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Sulfur isotopes in sulfate in the inputs and outputs of a Canadian Shield watershed

R.H. HESSLEIN,[1] M.J. CAPEL[1] & D.E. FOX[2]
[1]Department of Fisheries & Oceans, Freshwater Institute, 501 University Crescent, Winnipeg, Manitoba R3T 2N6; [2]195 Alburg Drive, Winnipeg, Manitoba R2N 1V5, Canada

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Abstract. The isotopic composition of sulfur in sulfate from precipitation, stream inflows and outflow of the Lake 239 watershed at the Experimental Lakes Area, northwestern Ontario, was monitored for four years, 1982–1985. Rainfall had $\delta^{34}S$ of 3–9‰ and a three year mean value weighted by the mass of sulfate of 4.8‰. Sulfur in streams ranged from 5–15‰ and displayed a pronounced seasonal pattern in which $\delta^{34}S$ showed significant negative correlations with both streamflows and sulfate concentrations. Outflow values were much more constant and averaged 6.4‰ over the three year period. Sulfate reduction or sorption favoring retention of the lighter isotope in the watershed was the probable cause of the isotopic variation of the sulfur isotopes in the streams. A sulfur isotope budget for the lake balanced within 1‰.

Introduction

Because of the growing interest in acid precipitation, a considerable amount of research has recently been reported on sulfur isotopes in lakes and their sediments (Nriagu & Soon 1984 1985; Nriagu & Coker 1983; Mitchell 1984; Nriagu & Harvey 1978). These works have emphasized the paleolimnological application of the isotope data and have examined the distribution of the sulfur into different forms in the sediments. Fuller et al. (1986) have described the use of radioactive ^{35}S as a tool for the examination of sulfur cycling in soils of the Hubbard Brook watershed. Other workers have used the radioisotope ^{35}S to explore the processes and rate constants for the deposition of sulfur diffusing into the sediments as sulfate, and to determine the persistence of the various forms of sulfur in the sediments (Rudd et al. 1986; Kelly & Rudd 1984). Although some data have been presented for the isotopic composition of sulfur in precipitation, lake water, and sediments in areas essentially free of major anthropogenic sulfur inputs (Nriagu & Soon 1985; Nriagu & Coker 1976, 1983), there has not been a systematic study of the isotopic and mass balances of sulfur in such remote areas. We felt that this kind of study was essential as background to the interpretation of the differences observed in sulfur isotope profiles from sediments of impacted lakes and the assignment of these differences to historical changes in sulfur deposition.

Since 1982 we have monitored the sulfate concentrations and the isotopic composition of sulfur as sulfate in precipitation, stream inflows, lake water at several depths, and the outflow of Lake 239 at the Experimental Lakes Area (ELA), northwestern Ontario, Canada. The hydrologic flows, and the inputs and outputs of nutrients and major dissolved ions of Lake 239 have been monitored since 1969 (Schindler et al. 1976; Schindler 1986). The lake is oligotrophic with a mean depth of 10 m, area of 56.1 ha, and a total drainage basin area (including the lake) of 391 ha. The average water renewal time since 1969 has been 10 years (Newbury & Beaty 1977; Beaty, unpubl. data). Streams enter this headwater lake from three sub-basins; the East, the Northwest, and the Northeast. The areas drained by these streams are, respectively, 170 ha (44% of total), 56.4 ha (14%), and 10.6 ha (2.7%) (Newbury & Beaty 1977). The remaining area (98 ha, 25%) is drained by overland runoff, the chemistry and water yield of which has been assumed to be best represented by a 50/50 mixture of the Northwest and East sub-basins. The streamflow is characteristically large early in spring due to snowmelt and decreases throughout the summer frequently ceasing in August. The lake outflow follows the same pattern damped somewhat by the lake. The soils (Brunskill & Schindler 1971) in the drainage basin are generally thin (10–50 cm) except in the East sub-basin which has some deposits of 18 m. The bedrock is primarily granodiorite. Forested areas have a layer of detrital organic material of 10–30 cm.

