

## **$^{13}\text{C}$ natural abundance variations in carbonates and organic carbon from boreal forest wetlands**

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**Abstract.**  $^{13}\text{C}$  natural abundance variations were measured in peat soil and vegetation from two contrasting boreal forest wetlands: an upland watershed basin and a permanently saturated lowland mire. Evidence of methane oxidation was shown in the permanently saturated wetland with  $\delta^{13}\text{C}$  values as low as  $-97\text{‰}$  in carbonate minerals found in floating peat mats. It is postulated that  $^{13}\text{C}$  depleted  $\text{CH}_4$  is oxidized in the mat and reacts with calcium ions to form calcite (identified through x-ray diffraction). Methane flux measurements during the summer of 1992 showed much lower fluxes in areas with floating peat mats relative to open water. Secondary carbonates in the basin peat have isotope compositions close to the  $\delta^{13}\text{C}$  values of the peat organic carbon ( $-25\text{‰}$ ), indicating their origin from fermentation and possibly from sulfate-reduction. In the upland basin peat deposits, the  $\delta^{13}\text{C}_{\text{PDB}}$  values of organic C were constant with depth, while the permanently saturated mire had localities of  $^{13}\text{C}$  enrichment in deeper layers of the peat. The  $^{13}\text{C}$  enrichment may reflect areas of intense  $\text{CH}_4$  production in which  $^{13}\text{C}$  enriched residual substrate is left behind during the production of highly  $^{13}\text{C}$  depleted  $\text{CH}_4$ .

### **Introduction**

Over the last 400 years,  $\text{CH}_4$  concentration in the atmosphere has nearly tripled (Khalil & Rasmussen 1983) and ambient air measurements have indicated an increase in atmospheric  $\text{CH}_4$  concentrations of  $\sim 1\%$  per year from 1951 to 1981 (Ramanathan 1988; Rinsland et al. 1985). Modelling global  $\text{CH}_4$  balances and identifying sources of atmosphere  $\text{CH}_4$  require an understanding of carbon cycling throughout the surface of the earth. Northern wetlands ( $>40^\circ\text{N}$ ) are believed to produce about 66% of the total global  $\text{CH}_4$  emissions (Matthews & Fung 1987). The boreal forests of Canada contain a large portion of the northern wetlands and it is important to understand which wetland types are substantial methane producers. Several studies have recently addressed methane

dynamics through surface-based measurements of methane fluxes in the Canadian wetlands (Moore & Knowles 1989; Moore et al. 1990; Roulet et al. 1992; Whalen & Reeburgh 1992). Stable carbon isotope variations ( $\delta^{13}\text{C}$ ) can also provide clues about carbon cycling (Natelhoffer & Fry 1988; O'Brien & Stout 1978) and are used here along with flux measurements, to reveal C transformation processes in two boreal forest wetland types.

## Methods

### Sites

The sampling sites are located in Prince Albert National Park in central Saskatchewan, Canada ( $106^\circ\text{W}$  &  $54^\circ\text{N}$ ). Site 1 consists of a small lake surrounded by a large peat lowland and a series of hummocky hills (Fig. 1). The lowland is filled with 2–2.5 m of poorly decomposed peat which is permanently water saturated. The vegetation growing on the peat mat consists of *Sphagnum* moss species, several sedges of the *Carex* species, *Larix laricina*, *Ledum groenlandicum* and *Betula pumila*. Samples were taken from three areas within the wetland: a highly decomposed sediment below the open water (profile 1), a floating peat mat overlying sunken peat on top of mineral (inorganic) material (profile 2), and a continuous peat profile extending from the surface down to mineral material (profile 3). A soil profile from an upland hummock was also sampled (profile 4).

