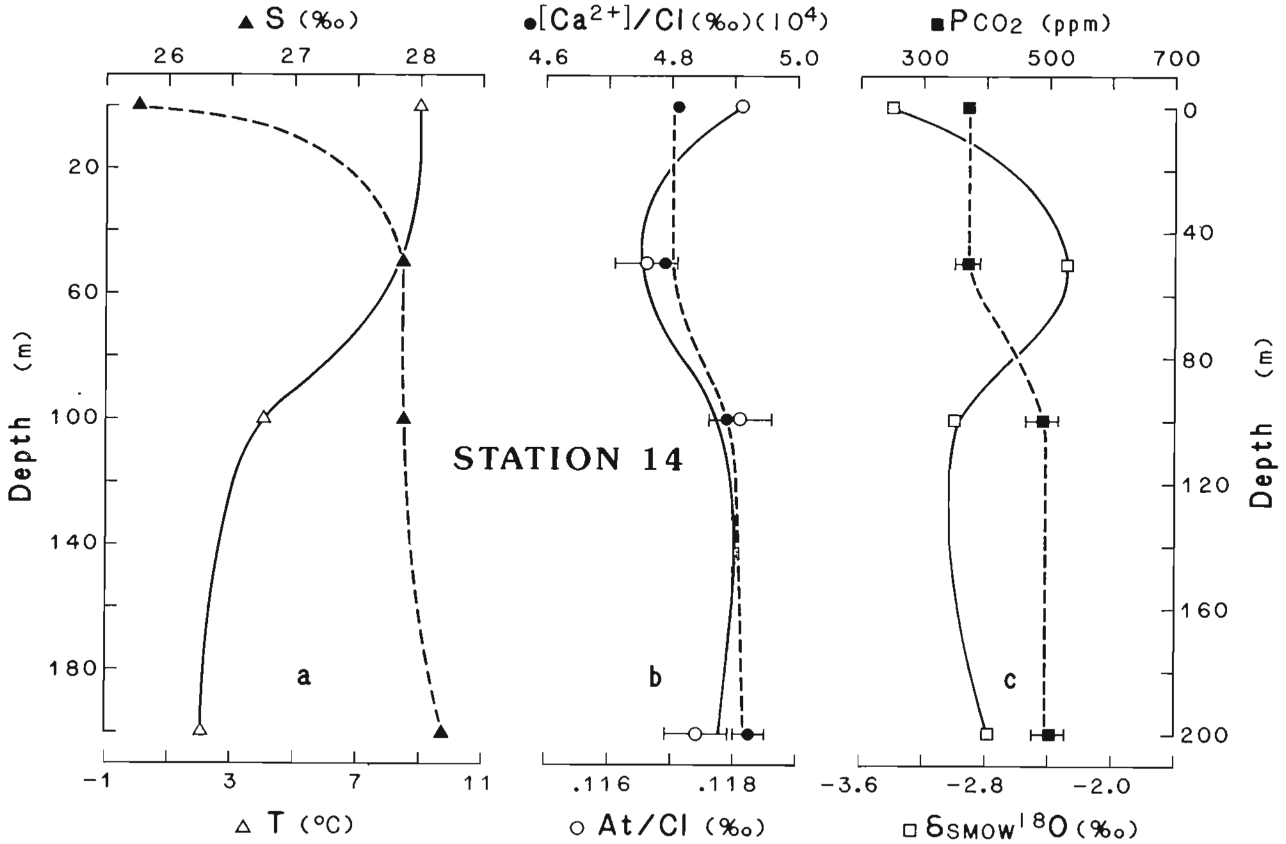

Figure 3.3. Depth profiles at station 14

DISCUSSION

Salinity distribution and stratification

As expected from the configuration of the lake (Fig. 3.1), the salinity of surface waters decreases regularly from 28.76 ‰ at the entrance of Great Bras d'Or Channel to 24.56 ‰ at the end of East Bay in the Great Bras d'Or Lake. An opening to the Atlantic Ocean through Little Bras d'Or Channel is responsible for the slight increase in the surficial salinity of water collected in St-Andrew's Channel. Mass balance calculations indicate that fresh water accounts for 20 to 30% of the surface water mixture.