Methods

Samples of precipitation were collected at the ELA meteorological site by a one meter square acrylic plastic container which drained into a 20 L carboy. The carboy was emptied only after each rainfall of 3 mm or more because at least 3 L were required to produce enough sulfur for isotopic analyses. Rainfall from smaller events was allowed to accumulate to the required volume. Stream samples were collected weekly during the ice-free season at the weirs installed for flow measurement (within 50 m of the point of inflow to the lake) using polyethylene bottles rinsed with distilled water. The sampling record length was also affected by the duration of streamflow and the length of employment of summer students. Lake water samples were collected using a 0.5 m long Van Dorn bottle centered at the nominal depth.

Because of the very low concentrations of sulfate in the waters sampled (0.5–10 mg $\cdot$ L^{-1}) it was not possible to directly precipitate $BaSO_4$ (Cook 1981). It was therefore necessary to concentrate the sulfate before addition of $BaCl_2$. Initially this was accomplished by the tedious procedure of boiling down the samples to ≈20% of the original volume. For 1982 and subsequent years we developed a method of sulfate extraction by ion exchange.

An ion exchange column (Dowex AG 1-X4, 100–200 mesh, chloride form) was prepared in two sections of 1 cm dia. tubing (Fig. 1). The lower section, 11.5 cm long, was packed with 10 cm of resin and stoppered with a one hole stopper at the top. The upper section, 2.5 cm long, was packed into a 30 cm funnel topped column. A glass wool plug was placed on top of the resin in each section. The upper section, which was discarded after each sample, was required because dissolved organic material binds very tightly to the resin, was not removed with the normal elution, and eventually clogged the column. When samples of very high organic content were processed, the lower section also eventually became stained and was replaced. The column was conditioned with 30 mL of 3 N HCl followed by 100 mL of distilled water. High variance in replicate $\delta^{34}S$ analyses of early tests of the ion exchange extraction were attributed to microbial activity associated with the organic matter extracted by the column resulting in reduced oxygen con-

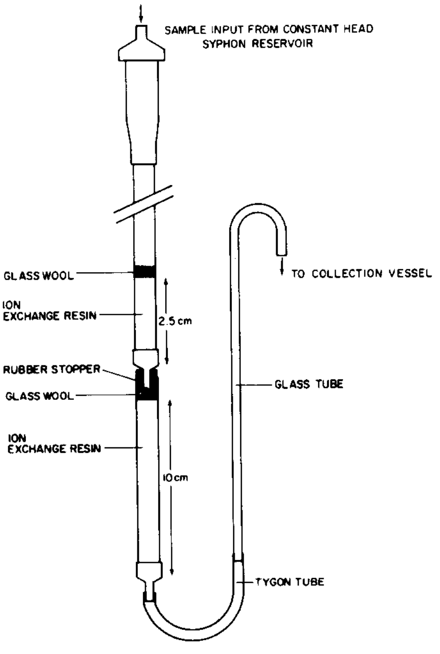

Fig. 1. The ion exchange system for extraction of sulfate from lake water.

centration and sulfur reduction. Addition of 0.7 g sodium azide per liter served to preserve the sample while awaiting extraction and to preserve the column from any possible sulfate reduction during extraction (some of the azide is removed by the column). Sulfate reduction during storeage in well oxygenated samples is not significant. The samples were passed through the column at a rate of 3 mL $\cdot$ min^{-1}. The sulfate was eluted with 30 mL 3N HCl followed by 100 mL distilled water as in the conditioning step. (Good ventilation must be provided during the elution because the sodium azide is converted to gaseous azoic acid which is toxic). The eluent volume was brought up to 200 mL with distilled water, 2 mL of 1N $BaCL_2$ added to precipitate the $SO_4^=$ as $BaSO_4$, and precipitate digested on a hot plate overnight. The precipitated $BaSO_4$ was filtered onto ashless paper (Whatman 42). The sulfate yield and isotopic ratios determined by standing additions of Na_2SO_4 to lake water and ion exchange extraction were indistinguishable from direct precipitation of $BaSO_4$.

