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Stable sulfur isotopic distributions and sulfate reduction in lake sediments of the Adirondack Mountains, New York

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Abstract. Cores from five lakes of the Adirondack Mountains, New York, were analyzed for sedimentary sulfur concentrations and stable sulfur isotopic compositions. Isotopic values of total sedimentary sulfur were as much as 6 to 8‰ lower than isotopic values of sulfur sources (soils, tree leaves and lake water sulfate) which showed little isotopic variation in the Adirondacks. The low isotopic values of recent sediments indicate increased sulfate reduction, probably in response to increased sulfate loading and acid deposition. Detailed historical reconstruction of sulfate loading histories from sedimentary sulfur profiles is premature, however, since model calculations indicate that sulfur can be added to deeper older sediments by ongoing, contemporary sulfate reduction.

Introduction

Dissimilatory sulfate reduction is an important decomposition process in sediments of freshwater lakes. Sulfate reduction by anaerobic bacteria leads to marked vertical depletions in sulfate concentrations to near-zero levels within 1–10 cm of sediment surfaces (Kelly and Rudd 1984). The resulting sulfides can add to the total amount of sulfur stored in sediments during reactions with iron and organic matter (Nriagu and Soon, 1985). Since experimental addition of sulfate to whole lakes and to experimental enclosures within lakes stimulates sulfate reduction, the low 10–200 μM sulfate concentrations typical of most lakes appear to wholly or partially limit the extent of sulfate reduction (Cook, 1981; Cook and Schindler, 1983; Kelly and Rudd, 1984). Increased sulfate loading from atmospheric acid deposition often has the effect of stimulating sulfate reduction in lake sediments (e.g., Holdren et al., 1984).

In this paper, I use stable sulfur isotopic analyses of sediment cores to evaluate dissimilatory sulfate reduction in lakes of the Adirondack Mountains, New York. Sulfate levels in these lakes have increased from about 15 to 70 μM over the last century due to atmospheric deposition (Galloway et al., 1983; Wright, 1983; Galloway et al. 1984), potentially causing increases in dissimilatory sulfate reduction. Increased sulfate reduction should lead to lower $\delta^{34}S$ values in sediments for two reasons. Dissimilatory sulfate reduction occurs with a normal isotope effect such that product sulfides are depleted in ^{34}S relative to ^{32}S and have low $\delta^{34}S$ values (Chambers and Trudinger, 1979). Increased production and retention of sulfides in sediments will result in lower $\delta^{34}S$ values. Secondly, isotopic fractionations may increase as sulfate levels increase. The isotopic composition of sulfides is approximately equal to that of sulfate when sulfate is present at the 10–15 μM concentrations characteristic of many undisturbed lakes (Harrison and Thode, 1958), but becomes increasingly depleted in ^{34}S as sulfate concentrations increase (Nakai and Jensen, 1960; Nakai and Jensen, 1964; Matrosov et al. 1975; Migdisov et al. 1974; Migdisov et al., 1983). The magnitude of this ^{34}S depletion is variable, but typically ranges between 10 and 70‰ (Chambers and Trudinger, 1979). If increased environmental sulfate levels lead to increased sulfate reduction in lakes, the combined effects of increased sulfide addition and increased isotopic fractionation should result in ^{34}S depletions in lake sediments. These depletions may function as indicators of sulfate loading and sulfate reduction activities.

To test these ideas, I analyzed %S and $\delta^{34}S$ of cores from five Adirondack lakes. The results show considerable between-lake differences in both %S and $\delta^{34}S$ profiles. Contemporary sulfate reduction can account for some of these variations, so that sedimentary sulfur profiles represent a mixture of historical and ongoing patterns of sulfur deposition.