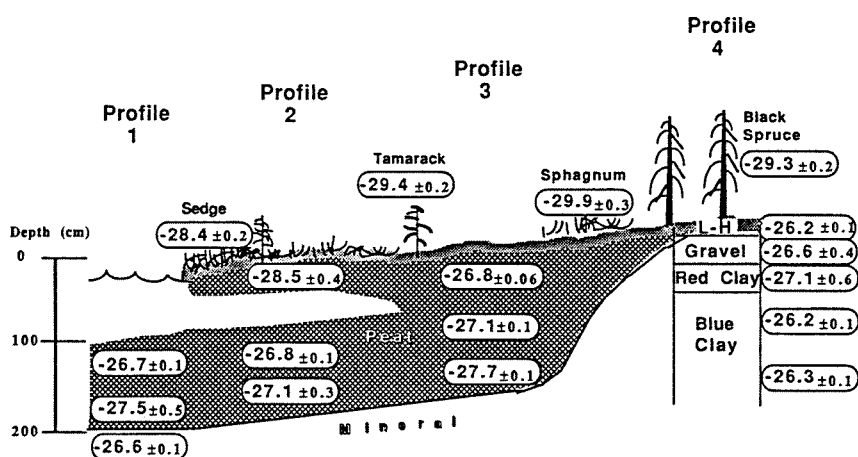


Fig. 1.  $\delta^{13}\text{C}$  values of organic C in the saturated mire.

Neutral to basic pH values (6.4–7.6) were observed in the peat layers, reflecting a high input of basic cations from lateral subsurface water flow in upland areas. The high pH and abundance of calcium in the water create conditions conducive for precipitation of carbonate as  $\text{CaCO}_3$ . Wetlands with neutral pH are found on the calcareous glacially-derived parent materials found in the mid-boreal wetland district (Zoltai & Pollett 1983) in Canada. Low levels of sulfate (Table 1) and low sulfur loading may limit sulfate reduction, resulting in more C turnover occurring through fermentation and methanogenesis.

Table 1. C, N and S concentrations in the saturated mire.

Horizon depth cm	Organic C mg C/kg	Inorganic C mg C/kg	Nitrate mg N/kg	Reduced- inorganic-S mg S/kg	Inorganic sulfate mg S/kg
Profile 1					
0–80 (peat)	267800	5000	38.4	18.4	6.1
80–150 (mineral)	19500	19000	0.4	7.3	7.8
Profile 2					
surface mat	430500	3500	347.7	12.5	18.0
120–160 (peat)	446500	3600	66.0	10.6	7.3
160–230 (peat)	456000	3600	4.8	8.8	3.9
Profile 3					
1–100 (peat)	451300	3500	10.1	9.0	5.1
100–180 (peat)	450500	3700	17.4	7.6	3.9
180–200 (peat)	457100	3300	20.6	8.9	12.7
Profile 4					
0–20 (L-H)	475100	2700	0.5	14.5	30.6
20–56 (gravel)	75300	1700	0.3	2.4	3.2
56–70 (red clay)	3000	19400	0.1	2.4	2.9
70–160 (blue clay)	3600	22200	0.2	2.5	1.9
160–180 (blue clay)	1900	14400	0.1	2.5	8.6

Values reported are means of triplicate analyses (C.V. < 5%).

Measurements expressed on air-dried weight basis.

The second site consists of an upland catchment basin which collects runoff from surrounding slopes. Accumulation of water in the basin during the spring results in saturated conditions for part of the year, while aerobic conditions prevail in late summer and fall after the basin has dried. The vegetation canopy is made up of *Picea mariana* with a floor vegetation comprised predominantly of *Sphagnum* and *Pleurozium*

*schreberi*. The soil in the basin consists of 60 cm of peat which is increasingly decomposed with depth. A higher content of nitrate and sulfate, and a higher amount of reduced inorganic S species was observed with increasing peat depth (Table 2). The peat horizons are neutral to basic in pH (6.8–7.8). In the upslope region an Orthic Gray Luvisol soil was sampled. The eluvial Ae and illuvial Bt horizons are acidic (pH 4.8–6.5) while the Ck horizon is alkaline (pH 8.9).

Table 2. C, N and S concentrations in the upland watershed.