Sulfur dioxide for mass spectrometric analyses was prepared by thermal decomposition of the $BaSO_4$ after ashing the filtered $BaSO_4$ at 800 °C for 1 h in a platinum crucible in order to remove the filter paper and any organic impurities. Total sulfur was estimated from the weight of $BaSO_4$ after ashing. The thermal decomposition was performed following the method of Halas & Wolacewicz (1981). Water sample volumes were chosen so that $\approx$ 1 atm.cc of SO_2 was produced ($\approx$ 5 mg sulfate) except when limited sample volume was available.

All isotopic ratio measurements were made using a VG Micromass 602E mass spectrometer with the changeover valve, capillaries, and inlet system heated to 110 °C. A tank of SO_2 was used as a machine reference. All ratio values of ^{34}S to ^{32}S are expressed in per mil units relative to Canyon Diablo troilite. Pacific seawater sulfate (21.0‰) (Rees et al. 1978) was used to standardize the machine reference. Aliquots of $BaSO_4$ batch precipitate were analysed with each sample set. Standard deviations of replicate analyses were routinely 0.1‰. Overall precision is estimated to be 0.3‰. Precision in estimating total sulfur was 0.5 mg which typically represented 5–10% of the total weight of $BaSO_4$, but up to 40% of some precipitation samples and stream samples at low flow.

Results

The sulfur isotopic composition of rain for 1982–1985 (Fig. 2) ranged from 3–9‰. The mean values, weighted by the mass of sulfate in rainfall, for four

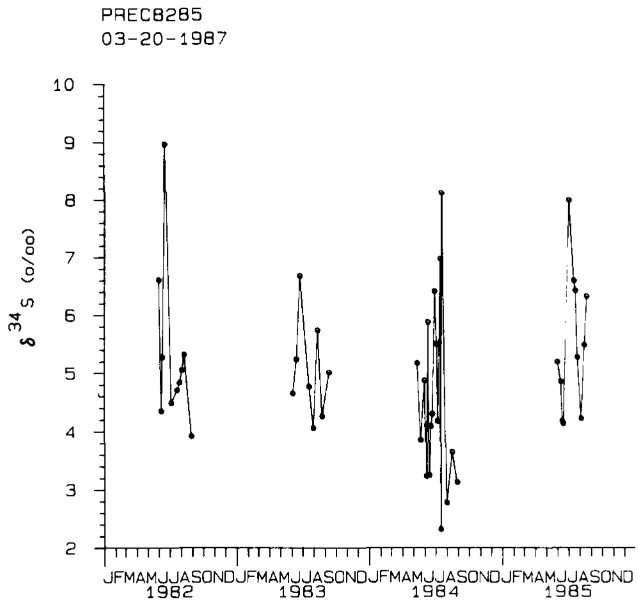

Fig. 2. The sulfur isotope compostion of rainfall events at ELA, 1982–1984.

years were respectively 4.62, 4.97, 4.44, and 5.93‰ (Table 1), quite consistent when compared with the event to event variance. Samples of total accumulated snowpack on March, 1985 and February, 1986 had delta values of 6.15 and 2.38‰ respectively. Based on a 15 years record, precipitation at the Experimental Lakes Area averages 29% snow and 71% rain (Beaty 1984). We estimate that the average sulfur isotopic composition of

Table 1. Mass weighted mean values of sulfate concentrations and δ^{34}S values for precipitation, inflows and outflow of Lake 239 drainage basin.

	Sulfate (mg · L^{-1})				δ^{34}(‰)			
	82	83	84	85	82	83	84	85
NEIF	2.5	0.88	2.1	1.9	8.17	7.59	11.66*	10.09*
NWIF	7.4	5.5	5.4	3.3	6.24	6.48	8.88	8.75
EIF	4.4	3.3	4.1	4.4	6.69	6.70	8.70	7.31
Outflow	4.2	4.6	4.1	4.3	6.25	5.91	6.78	6.57
Rain precipitation	0.63	0.57	1.03	0.81	4.62	4.97	4.44	5.93
Snow pack								
(March 1985)			0.77				6.15	
(Feb. 1986)			0.27				2.38	

* Irrigation of wetland with sulfuric acid having δ^{34}S = + 18‰.

the precipitation has been 4.8 ± 0.5‰ (std. dev.). Correlation of the $\delta^{34}S$ values with sulfate concentration was not significant ($p > 0.5$), but the precision of the sulfate analyses is poor in precipitation due to the low concentrations. Sea salt corrections were not made because they would be very small due to the low chloride and because the area is 900 km from Hudson Bay, the nearest oceanic water. Cortecci & Longinelli (1970) showed that the sea salt corrections in rain in Pisa, Italy, only 10 km from the Mediterranean, averaged < 6%.