The only important continental inflows to the lake are located in sub basins on the north-western side of Great Bras d'Or Lake. They are the Middle and Baddeck rivers which flow into the St-Patricks Channel and the Denys River which runs into the Denys Basin. Many short brooks also drain the highlands around the lake and one might expect a relatively small land drainage component to the lake waters.

Figures 3.2a, 3.3a and 3.4a indicate that stratification of the water column is characterized by a halocline situated between 40 and 60 m depth. The lifetime of this halocline is unknown as data from other seasons are unavailable. However, as the lake is known to freeze in winter, the stratification is probably destroyed during this season and re-established during the summer. Similarly, Vilks (1967) noted that deep basins, such as the ones we sampled (Stations 11, 14, and 16), contain cold water all summer but that water in shallower localities may undergo extensive changes in temperature during the seasons.

Alkalinity-chlorinity relationship

Figure 3.6 shows the results of the alkalinity titrations as a function of chlorinity for each collected sample. All the data are grouped around a straight line with a slope of 0.1175 (meq/kg)/Cl‰. This is indicative of the conservative mixing behaviour of the total alkalinity in this lake. The lake waters would have obtained their present composition from the mixing of a fresh water source of negligible alkalinity (about 6 μeq/kg) and seawater typical of the Northwest Atlantic at this latitude. The GEOSECS station situated closest to the latitude of the lake is Station 26 (44° 57.6'N/42° 0.4.6'W). Surface waters (4 m) collected at Station 26 during the GEOSECS expedition had a salinity of 35.754‰ (or Cl‰ = 19.791) and a total alkalinity of 2.331 meq/kg (Bainbridge, 1981). This datum point is presented in Figure 3.6 and clearly demonstrates the conservative mixing of the two water masses to form the lake waters. In fact, nearly all the water

