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Evidence for influence of mineral weathering on stream water sulphate in Vermont and New Hampshire (USA)

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Abstract:

Mass balance studies in forested catchments in the northeastern USA show that S losses via streamwater SO_4^{2-} exceed measured atmospheric S inputs. Possible sources of the excess S loss include underestimated dry deposition, mineralization of organic S in soils, desorption of soil sulphate, oxidation of recently formed sulphides and mineral weathering. Evaluating the relative contribution of these sources and processes to SO_4^{2-} export is important to our understanding of S cycling as well as to policy makers in their evaluation of the efficacy of S emission controls. In order to evaluate the potential for mineral weathering contributions to SO_4^{2-} export, we measured concentration and isotopic composition ($\delta^{34}S$ and $\delta^{18}O$) of SO_4^{2-} in stream water, and concentration and $\delta^{34}S$ values of four S fractions in bedrock and soil parent material in catchments of varying geological composition. Geological substrates with low S concentrations were represented by catchments underlain by quartzite and granite, whereas geological substrates with high S concentrations were represented by catchments underlain by sulphidic slate, schist and metavolcanic rocks. Catchments with S-poor bedrock had stream-water SO_4^{2-} concentrations <100 μeq L^{-1} and isotopic values consistent with those of atmospheric SO_4^{2-} that had been cycled through the organic soil pool. Catchments with S-rich bedrock had stream-water SO_4^{2-} concentrations ranging from 56 to 229 μeq L^{-1}. Isotopic values deviated from those of SO_4^{2-} in atmospheric deposition, clearly indicating a mineral weathering source in some cases, whereas in others spatial variability of mineral $\delta^{34}S$ values precluded the isotopic detection of a weathering contribution. These results, along with evidence suggesting formation of secondary sulphate minerals in bedrock weathering rinds, indicate that mineral weathering may be an important source of S in the surface waters of some forested catchments in the northeastern USA. Copyright © 2004 John Wiley & Sons, Ltd.

KEY WORDS forest; mineral weathering; oxygen isotopes; stream water; sulphate; sulphur isotopes

INTRODUCTION

Atmospheric emissions and deposition of S have been declining in the northeastern USA since the early 1970s (Likens *et al.*, 2001). During this period, stream water SO_4^{2-} concentrations also have been declining (Likens *et al.*, 2002). However, watershed mass balances in this region show that stream-water output of SO_4^{2-}-S was in excess of S inputs measured by bulk precipitation collectors for at least the past 35 years (Hornbeck *et al.*, 1997; Likens *et al.*, 2002) indicating that either atmospheric S inputs were underestimated or that additional internal SO_4^{2-} sources contributed to outputs. Identification of the sources of stream-water SO_4^{2-} has important implications for understanding of forest nutrient cycles. Additionally, policy makers concerned with the efficacy of emission controls need more precise information on whether emission controls are having effects on ecosystem processes and target stream-water concentrations to indicate recovery from acidification. If atmospheric deposition is the only S source, stricter air quality control and further emission

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reduction will result in a concomitant decrease in drainage water SO_4^{2-}. However, if a major internal S source exists in catchments, the contribution of this source to SO_4^{2-} export must be quantified if accurate predictions are to be made of how changing atmospheric S inputs will affect the recovery of surface waters from acidification.

Possible explanations to account for the S mass balance discrepancies in watersheds include (i) unaccounted dry deposition inputs (Likens *et al.*, 1990), (ii) oxidation of soil organic (C-bonded) S (Dillon and LaZerte, 1992; Houle and Carignan, 1995), (iii) desorption of SO_4^{2-} from anion exchange sites (Nodvin *et al.*, 1988), (iv) oxidation of reduced inorganic S, and (v) mineral weathering (Mitchell *et al.*, 2001). By mineral weathering, we refer to dissolution or oxidation of primary S minerals derived from the geological substrate, either in bedrock or soil parent material. This process is distinct from oxidation of recently formed sulphides, precipitated under anoxic conditions. Formation and reoxidation of sulphides in anoxic soils may be regarded as an internal transformation of S that has already cycled within the watershed, whereas mineral weathering represents an additional S source, newly available to biogeochemical cycling through dissolution and oxidation processes. Desorption of previously retained inorganic SO_4^{2-} is not considered to be a significant SO_4^{2-} source in geologically young soils of northeastern North America because absorbed pools are often too small to account for the S balance discrepancy and desorption reactions are too rapid to account for the long period of observed net SO_4^{2-} loss (Driscoll *et al.*, 1999).