The natural sulfur isotopic composition of the three sub-basin streams flowing into Lake 239 ranged from 5–15‰ during 1982–1985 (Fig. 3). The Northeast basin had values of 12–16‰ in 1984 and 1985, but this was due to the irrigation of the wetland area in this basin with sulfuric acid having a $\delta^{34}S$ of 18‰. The inflow of this wetland contributes less than 0.33% of the sulfate input to the lake and the acid does not influence the budgets for the lake (Schindler et al. 1976; S. Bayley, Univ. of Manitoba, pers. comm.). The $\delta^{34}S$ in all three streams were consistently low in the spring, increased as the flow in the streams decreased during the summer, and decreased again in the fall of years when there was significant flow. The amplitudes of this seasonal cycle in the sub-basins were: East < Northwest < Northeast. The acid irrigation of the Northeast wetland obliterated the pattern in that stream during 1984 and 1985. The mass weighted yearly mean $\delta^{34}S$ for each of the four years were similar in the East and Northwest basins and higher in the Northeast. Much of the increase in the Northeast mean in 1984 and 1985 was of course due to the acid irrigation.

The sulfate in the outflow of Lake 239 (equivalent to lake surface water) had the smallest range of $\delta^{34}S$, 5.5–7.1‰ during 1982–85 (Fig. 3d). The mass weighted means for the four years were respectively 6.25, 5.91, 6.78 and 6.57‰ (Table 1).

No significant differences were noticed in the $\delta^{34}S$ for sulfate at different depths in Lake 239. The four year means at the seven depths monitored (Table 2) ranged from 6.21 to 6.44‰ with standard deviations of 0.32–0.56‰. Mean sulfate concentrations were slightly lower and showed a slightly higher variance for the samples from 30 m depth. This may have been due to the occasional occurence of anoxia for a short period in late summer at that depth which led to increased sulfate reduction. The mean value of all lake water measurements over the three year period was 6.34‰ with a standard deviation of 0.58‰.

Highly significant correlations for streamflow vs $\delta^{34}S$ and sulfate concentrations vs $\delta^{34}S$ were found on all three sub-basins using Spearman rank order analyses (Table 3). This non-parametric approach was used because we are not prepared to use a particular mathematical model to describe the

