Limnol. Oceanogr., 31(6), 1986, 1281–1291

The role of sulfate reduction in long term accumulation of organic and inorganic sulfur in lake sediments[1]

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Abstract

Sulfate reduction and the accumulation of reduced sulfur in epilimnetic sediments were studied in lakes in southern Norway, the Adirondack Mountains, and at the Experimental Lakes Area (ELA) of northwestern Ontario. In all of the lakes, in addition to the previously known formation of acid volatile sulfur, sulfate reduction also produced substantial quantities of pyrite and organic sulfur compounds. In 9-month in situ experiments at ELA using ^{35}S, there was a large loss (55%) with time of the S initially reduced and deposited in the sediments and a preferential loss of inorganic S compounds which led to a predominance of organic ^{35}S accumulation in the sediments. An intensive study of long term accumulation of sulfur in the epilimnetic sediments of four Adirondack lakes also showed that the most important long term end product of sulfate reduction was organic S and that sulfate reduction was the major source of S to the sediments.

Because of the high concentrations of iron in all of the sediments we sampled and because of the long term storage of sulfur in sediments, mostly as organic S, iron did not limit iron sulfide accumulation in these sediments. Iron limitation is unlikely to occur except in unusual circumstances.

This study indicates that formation of organic S in epilimnetic sediments is primarily responsible for H^+ consumption via sulfate reduction in acidified lakes.

Elevated amounts of sulfate are entering lakes in regions where the acidity of atmospheric deposition has increased (e.g. Wright and Snekvik 1978; Galloway et al. 1983; Jeffries et al. 1984). This has stimulated research into sulfur cycling to improve our understanding of the fate of sulfate in lakes. A topic of special interest is the process of bacterial sulfate reduction, which consumes H^+ in acidified lakes (Hongve 1978) by producing reduced S compounds (Kelly et al. 1982). Sulfate is reduced by bacteria in both the epilimnetic and hypolimnetic sediments of lakes (Schindler et al. 1980; Kelly et al. 1982; Cook and Schindler 1983; Kelly and Rudd 1984), and rates of sulfate reduction in sediments can increase as sulfate concentrations in the overlying lake water increase (Cook and Schindler 1983; Kelly and Rudd 1984).

Until recently, it was thought that the sole end product of sulfate reduction in lake sediments was acid volatile sulfur (AVS: ΣH_2S) with later chemical conversion of FeS to FeS_2 (Berner 1984). This belief led to a hypothesis that the increased loading of sulfur to acidified lakes could result in the exhaustion of available reduced iron, which would in turn limit iron sulfide formation and thus consumption of H^+ by sulfate reduction (Schindler 1985). During the past few years we have studied sulfate reduction and end product formation in several lakes including some which might be expected to have iron limitation.

During the course of this research, in which we added $^{35}SO_4^{2-}$ to sediments, we could not account for all of the lost $^{35}SO_4^{2-}$ as [^{35}S]AVS. This led us to explore the possibility that pyrite, which has been observed to form rapidly in salt marshes (Howarth and Merkel 1984), might be an additional important end product of sulfate reduction

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[1] Funded by NSERC grant A2671 and by the Department of Fisheries and Oceans, Canada.

in lake sediments. We also investigated the possibility that organic S, which had been found in small quantities in one lake (Landers et al. 1983), might be another important end product of sulfate reduction. Our experiments showed that all of these end products were formed in the short term but that organic S formation was probably the most important long term source of S to epilimnetic sediments. The implications of this information with respect to sulfur cycling and H^+ consumption by sulfate reduction are discussed.

G. J. Brunskill and P. Kilham provided insights into iron and sulfur geochemistry in sediments. V. St. Louis, E. Schindler, and M. Holoka collected and analyzed many of the field samples. D. W. Schindler, R. H. Hesslein, R. E. Hecky, B. B. Jørgensen, and P. Campbell provided criticisms during the writing of this manuscript.

Methods

Study sites—Sulfate reduction was studied in the epilimnetic sediments of eight acidified soft-water lakes. One of these, the southern basin of Lake 302 (302S) in the Experimental Lakes Area (ELA) of northwestern Ontario, has been experimentally acidified since 1982 by addition of sulfuric acid (D. W. Schindler unpubl. data). At the time of our sampling the epilimnetic pH was 5.66. Five of the lakes (Woods, Sagamore, Big Moose, Darts, and Twitchell), in the Adirondack Mountains of upper New York State, are atmospherically acidified (Galloway et al. 1983; White and Driscoll 1986); at the time of our sampling epilimnetic pH values ranged from 4.66 to 5.31. The remaining two lakes, Hovvatn and Lille Hovvatn, in southern Norway, are also atmospherically acidified (Wright and Skogheim 1983) with epilimnetic pH values of 5.00 and 4.90 at the time of our sampling. Data in this paper were obtained at the same time and from the same sampling locations as those of Rudd et al. (1986).