A regional compilation of stream-water chemistry showed a large range in SO_4^{2-} concentrations (40 to 250 μeq L^{-1}) in stream water from small forested catchments in northern New England, USA (Hornbeck *et al.*, 1997). The mean drainage water SO_4^{2-} concentration for experimental watersheds was 105 μeq L^{-1} at Hubbard Brook Experimental Forest (HBEF), New Hampshire, 135 μeq L^{-1} at Cone Pond Watershed (CPW), New Hampshire, and 160 μeq L^{-1} at Sleepers River Watershed (SRW), Vermont. This range is greater than that expected from regional variability in bulk atmospheric S inputs (7·2 to 9·3 kg S ha^{-1} $year^{-1}$) and concentrations (36 to 43 μeq L^{-1}) (Hornbeck *et al.*, 1997), implying spatial variability in S sources. Compilations of bedrock chemistry likewise have shown great variability in S concentrations (Billings and Wilson, 1964), suggesting potential spatial variability in weathering contributions to surface water SO_4^{2-}. The iron sulphides pyrite (FeS_2) and pyrrhotite (FeS) are common S-bearing minerals, particularly in some bedrock formations of sedimentary and volcanic origin. Although they have received little attention in biogeochemical studies in the northeastern USA, secondary sulphate minerals, such as pickeringite, have also been identified in weathering rinds of sulphidic bedrock outcrops in Massachusetts (Parnell, 1983) and Connecticut (Schairer and Lawson, 1926), implying active S weathering. Thus, at least in some locales in the northeastern USA, weathering of S-containing bedrock is a potential contributor to SO_4^{2-} in surface waters.

Isotope measurements have proven useful in tracing S cycling in forested ecosystems (e.g. Mitchell *et al.*, 1998). It has been demonstrated that several sources of SO_4^{2-} can be differentiated, if both sulphur and oxygen isotope ratios are determined (Van Stempvoort and Krouse, 1994; Krouse and Mayer, 2000). Sulphate in atmospheric deposition in the northeastern USA has $\delta^{34}S$ values between +3 and +5‰ (Alewell *et al.*, 2000; Wadleigh *et al.*, 1996) with $\delta^{18}O$ values typically ranging between +7 and +17‰ (Krouse and Mayer, 2000). Sulphate formed by oxidation of organic (carbon-bonded) soil S is expected to have similar $\delta^{34}S$ values (+1 to +5‰) but lower $\delta^{18}O$ values (< +6‰), because water-oxygen (with negative $\delta^{18}O$ values) is introduced in the SO_4^{2-} molecule during the mineralization process (Mayer *et al.*, 1995a). Sulphate generated via oxidation of sulphide-containing minerals has similarly low $\delta^{18}O$ values (< +6‰) (e.g. Toran and Harris, 1989) and $\delta^{34}S$ values that may vary from < −20‰ to > +10‰ depending on the sulphur isotope ratios of the parent material. Hence, determination of the isotopic composition of stream-water SO_4^{2-} appears to be a promising tool for identifying sources of stream-water sulphate.