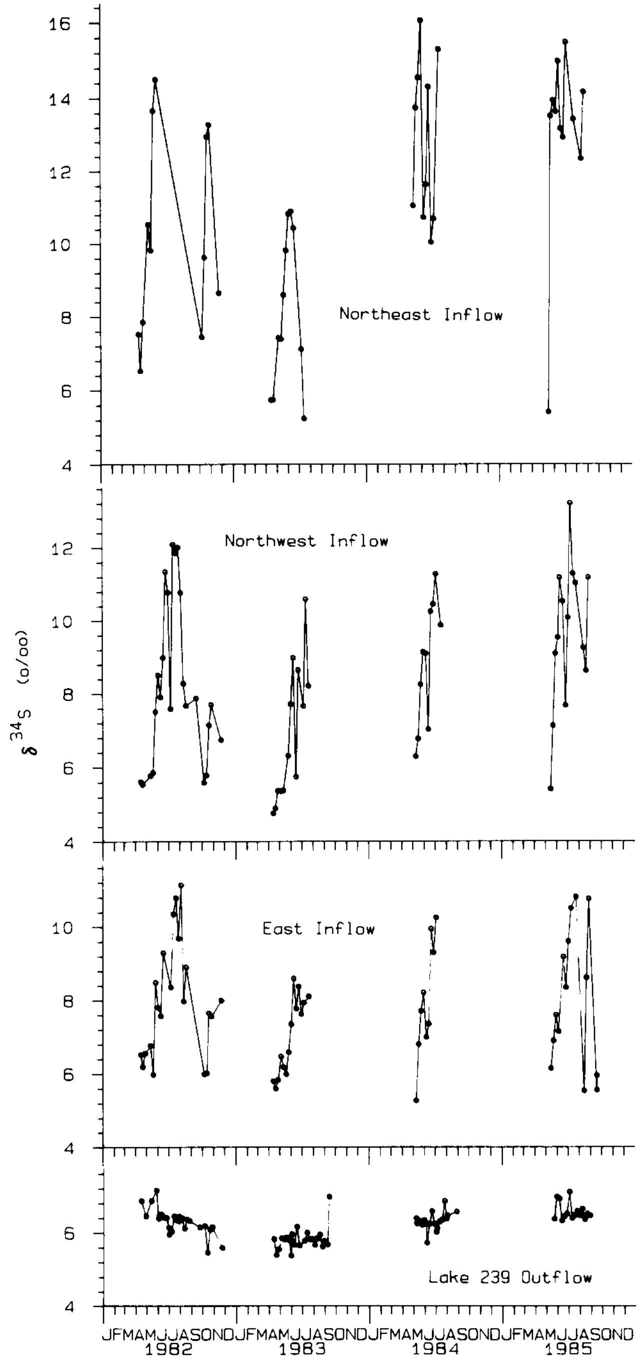

Fig. 3. The sulfur isotope composition of sulfate in the inflows and outflow of Lake 239, 1982–1985.

Table 2. Mean values for $\delta^{34}S$ and sulfate in lake 239, 1982–1985.

Depth (m)	$\delta^{34}S$ (‰)	Std. dev.	SO_4(mg L^{-1})	Std. dev.
1	6.35	0.70	4.24	0.71
5	6.27	0.54	4.21	0.62
10	6.24	0.32	4.34	0.49
15	6.43	0.56	4.10	0.71
20	6.21	0.34	4.42	0.57
25	6.40	0.49	4.20	0.66
30	6.44	0.52	3.87	0.98
All samples	6.34	0.58	4.21	0.72

Table 3. Statistical data for Spearman rank correlation of sulfate concentrations ($mg \cdot L^{-1}$) and streamflow ($m,^3 \cdot sec^{-1}$) against $\delta^{34}S$ (‰).

Variables	r_S	P
NEIF: [SO_4] vs $\delta^{34}S$	−0.466	< 0.01
NWIF: [SO_4] vs $\delta^{34}S$	−0.454	< 0.01
EIF: [SO_4] vs $\delta^{34}S$	−0.378	< 0.01
NEIF: flow vs $\delta^{34}S$	−0.711	< 0.001
NWIF: flow vs $\delta^{34}S$	−0.758	< 0.001
EIF: flow vs $\delta^{34}S$	−0.791	< 0.001

relationships. Data from the Northeast sub-basin for 1984 and 1985 was not included because of the influence of acid irrigation on flow and sulfate. Part of the reason for higher correlations with flow than sulfate concentration may be the considerable analytical imprecision in our determinations of sulfate by $BaSO_4$ precipitation for the very low concentrations during low flow.

Discussion

We feel that there is strong evidence in the data for fractionation of sulfur isotopes favoring retention of ^{32}S in the watershed of Lake 239 by either sulfate reduction or sorption. The consistently higher $\delta^{34}S$ in runoff relative to precipitation and the strong negative correlations of $\delta^{34}S$ to sulfate concentrations in streamflow support this conclusion. We envision the following scenario: during times of high flow, as in the spring or after storms the residence time of sulfate in the drainage basin is short and flow is in the shallow surface layer. There is little contact time for sorption or bacterial sulfate reduction and the oxygen concentrations are high. Little fractionation of sulfur isotopes occurs so the $\delta^{34}S$ is like that in precipitation and the concentration of sulfate in the runoff is effected only by evapotranspiration.