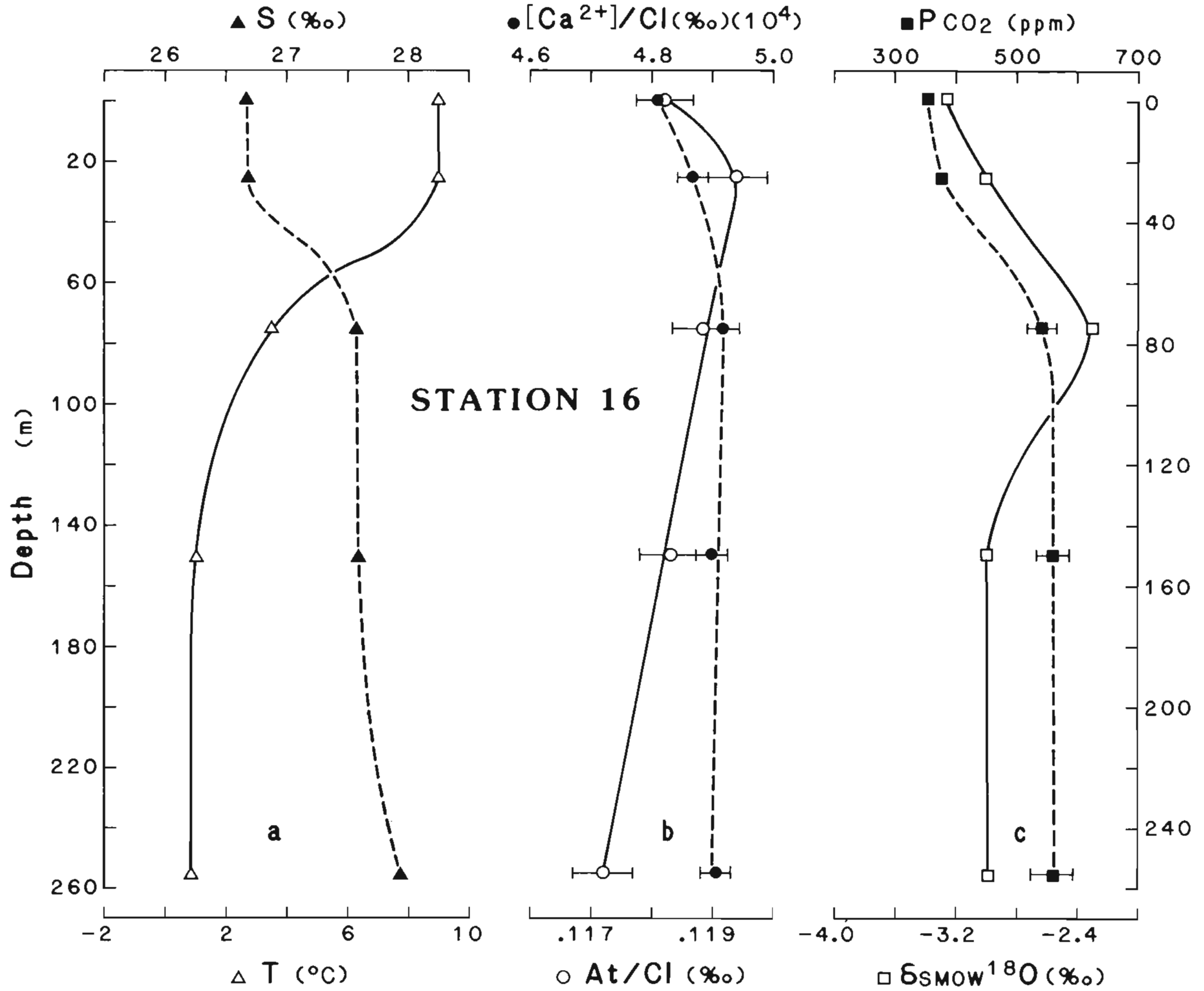

Figure 3.4. Depth profiles at station 16

samples collected in the lake possess a specific alkalinity (see Table 3.2) equal to the Northwest Atlantic Ocean water value (0.1178 ± .0005).

However, the [Ca^{2+}]/Cl‰ ratios of all the lake water samples (Table 3.2) are significantly lower than the value for standard seawater (5.31 × 10^{-5} (mole/kg)(Cl‰). The value of 4.98 × 10^{-5} determined for surface waters collected at Station 17, which is situated closest to the open sea channel, was the highest one measured in the lake. Lowered [Ca^{2+}]/Cl‰ ratios are most often associated with productivity of calcium sequestring organisms in surface waters. The [Ca^{2+}]/Cl‰ ratios are smaller in surface waters than at depth (Fig. 3.2b, 3.3b, 3.4b) which would support the hypothesis that biological activity is responsible for the low [Ca^{2+}]/Cl‰ ratios in the lake water. Even bottom waters however, at Stations 11, 14 and 16 have lower [Ca^{2+}]/Cl‰ ratios than standard seawater or surface waters at Station 17. Furthermore, no significant deviations of the specific alkalinity are associated with the surface [Ca^{2+}]/Cl‰ minima. This appears to rule out the possibility of important biogenic calcium carbonate production as calcium carbonate frustules would be expected to dissolve and increase the [Ca^{2+}]/Cl‰ in the deep basin waters of the lake since these are often undersaturated with respect to calcite (Table 3.2).

CO_2 partial pressure-depth relationship

The CO_2 partial pressures calculated from in situ pH and carbonate alkalinity indicate that surface waters are close to equilibrium with the atmosphere. Surface water values vary between 335 and 424 ppm with an average of 358 ± 23 ppm.