Depth cm	Organic C mg C/kg	Inorganic C mg C/kg	Nitrate mg N/kg	Reduced- inorganic-S mg S/kg	Inorganic sulfate mg S/kg
Upland					
0–7 (L-H)	320700	2000	0.2	19.1	14.4
7–27 (Ae1)	5200	n.d.	0.1	2.1	2.5
27–52 (Ae2)	5500	n.d.	0.2	2.0	n.d.
52–127 (Bt)	2900	200	0.1	2.2	1.8
127–147 (Ck)	1800	9300	0.2	2.1	13.2*
Basin					
1–10 (L-H)	428100	2600	0.8	23.1	16.3
10–20 (peat)	415400	4600	1.1	26.4	18.6
20–30 (peat)	367500	7200	5.9	85.0	24.5
30–40 (peat)	328600	4000	2.9	141.0	18.5
40–60 (peat)	225900	2700	4.8	124.3	11.1
60–80 (mineral)	2600	1900	0.2	13.1	1.4
80–110 (mineral)	1900	1800	0.1	14.6	1.4
110–134 (mineral)	1900	4000	n.d.	5.2	2.1

\* Sulfate co-precipitated with  $\text{CaCO}_3$  was included.

n.d. denotes not detectable.

Values reported are means of triplicate analyses (C.V. < 5%).

Measurements expressed on air-dried weight basis.

### Analytical

Fresh peat samples were obtained using a hand-held coring device in the summer of 1990. Samples were then refrigerated and analyzed for inorganic sulfate and reduced inorganic sulfur. Subsamples were air-dried, ground to pass a 0.15 mm sieve and analyzed for total inorganic C,  $\text{NO}_3^-$  and  $\delta^{13}\text{C}$ . Total carbon content was measured using dry combustion and two end-point titration (Tiessen et al. 1981). The addition of HCl and a two-endpoint titration was used to determine inorganic C (Tiessen et al.

1983). Soil organic C was calculated as the difference between total and inorganic C. Soluble  $\text{NO}_3^-$  was determined by a 2M KCl extraction followed by colorimetric analysis (Technicon 1973). Inorganic sulfate was removed in a 0.05 M  $\text{KH}_2\text{PO}_4$  extraction and analyzed colorimetrically by the methylene blue procedure (Johnson & Nishita 1952). Reduced inorganic sulfur (elemental S, hydrogen sulfide and pyrite sulfur) was measured using a modified version of the Zn HCl reduction procedure described by Aspiras et al. (1972). All sulfur determinations were carried out on field moist samples with concentrations expressed on an air-dry basis. Values reported are means of triplicate analyses.

The preparation method for  $\delta^{13}\text{C}_{\text{PDB}}$  determination of inorganic C used a carbonate/ $\text{H}_3\text{PO}_4$  reaction under vacuum, producing  $\text{CO}_2$  which was purified through cryogenic separation. The precision for inorganic C using this method is  $\pm 0.03$  ‰. Carbon dioxide was produced from organic C through combustion at 900 °C with  $\text{Cu}_2\text{O}$  under vacuum. The  $\delta^{13}\text{C}$  reproducibility for typical replicated organic C measurements in soils and plants is  $\pm 0.3$  ‰. Purified  $\text{CO}_2$  was analysed in a VG Iso Gas SIRA 12 dual inlet, triple collector mass spectrometer.  $\delta^{13}\text{C}$  values for organic or inorganic C produced on this system are in excellent agreement with two different NBS standards referenced against PeeDee belemnite (PDB) as well as an independent laboratory, making results comparable to external studies. Carbonates in the peat were identified as calcite through x-ray diffraction.

