

Sulfur during early diagenesis in *Sphagnum* peat: Insights from $\delta^{34}\text{S}$ ratio profiles in ^{210}Pb -dated peat cores

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Abstract

^{210}Pb chronologies and depth profiles of stable S isotope ratios ($\delta^{34}\text{S}$) and concentrations of organic and inorganic S fractions were determined in peat cores from nine sites in the U.S. and the Czech Republic. Results indicate that depth profiles in S concentrations, S accumulation, and $\delta^{34}\text{S}$ ratios in peat deposits are affected not only by historical patterns in atmospheric S deposition but also by ongoing depth-dependent changes in S reduction-oxidation and S immobilization-mineralization processes within a peat deposit. These processes impart a certain degree of mobility to S in peat, bringing into question the validity of reconstructing historical records of S accumulation using dated peat profiles. Over long-term diagenesis, isotopically light S may be continually released from deep peat. This release may result in redistribution of S and S isotopes in peat and suggests that short-term patterns in S accumulation may not persist over much longer time scales.

Sphagnum-dominated wetlands often exhibit a net retention of atmospherically deposited S (cf. Bayley et al. 1986; Urban et al. 1989; Spratt and Morgan 1990). Sulfur retention apparently is not the result of a fraction of the incoming S atoms becoming immobilized within the peat, with the remaining fraction passing through the peatland unaltered. Rather, the biogeochemical cycling of S in peat is quite dynamic. The quantity of S that cycles internally through oxidation and reduction reactions in peat may far exceed S inputs (Urban et al. 1989; Spratt and Morgan 1990; Wieder et al. 1990). Subsurface peaks in total S, organic S, and FeS_2 -S concentrations, typically

located near the top of the permanently saturated peat (Urban et al. 1989; Novák and Wieder 1992), have been interpreted as resulting from bacterial sulfate reduction and the formation of both organic C bonded S (formed relatively slowly, but relatively stable once formed) and reduced inorganic S (e.g. FeS -S and FeS_2 -S; formed relatively rapidly, but relatively labile once formed). Thus, localized accumulation of the reduced S end products of sulfate reduction has been implicated as the key process contributing to the generally reported retention of S in *Sphagnum* peatland ecosystems. However, little is known about the long-term fate of S in peatlands as peat accumulation proceeds.

Previously (Novák and Wieder 1992), we reported changes in the concentrations of organic and inorganic S fractions as a function of depth in peat cores collected from nine sites. In this paper, we apply ^{210}Pb dating and stable sulfur isotope ($\delta^{34}\text{S}$) analyses to these same peat cores in an effort to better understand both the short-term cycling of S in near-surface peat and the longer term cycling of S during diagenesis.

Study sites

The nine sites, seven in the U.S. and two in the Czech Republic, have a predominantly

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Sphagnum-derived peat deposit. Four of the U.S. sites (Marcell S-2 Bog, Minnesota; Tamarack Swamp, Pennsylvania; Cranesville Swamp, on the Maryland-West Virginia border; Big Run Bog, West Virginia) are physiographically minerotrophic, receiving inputs of water both by directly incident precipitation and by runoff from the surrounding upland portions of their watersheds. However, vegetation and water chemistry (surface water pH, 3.6–4.4; dissolved $\text{Ca}^{2+} < 2.4 \text{ mg liter}^{-1}$) indicate that these sites are similar to ombrotrophic bogs. McDonald's Branch Swamp, in the New Jersey Pinelands, is predominantly groundwater fed; the wetland has a substantial cover of living *Sphagnum* and its surface waters are acidic, with pH values ranging from 3.2 to 3.5. Tub Run Bog, West Virginia, and Allegheny Mining Bog, Maryland, are *Sphagnum*-dominated wetlands that receive SO_4^{2-} inputs in acid coal mine drainage. Although Tub Run Bog has been receiving acid mine drainage (pH as low as 2.2; SO_4^{2-} as high as $276 \text{ mg liter}^{-1}$) since mining ended around 1950, the quantity of mine drainage entering the wetland is rather small in comparison to incident precipitation and runoff from the forested upland portion of its watershed; in contrast, Allegheny Mining Bog has been receiving acid mine drainage (pH of 2.8; SO_4^{2-} , $\sim 1,200 \text{ mg liter}^{-1}$) since 1985 from a fairly continuously discharging seep ($\sim 250 \text{ liter min}^{-1}$) at the toe of the regraded mine spoil.

The peat deposits at the two sites in the Czech Republic, Boží Dar Bog and Jezerní slat', are predominantly *Sphagnum* derived, but there is very little living *Sphagnum* at these sites today and therefore no current *Sphagnum* peat accumulation. Whereas Jezerní slat' is in the relatively pristine Šumava Mountains of southern Bohemia, Boží Dar Bog is in the Krušné hory Mountains of northern Bohemia, one of the most polluted regions of Europe. More detailed descriptions of the study sites are given by Novák and Wieder (1992); the data reported here are from the same cores as in that paper.

Methods

One intact peat core was collected from each site with a 10-cm-diameter, 50-cm-long PVC pipe with a sharpened bottom edge. All cores were collected from areas of the wetland where

microtopographic differences between hummocks and hollows did not exceed 20 cm; cores were not collected from either hummocks or hollows. Cores were sliced into 2-cm-thick sections, freeze-dried, and homogenized with a Tecator Cyclotec Sample Mill. Although Amaral et al. (1989) reported that (compared to other drying methods) freeze-drying caused a loss of total S and altered stable S isotope ratios in lake sediment samples, experience in our laboratory with freshwater peat has shown no statistically significant effect of drying method (freeze-drying, air-drying, oven-drying at 60 or 100°C) on total S concentrations (Baechler and Wieder unpubl.).

Peat profiles were ^{210}Pb dated by acid digestion of peat (W. R. Schell pers. comm.) and application of the constant rate of supply (CRS) model of Appleby and Oldfield (1978). A 3-g subsample from each peat core section, along with $\sim 15 \text{ dpm}$ of ^{208}Po as a chemical yield tracer, was digested with concentrated HCl, concentrated HNO_3 , and H_2O_2 . The Pb and Po isotopes were plated onto silver disks for activity measurement on an ORTEC 576 alpha spectrometer. There was enough variability in ^{210}Pb concentrations with depth in the Allegheny Mining Bog peat core that the CRS model failed to converge; the core from this site was not datable.

When ^{210}Pb is used to date the cores, each date has an error term comprised of both the counting error and propagated error associated with fitting the CRS model to the data. The magnitude of the error term increases with depth (Schell 1987). In this paper, depths for which the error term exceeded the estimated age (yr) of the section were not included in the construction of core chronologies. Additionally, the dates obtained with ^{210}Pb methodology represent the average date for each 2-cm section. To calculate apparent S accumulation rates ($\mu\text{g cm}^{-2} \text{ yr}^{-1}$), we estimated the dates for the top and the bottom of each 2-cm section by averaging the date for the section with those of the overlying and underlying sections, respectively; the difference between the estimated dates for the top and bottom of each section then represents the number of years over which the peat in a particular section accumulated.