The deep waters of the lake (Fig. 3.2c, 3.3c and 3.4c) are characterized by high P_{CO_2} values (about 600 ppm). This accumulation of CO_2 is most probably due to the oxidation of organic matter at depth and the limited exchange of these waters with the surface as a consequence of the stratification

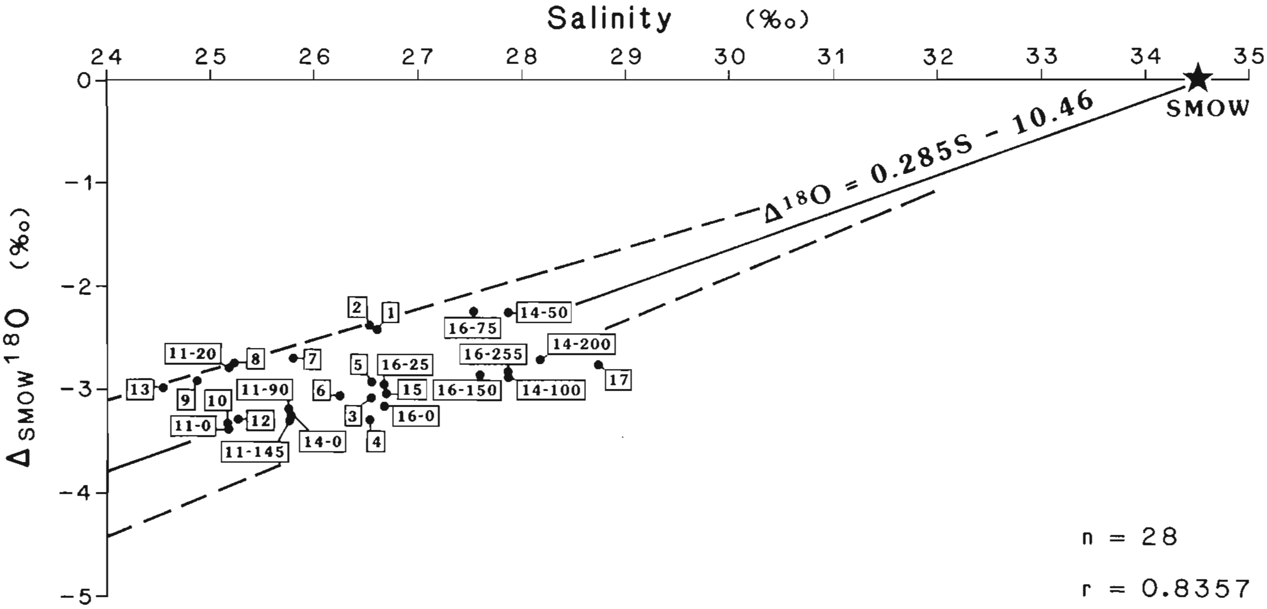

Figure 3.5. ^{18}O:^{16}O isotope ratios as a function of salinities.

over the summer and fall seasons. The increased CO_2 content of the deeper waters is responsible for the decrease in pH with depth as the carbonate alkalinity does not change significantly. This results in the deeper waters being undersaturated with respect to calcite ($\Omega < 1$).

Oxygen isotope-salinity relationship

Surficial water isotopic ratios do not show a trend similiar to salinity. Low values are found irregularly along the sampling track, either in the Great Bras d'Or Channel or Great Bras d'Or Lake, suggesting complex mixing between seawater and fresh water of variable isotopic composition. The relationship between mean annual $\delta^{18}O$ in precipitation and latitude (Yurtsever and Gat, 1981) indicates that precipitation over Cape Breton Island should reach a value of -10‰. Taken altogether, the data fit a regression line with an intercept of -10.46 (Fig. 3.5). All the data are bracketed between mixing lines which intercept the $\Delta^{18}O$ axis at -10‰ and -14‰ when linearly extrapolated to zero salinity.

Since seawater flowing through the northern channels originates from the Labrador Current, it must be diluted by meteoric waters collected around the Gulf of St-Lawrence or the Labrador coast where the precipitation exhibits lower $\delta^{18}O$ values than on Cape Breton Island. Supporting this view, waters collected at Stations 15, 16, and 17 which are closest to the oceanic inlets give $\delta^{18}O$ values near the lower mixing line. In addition, most of the deep water samples, and in particular those collected in St-Andrew's Channel below 90 m (Stations 14 and 16), are close to that lower line (they fit the following regression line: $\Delta^{18}O‰ = 0.398\ S - 13.91$). The salinity of these waters (>27.58‰) is also close to the salinity of waters entering the channel and indicates that they have not been influenced significantly by dilution from local precipitation. On the other hand, surficial and shallow waters fall in between, or even near the upper mixing line in Figure 3.5, indicating that local precipitation intervenes in the mixing. This pattern is clearly visible in the depth profiles (Fig. 3.2, 3.3 and 3.4). Salinity increases slightly below the halocline, while $\delta^{18}O$ values decrease slowly due to a fresh water contribution depleted in heavy isotope.