Methane flux measurements were carried out in 1992, by capturing methane in collection chambers located over profiles 1 through 3, plus a fourth location in shallow solid peat located half the distance between profile 3 and 4 of the permanently saturated wetland. Clear plastic storage tubs with a rubber septum installed in the bottom were inverted over surface peat and plants in the wetland. The opening of the tub was sealed air tight by sinking the open edge below the water surface. Air samples were taken every week from the chambers with a syringe and injected into evacuated vacutainers. After sampling, the chambers were opened to the atmosphere and then resealed. Atmospheric gas samples were taken at the same time as chambers were resealed and used as the initial  $\text{CH}_4$  concentration in the chambers. The next sample was taken 24 hrs later. The short sampling period was used to estimate measurement errors due to temperature alterations and methane accumulation over the week-long period. Methane samples were measured within 3 days of sampling on a Hewlett Packard gas chromatograph equipped with a flame ionization detector ran at 150 °C, using a 2 m long Poropak Q column.

Results and discussion

Peat soils tend to bear  $\delta^{13}\text{C}$  values for organic C which are constant with depth (Deines 1980) or values which decrease due to the accumulation of  $^{13}\text{C}$  depleted lignin (Benner et al. 1987). Compared to the surface peat, the lower peat in the saturated wetland (site 1) showed slight enrichments of  $^{13}\text{C}$  in organic C, despite the poorly decomposed peat appearing uniform with depth (Fig. 1). Slight  $^{13}\text{C}$  enrichment in the organic matter may be ascribed to fractionation during methanogenesis. Organic substrates left behind during methanogenesis will be highly enriched in  $^{13}\text{C}$ , creating a slight increase in total organic  $\delta^{13}\text{C}$  values. Sulfate and reduced inorganic S levels are too low in the permanently saturated site to suggest a substantial impact of sulfate-reduction activity on the C cycle (Table 1), especially when the sulfur load is mainly from decomposition of litter.

The inorganic  $\delta^{13}\text{C}$  values in the wetlands provides information on carbon origin. Carbonates in the mineral (inorganic) material have  $\delta^{13}\text{C}$  values which are near zero per mil ( $-0.02$  to  $-4.4$  ‰) (Figs. 2 & 5), indicating the carbonates are from fossil (primary) origin. Carbonates associated with the peat have more negative  $\delta^{13}\text{C}$  values, suggesting that they are secondary carbonates formed from biogenically produced  $\text{CO}_2$  (Rightmire & Hanshaw 1973). Most  $\text{CO}_2$  in wetlands originates from fermentation, sulfate reduction, and/or methane oxidation (Wieder et al. 1990). Although the carbonates will only dominate in wetlands formed on calcareous parent materials, the clues they provide about C cycling in wetlands will likely apply to most wetlands in the mid-boreal forest regions of Canada.

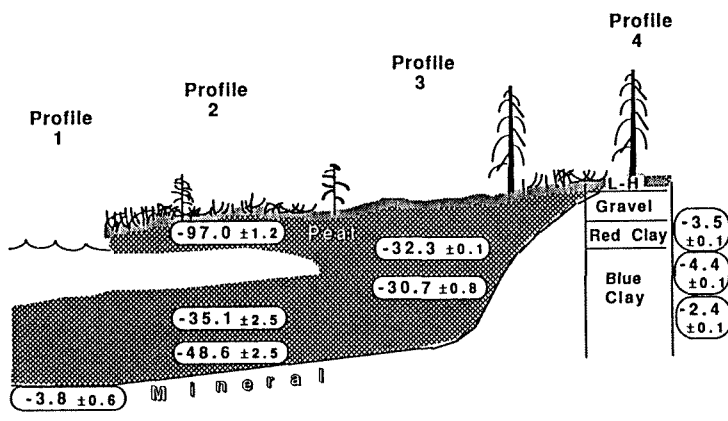


Fig. 2.  $\delta^{13}\text{C}$  values of carbonate C in the saturated mire.