Methods

Cores were collected from the deepest parts of lakes using a 10 cm diameter piston-corer in the summers of 1982 and 1983. Cores were sectioned at 0.5 cm intervals in the field, and stored in plastic bags until returned to the laboratory. Samples of about 150 mg were dried to constant weights in glass vials at 60°C, then combusted as follows using about 1 g per sample of Eschka's mixture (two parts MgO, one part $NaCO_3$) as an oxidant in a muffle furnace: 275°C (12 hr), 450°C (3 hr), 850°C (0.5 hr). Cooled samples were digested and leached with boiling HCl, filtered, the filtrate heated and $BaCl_2$ added to precipitate $BaSO_4$. After standing overnight, $BaSO_4$ was recovered by filtration onto #42 Whatman filters, then combusted at 850°C. The remaining $BaSO_4$ powder was weighed to the nearest 0.01 mg for calculation of %S, then thermally decomposed at 1600°C under vacuum to SO_2 (Fry et al., 1982). Contaminating CO_2 and H_2O were removed during vacuum distillations with pentane/liquid nitrogen and dry ice/ethanol slushes. Purified SO_2 was measured for its isotopic content using a Nuclide 6-60 isotope ratio mass spectrometer by comparison to a laboratory standard (lecture bottle SO_2) that had been calibrated against seawater sulfate (assumed to be + 20.1‰ vs. Cannon Diablo Troilite, CDT, for SO_2 measurements; Rees et al., 1978). Isotopic results are reported as $\delta^{34}S$ values versus CDT where

$$\delta^{34}S = [(R_{SAMPLE}/R_{STANDARD}) - 1] \times 1000.$$

Replicate analyses of sediments showed that $\delta^{34}S$ measurements were reproducible to ± 0.2‰, and %S to ± 0.05%.

Results

Sulfur in lake sediments is derived from two sources: sedimenting organic matter and sulfate in lake waters. The sulfur isotopic composition of these source materials was fairly constant among 14 watersheds located in the western, central and northeastern Adirondacks (Table 1). The isotopic compositions of tree leaves and soils each averaged + 2.9‰, and were not significantly different from the average value of sulfate in lake waters (mean = 3.7‰, Table 1). These results indicate little isotopic fractionation of sulfur during a) incorporation of inorganic sulfur into plant leaves, and b) decomposition of plant litter. The isotopic similarity of sulfur in soils and leaves was independent of tree species (Table 1) and soil type (personal observation). Lakes believed to be strongly acidified due to atmospheric deposition (e.g. Big Moose Lake; Charles, 1982; Charles, 1984) had sulfate isotopic values only marginally lower than larger lakes (Lake Placid, Sixth Lake) which are probably much less acidified (Table 1).

Although source materials thus had fairly uniform isotopic compositions in the Adirondacks, sulfur present in lake sediments was not similarly uniform in its isotopic composition. All cores had the most ^{34}S enriched values (most positive values) at depth and most ^{34}S depleted values (most negative values) at or near the surface (Figure 1), but cores differed sufficiently to warrant description in terms of three different patterns. Pattern 1. Although the absolute magnitudes of the %S and $\delta^{34}S$ values differed between Big Moose Lake, Windfall Pond and South Lake, cores from these lakes were qualitatively similar. They had subsurface maxima in %S with a nearly coincident minimum in $\delta^{34}S$. In these cores, %S and $\delta^{34}S$ were inversely related, since at mid-depth in the cores, increases in %S were accompanied by decreases in $\delta^{34}S$, and also near the surface, decreases in %S were accompanied by increases in $\delta^{34}S$ (Figure 1). This general inverse relationship between %S and $\delta^{34}S$ characterizes these cores. Pattern 2. Results from Upper Wallface Pond (located at 44 08 47 N, 74 03 15 W) showed that $\delta^{34}S$ changes in lake cores can occur independently from %S changes. In this core, %S was essentially constant at ~ 0.4%, even in the top 10 cm where a marked subsurface minimum in $\delta^{34}S$ occurs (Figure 1). This core is characterized by constant %S and an independent variation in $\delta^{34}S$. Pattern 3. In Deep Lake, %S reached unusually high values of about 5%, and no subsurface minimum in $\delta^{34}S$ occurred (Figure 1). Also, changes in %S and $\delta^{34}S$ were not inversely correlated in either the lower portion of the core or near the surface (Figure 1). This pattern is characterized by a very well-developed subsurface maximum in %S but no accompanying $\delta^{34}S$ minimum.