A prerequisite for successful source apportionment using stable isotopes is that S transformation processes do not change the isotopic composition of SO_4^{2-}. During bacterial (dissimilatory) SO_4^{2-} reduction for instance, the light isotopes ^{32}S and ^{16}O are preferentially metabolized by bacteria, leaving the remaining SO_4^{2-} progressively enriched in ^{34}S and ^{18}O (e.g. Harrison and Thode, 1958; Canfield, 2001). This results in a

characteristic pattern of increasing $\delta^{34}S_{sulphate}$ and $\delta^{18}O_{sulphate}$ values as SO_4^{2-} concentrations decrease during bacterial (dissimilatory) SO_4^{2-} reduction (e.g. Strebel *et al.*, 1990). Consequently, bacterial (dissimilatory) SO_4^{2-} reduction is a process that may complicate the identification of sources of stream-water SO_4^{2-}. In contrast, oxidation of sulphides and dissolution of sulphate minerals typically results in only minor sulphur isotope selectivity (e.g. Holser and Kaplan, 1966; Chambers and Trudinger, 1979). Dissolved SO_4^{2-} generated by these processes therefore has S isotope ratios similar to those of the S-containing minerals in the parent soil or bedrock. Also, immobilization of SO_4^{2-} and mineralization of soil organic S are believed to be accompanied by only minor sulphur isotope fractionation (Krouse *et al.*, 1991).

The objective of this study was to determine if concentration and isotopic composition ($\delta^{34}S$ and $\delta^{18}O$) of SO_4^{2-} in drainage waters can be used to detect a contribution of mineral weathering to SO_4^{2-} export from forested catchments in New Hampshire and Vermont, USA. We measured concentration, $\delta^{34}S$ values and $\delta^{18}O$ values of SO_4^{2-} in stream water, and concentration and $\delta^{34}S$ values of four S fractions in bedrock and soil parent material in catchments of varying geological composition. Two groups of catchments were chosen—those where previous S mass balance studies had been conducted, and a regional group chosen to reflect uniform geological substrate of either high or low S content.

MATERIALS AND METHODS

Stream-water samples were collected in late August to early September 1998 during baseflow conditions. This period was chosen because it should maximize the proportion of stream water derived from deeper flow paths, thereby increasing the likelihood of detecting products of mineral weathering from bedrock or deeper soil horizons. Two types of catchments were chosen for sampling, the first being catchments with established mass balance studies. These included the HBEF (3037 ha), CPW (33 ha) and SRW (W-9; 41 ha; Figure 1), which span a range of SO_4^{2-} concentrations in stream water (Hornbeck *et al.*, 1997). Both HBEF and SRW are partially underlain by sulphidic bedrock. The HBEF bedrock includes the Rangeley Formation, composed of sulphidic schist and calc-silicate granulite, and the Kinsman Granodiorite. The SRW bedrock includes sulphidic schist, phyllite and calcareous granulite of the Waits River Formation, and schist and phyllite of the Gile Mountain Formation. The CPW is underlain by relatively S-poor Perry Mountain Formation schist and Kinsman Granodiorite. At HBEF, spatial variability of the chemical and isotopic composition of stream-water SO_4^{2-} within the valley was explored by collecting samples from all nine experimental catchments (ranging in area from 12 to 68 ha) and from a number of other unmonitored catchments and longitudinally on the main stem of Hubbard Brook itself. Available stream sampling locations at CPW and SRW were more limited by baseflow conditions, which resulted in much of the stream channel network being dry in these smaller catchments. The stream at CPW was sampled just above the weir, whereas SRW was sampled above the weir and at the mouth of two tributaries.

The second group of catchments, referred to as regional streams, drain bedrock with varying S concentrations. The Cheshire Quartzite and Conway Granite were chosen as examples of bedrock with low S concentrations. The Ammonoosuc Volcanics are composed of metamorphosed lava flows and volcanic sediments with moderate to high S concentration. The Rangeley, Partridge and Smalls Falls Formations are metasedimentary units with the highest S concentrations of rocks in the region. Samples from these metasedimentary units have up to 10 mg S g^{-1} (Billings and Wilson, 1964). Geological maps (Doll *et al.*, 1961; Lyons *et al.*, 1997) and US Geological Survey topographic maps were consulted to locate small catchments (10s to 100s ha) underlain by a single bedrock map unit and also with forest cover, minimal roads or cultural development. Additionally, catchments were selected where as large a region as possible immediately north and west of the candidate catchment was underlain by the same bedrock map unit, minimizing the contribution of other rock units in glacial drift derived from material transported to the south and east by Pleistocene glaciation (Bailey and Hornbeck, 1992).