Measurement of chemical concentrations in porewater and sediments—Dissolved NO_3^-, Fe, and SO_4^{2-} in the epilimnetic sediments of the four Adirondack lakes were obtained with in situ membrane samplers (Hesslein 1976). The samplers were deoxygenated, inserted into the sediments, left to equilibrate for 1 week before sampling, and the samples withdrawn and stored until analysis (Kelly and Rudd 1984). Nitrate and dissolved iron were determined as described by Stainton et al. (1977), sulfate by ion chromatography. The pH of the porewater was measured at 0.7-mm intervals by mechanically inserting a micro-pH probe into intact cores with a motor-driven, threaded-rod assembly (Kelly and Rudd 1984). Depth profiles of total extractable iron concentration (porewater + particulate) were determined for 1-cm slices of cores: after combustion of organic material, iron was extracted with dilute HCl and quantified (Stainton et al. 1977). This method does not include highly stable iron minerals but does include iron present as sulfides and iron associated with organic materials. Total sulfur concentrations in the sediments were determined in 1-cm slices of the epilimnetic sediments. The sediments were heated to 290°C for 16 h with magnesium nitrate to oxidize the sulfur compounds to sulfate, then heated to 500°C for 4 h to remove the nitrate. Following combustion, the sulfate was extracted for 4 h in an aqueous solution at 100°C and then quantified by ion chromatography.

Measurement of end products of sulfate reduction—Relative abundances of the short term end products of sulfate reduction were measured with $^{35}SO_4^{2-}$. Radiolabeled sulfate was either injected directly into undisturbed cores (Norway) or allowed to diffuse into the sediment from the overlying water of intact cores (Adirondacks and ELA). The cores were incubated for 18–24 h at in situ temperature, sliced, and 1-cm sections frozen within 30 s between two pieces of Dry Ice. This prevented oxidation of the reduced S for at least 2 weeks. The frozen sediment slices were put into an anoxic HCl sparger for collection of the [^{35}S]AVS (Kelly and Rudd 1984). The AVS fraction consists of acid volatile sulfides including FeS and total H_2S. In our case, the fraction was composed almost entirely of FeS; H_2S was usually undetectable either by odor or by colorimetric analysis (i.e. <0.2 µmol liter^{-1}, Stainton et al. 1977).

After sparging, each sediment section was divided in two. Half was rinsed with 6 N $MgSO_4$ or 6 N H_2SO_4 and then distilled water to remove unreduced $^{35}SO_4^{2-}$, and the sum of $^{35}S^0$ + $Fe^{35}S_2$ + organic ^{35}S determined with aqua regia digestion (Howarth and Teal 1979). The other half was used to determine the production of $^{35}S^0$ + $Fe^{35}S_2$ by converting the reduced ^{35}S to $H_2{}^{35}S$ with the chromium reduction technique of Howarth and Merkel (1984). In some cases, we analyzed part of this section for $^{35}S^0$ (Zhabina and Volkov 1978), which was always <10% of the CRS (chromium reducible sulfur) fraction. The quantity of organic ^{35}S formed during sulfate reduction was calculated as the difference between the aqua regia and CRS fractions.

Zero-time blanks used as a check for contamination of the various fractions with unreduced $^{35}SO_4^{2-}$ consisted of sediments killed immediately after $^{35}SO_4^{2-}$ was added by addition of the sparging acid. Contamination, a potential problem especially for the aqua regia fraction, was prevented by using $MgSO_4$ or H_2SO_4 as above in the first rinse following the sparging of AVS.

The quantities of AVS and CRS naturally deposited in the sediments were separated as described above but quantified by thiosulfate-iodine titration of the trapped sulfide. The recovery efficiency of the AVS method, determined by using H_2S and CdS standards, was 95%. The efficiency of the chromium reduction method, determined from FeS_2 standards, was 85%. Possible interference in the chromium reduction fraction from reduction of organic S was examined with yeast extract and found to be zero. The concentration of organic S in the sediments was determined as the difference between the total sulfur concentration (measured as described above) and the CRS plus AVS fractions.

The same methods were used for three in situ experiments in Lake 302S to determine the long term retention of the various end products of sulfate reduction in the sediments. We added 2 mCi of $^{35}SO_4^{2-}$ to 1-m^2 Plexiglas chambers that enclosed 6 cm of water above the sediment–water interface. After the sediment had been labeled for 8 days, the chambers were removed. After an additional 11 days, the labeled sediment was cored to determine the initial activities of the [^{35}S]AVS, [^{35}S]CRS, and [^{35}S]aqua regia, and then cored again the next spring and analyzed for the same compounds.

The carbon content of the sediments was determined by methods of Stainton et al. (1977).

Rates of daily net sulfate reduction in the sediments were estimated as described by Rudd et al. (1986). These rates were calculated from the measured porewater sulfate gradients and from the diffusion rate of sulfate in the sediments. The coefficient of diffusion of sulfate in the sediments was calculated from the functional diffusion coefficient of ^3H_2O which was determined by direct measurement of the sediment porosities and by measurements of rates of ^3H_2O diffusion in the sediment porewater of undisturbed cores at in situ temperatures.