Table 1. $\delta^{34}S$ values of lake water and watershed soils and tree leaves from the Adirondack Mountains

Lake	Location	$\delta^{34}S_{CDT}$		
		Water	Soil	Tree leaves
Big Moose Lake	43 49 02N 74 51 23W	3.7, 4.4^a	3.5	2.7^b
Clear Pond	43 59 50N 73 49 50W	3.9	3.5	3.5^c
Dart Lake	43 47 36N 74 52 13W	3.4	—	—
Deep Lake	43 36 58N 74 39 52W	3.0	1.8	2.7^d
Durant Lake	43 50 26N 74 23 03W	3.8	2.4, 2.9^a	2.4, $2.7^{a,b}$
Elk Lake	44 01 23N 73 34 02W	3.4	3.4	3.6^c
Heart Lake	44 10 50N 73 58 03W	3.6	2.4	3.3^d
Lake Placid	44 18 16N 73 59 43W	5.6	—	—
Moss Lake	43 46 52N 74 51 11W	3.4	—	—
North Lake	43 31 20N 74 56 55W	3.0	—	—
Queer Lake	43 48 49N 74 48 25W	3.5	4.1	3.0^d
Sixth Lake	43 44 40N 74 46 58W	4.5	—	—
South Lake	43 30 34N 74 52 38W	3.2	1.9	2.0b
Windfall Pond	43 48 15N 74 49 52W	2.9	3.0	3.0^d
	$\bar{x}$ ± S.D.	3.7 ± 0.7	2.9 ± 0.8	2.9 ± 0.5

[a] Separate samples.
[b] *Fagus grandifolia* (American beech).
[c] *Acer rubrum* (red maple).
[d] Unidentified deciduous species.

Organic carbon varied from 10–30% in sediments of the Adirondack lakes, and iron was also abundant, as iron oxides measured after ashing comprised at least 3–15% of dry sediment weight (S. Norton, personal communication). Sulfate levels in most Adirondack lakes are fairly uniform at 50–75 μM (C. Driscoll, personal communication), so that in sum, the observed differences among the sulfur profiles could not be readily linked to variations in organic carbon, iron,or sulfate levels.

Discussion

Isotopic values of total sulfur in recent sediments of the five Adirondack lakes reach minimal values at or near the surface. These minimal values are

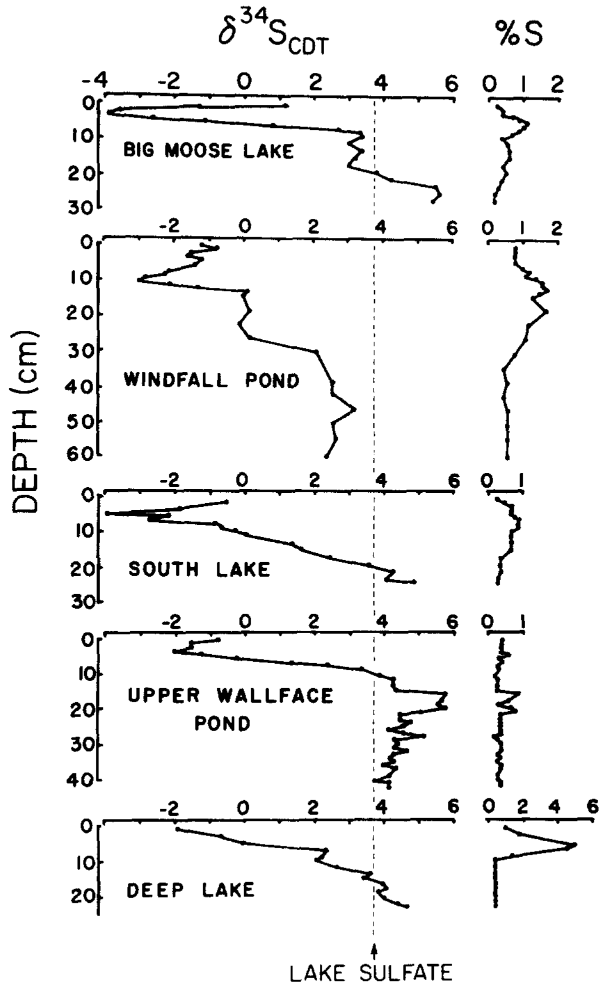

Figure 1. $\delta^{34}S_{CDT}$ and %S profiles of total sulfur for cores from five Adirondack lakes. Dashed line at + 3.7‰ indicates average value of lake water sulfate from 14 Adirondack lakes (Table 1).