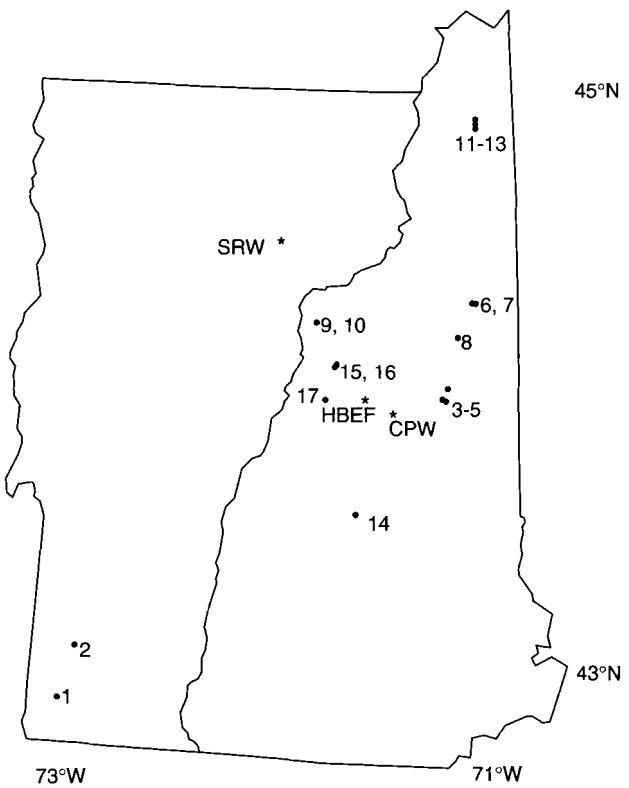

Figure 1. Index map of Vermont and New Hampshire showing locations of experimental catchments (stars) and regional streams (circles) sampled in this study. Experimental catchments include Cone Pond Watershed (CPW), Hubbard Brook Experimental Forest (HBEF) and Sleepers River Watershed (SRW). Regional stream locations are listed in Table III

Rock samples were collected from each of the bedrock map units for chemical and isotopic characterization of four different S fractions. To the extent possible, only unweathered portions of rock samples were chosen for analysis. This was more feasible for samples collected from recent road cuts. Fresh samples from natural exposures of sulphidic rocks were more difficult to collect owing to deep weathering rinds. In experimental catchments, where soil parent material was derived from a variety of lithological sources, till (lower C-horizon) samples from a portion of the watershed with the deepest soils were also analysed for concentration and isotopic composition of S compounds. This sample was chosen to represent the least weathered soil parent material available in order to minimize the chance that a potential mineral S source would be overlooked owing to weathering depletion. Soil and rock samples were pulverized in a tungsten carbide shatterbox prior to chemical and isotopic analyses.

Water samples were collected in collapsible 10 L polyethylene jugs with Tygon® tubing. Sulphate concentrations in stream water were measured on an ion chromatograph. For isotope analyses, water samples were passed through anion exchange resin columns (Bio-Rad Polyprep, AG 1X-8) to retain the SO_4^{2-}. Sulphate was eluted from each column with 15 mL 3M HCl; 0·5 M $BaCl_2$ solution was added to precipitate $BaSO_4$, which was recovered by filtration, washed with deionized water, air-dried, weighed and stored for isotope analysis. Total S concentrations in bedrock and soils were determined using a LECO SC-444 analyser. To determine concentration and the isotopic composition of total S in soil and bedrock pulverized samples were digested in a concentrated HNO_3/Br_2 mixture to oxidize the S to SO_4^{2-} (Zhabina and Volkov, 1978). After removing the undigested material by filtration, SO_4^{2-} was precipitated as $BaSO_4$ and further processed as described for the water samples.