It has been suggested that ^{210}Pb is mobile, especially in the hollows of acidic peats (cf. Urban et al. 1990). However, palynological

analysis of the peat cores from Marcell S-2 Bog (timing of the rise in *Ambrosia* pollen) and Big Run Bog (timing of the disappearance of *Castanea* pollen) has corroborated the ^{210}Pb dates (Wieder et al. in press). Thus, in this paper we evaluate S fraction and $\delta^{34}\text{S}$ profiles assuming the validity of ^{210}Pb dates.

Total sulfur for $\delta^{34}\text{S}$ determination was extracted by Eschka's procedure (Chakrabarti 1978). The bottom of a 50-ml porcelain crucible was covered with 0.5 g of Eschka's mixture (MgO and Na_2CO_3 ; 2:1 wt/wt). A 1-g subsample from each depth interval was mixed thoroughly with 2.5 g of Eschka's mixture and added to the crucible. An additional 1 g of Eschka's mixture was added to the crucible which was then placed in a muffle furnace. The temperature was gradually raised to 800°C over a 1-h period; heating at 800°C continued for another 90 min. The resulting ash was transferred to a beaker containing 30 ml of distilled, deionized water, and 17 ml of concentrated HCl were added. The beaker was covered with a watch glass, and the mixture was boiled for 5 min, then passed through Whatman 541 filter paper. Two drops of methyl red indicator were added to the filtrate, and 30% NH_4OH was added until the color changed to light green and a trace of precipitate formed. A sufficient amount of concentrated HCl was added to just redissolve the precipitate plus 1 ml of HCl in excess. The beaker was covered and heated until the solution boiled. The temperature was reduced to just below the boiling point, and 10 ml of 0.48 M BaCl_2 were added while the beaker was agitated; heating was continued for another 30 min. The mixture was passed through Whatman 541 filter paper, and the wet filter paper was placed in a crucible and ignited at 800°C for 15 min, yielding solid BaSO_4 .

Stable sulfur isotope determinations of the resulting BaSO_4 from the North American cores were conducted by Geochron Laboratories (Cambridge, Massachusetts). Stable sulfur isotope determinations for the two Czech cores were conducted by the Czech Geological Survey (cf. Yanagisawa and Sakai 1983). In both cases, analysis involved thermal decomposition of the BaSO_4 to SO_2 and subsequent isotopic determination with a dual collector isotope ratio mass spectrometer.

Results and discussion

S accumulation in peat deposits—Previously (Novák and Wieder 1992) we reported that, for peat cores from the four relatively undisturbed sites in the U.S. that are not groundwater fed (Marcell S-2 Bog, Tamarack Swamp, Cranesville Swamp, Big Run Bog), total S concentrations gradually increased with depth, reaching maximum values between 10 and 20 cm, and then decreased with depth. Although we did not have detailed measurements of water-table fluctuation at any of the sites, the locations of the subsurface maxima in total S concentrations corresponded closely with field observations of minimum water-table elevation. Furthermore, among these four sites, there were only weak trends of increasing total S concentration in living *Sphagnum* and of increasing values for the subsurface total S concentration maxima with increasing atmospheric S deposition. Generally, the depth profiles for concentrations of organic and inorganic S fractions provided only weak evidence to support a hypothesis of greater S retention with greater atmospheric S deposition. Reassessment of these same cores using bulk densities to replace S concentrations with S contents and replacing depths with ^{210}Pb dates (Fig. 1), however, provides considerably more insight into S accumulation.

For the U.S. sites, there was a general trend of increasing S accumulation with increasing atmospheric S input (Fig. 1). Whereas all of these sites are surrounded by upland watershed areas and hence are physiographically minerotrophic, field observations suggest that much of the S in runoff from the upland areas is funneled through lags to the outlets or travels through the peatlands in small stream channels. Care was taken to collect cores at locations distant from both the upland boundary and stream channels; the extent to which any of the cores may have been influenced by upland runoff is difficult to determine quantitatively. Certainly, the greater accumulation of S in Tub Run Bog peat than in Big Run Bog peat (the sites are separated by <10 km) is a result of enhanced S inputs to Tub Run Bog in acid coal-mine drainage.

At the two Czech sites, the deeper parts of

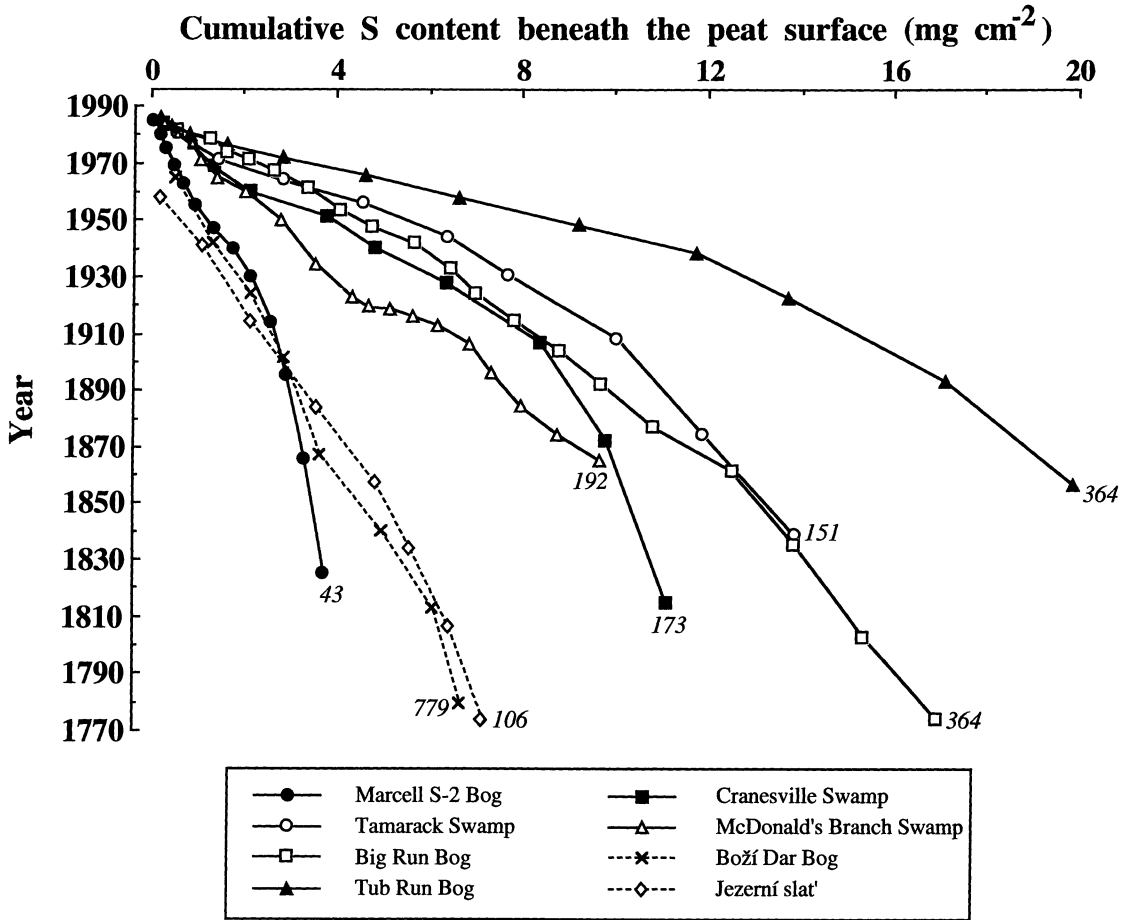


Fig. 1. Cumulative S contents beneath the peat surface as a function of year, determined by ^{210}Pb -dating of peat cores. Values on each curve represent current atmospheric S deposition in bulk precipitation ($\mu\text{g cm}^{-2} \text{ yr}^{-1}$), from Novák and Wieder (1992).