The saturated wetland (site 1) contains secondary carbonates with highly negative  $\delta^{13}\text{C}$  values ( $-97\text{‰}$ ) in the floating peat mat of profile 2 (Fig. 2). Carbonate  $\delta^{13}\text{C}$  values near  $-97\text{‰}$  are on the outer limits of the terrestrial C isotopic scale and provide evidence of methane oxidation in the peat mat. While carbonates originating from methane oxidation with  $\delta^{13}\text{C}$  values of  $-25$  to  $-50\text{‰}$  PDB have been reported in a few marine environments (Matsumoto 1990; Beauchamp et al. 1989; Thyne & Boles 1989; Hovland et al. 1987), this carbonate with a  $\delta^{13}\text{C}$  value as low as  $-97\text{‰}$  is being reported for a terrestrial environment. The highly  $^{13}\text{C}$  depleted nature of the calcite suggests that it may originate from the oxidation of methane to  $\text{CO}_2$  in the surface peat layer. Methane production is accompanied by a  $-21$  to  $-73\text{‰}$  fractionation (Krzycki et al. 1987) and is the only natural process which produces  $\delta^{13}\text{C}$  values below  $-45\text{‰}$  (Zyakun et al. 1988; Whiticar et al. 1986). Methane produced in freshwater wetlands tends to have  $\delta^{13}\text{C}$  values near  $-50$  to  $-70\text{‰}$  (Quay et al. 1988; Kelley et al. 1992; Lansdown et al. 1992). Aerobic methane oxidation pathways cause a further  $^{13}\text{C}$  depletion in the product  $\text{CO}_2$  by  $-5$  to  $-31\text{‰}$  relative to residual methane (Barker & Fritz 1981; Games et al. 1978). As a result, methane emitted from high oxidation areas is enriched in  $^{13}\text{C}$  relative to  $\text{CH}_4$  below the oxidation zone (Oremland et al. 1987; Kelley et al. 1992).

The floating mat provides an ideal environment for oxidation of methane produced at depth in the mire. Methane rising from below is captured by the mat, and may be oxidized by  $\text{O}_2$  moving down roots of vascular plants, such as sedges, growing in the mat. The aerobic surface peat in wetlands has been found to be an active  $\text{CH}_4$  oxidation zone consuming 11 to 90% of the  $\text{CH}_4$  produced (Yavitt et al. 1988; King et al. 1990; Fechner & Hemond 1992) and plant photosynthetic processes greatly affect the oxidation rates (King 1990). High  $\text{NO}_3^-$  concentrations found in the floating peat mat may be associated with this zone of methane oxidation (Table 1). Nitrate can accumulate during the co-oxidation of ammonia and methane by methanotrophic bacteria in the areas of intense methane oxidation (Harrits & Hanson 1980).

Methane oxidation appears to occur in buried peat below the floating mat in profile 2 of site 1 (Fig. 2). The calcite in this poorly decomposed peat also bears a low  $\delta^{13}\text{C}$  value ( $-48.6\text{‰}$ ), indicative of methane oxidation. Since  $\text{O}_2$  is usually present only within the first few millimeters of sediment under a water body (Kuivila et al. 1988; Lidstrom & Somers 1984), methane oxidation could be occurring under anaerobic conditions in this layer. Anaerobic methane oxidation has been documented in fresh water environments (Panganiban et al. 1979; Zehnder & Brock 1980;

Iversen et al. 1987) and has been predicted through models to cause a fractionation of  $-8.8\text{‰}$  in product  $\text{CO}_2$  relative to substrate  $\text{CH}_4$  (Alperin et al. 1988).

The carbonates in the saturated wetland peat have  $\delta^{13}\text{C}$  values of around  $-30\text{‰}$ . As the conversion of  $\text{CO}_2$  to bicarbonate will cause  $^{13}\text{C}$  enrichment in the bicarbonate by about 9 to 12 ‰ at 25 to 0 °C (Mook et al. 1974), the  $^{13}\text{C}$  depletion relative to the original organic matter may reflect the inclusion of highly  $^{13}\text{C}$  depleted  $\text{CO}_2$  produced from  $\text{CH}_4$  oxidation.