In addition to total S, three S fractions were extracted from the solid samples and their S concentrations and isotope ratios were determined. Acid-volatile S (mostly monosulphide minerals such as pyrrhotite), HCl-soluble S (mostly sulphate minerals), and Cr-reducible S (mostly disulphide minerals, such as pyrite) were sequentially extracted from the soil and rock samples following the procedure of Rice *et al.* (1993). The concentrations of all S fractions were determined gravimetrically.

Sulphur dioxide (SO_2) for mass spectrometric analyses was generated by high temperature decomposition of $BaSO_4$ or Ag_2S mixed with V_2O_5 and SiO_2 (Yanagisawa and Sakai, 1983; Ueda and Krouse, 1986). Sulphur isotope ratios were determined by conventional dual inlet isotope ratio mass spectrometry (DI-IRMS). For oxygen isotope analyses on SO_4^{2-}, $BaSO_4$-oxygen was converted to CO at 1450 °C in a pyrolysis reactor (Finnigan TC/EA). The resultant gas was subsequently swept with a He stream into a mass spectrometer (Finnigan MAT delta plus XL) for isotope ratio determinations in continuous-flow mode (CF-IRMS). For comparison, some $BaSO_4$ samples were mixed with graphite and converted to CO and CO_2 at 1000 °C followed by a high voltage conversion of CO to CO_2 in a discharge chamber (Holt and Kumar, 1991). Oxygen isotope ratios obtained with both techniques typically agreed within the uncertainty of the respective analytical procedures provided below.

Isotope ratios are reported using the δ-scale in parts per thousand

$$\delta_{\text{sample}}(‰) = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000 \quad (1)$$

where R is the $^{34}S/^{32}S$ or $^{18}O/^{16}O$ ratio of a sample or a standard, respectively. The internationally accepted standards are CDT (troilite from the Canyon Diablo meteorite) for S isotope ratio measurements and V-SMOW (Vienna Standard Mean Ocean Water) for oxygen isotope analyses. The reproducibility for S isotope measurements on aqueous SO_4^{2-} was better than ±0·3‰. The overall reproducibilities of extractions, gas preparations and mass spectrometric analyses for S isotope determinations on acid-volatile S, HCl-soluble S and Cr-reducible S, determined by duplicate analyses, were better than ±1·0‰. The analytical reproducibility of O isotope measurements on SO_4^{2-} was ±0·8‰.

RESULTS AND DISCUSSION

Bedrock

Bedrock S concentrations were consistent with limited previously published results (Billings and Wilson, 1964; Table I). The Cheshire Quartzite and Conway Granite, chosen to represent S-poor lithologies, had total S concentrations <0·1 mg g^{-1}. The total S concentrations of the other rock samples, including Ammonoosuc Volcanics, Rangeley Formation schist and Smalls Falls Formation schist, ranged from 1·9 to 25·4 mg g^{-1}. In most rocks with intermediate to high S concentrations, acid-volatile S represented 31–81% of total S, Cr-reducible S comprised 3–53% of total S, and HCl-soluble S was ≤28% of total S. The only exception was in two schist samples from the Rangeley and Waits River Formations where acid-volatile S and Cr-reducible S represented less than 5% of total S, indicating that the majority of the S occurred in the HCl-soluble or insoluble S fractions. The insoluble S fraction was highly variable, representing from 0 to 85% of total S.

In all bedrock samples, $\delta^{34}S$ values of Cr-reducible and acid-volatile S were similar to those of total S. In general, $\delta^{34}S$ values of total S in bedrock samples were either lower than −1‰ or higher than 6‰ (Table I), and thus distinct from the sulphur isotope ratios of SO_4^{2-} in atmospheric deposition in the northeastern USA (e.g. Alewell *et al.*, 2000). However, within map units, there was great variability in the isotopic composition of total S. For example, samples from the Smalls Falls Formation collected in different parts of New Hampshire (ca. 120 km apart) had $\delta^{34}S$ values of total S that ranged from −28·3‰ to 17·1‰, covering almost the entire range of measured bedrock values. Differences in sedimentary environment (e.g. Strauss, 1997) or metamorphic grade may cause such variability within map units. These results are similar to those

Table I. Concentration and isotopic composition of total S and three S fractions in bedrock samples