the peat appeared to be predominantly *Sphagnum* derived, but the upper 6 cm of each core consisted of an admixture of partially decomposed pine needles (dwarf pine, *Pinus mugo*). Nonetheless, the general pattern of long-term S accumulation at Jezerní slat' (Figs. 1, 2) is consistent with what would be expected at a low S deposition site. Surprisingly, however, S accumulation was similar at the two Czech sites, despite a present 7.4-fold greater atmospheric S deposition at Boží Dar Bog than at Jezerní slat'. The factors that contribute to the unexpectedly low S accumulation at Boží Dar Bog remain unknown.

For the U.S. sites, the S accumulation curves

(Fig. 1) appear slightly sigmoidal, with steeper slopes (less rapid S accumulation) near the upper and lower ends of the profiles and a middle section with a somewhat flatter slope (more rapid S accumulation). The more rapid S accumulation in the middle sections of the profiles is also evident in plots of S accumulation per year in each 2-cm section of each core (Fig. 2). The zone of relatively rapid S accumulation at McDonald's Branch Swamp (between 17 and 25 cm) is deeper than at the other U.S. sites and corresponds to a period of apparently rapid peat accumulation (each 2-cm section accumulating in <4 yr; see Fig. 2). Unlike the other sites, McDonald's Branch Swamp is

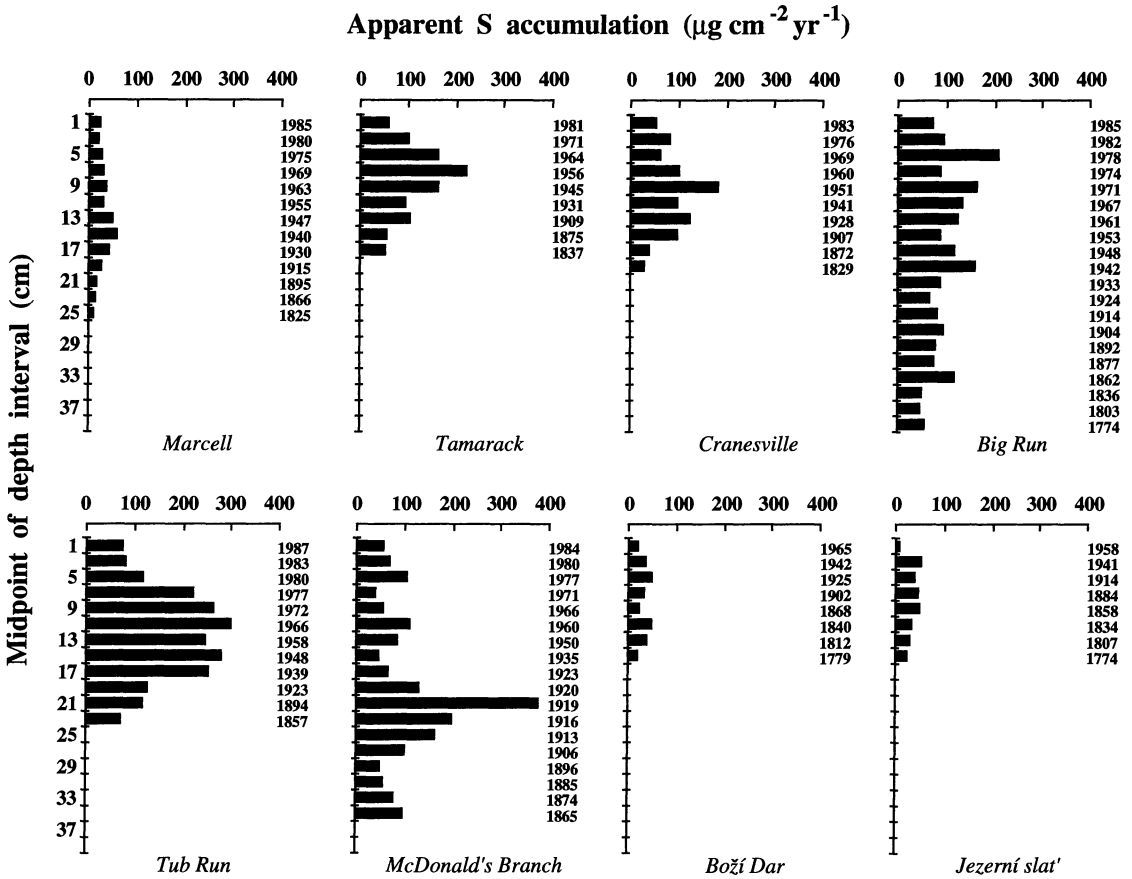


Fig. 2. Apparent S accumulation as a function of depth; to the right of each panel is the date for each section of the core, determined with ²¹⁰Pb methodology.

groundwater fed. We do not know whether the patterns of S and peat accumulation at McDonald's Branch Swamp have been affected by hydrology or possibly by past local disturbance at the site.

We note, however, that interpretation of S accumulation curves requires caution. For atmospherically deposited elements that are efficiently retained in the surface layers of an aggrading peat deposit, analysis of dated peat profiles may realistically represent element accumulation per year in each 2-cm section. However, for elements which are mobile (like S), organic matter accumulation and S accumulation are decoupled. Therefore, a more conservative interpretation is that each bar in Fig. 2 represents the quantity of S that presently exists in a 2-cm section of peat; the peat

itself is comprised of organic matter remaining from net primary production that had occurred over a certain number of years in the past. Thus, the x-axis in Fig. 2 has been labeled "apparent" S accumulation.

Apparent S accumulation values obtained in this study are similar to others reported in the literature. Using a different dating technique (acid-insoluble ash), Urban et al. (1989) reported apparent S accumulation for the Marcell S-2 Bog as being greatest at the surface (~125 µg cm⁻² yr⁻¹) and decreasing to a fairly constant rate of 24 µg cm⁻² yr⁻¹ below 10 cm. We obtained values for the Marcell S-2 Bog ranging from 10 to 58 µg cm⁻² yr⁻¹ (Fig. 2). Schell et al. (1986) reported apparent S accumulation for ²¹⁰Pb-dated peat bogs in New York and Pennsylvania ranging from 2 to 280

Table 1. Mean concentrations (averaged across all depths within a single core from each site) of the various S fractions in peat cores from all nine sites (cf. Novák and Wieder 1992).