Results

Porewater chemistry—Nitrate concentration gradients were very steep in all of the Adirondack lakes (Fig. 1A). Amounts in the overlying water were consistently reduced to undetectable values 1.5 cm beneath the sediment surface. Depth profiles of sulfate concentration were of two types (Fig. 1B). In Woods and Darts sediments, sulfate was reduced to minimum values within about 3 cm of the sediment surface. In Sagamore and Big Moose sediments, the sulfate was consumed rapidly near the interface, but, below this, concentrations decreased much more slowly than in the other two lakes and had not reached the lowest concentrations of Darts and Woods lakes by 10–11 cm below the interface. Concentrations of dissolved iron in the porewater of Big Moose and Sagamore lakes increased only slightly with depth, reaching maxima of 17 and 23 μmol liter^{-1} (Fig. 1C). In Darts Lake, dissolved iron in the porewater increased to 225 μmol liter^{-1} at a depth of 4 cm and then declined to 130 at 13.6 cm below the sediment–water interface. The pH of the porewater increased with depth in all four lakes (Fig. 1D). The pH profiles of cores from Woods and Darts lakes were very similar, increasing to about 6.2 at 4 cm below the surface. The pH of Big Moose and Sagamore

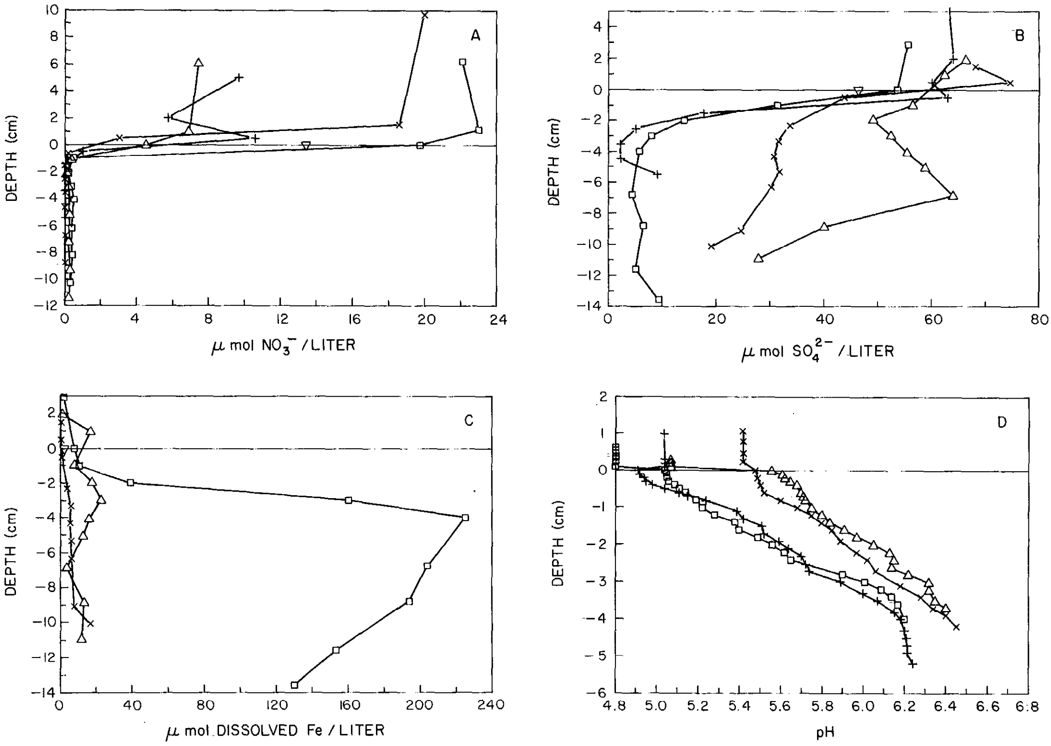

Fig. 1. Concentrations of NO_3^-, SO_4^{2-}, Fe, and pH in the porewater of epilimnetic sediments of Darts (□), Woods (+), Sagamore (△), and Big Moose lakes (×). Profiles for Woods, Darts, and Sagamore sediments were obtained in June 1984. The Big Moose data were obtained in July 1983.

cores was consistently about 0.15–0.5 units higher than that of the other two lakes.

Sediment chemistry—Concentrations of extractable iron in epilimnetic cores from Darts and Woods lakes ranged from 63 to 224 μmol Fe cc^{-1}. Extractable iron concentrations in Big Moose and Sagamore sediments were higher, increasing with depth to 646 and 551 μmol Fe cc^{-1} of sediment (Fig. 2).