Map unit	Lithology	Location	S fraction (mg S g^{-1})				S fraction ($\delta^{34}S$ [‰])			
			Total	Cr-reducible	Acid-volatile	HCl-soluble	Total	Cr-reducible	Acid-volatile	HCl-soluble
Cheshire	Quartzite	Sunderland, VT	0·072	0·022	—	—	12·0	—	—	—
Conway	Granite	Albany, NH	0·090	0·019	0·041	—	−1·9	−3·6	0·0	—
Ammonoosuc	Metatuff	Benton, NH	25·370	1·339	18·214	0·078	−15·3	−15·1	−14·8	−10·1
Rangeley	Schist	HBEF, W5	8·340	0·288	—	2·331	−11·5	−9·9	—	−12·9
Rangeley	Schist	HBEF, W9	1·920	0·600	0·602	0·098	6·0	5·9	6·6	4·3
Smalls Falls	Schist	Plymouth, NH	15·710	8·409	7·372	1·280	−21·0	−21·1	−23·4	15·2
Smalls Falls	Quartzite	Plymouth, NH	8·920	0·803	5·103	0·042	−28·3	−27·4	−28·1	−0·9
Smalls Falls	Schist	Dixville, NH	7·050	0·635	5·685	0·618	17·1	16·9	17·4	15·1
Waits River	Schist	Danville, VT	7·810	0·103	0·402	0·666	8·5	7·7	7·8	5·8

—, insufficient S for analysis.

of Oliver *et al.* (1990), who found similar variation in $\delta^{34}S$ values in high-grade pelitic rocks in Maine. Our results from bedrock samples in New Hampshire of sulphidic sedimentary constituents and $\delta^{34}S$ values also suggest that high-grade regional metamorphism did not homogenize the wide variation in S constituents. Additionally, two samples of the Rangeley Formation collected at HBEF (*c.* 4 km apart), although collected in relatively close proximity, and within the same metamorphic grade, had $\delta^{34}S$ values of total S that varied from −11·5‰ to 6·0‰ (Table I). A previously published value (Fuller *et al.*, 1986) of 9·2‰ for a sample of Littleton Formation (now mapped as Rangeley Formation) from HBEF further extends the range in $\delta^{34}S_{total}$ values reported for this map unit. The variation of $\delta^{34}S$ for total S in the Rangeley Formation bedrock at HBEF encompasses $\delta^{34}S$ values measured in atmospheric SO_4^{2-} deposition at this site (range from 3·2 to 5·0‰, mean 4·4‰; Alewell *et al.*, 2000), suggesting that a composite $\delta^{34}S$ value for bedrock at HBEF could be coincident with that of atmospheric SO_4^{2-} deposition.

For most rock samples, the Cr-reducible or acid-volatile S fractions were dominant over the HCl soluble S fraction, consistent with pyrite and pyrrhotite being the dominant S minerals in these formations (Moench *et al.*, 1995). The two exceptions, a Rangeley Formation sample collected from Watershed 5 at HBEF and a Waits River Formation sample collected from the vicinity of SRW, were dominated by HCl-soluble S, suggesting that soluble sulphate minerals were present in these samples. In both samples more than 70% of the S was not accounted for by our extraction scheme. As organic S is assumed to be negligible, we suggest that the unaccounted fraction is comprised of secondary sulphate minerals, which are insoluble in acid. This is consistent with both samples showing pitting and extensive iron oxide staining, as they were collected from weathered natural bedrock exposures. In contrast, the sample from HBEF Watershed 5 showed an unidentified bright yellow material that was partially soluble upon soaking in deionized water, yielding a solution with a pH of 2·9, suggesting the presence of a more soluble secondary sulphate mineral. We hypothesize that both insoluble and soluble secondary minerals, possibly including barite and a variety of hydroxy sulphate minerals may be present in the bedrock weathering zone. The $\delta^{34}S$ values of the HCl-soluble SO_4^{2-} fractions were similar to those of the reduced inorganic S forms, consistent with the secondary minerals having been formed by sulphide oxidation.