Site	Concentration ($\mu\text{g g}^{-1}$ dry mass) of S as				
	Total S	Organic S	FeS ₂ -S	FeS-S	SO ₄ ²⁻ -S
Marcell S-2 Bog	1,741	1,369	191	94	87
Tamarack Swamp	5,653	4,865	562	105	122
Cranesville Swamp	2,954	2,598	223	80	53
Big Run Bog	5,272	4,666	367	113	126
Tub Run Bog	3,905	3,059	631	92	123
Allegheny Mining Bog	11,345	7,015	305	164	3,861
McDonald's Branch Swamp	4,319	3,639	444	136	101
Boží Dar Bog	2,179	1,979	89	37	74
Jezerní slat'	2,064	1,742	170	86	65

$\mu\text{g cm}^{-2} \text{yr}^{-1}$. A subsurface peak was obtained for the New York peat core, but the pattern for the Pennsylvania core was more similar to that found by Urban et al. (1989), with highest values in the surface peat sections.

S fraction and $\delta^{34}\text{S}$ ratio profiles—In all peat cores, organic S was much more abundant than inorganic S, even at Allegheny Mining Bog, where exceptionally high SO₄²⁻ concentrations (34% of total S) are attributable to the considerable inputs of acid mine drainage (Table 1). Excluding Allegheny Mining Bog, on average, organic S, FeS₂-S, FeS-S, and SO₄²⁻-S contributed 85, 9, 3, and 3% of total S respectively. Previously, we reported depth profiles in the concentrations of these S fractions (Novák and Wieder 1992); these profiles are provided in Fig. 3 so they can be compared with profiles for $\delta^{34}\text{S}$ ratios from the same cores.

Several aspects of the $\delta^{34}\text{S}$ ratio depth profiles (Fig. 3) are worthy of mention. At most sites (less so at Marcell S-2 Bog, Cranestville Swamp, McDonald's Branch Swamp), the signal-to-noise ratio (sensu Fry 1989) was rather high (i.e. the overall range in $\delta^{34}\text{S}$ ratios was substantially greater than differences between $\delta^{34}\text{S}$ ratios for adjacent depth intervals), making it possible to identify shifts in $\delta^{34}\text{S}$ ratios that were localized within a series of adjacent depths.

At all U.S. sites, a decrease in $\delta^{34}\text{S}$ ratios between the topmost section and the sections immediately below was observed, although the magnitude and depth over which this decrease occurred differed considerably between sites. In contrast to decreases in $\delta^{34}\text{S}$ ratios of 1.9, 2.4, and 4.3‰ in the top 4–6 cm of depth at Tamarack Swamp, Cranestville Swamp, and Marcell S-2 Bog, respectively, a decrease of

11.7‰ was observed in the top 6–8 cm of depth at McDonald's Branch Swamp. The surface section (living *Sphagnum*) from McDonald's Branch Swamp had the highest $\delta^{34}\text{S}$ ratio (+8.7‰), probably reflecting S inputs from storms originating in the Atlantic Ocean, ~40 km away (oceanic SO₄²⁻ with a $\delta^{34}\text{S}$ ratio of about +21‰; Rees 1970). $\delta^{34}\text{S}$ ratios decreased by 6.8 and 11.7‰ in the top 10–14 cm at the two mine-drainage-impacted sites, Tub Run Bog and Allegheny Mining Bog. Among all sites, Tub Run Bog and Allegheny Mining Bog were further characterized as having the lowest $\delta^{34}\text{S}$ ratios throughout their profiles. We do not know the $\delta^{34}\text{S}$ ratios for the pyrite and other sulfidic minerals that gave rise to the acid mine drainage. Nonetheless, it seems likely that the generally low $\delta^{34}\text{S}$ ratios in the peat from Tub Run Bog and Allegheny Mining Bog reflect inputs to the peat deposits of isotopically light S in the acid coal-mine drainage (cf. Smith and Batts 1974).

Neither of the Czech sites had living *Sphagnum*, although the peat below a depth of ~6 cm appeared to be predominantly *Sphagnum* derived. Both Czech sites had decreases in $\delta^{34}\text{S}$ ratios between the top and next-deepest sample, but these differences were quite small in magnitude (1.6‰ at Boží Dar Bog and 1.9‰ at Jezerní slat').

At some of the sites, near-surface decreases in $\delta^{34}\text{S}$ ratios with increasing depth culminated in the minimum $\delta^{34}\text{S}$ ratio obtained in the entire core; with further increases in depth, $\delta^{34}\text{S}$ ratios generally increased (this pattern is best illustrated at Tamarack Swamp, Big Run Bog, and Jezerní slat', Fig. 3). Corresponding to the near-surface decreases in $\delta^{34}\text{S}$ ratios with depth were increases in both organic S and, to a much

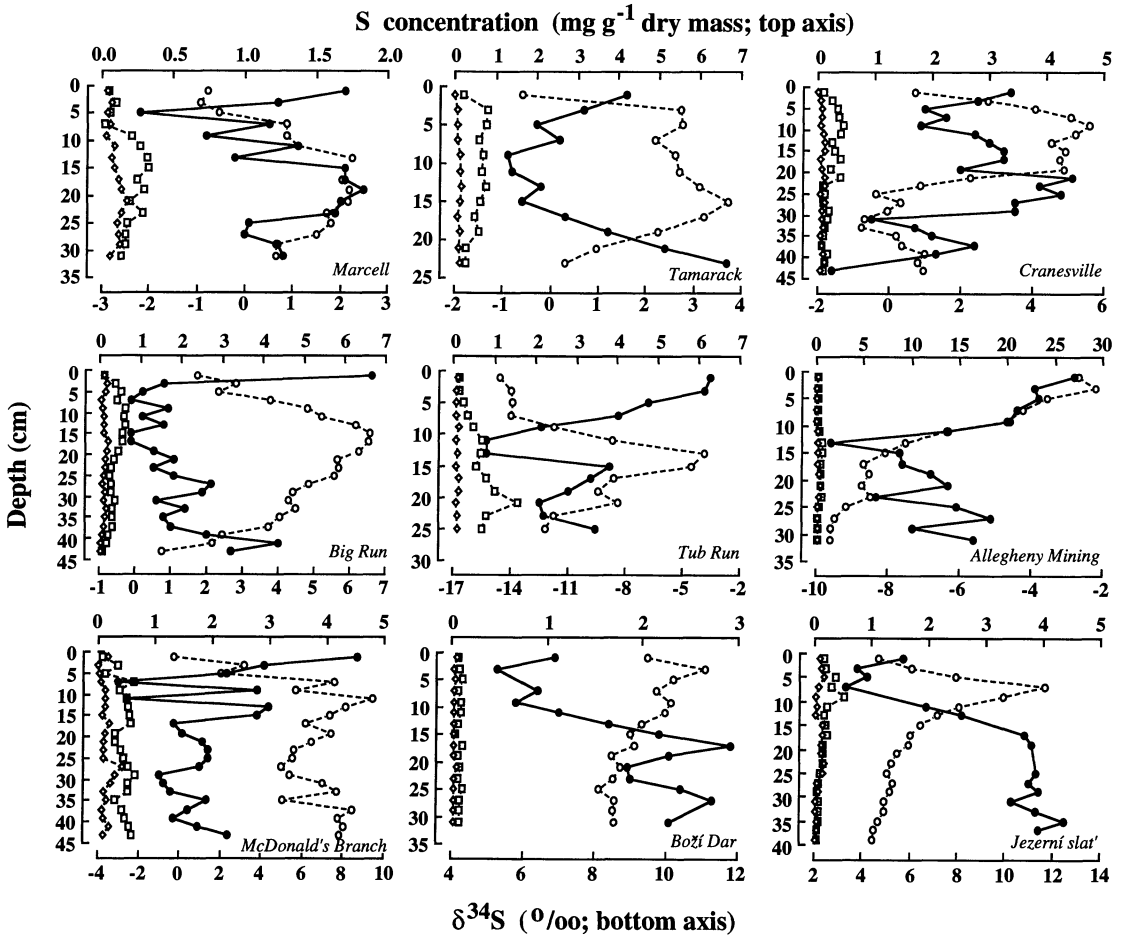


Fig. 3. Depth profiles for organic S (○), FeS₂-S (□), and FeS-S (◇) concentrations (all in mg g⁻¹ dry mass) and for δ³⁴S ratios (●; in ‰) in peat cores from all nine sites. Not shown are depth profiles for SO₄²⁻-S, concentrations of which were either uniform with depth or slightly elevated in near-surface (top 6 cm) peat (Novák and Wieder 1992).