6–8‰ lower than values of sulfate in the water column (Figure 1, Table 1). Several explanations can be advanced to explain this general observation, including isotopic changes introduced by loss of sulfur from sediments, changes in the isotopic composition of source materials, increased esterification of sulfate in sediments, changes in sulfate adsorption by sediments, and increased dissimilatory sulfate reduction. The importance of dissimilatory sulfate reduction has been shown in several Canadian lakes near Sudbury, Ontario, where more than 50% of total sulfur in sediments is composed of reduced inorganic sulfur compounds (FeS, FeS_2, S^0, H_2S)

that are formed where sulfate reduction is active (Nriagu and Soon, 1985). No similar direct evidence for sulfate reduction is available for the lakes of this study since only total sulfur was analysed. However, the following discussion shows that isotopic changes associated with the other processes are too small to account for the observed isotopic minima in the Adirondacks.

Any losses of organic sulfur from sediments could potentially entail isotopic changes, but field studies in two relatively pristine lakes of northern Ontario show essentially constant %S and δ^{34}S values with depth (Nriagu and Soon, 1985). Isotopic similarity among leaves and soils of the Adirondacks (Table 1) and one laboratory study of plant decomposition (Mekhtiyeva et al., 1976) also confirm that isotopic changes accompanying degradation of organic sulfur are small, < 1.5‰.

Some historical decline in δ^{34}S of source materials may be indicated, since deepest sediments in four of the five Adirondack cores average about 5‰ (Figure 1) whereas modern source materials average 3‰ (Table 1). However, this decline is not large enough to account for the low − 2 to − 4‰ minimal values observed in Adirondack sediments.

David and Mitchell (1985) have recently proposed that sulfur may be incorporated into sediments of Adirondack lakes by various processes other than dissimilatory sulfate reduction, including assimilatory sulfate reduction in sediments, increased inputs of planktonic biomass that is relatively rich in sulfur, and sulfate esterification in sediments. Laboratory and field studies show that isotopic fractionations associated with assimilatory sulfate reduction by bacteria and plants are small, averaging about − 1.5‰ (Kaplan and Rittenberg, 1964; Mekhtiyeva and Pankina, 1968; Chambers and Trudinger, 1979); Nriagu and Wong (1975) found small fractionations of 0 to − 0.5‰ for *Chlorella pyrenoidosa* grown at sulfate concentrations < 100 μM that are typical of Adirondack lakes. Isotopic changes associated with assimilatory sulfate reduction in sediments or increased planktonic inputs should thus be minor relative to larger changes actually observed. Esterification also appears to involve very minor isotopic fractionations, since algae rich in sulfate esters show δ^{34}S values that average only 1–2‰ lower than those of environmental sulfate (Kaplan et al., 1963; Mekhtiyeva and Pankina, 1968; Fry et al., 1982).

Sulfate adsorption can also potentially lower isotopic values of sediments. Adsorption can be accompanied by strong isotopic fractionations such that adsorbed sulfate is strongly depleted in ^{34}S by 22 to 34‰ vs. initial sulfate (Nriagu, 1974; Cortecci, 1978). However, the regularity of isotopic fractionation by this mechanism is somewhat questionable, since in one of three sediments thus far tested, no isotopic fractionation was observed during sulfate adsorption (Cortecci, 1978). More importantly, Nriagu (1974) has calculated that sulfate adsorption is quantitatively of minor importance in changing isotopic values of total sedimentary sulfur, i.e., adsorption of sulfate for a sediment containing 0.5% S changes isotopic values by only − 0.2 to − 0.5‰.