Methane fluxes in the permanently saturated mire revealed different methane production/oxidation balances in the different peat conformations during the major  $\text{CH}_4$  flux period of the year (Fig. 3). The shallow solid peat (1.4 m peat) emitted less  $\text{CH}_4$  than profile 3 (2 m peat) because of less saturated peat area relative to the aerobic peat at the surface. Profile 2, which contains the floating peat mat, had much lower  $\text{CH}_4$  fluxes than profiles 1 or 3. The highly depleted  $\delta^{13}\text{C}$  values in the carbonates from the peat mat indicate the mat is an active oxidation zone which may be consuming  $\text{CH}_4$  produced below. The lower net fluxes observed from the floating mat support this. Profile 1 has high  $\text{CH}_4$  fluxes presumably because of a lack of surface peat to promote the oxidation of  $\text{CH}_4$ .

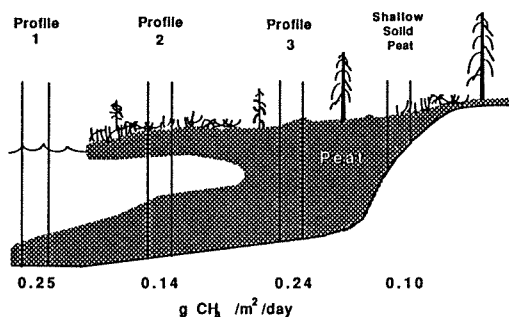


Fig. 3. Mean methane fluxes in saturated mire from June 24 to July 25, 1992.

In the second site, the peat accumulation bears a  $\delta^{13}\text{C}$  signature for organic C which remains constant with depth below the litter layer (Fig. 4). The dominant processes controlling C mineralization in saturated conditions, and therefore influencing the  $\delta^{13}\text{C}$  values, are methanogenesis and sulfate-reduction. Cumulative methane flux measured in the basin over the entire 1992 period was only  $0.0081\text{ g CH}_4\text{ m}^{-2}$ , and was only



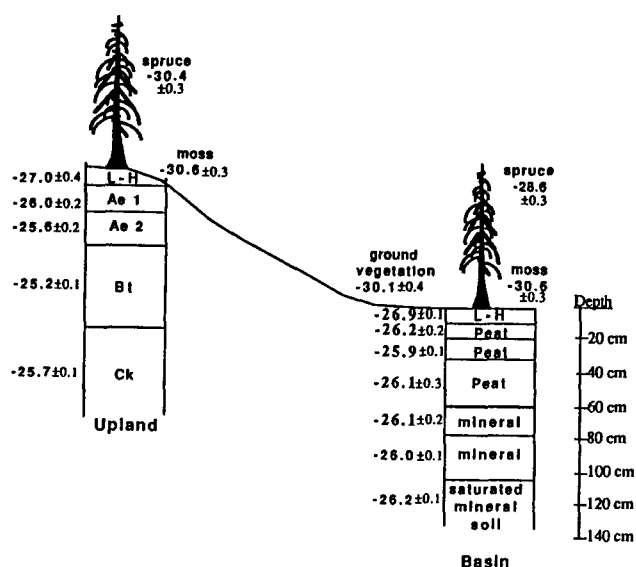


Fig. 4.  $\delta^{13}\text{C}$  of organic C in the upland watershed.

significant when the peat was thawing. The upland basin has greater amounts of available sulfate than the permanently saturated site presumably because aerobic decomposition periods release sulfate from the organic matter. This site had the distinct odour of sulfur gases which was never detected at any time in the permanently saturated site. High concentrations of reduced inorganic S at depth in the saturated zone of the basin suggest activity by sulfate reducers, especially at the 30 to 60 cm depth (Table 2). Depleted  $\delta^{34}\text{S}$  values measured in this site also support the occurrence of substantial sulfate-reduction activity below the 20 cm depth in the basin (Han 1991). It has been suggested that the mineralization of C during sulfate-reduction is not accompanied by  $^{13}\text{C}$  fractionation (Murphy et al. 1989), which creates  $\delta^{13}\text{C}$  values that remain constant with depth.