lesser extent, FeS₂-S concentrations, so that in many instances the δ³⁴S ratio within a core reached a minimum value at or near the depth of the maximum concentration of organic S or FeS₂-S. For these sites, the observed inverse relationship between δ³⁴S ratios and concentrations of organic S or FeS₂-S is substantiated by significant negative correlations between the δ³⁴S ratios and concentrations of organic S or FeS₂-S (Table 2). In most cores, FeS-S concentrations are lower than FeS₂-S concentrations; a significant negative correlation between δ³⁴S ratio and FeS-S concentration was obtained in only one of the cores (Table 2).

δ³⁴S ratios and S cycling in peatlands—As a descriptive tool, δ³⁴S ratios, when considered

along with depth profiles in the concentrations of organic and inorganic S fractions in ²¹⁰Pb-dated peat, may provide insight into S cycling and S accumulation in peatland ecosystems. In the ensuing discussion, we focus primarily on four of the study sites (Marcell S-2 Bog, Tamarack Swamp, Cranesville Swamp, Big Run Bog) and make reference to the other sites when appropriate. Tub Run Bog exhibited patterns similar to these four sites, but Tub Run Bog is relatively disturbed because of its chronic, low-level S input from acid mine drainage. Allegheny Mining Bog was not datable with ²¹⁰Pb, and its S fraction depth profiles are unique and unusual because of the considerable S input of acid mine drainage. Mc-

Table 2. Pearson correlations between $\delta^{34}\text{S}$ ratios and concentrations of S fractions for each site. An asterisk indicates a significant correlation ($P \leq 0.05$; one-sided test for negative correlation between $\delta^{34}\text{S}$ and either organic S, $\text{FeS}_2\text{-S}$, or FeS-S). Sulfur fraction data were taken from Novák and Wieder (1992).

Site	Pearson's coefficient for correlations between $\delta^{34}\text{S}$ ratios and concentrations of		
	Organic S	$\text{FeS}_2\text{-S}$	FeS-S
Marcell S-2 Bog	0.363	0.391	0.563
Tamarack Swamp	-0.785*	-0.780*	-0.146
Cranesville Swamp	0.025	0.076	0.297
Big Run Bog	-0.609*	-0.726*	-0.289
Tub Run Bog	-0.647*	-0.634*	-0.080
Allegheny Mining Bog	0.659	-0.851*	-0.450*
McDonald's Branch Swamp	-0.640*	-0.565*	-0.145
Boží Dar Bog	-0.841*	0.180	-0.092
Jezerní slat'	-0.589*	-0.746*	-0.324

Donald's Branch Swamp is characterized by a hydrologic setting that is different from the other sites. The two Czech sites are no longer accumulating *Sphagnum*-derived peat and have much less S accumulation than would be expected from atmospheric S deposition levels (Figs. 1, 2).

The peat cores from Marcell S-2 Bog, Tamarack Swamp, Cranestville Swamp, and Big Run Bog all exhibited sigmoidal cumulative S content curves (Fig. 1), subsurface maxima in apparent S accumulation (Fig. 2), and subsurface maxima in total S and organic S concentrations (Fig. 3). One possible explanation for the depth patterns observed at these four sites is that S accumulation with depth reflects changes in atmospheric S deposition over the past 100–200 yr (i.e. periods of high atmospheric S deposition should be reflected in high S accumulation in peat formed during those periods). There are two variants of this explanation. Based on between-site comparisons of estimates of S accumulation in peat bogs, Urban et al. (1989) suggested that S accumulation in peat deposits increases proportionally with SO_4^{2-} inputs; increasing S input does not affect S retention efficiency. Alternatively, Fry (1986) suggested that in the sediments of low- SO_4^{2-} Adirondack Lakes, recently elevated S deposition in acid rain has stimulated dissimilatory sulfate reduction, leading to a greater proportion of the S input to the sediment being retained during periods of elevated atmospheric S deposition. Stable S isotope profiles can help distinguish between these two variants.

In theory, increased S input (with no change

in the $\delta^{34}\text{S}$ ratios of the S inputs) could lead to increased S retention without affecting $\delta^{34}\text{S}$ ratios in a lake sediment or peat deposit. If enhanced S retention occurs without a substantial fractionation of S isotopes (e.g. by assimilatory uptake and reduction or by dissimilatory sulfate reduction at SO_4^{2-} concentrations below 10–15 μM , cf. Harrison and Thode 1958), then S concentrations and retention could vary considerably with depth while $\delta^{34}\text{S}$ ratios would remain uniform. Alternatively, if enhanced S input increases SO_4^{2-} concentrations enough to increase the extent of fractionation during dissimilatory sulfate reduction, high values for S concentration and S retention will be accompanied by low $\delta^{34}\text{S}$ ratios of the S retained in the sediment or peat deposit. This latter scenario was obtained in Adirondack Lake sediments, where in deeper sediments total S concentrations and $\delta^{34}\text{S}$ ratios were fairly uniform, and near the surface total S concentrations increased and $\delta^{34}\text{S}$ ratios of total S decreased (Fry 1986). A similar depth pattern for total S concentrations and $\delta^{34}\text{S}$ ratios was obtained in lake sediments that were believed never to reach a level of anoxia capable of supporting dissimilatory sulfate reduction (Nriagu and Coker 1983). Although the near-surface increases in total S were attributed to recently elevated atmospheric S deposition, a mechanism of S retention that would lead to the observed isotopic fractionation (other than dissimilatory sulfate reduction) was not postulated.