In summary, although dissimilatory sulfate reduction was not directly confirmed as the cause of low $\delta^{34}S$ values in Adirondack lake sediments, this process appears to be the only one of several potential mechanisms that can add significant quantities of ^{34}S depleted sulfur to sediments. Sulfate depletion and presence of sulfides in sediments of at least one Adirondack lake (Holdren et al., 1984) indicates that dissimilatory sulfate reduction occurs in Adirondack lake sediments. Two general observations from this study support the importance of dissimilatory sulfate reduction. First, the $\delta^{34}S$ minima in Adirondack cores (Figure 1) occur near the surface where sulfate reduction is typically most intense (Kelly and Rudd, 1984). Second, surface sediments typically have lower %S and higher $\delta^{34}S$ values than sediments a few centimeters deeper (Figure 1). Oxidation of surface sediments could account for these features, since sulfides may be lost from oxidized surface sediments (Aller, 1980) or the depth at which anaerobic sulfate reduction starts may be lowered where surface sediments are oxidized (Holdren et al., 1984).

The %S and $\delta^{34}S$ profiles of the five lakes (Figure 1) show that even within a relatively small geographical area like the Adirondacks, sulfur accumulation in lake sediments is not uniform. The most common pattern of increasing %S and decreasing $\delta^{34}S$ towards the surface (Figure 1, Big Moose Lake, Windfall Pond, South Lake) has also been observed in sediments of Canadian lakes that have received increased sulfate loading (Nriagu and Coker, 1983; Nriagu and Soon, 1985; Dickman and Thode, 1985). Detailed interpretation of these profiles may be premature, however, until we reach a better understanding of their historical development. The production and reaction of sulfides strongly affects profile development, but the following shows that sulfide isotopic data can be interpreted to support either of two opposite hypotheses – that the sulfur profiles primarily reflect historical patterns of sulfur deposition, or that they are primarily the result of contemporary sulfate reduction processes.

To illustrate vertical changes occurring in sulfide $\delta^{34}S$, I have selected cores from three representative lakes which have experienced recent increases in sulfate loading: Big Moose Lake (this study), McFarlane Lake near Sudbury, Canada (Nriagu and Coker 1985) and Lake Ontario (Nriagu and Coker 1976). For the first two lakes, sulfide $\delta^{34}S$ values are not available, but can be estimated by mass balance considerations. Isotopic values of sulfides can be calculated by assuming that sulfur in lake sediments is a mixture of two components, detrital sulfur from plants and sulfate reduction or sulfide sulfur (Holdren et al., 1984). Calculations were made using a mass balance equation:

$$\delta_T = [\delta_{SRS}(\%_T - \%_{DS}) + \delta_{DS}\%_{DS}]/\%_T \qquad (1)$$

where δ and % refer to $\delta^{34}S$ and %S and the subscripts T, SRS, and DS refer respectively to total sulfur, sulfate reduction sulfur and detrital sulfur.

Judicious selection of %S and $\delta^{34}S$ values for detrital sulfur is important in these calculations. For Big Moose Lake, 0.3% and 3.2‰ values were selected since these are respectively the extrapolated surface %S concentration and, for δ_{DS}, an average value of sulfur in the mid-portion of the core (Figure 1) that is near the 2.9‰ average for Adirondack leaves and soils (Table 1). The 0.3% value is reasonable, since it is slightly higher than a 0.2% average value for terrestrial vegetation (David et al., 1984) but slightly lower than a 0.35 average %S value of profoundal sediments from a relatively pristine lake (Nriagu and Soon, 1985). For the McFarlane Lake core, very constant values of 0.15% S and 5.1‰ $\delta^{34}S$ are observed at depth (Nriagu and Coker, 1983); these values were used as estimates of $\%_{DS}$ and δ_{DS}.

The isotopic compositions of sulfate reduction sulfur calculated by means of equation 1 for Big Moose Lake and McFarlane Lake show rapid vertical changes that are similar to, although somewhat less pronounced than changes observed in a core from Lake Ontario where isotopic values of sulfate reduction sulfur (acid volatile sulfides) were directly measured rather than calculated (Figure 2). For all three cores, values are most negative (most depleted in ^{34}S) near the surface but approach or surpass that of lake water sulfate at depth. The −10 to −22‰ maximal ^{34}S depletions found near the surface between SRS and lake sulfate in the three lakes are consistent with active sulfate reduction in near-surface sediments.