Total sulfur concentrations in Big Moose and Sagamore sediments were very low, decreasing with depth in the core to 0.9 and 5.6 μmol cc^{-1} (Fig. 3A). The total sulfur concentrations were much higher in Woods and Darts lakes and increased with depth in the cores, reaching 107 and 39 μmol cc^{-1}. Concentrations of AVS increased with depth in sediments of all four lakes (Fig. 3B) and appeared to peak 2.5–3.5 cm below the sediment interface. Concentrations of CRS generally increased with depth and were 5–10 times higher than the AVS (Fig. 3C). A more general picture of sulfur speciation in lake sediments is given in Table 1 where AVS and CRS concentrations are given for five Adirondack lakes and epilimnetic sediments of ELA Lake 302S and the Norwegian lakes. The shapes of the profiles were similar to those shown in Fig. 3B and C, but concentrations in the Norwegian lakes

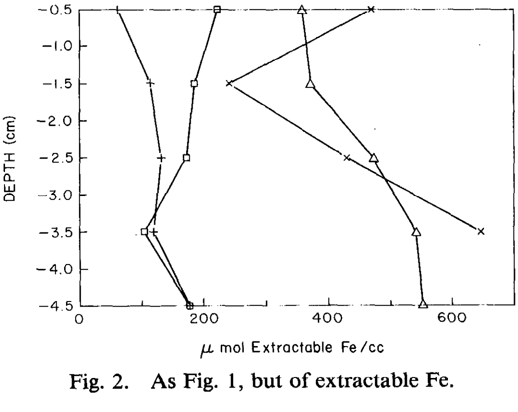

Fig. 2. As Fig. 1, but of extractable Fe.

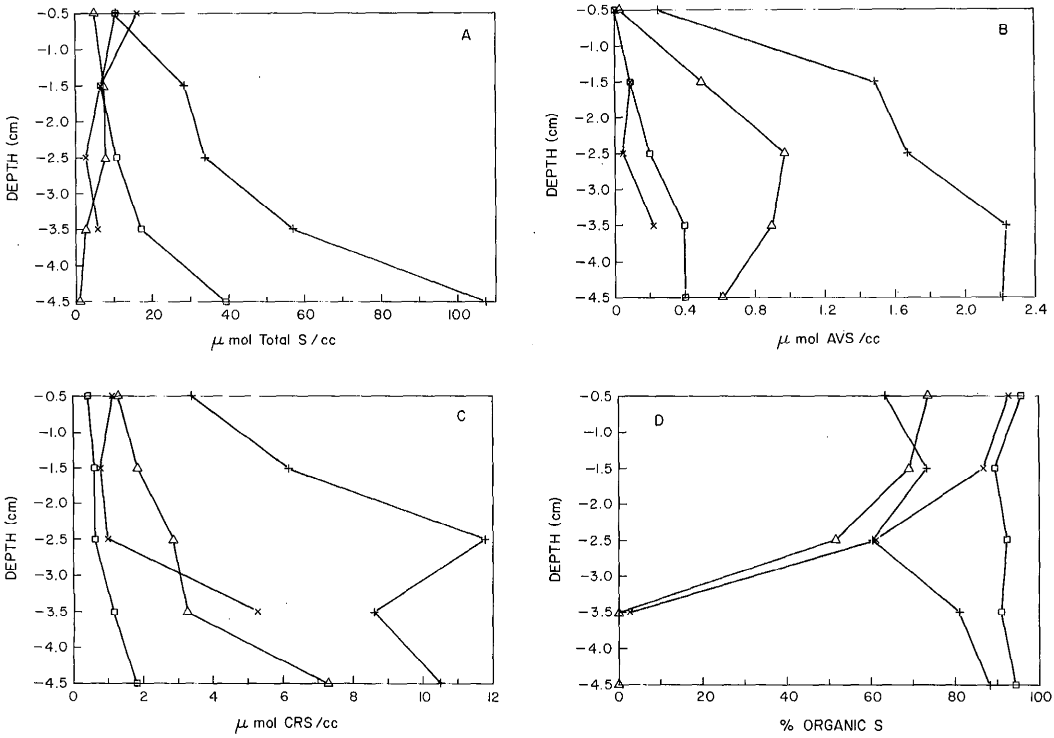

Fig. 3. As Fig. 1, but of total S, AVS, CRS, and percent of total sulfur which was organic S.

were generally much lower than in the others. Lake 302S sediment was similar in AVS and CRS content to the Adirondack sediments.

Depth profiles of the percentage of total sulfur in organic form are presented in Fig. 3D for four of the Adirondack lakes. In Big Moose and Sagamore, organic sulfur decreased rapidly with depth to near 0% at 3.5 cm below the sediment interface. In the epilimnetic sediments of Darts Lake, organic S was consistently >90%. Organic sulfur increased with depth in Woods Lake from 63.5% at the sediment surface to 88.2% at 4–5 cm below the sediment surface.

The maximum fraction of extractable iron present as iron sulfides can be approximated from the AVS + CRS measurements. The maximum S observed was 14.2 μmol S cc^{-1} (Fig. 3B, C). The associated iron as iron sulfides was 8.2 μmol cc^{-1} (a very small fraction of the extractable iron: 63–646 μmol cc^{-1}, Fig. 2).