With regard to the U.S. peat cores we analyzed, the patterns of S accumulation can be

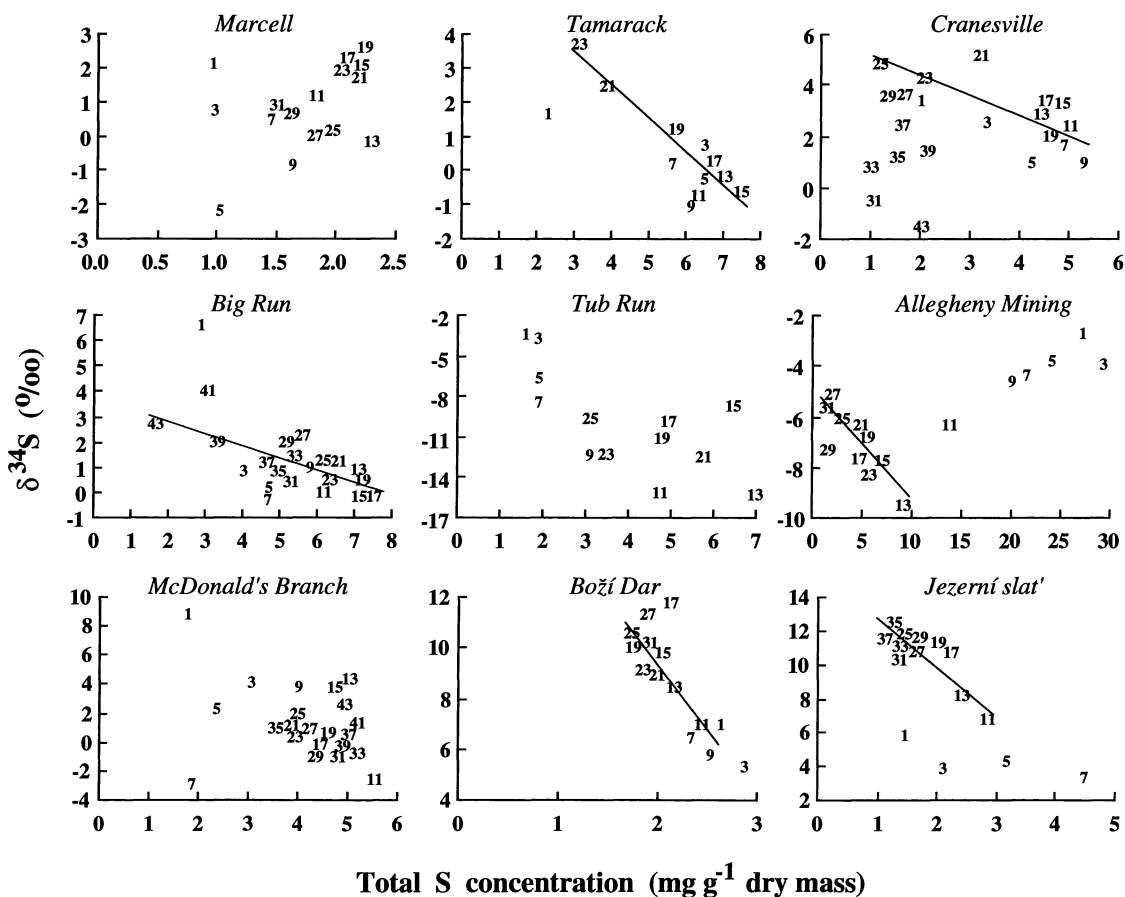


Fig. 4. Relationships between $\delta^{34}\text{S}$ and total S concentration for the 2-cm sections from the peat cores collected at all nine sites. Individual points are plotted as numbers which correspond to the midpoint of the depth interval within each core. For those sites where there was a significant relationship between the $\delta^{34}\text{S}$ ratio of total S and total S concentration within all or part of the anaerobic zone, the regression line is provided (cf. Table 3).

evaluated in light of the history of atmospheric S deposition. After the Industrial Revolution, atmospheric S deposition throughout eastern North America generally increased until the early 1970s and has subsequently declined. Superimposed on the pre-1970s pattern of generally increasing atmospheric S deposition were peaks in atmospheric S deposition around 1920 and 1945 and valleys in deposition in the early 1930s and 1950s (Husar et al. 1991). Moving upward through the peat at Marcell S-2 Bog, Tamarack Swamp, Cranesville Swamp, and Big Run Bog, total S and organic S concentrations (Fig. 3) as well as apparent S accumulation (Fig. 2) increased and then decreased. This pattern suggests a correspondence between the

temporal pattern of S deposition and the vertical spatial pattern of S retention. However, at these four sites respectively, S accumulation rates peaked at depths dated at 1940, 1956, 1952, and 1978 (Fig. 2), and total S concentrations peaked at depths dated at 1947, 1875 (with a second peak at 1964), 1951, and 1948. If it is the case that atmospherically deposited S is retained in peat primarily by dissimilatory sulfate reduction, retention will occur at a depth corresponding to the top of the saturated zone, where anaerobic conditions are first encountered by atmospherically deposited SO_4^{2-} ; S retention will not be substantial at the peat surface. As such, the vertical pattern of S accumulation will be offset as compared with the

Table 3. Results of linear regressions (estimated slope \pm SE of the estimate; *P* value associated with the null hypothesis that the slope of the regression is equal to 0) of $\delta^{34}\text{S}$ as a function of total S concentration (cf. Fig. 4) in peat samples considered to be at least occasionally exposed to anaerobic conditions in the field.

Site	Depths used in the regression	Slope \pm SE	<i>P</i>
Marcell S-2 Bog	≥ 7 cm	1.79 ± 0.94	0.0844
Tamarack Swamp	≥ 3 cm	-0.98 ± 0.46	0.0002
Cranesville Swamp	3–25 cm	-0.79 ± 0.23	0.0064
Big Run Bog	≥ 7 cm	-0.51 ± 0.11	0.0003
Tub Run Bog	≥ 9 cm	-0.31 ± 0.62	0.6307
Allegheny Mining Bog	≥ 13 cm	-0.42 ± 0.11	0.0045
McDonald's Branch Swamp	≥ 11 cm	-0.62 ± 0.94	0.5212
Boží Dar Bog	≥ 3 cm	-5.13 ± 1.05	0.0006
Jezerní slat'	≥ 7 cm	-2.72 ± 0.31	0.0001

dated chronology of a peat core. The magnitude of the offset will correspond spatially to the distance between the peat surface and the top of the anaerobic zone and will correspond temporally to the difference in age between the surface peat and the peat at the top of the anaerobic zone.

If the vertical patterns in S retention are related to historical changes in atmospheric S deposition, the $\delta^{34}\text{S}$ ratio depth profiles should reflect one of two predicted patterns: uniform $\delta^{34}\text{S}$ ratios throughout the entire peat deposit or uniform $\delta^{34}\text{S}$ ratios deep in the peat that become more negative only near the top of the anaerobic zone. Because the second pattern results from a stimulation of dissimilatory sulfate reduction and an attendant increase in the extent of S isotope fractionation, an inverse relationship between total S concentration and $\delta^{34}\text{S}$ ratio would be expected for peat in the anaerobic zone of a deposit. Present-day dissolved SO_4^{2-} concentrations in surface waters from Marcell S-2 Bog, Tamarack Swamp, Cranestville Swamp, and Big Run Bog average $< 10, 46, 63,$ and $60 \mu\text{M}$ (Urban et al. 1989; Sanguinetti 1992; Lang and Topa 1982; Wieder 1985). Therefore, minimal S isotope fractionation during dissimilatory sulfate reduction would be expected in Marcell S-2 Bog peat, whereas some degree of fractionation would be expected at the other sites. Accordingly, an inverse relationship between total S concentration and $\delta^{34}\text{S}$ ratio does not hold for Marcell S-2 Bog peat but does for Tamarack Swamp and Big Run Bog (Fig. 4, Table 3). For Cranestville Swamp, this relationship holds for peat between 3 and 25 cm deep, but below 25 cm, $\delta^{34}\text{S}$ ratios are independent of total S con-

centrations. These findings suggest that the vertical patterns of S retention in Marcell S-2 Bog, Tamarack Swamp, Cranestville Swamp, and Big Run Bog are related to historical changes in atmospheric S deposition. At the latter three sites, but not at Marcell S-2 Bog, retention may be the result of stimulated dissimilatory sulfate reduction in response to enhanced atmospheric S deposition.