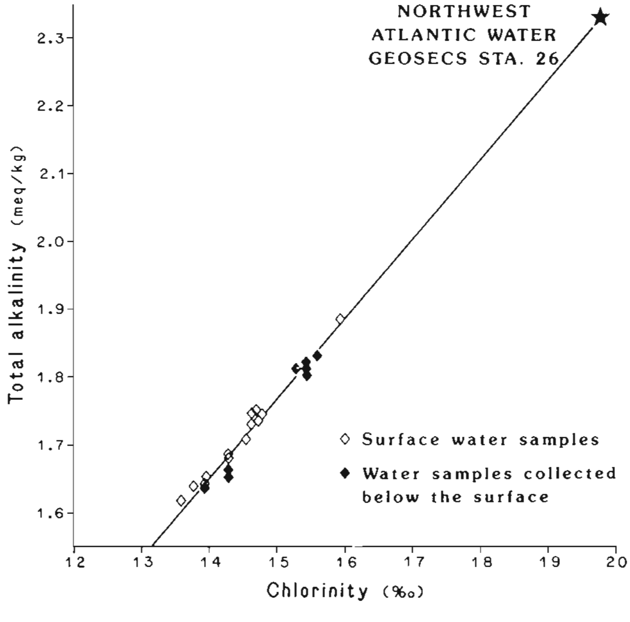

Figure 3.6. Conservative mixing in surficial and deep waters.

The seasonal precipitation could also explain the span of $\triangle^{18}O$ values. Winter snow and rain have lower isotopic ratios than summer rain since fractionation is thermodependent. Sinking and storage of cold isotopically lighter waters at depth would also result in depth profiles similar to those observed. The importance of this factor is determined by the flushing time of the fresh water fraction and is reflected by a more or less homogenized meteoric signal approximating the annual $\delta^{18}O$ value.

CONCLUSIONS

Bras d'Or Lake is a dominantly marine body of water possessing a slight longitudinal and vertical salinity gradient. The lake waters are composed of a nearly conservative mixture of seawater typical of the northwest Atlantic Ocean and fresh water. The fresh water end member is characterized by a very low alkalinity and a normal $\delta^{18}O$ value partly influenced by an allochthonous meteoric signal originating from the dilution of oceanic waters at higher latitudes.

It appears that fresh water from the deep underground drainage, which should have been mineralized following contact with the lithologies of this geological subprovince (for instance, dolomite, gypsum and limestone of the Carboniferous Windsor Group outcrop in the Middle and Baddeck river watersheds: Kelley, 1967), is not an important component of the lake water mixture. The presence of proximal runoff waters or even direct precipitation on the lake surface is supported by the fact that the $[Ca^{2+}]/Cl‰$ ratio of the lake water is always lower than the standard seawater value or even the maximum value measured in the lake at Station 17. The influence of the surrounding geology on the lake water composition is only slightly noticeable from the higher specific alkalinity of surficial waters at Stations 2, 5, 13 and 16 which are situated near outcrops of the Windsor Group.

The water column in the lake is stratified below approximately 60m, particularly in deep basins. The stratification is most likely destroyed during winter since the lake is known to freeze. The temporary stratification is responsible for limiting the exchange of gases in the deeper waters with the atmosphere. This results in an accumulation of CO_2 in the deeper portions of the lake following the degradation of organic matter at or near the sediment-water interface. As a consequence of the increased CO_2 concentration, bottom waters (>80m depth) are undersaturated with respect to calcite.

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