Soil parent material

In addition to bedrock, glacial till samples were analysed from the experimental catchments because, unlike the other study sites chosen for their relative uniformity of geological influences, the experimental catchments are underlain by at least two bedrock map units. Additionally, different bedrock map units immediately to the north and west of the experimental catchments suggests that soil parent materials formed in till of

mixed provenance. At HBEF and SRW, a portion of the till is derived from sulphidic bedrock, the Rangeley Formation and the Waits River Formation, respectively, with other contributions from a variety of S-poor metasedimentary and igneous bedrock units. In contrast, CPW is primarily underlain by the Perry Mountain Formation, a S-poor unit, and its till may be less influenced by sulphidic sources (Bailey and Hornbeck, 1992). Relatively unweathered till samples from HBEF and CPW had extremely low total S concentrations (<0·001 mg g^{-1}; Table II), suggesting that either the till deposited in these catchments contained few S-bearing minerals or that S minerals have been removed by 14 000 years of weathering since deglaciation. In contrast, SRW till samples contained between 1·4 and 11·6 mg g^{-1} of total S. HCl-soluble S was the only measurable fraction in these samples, suggesting that much of the S in the till at SRW is in a sulphate rather than a sulphide form. The negative $\delta^{34}S$ values of the HCl-soluble S fractions provide evidence that the sulphates were formed by sulphide oxidation. Because a significant portion of the total S was not accounted for, organic (carbon-bonded) S and/or insoluble sulphate minerals might also be an important S fraction in these soils.

Stream water in experimental catchments

Drainage waters at CPW, HBEF and SRW were sampled because intensive catchment-scale S mass balance evaluations had been conducted in these watersheds (Tables III and IV). Geological provenance of glacial till in these watersheds is mixed, with a number of lithological sources contributing to the substrate (Hornbeck *et al.*, 1997) and in some cases contrasting with the underlying bedrock. In general, CPW has till and bedrock with low S concentration (Bailey and Hornbeck, 1992). The bedrock at HBEF is primarily Rangeley Formation, one of the S-rich bedrock units. On the other hand, the till is dominated by Kinsman Granodiorite, with moderately low S concentrations (Bailey *et al.*, 2003). Finally SRW is mostly underlain by Waits River Formation bedrock (Hall, 1959), which is also the dominant influence in a mixed till. The Waits River includes highly sulphidic schist interbedded with calcareous granulite.

Of the experimental catchments, HBEF had somewhat higher atmospheric deposition of S owing to greater amount of precipitation (Hornbeck *et al.*, 1997; Table V). Sleepers River Watershed has substantially higher net S loss (9·9 kg S ha^{-1} $year^{-1}$) while CPW and HBEF had similar net losses of 5·6 and 4·4 kg ha^{-1} $year^{-1}$, respectively, suggesting greater contributions of watershed-internal S sources at SRW. Mean annual stream-water SO_4^{2-} concentrations followed a similar trend, with SRW having the highest value at 160 μeq L^{-1}, followed by CPW at 135 μeq L^{-1} and HBEF at 100 μeq L^{-1}. In comparison with the regional streams (Table III), SRW and CPW have SO_4^{2-} concentrations higher than the group of streams underlain by low-S substrates, suggesting greater SO_4^{2-} contributions via mineralization of soil organic S and/or mineral weathering at SRW and CPW.

Stream water from all nine experimental catchments at HBEF as well as a number of other tributaries and stations along the main stem of the Hubbard Brook itself were sampled in order to characterize spatial variability across this relatively well-studied valley. Sulphate concentrations ranged from 40 to 119 μeq L^{-1}

Table II. Concentration and isotopic composition of total S and three S fractions in soil parent material

Watershed	Sample depth	S fraction (mg S g^{-1})				S fraction ($\delta^{34}S$ [‰])			
		Total	Cr-reducible	Acid-volatile	HCl-soluble (cm)	Total	Cr-reducible	Acid-volatile	HCl-soluble
CPW	229–244	0·000	—	—	—	—	—	—	—
HBEF	165–170	0·000	—	—	—	—	—	—	—
SRW	61–81	11·620	0·000	0·000	5·051	−22·5	—	—	−22·9
SRW	132–158	1·400	0·000	0·000	0·085	−9·6	—	—	−19·0

—, insufficient S for analysis.