Other aspects of these relationships between $\delta^{34}\text{S}$ ratios and total S concentrations in peat merit mention. At Tub Run Bog, $\delta^{34}\text{S}$ ratios and total S concentrations were not related, whereas at Allegheny Mining Bog, the recent exposure of surface peat to severe acid mine drainage was clearly evident in the top 11 cm of peat. Most of the horizontal water movement in a peat deposit occurs near the peat surface (Boelter 1965). Below 13 cm at Allegheny Mining Bog, the peat has been less exposed to mine drainage, and the relationship between $\delta^{34}\text{S}$ ratios and total S concentrations is inverse. At the groundwater-fed McDonald's Branch Swamp, $\delta^{34}\text{S}$ ratios were independent of total S concentrations. Both Czech sites exhibited the inverse relationship expected from S retention by the stimulation of dissimilatory sulfate reduction but with slopes that were much steeper than for any of the U.S. sites. This result is surprising given the small degree of S accumulation at the Czech sites as compared to the U.S. sites (Figs. 1, 2).

The apparent relationship between S retention and historical changes in atmospheric S deposition at Tamarack Swamp, Cranestville Swamp, and Big Run Bog cannot explain the shifts toward more positive $\delta^{34}\text{S}$ ratios deeper in the cores. These positive shifts are especially

evident at Tamarack Swamp and Big Run Bog, where the lowest datable sections (1837 at 19 cm and 1774 at 39 cm, respectively) are in regions of the peat profile where total S concentrations decrease with depth and $\delta^{34}\text{S}$ ratios increase with depth (Fig. 3). Because these depths predate widespread industrialization in the U.S., and given that patterns of S retention in peat are vertically displaced downward (S deposited at Tamarack Swamp in 1837 and at Big Run Bog in 1774 would be retained in peat deeper than 19 or 39 cm, respectively), these shifts cannot be related to increasing atmospheric S deposition.

We suggest a more complex scenario by which depth profiles in S concentrations, S accumulation, and $\delta^{34}\text{S}$ ratios in peat deposits are affected not only by historical patterns in atmospheric S deposition but also by ongoing depth-dependent changes in S reduction-oxidation and S immobilization-mineralization within a peat deposit. Sulfur entering the surface layers of a peatland, either from atmospheric deposition or minerotrophic runoff, can be retained in the aerobic surface peat by assimilatory uptake of both plants and microbes. Isotopic fractionation during assimilatory uptake and reduction of S appears to be minimal (cf. Krouse 1988; Thode 1991), so that across broad geographic scales, $\delta^{34}\text{S}$ ratios in living *Sphagnum* reflect the $\delta^{34}\text{S}$ ratios of atmospherically deposited S (Nriagu and Glooschenko 1992). Thus, differences in $\delta^{34}\text{S}$ ratios in the 0–2-cm depth interval (living *Sphagnum*) among the seven U.S. sites (Fig. 1; note the Czech sites do not have living *Sphagnum*) probably reflect $\delta^{34}\text{S}$ ratio differences in the S input to these peatlands.

Downward movement of SO_4^{2-} through unsaturated peat delivers the SO_4^{2-} to the anaerobic layer, where the decomposition of relatively young organic material provides the soluble organic molecules to fuel sulfate reduction. It is well documented that dissimilatory sulfate reduction discriminates against the heavier S isotope and results in a depletion of ^{34}S in the products of sulfate reduction by as much as -46% (see Krouse and Tabatabai 1986). The magnitudes of the near-surface decreases in $\delta^{34}\text{S}$ with depth for the peat cores analyzed in this study certainly could have arisen from bacterially mediated dissimilatory sulfate reduction.

Dissimilatory sulfate reduction has received little study in freshwater peatlands. Despite dissolved SO_4^{2-} concentrations of $<100\ \mu\text{M}$, rates of sulfate reduction in peat from Big Run Bog (Wieder et al. 1990) and McDonald's Branch Swamp (Spratt and Morgan 1990), measured with $^{35}\text{SO}_4^{2-}$ methodology, have approached those reported for coastal marine sediments. Although at Big Run Bog rates of sulfate reduction were positively correlated with dissolved SO_4^{2-} concentrations, experimental augmentation of the dissolved SO_4^{2-} pool failed to stimulate sulfate reduction (Wieder et al. 1990). High rates of sulfate reduction at Big Run Bog appear to be fueled by continual replenishment of the dissolved SO_4^{2-} pool by S oxidation reactions in the peat. The dissolved SO_4^{2-} pool in Big Run Bog peat turns over on the order of 1–2 d (Wieder and Lang 1988). In a closed system, the degree of isotope fractionation during sulfate reduction decreases as the dissolved SO_4^{2-} pool is depleted. However, a peat deposit is an open system in which the dissolved SO_4^{2-} pool can be replenished, either by S turnover within the peat deposit or by addition of new SO_4^{2-} in episodic rain events. Such a replenishment of the dissolved SO_4^{2-} pool could lead to a greater degree of S isotope fractionation than would be predicted from laboratory studies in closed systems.

Further, in freshwater peatlands, the dominant short-term end product of sulfate reduction is reduced inorganic S, which has a relatively rapid turnover rate. C-bonded S, a less important short-term end product of sulfate reduction, has a relatively slow turnover rate, so that over time C-bonded S becomes the dominant S fraction in peat (Wieder and Lang 1988). If most of the C-bonded S in peat is formed as a relatively stable end product of dissimilatory sulfate reduction, and given that most of the S in freshwater *Sphagnum*-derived peat is C-bonded S, then the $\delta^{34}\text{S}$ signature of total S is determined largely by C-bonded S formed by sulfate reduction. The pattern of coincidence of minimum $\delta^{34}\text{S}$ ratios with maximum organic S concentrations in several of the peat profiles in Fig. 3 is consistent with the view that the frequently observed peaks in C-bonded S concentration near the top of the permanently saturated peat result from dissimilatory sulfate reduction.

Deeper in the peat profiles at Tamarack Swamp and Big Run Bog, $\delta^{34}\text{S}$ ratios increased and concentrations of organic S and reduced inorganic S decreased. In theory, slow, long-term removal of reduced inorganic S from deep peat could contribute to an increase in the $\delta^{34}\text{S}$ ratio of the residual total S in the peat with depth if the anaerobic oxidation discriminates against ³⁴S. The oxidation of soluble sulfides, either aerobically or in sulfureta (cf. Krouse and Tabatabai 1986; Fry et al. 1988), at least sometimes exhibits such a fractionation. However, at the low percentages of total S contributed by reduced inorganic S characteristic of the peat profiles in Fig. 3, an unrealistically large isotopic fractionation during anaerobic oxidation of reduced inorganic S would be required to cause the observed increases in $\delta^{34}\text{S}$ ratios with depth. For example, at Tamarack Swamp, assume that at 15 cm the reduced inorganic S and organic S fractions had identical $\delta^{34}\text{S}$ ratios. As the peat matured to a state characteristic of the 23-cm depth, if only reduced inorganic S underwent fractionation during oxidation, a fractionation of 34‰ (oxidized and removed soluble S products isotopically lighter than the remaining solid-phase reduced inorganic S) would be required to obtain the $\delta^{34}\text{S}$ ratio for total S obtained at 23 cm; in contrast, if only organic S underwent fractionation during mineralization, a fractionation of 5‰ (mineralized and removed S isotopically lighter than the remaining solid-phase organic S) would be required to obtain the $\delta^{34}\text{S}$ ratio for total S obtained at 23 cm.