^{35}S end products of sulfate reduction—The initial (radiolabeled) formation of the end products of sulfate reduction were determined in the sediments of the Adirondack and Hovvatn lakes and for Lake 302S (Table 2). In addition to the formation of [^{35}S]AVS, which has been observed by others, we also found rapid formation of [^{35}S]CRS, which often amounted to more than half of the reduced inorganic S produced by sulfate reduction. In our case, the CRS fraction consisted of >90% FeS_2 (*see methods*). Although rapid formation of pyrite has been demonstrated in salt marshes (Howarth and Merkel 1984), this is the first report of it in lake sediments. In addition to inorganic S species we also observed the formation of organic ^{35}S (Table 2). In the Hovvatn lakes, 1.5–14% of the sulfate reduced appeared in the sediments as organic ^{35}S. In the other lakes, the proportion of reduced ^{35}S that was organic was always much higher (28–90%).

At ELA, where we were able to expose sediments to $^{35}SO_4^{2-}$ in situ, we examined the long term retention of the radiolabeled end products of sulfate reduction. We did

Table 1. Concentrations of AVS, CRS, and percent org C in epilimnetic sediments of acidified North American and Norwegian lakes. Maximum and minimum concentrations over the depths sampled are presented.

		AVS	CRS	
	Sediment depth (cm)	(μmol cc^{-1})		% C (wt/wt)
302S (3 m)	0.5–3.5	0.75–2.1	2.1–6.5	1.2–0.4
Twitchell (1 m)	0.5–5.5	0.7–1.7	4.6–68	14.4–11.5
Big Moose (3.5 m)	0.5–4.5	0.001–0.43	1.5–11	7.3–0.7
Woods (1.5 m)	0.5–4.5	0.51–4.4	6.8–24	15.7–7.6
Sagamore (2.5 m)	0.5–4.5	0.066–2.0	2.6–15	1.2–0.4
Darts (2.5 m)	0.5–4.5	0.01–0.8	0.86–3.6	2.2–0.5
Hovvatn (5 m)	0.75–6.0	0.01–0.78	0.88–5.6	26.8–19.4
Hovvatn (2 m)	0.75–6.0	0.004–0.31	0.46–4.0	19.4–13.6
Lille Hovvatn (5 m)	0.75–6.0	0.01–0.78	0.50–1.6	18.1–5.2
Lille Hovvatn (2 m)	0.75–6.0	0.00–0.20	0.26–0.65	18.1–11.4

three separate experiments at three depths in the epilimnion of Lake 302S (Table 3). There was substantial loss of both organic and inorganic sulfur over the winter, probably by reoxidation of reduced S compounds. Losses were greatest in the top 2 cm (Fig. 4), where it is known that oxygen penetrates deeper into the sediments during winter (unpubl. data). Overall, the inorganic S species showed greater losses than the organic S. The percentage loss of inorganic S was also much more variable (Table 3), suggesting that it was more affected by variations in conditions, such as oxygen penetration, than was the loss of organic S. The average retention of total ^{35}S over 9 months, including winter, was 45%.

Discussion

Microbial activity was high at the sediment–water interface of all four Adirondack lakes investigated in detail. Nitrate was rapidly consumed in the surficial sediments of all four (Fig. 1A). Rates of denitrification for Big Moose, Woods, Darts, and Sagamore lakes were 602, 376, 406, and 556 μeq m^{-2} d^{-1} (Rudd et al. 1986). Sulfate was also reduced near the surface of the sediments, most rapidly in Big Moose, Woods and Darts sediments (400, 362, 126 μeq m^{-2} d^{-1}) and least rapidly in the Sagamore sediments (66 μeq m^{-2} d^{-1}; Fig. 1B, Table 4). With the exception of sulfate reduction in Sagamore Lake, the activity in surficial sediments of all the lakes was as high as that of other unacidified lakes (Rudd et al. 1986).

At depths >1 cm below the sediment–water interface, our data and flux calculations (Fig. 1C; Table 4) indicate that sulfate reduction rates (and probably microbial activity in general) were much lower in Sagamore and Big Moose lakes than in Darts and Woods lakes. Despite the comparatively low rates of sulfate reduction below the interface in Big Moose sediment and throughout the Sagamore sediments, the pH

Table 2. Percentages of [^{35}S]AVS, [^{35}S]CRS, inorganic ^{35}S ([^{35}S]AVS + [^{35}S]CRS), and organic ^{35}S produced during 24-h incubations of epilimnetic sediments from acidified North American and Norwegian lakes. Sampling sites as in Table 1.