Three hypotheses may be advanced to explain the vertical isotopic changes of sulfate reduction sulfur in freshwater lake sediments (Figure 2). First, emission of ^{34}S-depleted volatile sulfur compounds could cause residual sulfur to become enriched in ^{34}S with depth (Nriagu and Coker, 1976). Second, historical increases in isotopic fractionations could cause a pattern of decreasing isotopic compositions towards the surface. Third, contemporary sulfate reduction could cause ^{34}S increases with depth since such enrichment occurs in marine sediments where sulfate reduction is active (Hartman and Nielsen, 1969).

The first hypothesis of emission of ^{34}S depleted volatile sulfur compounds is not supported by available evidence. In formulating this hypothesis, Nriagu and Coker (1976) assumed a large −30‰ fractionation between FeS and a volatile sulfur compound such as H_2S or dimethyl sulfide. However, occurrence of such a fractionation has not been shown in laboratory experiments (Price and Shieh, 1979), and marine field studies show that isotopic differences between FeS and dissolved sulfides are approximately zero rather than −30‰ (Goldhaber and Kaplan, 1975). In the absence of large fractionations, ^{34}S enrichments in residual sulfur are not expected.

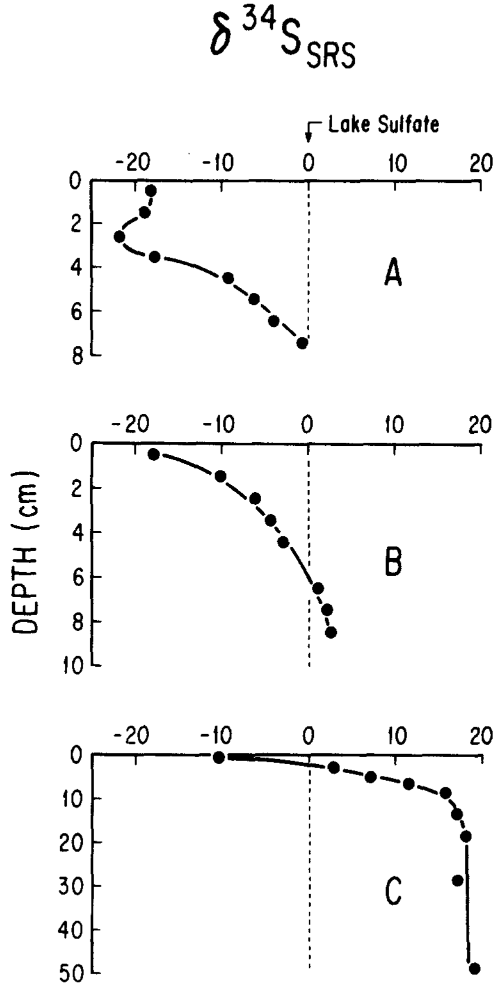

Figure 2. Isotopic variations in sulfide or sulfate reduction sulfur (SRS) with depth vs. lake sulfate (0‰) in three lakes. Values of SRS were calculated for A (Big Moose Lake) and B (McFarlane Lake) as described in the text; values for C (Lake Ontario) are acid volatile sulfide values for a core from Lake Ontario (Nriagu and Coker, 1976).

The second hypothesis of historical increases in isotopic fractionation may apply when sulfate levels are increased from near-zero concentrations (Harrison and Thode, 1958; Nakai and Jensen, 1960, 1964; Migdisov et al., 1974). A concentration dependence of the magnitude of isotopic fractionation could explain results from Deep Lake and Upper Wallface Pond as well as the near-surface ^{34}S depletions shown in Figure 2.

Sulfur accumulates in sediments of lakes undergoing meromixis (Harmsworth, in press) so that the very high 5% S maximum in Deep Lake