Strictly speaking, preferential mineralization of isotopically light S over isotopically heavier S from C-bonded S in the peat involves the preferential breaking of C-³²S bonds over C-³⁴S bonds and hence a proportionately greater loss of the light isotope from the solid-phase organic matter in the peat. The same effect could be achieved if the organic molecules to which sulfides initially attach to form C-bonded S are relatively more labile than the organic molecules containing S which was not formed by dissimilatory sulfate reduction. More rapid mineralization of the relatively labile organic molecules (with a relatively more negative ³⁴S ratio) than of the more recalcitrant organic molecules also could lead to a proportionately greater loss of the light isotope from the solid-phase organic matter in the peat. We suggest

that beneath the depths where minimum $\delta^{34}\text{S}$ ratios were obtained, increases in $\delta^{34}\text{S}$ ratios with increasing depth are probably more related to isotope fractionation during the net mineralization of S-containing solid-phase organic matter (and removal of the isotopically lighter S in the mineralization products) than to oxidation of reduced inorganic S (and removal of the isotopically lighter S in the oxidation products).

Urban et al. (1989) interpreted depth profiles in the C:S ratios in peat at Marcell S-2 Bog as indicating that S was mineralized more rapidly than C in the aerobic, surface peats, but deeper in the peat there were regions where C was mineralized more rapidly than S, and eventually depths were reached where C and S were mineralized at similar rates. Although little work has addressed changes in $\delta^{34}\text{S}$ ratios of decomposing plant materials, Schoenau and Bettany (1989) suggested that labile organic S fractions tended to have more positive $\delta^{34}\text{S}$ ratios than relatively recalcitrant organic S fractions. During the early stages of decomposition and S mineralization, $\delta^{34}\text{S}$ of the residual plant material should decrease, reflecting the preferential loss of the isotopically heavier fractions. Thus, S mineralization in near-surface (i.e. relatively undecomposed) peat could have contributed to our observed decreases in $\delta^{34}\text{S}$ ratios from the tops of the peat profiles downward. Below the depths where the minimum $\delta^{34}\text{S}$ ratios were obtained, the peat is older and relatively decomposed.

The effects of further S mineralization on the $\delta^{34}\text{S}$ ratios of total S in deeper peat are unknown. However, it has long been recognized that anaerobic mineralization of C-bonded S molecules can produce volatile S (Kadota and Ishida 1972) which would move upward through the peat deposit and potentially could be emitted from a peatland. Although little work has addressed S isotope fractionation during the production of S gases under anoxic conditions, in the laboratory direct cleavage of the sulfhydryl group from cysteine by *Proteus vulgaris* generated H₂S that was depleted in ³⁴S by -4 to -5‰ (Kaplan and Rittenberg 1964). Most studies have shown that S gas emission from *Sphagnum* peatlands is negligible (cf. Giblin and Wieder 1992), but Nriagu et al. (1987) suggested that substantial emission of dimethyl sulfide from Canadian

peatlands may explain the observed seasonal pattern of lower summertime $\delta^{34}\text{S}$ ratios than wintertime $\delta^{34}\text{S}$ ratios in bulk precipitation S across Canada.

Reciprocal depth patterns between organic S concentrations and $\delta^{34}\text{S}$ ratios observed at some of the sites (Fig. 3, Table 2) are consistent with a scenario of downward movement of incoming SO_4^{2-} to the anaerobic layers of the peat, followed by sulfate reduction and the formation of isotopically light reduced organic S and to a lesser extent reduced inorganic S, and then the slow release of isotopically light S by mineralization processes in even deeper peat layers. Moreover, the internal cycling of S near the top of the permanently saturated zone may accentuate the reciprocal patterns between organic S concentrations and $\delta^{34}\text{S}$ ratios in the peat profiles.

If the lower portions of the depth profiles represent regions of ongoing removal of isotopically light, reduced S compounds released by mineralization processes, such compounds would be expected to move upward, potentially becoming oxidized upon reaching the aerobic layers of the peat. Regardless of whether this oxidation discriminates against the heavier ^{34}S , reduction of this already isotopically light sulfur, with attendant discrimination against the heavier ^{34}S , would exaggerate the already low $\delta^{34}\text{S}$ ratios in the peat near the top of the permanently saturated zone. This argument has been used to explain changes in $\delta^{34}\text{S}$ ratios for SO_4^{2-} , S^0 , and FeS_2 with depth in a peat deposit in the Peace River area of Canada (Krouse 1980).

The depth profiles for $\delta^{34}\text{S}$ ratios that we have reported for freshwater *Sphagnum*-derived peat deposits are different from those that have been reported for lake sediments (e.g. Nriagu and Coker 1983; Fry 1986). Perhaps this should not be surprising because freshwater *Sphagnum* peat deposits differ in many ways from lake sediments. In peat deposits, unlike lake sediments, sharply decreasing dissolved SO_4^{2-} concentrations with depth may not be typical (cf. Urban et al. 1989; Wieder et al. 1990). Compared to lake sediments, peat deposits tend to have higher organic matter contents, a higher percentage of total S as organic S (rather than reduced inorganic S), and often lower concentrations of Fe oxides. Furthermore, in peat deposits, mass movement of

water occurs predominantly in a horizontal direction (Boelter 1965) and water-table levels fluctuate, potentially exposing the surface layers of the peat to frequently changing redox conditions. In contrast, because lake sediments are permanently overlain by water, materials move more by diffusion and advection than by mass movement of water. Redox conditions of lake sediments may change, especially during turnover, but the frequency of redox changes is likely to be much lower than for the surface of a peat deposit.

In both peat deposits and lake sediments, sulfate reduction has been implicated as causing subsurface minima in $\delta^{34}\text{S}$ ratios; however, interpretations based on depth profiles of S fractions and $\delta^{34}\text{S}$ ratios for both lake sediments and peat deposits suggest mobility of S. This apparent mobility brings into question the validity of reconstructing historical records of S accumulation in either lake sediments or peat deposits by combining peat dating techniques with S concentration data (e.g. Schell 1987; Urban et al. 1989; Baker et al. 1992). Moreover, although S accumulation in peat deposits responds to changes in atmospheric S deposition (both along present-day spatial gradients in deposition and in association with temporal changes in historical deposition), over long-term diagenesis, isotopically light S may be continually released from deep peat. This release may result in redistribution of S and S isotopes in peat and suggests that short-term patterns in S accumulation may not persist over much longer time scales.

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