	[^{35}S] AVS	[^{35}S] CRS	Inorg ^{35}S	Org ^{35}S
302S (3 m)	30	23	53	47
Twitchell	22	31	53	47
Big Moose	6.0	33	39	61
Woods	26	46	72	28
Sagamore	11	39	50	50
Darts	2.0	8.5	10	90
Hovvatn (5 m)	43	41	85	14
Hovvatn (2 m)	43	45	86	13
Lille Hovvatn (5 m)	76	18	94	6.0
Lille Hovvatn (2 m)	83	16	98	1.5

Table 3. Percent retention of inorganic ^{35}S, organic S, and total ^{35}S in the epilimnetic sediments of Lake 302S during three 9-month in situ experiments in which sediments (0–5 cm) were labeled by exposure to $^{35}SO_4^{2-}$ one summer and resampled the next.

	Depth (m)	[^{35}S]AVS + [^{35}S]CRS	Org ^{35}S	Total ^{35}S
Aug 84–May 85	1	26	59	33
	4	69	54	67
Aug 83–May 84	3	17	57	36
$\bar{x}$		37±28	57±3	45±19

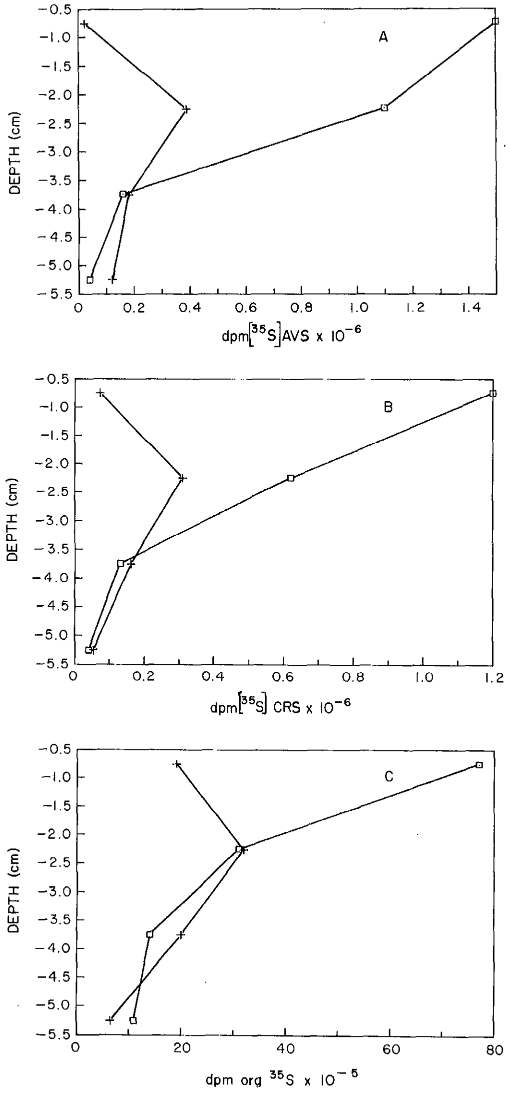

Fig. 4. Depth profiles of activities of [^{35}S]AVS, [^{35}S]CRS, and organic ^{35}S in Lake 302S sediments initially (□) and 9 months after (+) exposure to $^{35}SO_4^{2-}$; 1-m Lake 302S August 1984–May 1985.

of these sediments was much higher than that of the water, as in the other lakes. This was probably due, in all four lakes, to rapid rates of denitrification at the sediment–water interface (Rudd et al. 1986).

Table 4. Porosity (vol/vol), ^3H_2O diffusion coefficients (10^{-5} cm^2 s^{-1}), and rates of sulfate reduction (μmol m^{-2} d^{-1}) in subsurface sediments of four Adirondack lakes.

	Depth interval (cm)	Porosity	Diff. coeff. ^3H_2O	SO_4^{2-} reduction
Sagamore	Interface			66*
	1–3	0.57	1.07	0.0
	8–10	0.56	1.07	23
Big Moose	Interface			400*
	1–3	0.60	1.22	24
	8–10	0.47	1.22	15
Darts	Interface			126*
	1–3	0.57	1.00	62
	8–10	0.52	1.00	ND†
Woods	Interface			362*
	1–3	0.91	1.70	226
	8–10	0.70	1.70	ND†

* Calculated from diffusion of SO_4^{2-} across the sediment–water interface (Rudd et al. 1986).

† Sulfate reduction rates could not be calculated because porewater sulfate concentrations had been reduced to background at these depths.

The concentrations of iron in the porewater of Big Moose and Sagamore sediments (Fig. 1C) were the lowest recorded in a survey of porewater iron concentrations in 11 acidified lakes (Rudd et al. 1986). It was because of this that we decided to study these two lakes further to determine if these were, in fact, examples of iron limitation of the storage of reduced sulfur in the sediments as iron sulfides (Schindler 1985). Our data indicate that even though porewater iron concentrations were very low in these two lakes, iron was not limiting. Extractable iron concentrations in Sagamore and Big Moose sediments were the highest of the four Adirondack sites that we tested (Fig. 2). These concentrations exceeded the porewater iron concentrations by 10^4, suggesting that there was an abundance of iron potentially available for iron sulfide formation (note that porewater concentrations are per liter and sediment concentrations are per cm^3). Furthermore, the concentrations of extractable iron (Fig. 2) were more than 30 times the total sulfur concentrations on a molar basis (Fig. 3A). The low porewater iron concentrations could not be explained by high rates of iron sulfide formation depleting the porewater iron. Sulfate reduction rates were low in these sediments and concentrations of reduced S compounds (organic + inorganic) were also very low (Fig. 3B, C, D). There was no sulfide odor in the Sagamore and Big Moose sediments, which suggests that sulfide formation was not in excess of iron sulfide formation (i.e. iron