The upland basin contains carbonates in the peat horizons with depleted  $\delta^{13}\text{C}$  values indicating a biogenic origin (Fig. 5). Substantial amounts of  $\text{CO}_2$  or bicarbonate can be released as a byproduct of sulfate-reduction or fermentation from low molecular weight organic compounds. Carbon isotopic values of dissolved inorganic carbon (DIC) tend to approach the values of dissolved organic carbon (DOC) in environments conducive to sulfate-reduction (Carothers & Kharaka 1980; Nissenbaum et al. 1972; Presley & Kaplan 1968). Carbonate  $\delta^{13}\text{C}$  values in the 30 to 60 cm depth are  $-25.7$  to  $-21.9$  ‰ compared with the surrounding

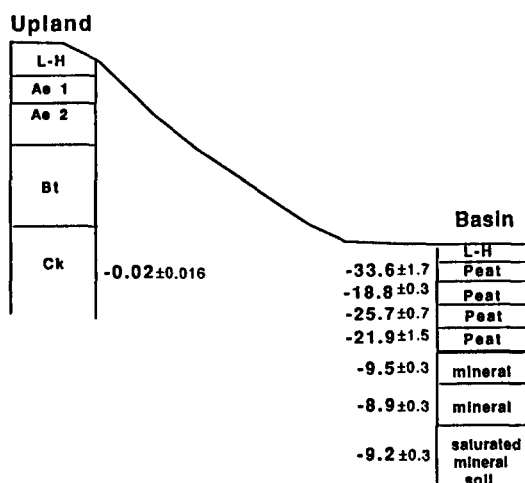


Fig. 5.  $\delta^{13}\text{C}$  of carbonate carbon in the upland watershed.

organic matter with a  $\delta^{13}\text{C}$  of  $-26\text{‰}$ . The mineral soils below the peat horizons contain carbonates with an isotopic value near  $-9\text{‰}$ , a value likely reflecting a combination of fossil carbonates (near  $0\text{‰}$ ) and biogenic carbonates produced during sulfur reduction. The largest carbonate accumulation, at 20–30 cm (Fig. 5), with a  $\delta^{13}\text{C}$  of  $-18.8\text{‰}$ , could be derived from sulfate reduction and possibly aerobic decomposition. Carbonate produced from aerobic decomposition has an estimated  $\delta^{13}\text{C}$  value of  $-10\text{‰}$  since isotopic values of  $\text{CO}_2$  produced will be equal to or slightly depleted relative to the organic matter (O'Brien & Stout 1978) and the conversion of  $\text{CO}_2$  to carbonate creates a  $\text{C}^{13}$  enrichment of 14 to 16  $\text{‰}$  (Cerling et al. 1989). Measured  $\delta^{13}\text{C}$  values for carbonates in the upper 10–20 cm peat layer (Fig. 5) were quite depleted at  $-33.6$  to  $-32.5\text{‰}$ . These carbonates may originate from methane oxidation and sulfate reduction. Methanogenesis has been shown to coexist with sulfate-reduction when different substrates are available for each process (Wieder et al. 1990; Oremland et al. 1987).

## Conclusion

The  $\delta^{13}\text{C}$  distribution and methane fluxes observed in the two types of boreal forest wetland supports methanogenesis as an important C mineralization process in permanently saturated wetlands. However, in wetlands which become aerobic for part of the year, such as the upland basin, there

may be a release of sulfate which may stimulate sulfate-reduction and inhibit methanogenesis. The variation of  $\delta^{13}\text{C}$  values in the carbonates indicate a number of possible C mineralization processes in the basin. In permanently saturated wetlands, the floating peat mats may be active oxidation zones because they contain highly depleted  $^{13}\text{C}$  carbonates ( $-97\text{‰}$ ) and emit lower amounts of  $\text{CH}_4$  than open water. As bogs mature, floating peat mats growing in to cover more open water may result in lower total  $\text{CH}_4$  fluxes.

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