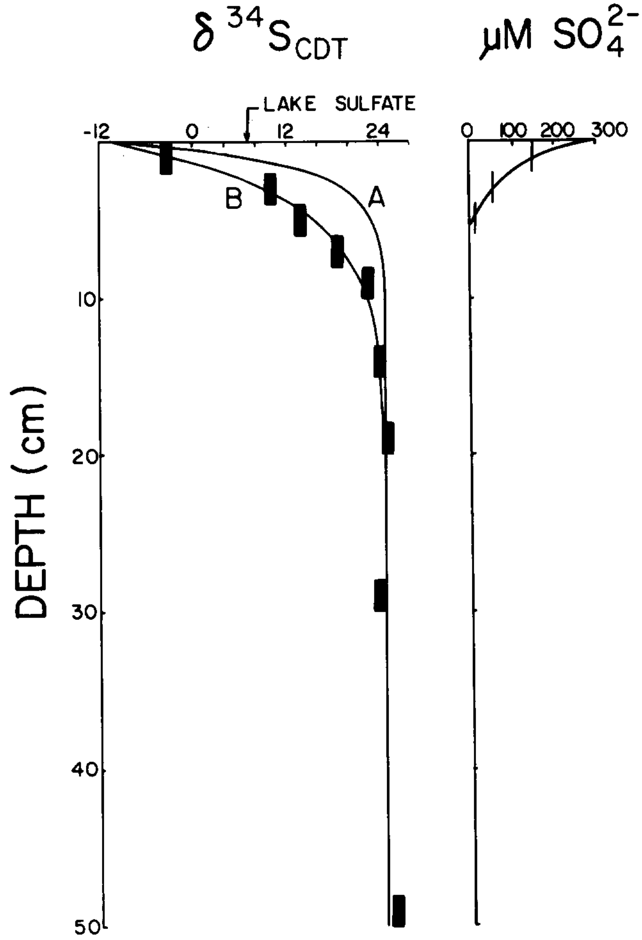

Figure 3. ^{34}S enrichment (increasing $\delta^{34}S_{CDT}$) of acid volatile sulfur (AVS) with depth in a core from Lake Ontario (Nriagu and Coker, 1976). Vertical bars show measured data. Curves fit general shape of AVS profile, indicating that closed system enrichment of ^{34}S and a decreasing isotopic fractionation may occur at depth in lake sediments. Curves were calculated using observed (A) and a more gradual (B) decline in porewater sulfate concentrations (see text).

may result from a temporary meromixis. Laminations observed in one core from this lake (D. Charles, personal communication) may indicate a temporary meromixis. Because bottom-water sulfate concentrations can approach zero during prolonged stratification (Ingvorsen et al., 1981), isotopic fractionations should also approach zero. A small isotopic fractionation is consistent with the small 1–2‰ decline in $\delta^{34}S$ that occurs at the 5% S maximum in Deep Lake (Figure 1).

Upper Wallface Pond represents an opposite extreme in which isotopic values decrease even though %S remains constant (Figure 1). A carbon limitation of sulfate reduction rates but not isotopic fractionation may be indicated. Carbon limitation of sulfate reducing bacteria could hold the rate of sulfide production constant over time so that %S remains constant, but isotopic fractionation could still increase in response to increased sulfate levels. Corroborative evidence for carbon limitation of sulfate reducers is unavailable at present, but diatom reconstruction of the pH history of this lake indicates a pH of 5 or less for a least the past five thousand years (Whitehead et al., in press), so that decomposition rates may be low in this oligotrophic lake.

Although an historical increase in isotopic fractionation in response to increasing sulfate levels can thus account for many aspects of sulfur profiles, sulfide $\delta^{34}S$ values that are higher than those of lake sulfate cannot be explained by this mechanism. Higher values do occur, as for instance, a large $\sim +18‰$ ^{34}S enrichment relative to lake sulfate is observed at depth in the core from Lake Ontario (Figure 2) and small enrichments occur in cores from lakes of the Sudbury region (Nriagu and Coker, 1983). Such ^{34}S enrichments would necessitate inverse isotope effects that have not been found in laboratory or marine field studies of sulfate reduction (Chambers and Trudinger 1979).

Contemporary sulfate reduction seems important in explaining ^{34}S enrichments observed at depth in many lake cores. Substantial ^{34}S enrichment in both sulfate and sulfide can occur at depth when dissimilatory sulfate reduction is active, since ^{34}S depleted sulfur is removed in upper sediment layers during sulfate reduction.