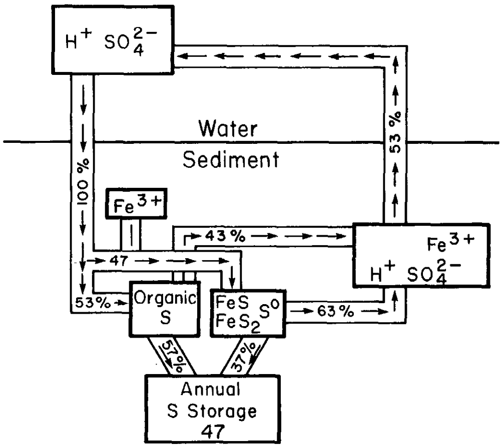

Fig. 5. Conceptual model for the fate of the end products of sulfate reduction in sediments.

was not a limiting factor). It is more likely that the low porewater iron concentrations in Big Moose and Sagamore lakes were a result of low rates of iron reduction than of its exhaustion by sulfide formation. This conclusion is supported by the low rates of sulfate reduction in the sediments, which suggest that, in general, the reducing power produced by microbial activities in these sediments was low. The rust color of the sediments also supports the conclusion that ample oxidized iron was present but that iron reduction was not taking place in the sediments because of low microbial activity. In these two lakes, it appeared that the organic carbon reaching the sediments was supplying surficial microbial activity, which was very active, but that very little of it was reaching the microorganisms below the sediment surface. From this detailed examination, plus the data on 9 other acidified lakes (Rudd et al. 1986), we conclude that iron limitation of sulfur storage in sediments is uncommon.

For many years there has been controversy over the origin of the sulfur components of sediments (e.g. Nriagu and Coker 1983; Kilham 1984; Holdren et al. 1984; Mitchell et al. 1985), with the discussion centering on whether the primary source of sulfur to the sediments is sedimenting particles (assumed to be mostly organic S) or sulfate reduction (assumed to lead primarily to inorganic reduced S). The controversy stemmed from the apparently incompatible facts that organic sulfur sedimentation rates are low compared to sulfate reduction rates (Cook and Schindler 1983; King and Klug 1982), yet most of the sulfur in sediments is organic. Nriagu and Soon (1985) found, through stable isotope measurements, that the origin of the most abundant S form in lakes, organic S, was compatible with the stable isotope signal of H_2S and not with the signal of organic sulfur in sedimenting particles. It has also been shown with $^{35}SO_4^{2-}$ that small amounts of organic S are formed via sulfate reduction in South Lake sediments (Landers et al. 1983). Our research has demonstrated that in many lakes a large proportion of the $^{35}SO_4^{2-}$ reduced is rapidly converted to organic ^{35}S (Table 2). In addition, this organic ^{35}S was more persistent in the sediments than were the iron sulfides (Table 3, Fig. 4), suggesting that with time the distribution of sulfur among the end products will be dominated increasingly by organic sulfur.

A conceptual model which fits our experimental ^{35}S data and our observations of natural sulfur accumulation in the four Adirondack lakes is shown in Fig. 5. The arrows show general pathways (but may not include all steps) and the numbers express in relative proportions the fate of 100 units of SO_4^{2-} after reduction in the sediments. The numbers for initial formation of end products were taken from the average distribution of $^{35}SO_4^{2-}$ into organic and inorganic end products in all but the Norwegian lakes (Table 2; *see later discussion*). The percentages for annual storage and recycling of S are taken from our three long term (9 month) experiments in Lake 302S (Table 3). This model should approach annual values and it demonstrates how, with time, there is a preferential retention of organic S in the sediments because of more complete loss of inorganic S from the sediments.

Of course all sediments will not have the same number of units of sulfate being reduced, and if sulfate reduction is the primary input of S to the sediments, different rates of sulfate reduction should be reflected in different rates of S storage within the sediments. Such differences seem to be occurring in the Adirondack lake sites shown here (Fig. 3A–D). The two sites with higher rates of sulfate reduction in the sediments (Darts and Woods, Table 4) also had the higher concentrations of total S per volume (Fig. 3A) and higher % organic S (Fig. 3D) in the sediments. Furthermore, the shapes of our depth profiles of organic S in sediments indicated that, where sulfate reduction was active, most of the organic S in the sediments originated from sulfate reduction and not from the sedimentation of organic S in particles. If sedimentation of organic S were the most important input of sulfur to sediments, one would not expect to see the increasing concentrations of organic S with depth that we observed in Darts and Woods sediments (Fig. 3A, D). The increasing concentrations of total and organic S that Nriagu and Soon (1985) and we have observed could be explained by diffusion of sulfate a few centimeters into the porewater, where it is initially converted to both organic and inorganic end products. With time (probably during fall and winter, Table 3, Fig. 4), a preferential loss of iron sulfide results in long term accumulation of primarily organic S. Further, the shape of the total S profiles suggests that organic S derived in this way predominates over sulfur originating from sedimentation of particulate organic S.