As the flows decrease, the residence time of sulfate in the soil increases and the concentration of oxygen decreases, especially in the wetland areas (Bayley et al. 1986). Sulfate reduction and sorption proceeds resulting in the observed decreased sulfate concentrations in the runoff in spite of the increased influence of evapotranspiration. The ^{32}S is more rapidly removed resulting in the observed increase in the delta values.

Fuller et al. (1986) suggested that large quantities of sulfur could cycle through organic fractions in the soil. They determined rate constants for immobilization of sulfate-S that would show significant concentration effects on the order of days. Longinelli & Cortecci (1970) claimed that biological activity was responsible for the increase in $\delta^{34}S$ of sulfate in the Arno and Serchio rivers of Italy, but they showed a positive correlation between sulfate and $\delta^{34}S$.

By using the yearly mean delta values for the inputs to Lake 239 given in Table I and the proportional contribution of each input to the sulfate budget of the lake derived from our sulfate data and a budget presented by Schindler (unpubl. data), an isotopic budget can be produced for the lake. If we assume that the three years of isotopic record are representative of the long-term record (Lake 239 has a mean water residence time of 10 yr), the budget calculation (Table 4) shows a mean delta value of all inputs of 7.01 ‰. This compares fairly well with the mean measured outflow value (Table 1) of 6.41 ‰. Schindler et al. (1976; unpubl. data) found that about 10–20% of the sulfur entering Lake 239 is retained by the sediments.

Although studies of sulfur isotopes in sulfate resulting from bedrock or soil weathering have not been done, we feel this is an unlikely source for the high $\delta^{34}S$ at low flows. The most mineral basin, that of the East inflow, shows the lowest $\delta^{34}S$ at low flow while the bog dominated Northeast basin shows the highest values. Sulfur reduction has been demonstrated in the Northeast basin wetland (Bayley et al. 1986).

Table 4. Isotopic balance for sulfur in Lake 239.

Input/output	(%) Contribution to sulfate budget	Mean $\delta^{34}S$ (‰)
NWIF	22	7.35
NEIF	1	9.54
EIF	40.5	7.25
Direct runoff	24	7.28
Precipitation (rain and snow)	12.5	4.82
Total input	100	7.01
Measured lake (see Table 2)		6.34
Measured outflow		6.41

A mass balance using our estimates of sulfate concentrations from the yield of $BaSO_4$ for isotopic measurements over four years suggests that only 5–10% of the sulfur is retained. A few cores from Lake 239 have been analysed and show $\delta^{34}S$ of 2–3 ‰ for total sulfur in the top few centimeters (Hesslein et al. unpubl.). The portion of the total sediment sulfur which is resultant from the sulfate in water is not known so the $\delta^{34}S$ for the mass balance cannot be specified. If the 5–10% defect in the mass balance had a $\delta^{34}S$ of 2.5 ‰, the expected lake water $\delta^{34}S$ would be 7.2–7.5 ‰. There is probably some bias in our estimate of the mean input value of the sulfur isotopes because our sampling often did not include the earliest spring runoff. Flows are typically high at this time and the isotopic values are consistently low in the early spring measurements that we do have. Correction of this probable high bias would improve the balance of the isotopic budget.

Other values of sulfur isotopic composition which have been reported for Canadian waters are generally similar to our values. Nriagu & Harvey (1978) reported values in precipitation of 3–8 ‰ in the Sudbury area. Nriagu & Soon (1985) reported mean delta values for precipitation; 3.7 ‰, and streams and lakes; 3.2 ‰, from the Turkey Lakes area near Sault Ste. Marie, Ontario. Fry (1986) reported values of 2.9 to 5.6 ‰ in lakes in the Adirondack Mountains of New York. The Great Lakes are typically 5–8 ‰. Some of these values from eastern Canada and the United States may be influenced to a greater extent by anthropogenic inputs to the atmosphere but the isotopic data is quite similar. The typically higher sulfate concentration observed in eastern Canadian waters may diminish the influence which the watershed processes can exert on the sulfur isotopic composition of runoff, however, Fuller et al. (1986) conclude that the reactions immobilizing sulfur are first order.

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