The most direct test of the contemporary sulfate reduction hypothesis is measurement of isotopic changes in porewater sulfates and sulfides which should show progressive ^{34}S enrichment with depth. Unfortunately, dissolved sulfate and sulfide pool sizes are so small as to preclude accurate measurements at present. In lieu of a direct test, a simple model was applied to examine effects of contemporary sulfate reduction as a possible cause of ^{34}S enrichment in freshwater sediments. The model assumes that isotopic fractionations decline in proportion to sulfate levels in sediments, and that diffusion of sulfides is negligible. Cook (1981) has shown that when isotopic fractionations are proportional to sulfate concentrations, approaching zero at zero sulfate concentration, the isotopic composition of sulfates in a closed system is given as:

$$\delta_{\text{SULFATE}} = -\epsilon f \tag{2}$$

where ϵ is the per mil fractionation factor associated with sulfate reduction at ambient lake water sulfate concentrations, f is the fractional extent of reaction, varying from 0 to 1 as sulfate consumption proceeds towards completion, and isotopic compositions are measured relative to initial sulfate. (Equation 2 is a simplified equivalent of the equation derived by Cook 1981). Because sulfide produced at any depth from sulfate differs in isotopic composition by $\epsilon\,(1-f)$ when isotopic fractionations decrease in proportion to sulfate concentration,

$$\delta_{\text{SULFIDE}} = -\epsilon\,(2f-1) \tag{3}$$

Application of equation 3 produces curves that approach ϵ at the surface and a constant value of $-\epsilon$ at depth when porewater sulfate concentrations approach zero. For example, in the case of Lake Ontario acid-volatile sulfides, ϵ was estimated from the 17.7‰ average isotopic difference that exists between acid-volatile sulfide at depth and lake water sulfate (Figure 3). This difference should equal $-\epsilon$, since sulfate was depleted to near-zero concentrations at depth, f was therefore ~ 1 and from equation 3, $\delta_{\text{SULFIDE VS. LAKE WATER}} = -\epsilon$. The extent of reaction, f, was estimated from observed porewater sulfate profiles; a best fit equation was μM sulfate $= 306\,e^{-0.6622z}$, $r^2 = 0.99$, where z is the depth from the sediment surface in centimeters. Values for f were then calculated as $f = e^{-0.6622z}$. The fit between calculated isotopic compositions and observed isotopic values in the upper 10 cm was not exact; observed isotopic values in the upper 10 cm were more depleted in ^{34}S than predicted (Figure 3, curve A). Several factors, including downward diffusion of sulfides, differential diffusion of $^{32}SO_4^{2-}$ and $^{34}SO_4^{2-}$ in response to different vertical concentration gradients (Jorgensen 1979; Goldhaber and Kaplan 1980) or a slower overall rate of sulfate reduction than in May when sulfate concentrations were measured at this site (Nriagu and Coker, 1976), could account for the discrepancy between observed and calculated results. For instance, assumption of a more moderate sulfate reduction rate and less steep sulfate concentration profile so that $f = e^{-0.27z}$ leads to a closer fit to field data (Figure 3, curve B).

The main point of presenting this model is to show that marked ^{34}S enrichments in SRS that are observed with depth (Figure 2) can be logically predicted solely on the basis of processes involving contemporary sulfate reduction. Moderate ^{34}S enrichments at depth such as those observed in Adirondack lakes and McFarlane Lake (Figures 1 and 2) may occur if sulfate reduction does not proceed to completion, if closed system conditions do not truly apply (Jorgensen 1979) or if migration of sulfides is extensive.

Conclusion

It is likely that sulfur profiles (%S, δ^{34}S) represent a combination of historical and contemporary processes. Especially surface features may be most variable since sulfate reduction is concentrated in the top 5 cm of freshwater sediments, and oxidation of sulfides is also expected to be most pronounced in this region. Increased sulfate loading in freshwater lakes may stimulate sulfate reduction so that ^{34}S depleted sulfides are added to surface sediments while ^{34}S enriched sulfides are added to deeper sediments. Field experiments are needed to quantitatively assess the importance of sulfide mobility as it relates to addition of sulfur to older deeper sediments. Until the seasonal spatial variation in sulfate reduction rates is better known for lake sediments, detailed historical reconstruction of sulfate loading histories from sedimentary sulfur profiles should be offered with caution.

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