Nriagu and Soon (1985), studying hypolimnetic sediments, and we, studying epilimnetic sediments, have independently and concurrently concluded that organic S formed via sulfate reduction in sediments can be the most important source of sulfur to freshwater sediments on a long term basis. The fact that these conclusions were drawn at widely separated locations by workers using entirely different approaches and methodologies demonstrates that they are of widespread significance. It should not be concluded that organic S formation is most important at all locations. We found that in the Hovvatn sediments (Table 2) organic S was a minor end product of sulfate reduction. However, our data (Table 2 and unpubl. data from other ELA lakes) suggest that the Hovvatn situation is unusual and may have been related to the very low pH (4.5: Rudd et al. 1986) of those sediments. Howarth and Merkel (1984) found no organic ^{35}S formation from $^{35}SO_4^{2-}$ in salt marsh sediments, but the formation of organic S by reaction of H_2S with organic materials has been observed in another salt marsh (Boulegue et al. 1982). A better understanding of the origin of these differences in the relative abundances of end products would certainly improve our understanding of sulfur cycling in sediments.

Peaks of sulfur concentration in sediments have been used as an indicator of the onset of acid precipitation (Nriagu and Coker 1983; Holdren et al. 1984; Mitchell et al. 1985). Since a large proportion of the sulfur in the sediments of many acidified lakes is produced within the sediments, and since sulfate diffuses as much as a few centimeters into the sediments before it is reduced and deposited, the age of the sediments at the depth of the peak should not be used as an indicator of the time of onset of acid precipitation. This conclusion is in agreement with that of Holdren et al. (1984).

When sulfate is lost from the water of a lake, H^+ is also lost, with the stoichiometric relationship of H^+ to sulfate loss depending on the specific reactions involved (Kelly et al. 1982). In the case of iron sulfide formation, sulfate and iron reduction processes must occur together for net consumption of H^+, and these reactions are well studied. The combined reduction of sulfate and iron consumes H^+ and produces FeS and FeS_2 as follows.

FeS formation—$2H^+$ consumed per mole of SO_4^{2-} reduced:

$$9CH_2O + 4FeOOH + 4SO_4^{2-} + 8H^+ \rightarrow 9CO_2 + 4FeS + 15H_2O. \quad (1)$$

FeS_2 formation—$2H^+$ consumed per mole of SO_4^{2-} reduced:

$$8CH_2O + 4SO_4^{2-} + 8H^+ \rightarrow 8CO_2 + 4H_2S + 8H_2O$$
$$Fe_2O_3 + 4H_2S \rightarrow 2FeS_2 + 3H_2O + H_2. \quad (2)$$

Formerly it was assumed that the consumption of sulfuric acid in acidified lakes by sulfate reduction resulted only in the formation of iron sulfide (Eq. 1 and 2; Kelly et al. 1982). It now appears that the formation of organic S is an important pathway of long term sulfur deposition in sediments and that this pathway is primarily responsible for long term alkalinity production by sulfate reduction.

There are two classes of organic S compounds, carbon-bonded sulfur and sulfate esters. The production of carbon-bonded sulfur by reaction of H_2S from sulfate reduction consumes two H^+ per mole of SO_4^{2-} reduced. There are many possible reactions of H_2S with organic compounds, e.g. reaction with hydroxyl groups:

$$H_2S + R\text{-}C\text{-}OH \rightarrow R\text{-}C\text{-}SH + H_2O. \quad (3)$$

Sulfate ester formation does not involve sulfate reduction. The reaction of sulfate with organic matter consumes one H^+ per mole of sulfate lost:

$$ROH + 2H^+ + SO_4^{2-} \rightarrow ROSO_3^- + H^+ + H_2O. \quad (4)$$

At present it is not clear which is the major pathway of organic sulfur formation. In ELA Lake 223, which was experimentally acidified, about two equivalents of alkalinity were produced per mole of sulfate lost from the water on an annual basis (Cook et al. 1986), suggesting that ester formation was not a predominant long term sulfate-utilizing reaction. It seems reasonable that carbon-bonded sulfur would be more likely to remain in the sediments in the long term, since sulfate esters are quite labile (King and Klug 1980). The resolution of this question will have an important bearing on the mechanism by which sulfate reduction generates alkalinity in acidified lakes.

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Submitted: 28 August 1985
Accepted: 28 May 1986