Table III. Concentration and isotopic composition of SO_4^{2-} from regional stream-water samples. The numbers preceeding stream names indicate the locations shown in Figure 1. Streams draining the Cheshire Quartzite and Conway Granite were chosen to represent S-poor bedrock, whereas the other streams were chosen to represent the bedrock formations with the highest known S concentrations in the region

Location	Geologic Influence	SO_4^{2-} ($\mu eq\ L^{-1}$)	$\delta^{34}S_{sulphate}$ (‰)	$\delta^{18}O_{sulphate}$ (‰)
1. Unamed brook, Bald Mtn., Bennington, VT	Cheshire Quartzite	71	6·3	6·1
2. Cole Brook, Sunderland, VT	Cheshire Quartzite	88	5·5	3·7
3. Oliverian Brook, Albany, NH	Conway Granite	80	4·8	2·6
4. Unamed tributary to Oliverian Brook, Albany, NH	Conway Granite	68	4·5	2·7
5. Oliverian Brook, Albany, NH	Conway Granite	67	5·5	4·2
6. Nineteen Mile Brook, Beans Purchase, NH	Rangeley Formation	75	−2·8	—
7. unamed brook, Zeta Pass, Beans Purchase, NH	Rangeley Formation	77	−2·5	1·5
8. Upper Stairs Brook, Sargents Purchase, NH	Rangeley Formation	82	−1·9	—
9. Unamed brook near Pettyboro, Bath, NH	Partridge Formation	229	−4·3	1·2
10. Unamed brook near Pettyboro, Bath, NH	Partridge Formation	94	3·0	4·6
11. Unamed tributary to Nathan Pond Brook, Dixville, NH	Smalls Falls Formation	56	10·4	0·9
12. Unamed tributary to Dixie Brook, Dixville, NH	Smalls Falls Formation	80	7·2	1·6
13. Unamed tributary to Swift Diamond River, Dixville, NH	Smalls Falls Formation	79	9·0	4·5
14. Unamed brook, Wade State Forest, Hill, NH	Smalls Falls Formation	133	−5·7	5·6
15. Unamed brook, Clough Mtn., Benton, NH	Ammonoosuc Volcanics	115	3·1	4·4
16. Spillman Brook, Benton, NH	Ammonoosuc Volcanics	112	2·8	3·4
17. Unamed brook, Sentinel Mtn., Warrren, NH	Ammonoosuc Volcanics	116	5·2	0·9

—, quantity insufficient for analysis.

(Table IV), mostly in the range shown by streams draining low-S geological substrates (Table III), even though much of the HBEF is underlain by the sulphidic Rangeley Formation. The range in $\delta^{34}S_{sulphate}$ values exhibited by HBEF streams was also relatively narrow (1·4 to 5·6‰) compared with that shown by the regional streams (Table III), and almost identical with sulphur isotope values observed for SO_4^{2-} from atmospheric deposition at this site (Alewell *et al.*, 2000). These $\delta^{34}S$ values and all but one of the $\delta^{18}O_{sulphate}$ values <6‰ indicate that atmospherically deposited SO_4^{2-} had cycled through the organic soil S pool before reaching the streams at HBEF. One exception (Table IV) was stream T7 which had the highest SO_4^{2-} concentration (119 $\mu eq\ L^{-1}$), among the lowest $\delta^{34}S$ values (1·6‰), as well as very high concentrations of base cations and alkalinity (unpublished data), suggesting that stream T7 was more influenced by mineral weathering than other streams at the HBEF. However, in general, the HBEF mass balance, stream-water chemistry and isotope data do not provide a clear indication of significant S mineral weathering influence, despite relatively high S concentrations in bedrock and evidence of secondary sulphate minerals in weathering rinds of bedrock exposures. A possible coincidence of $\delta^{34}S$ values of SO_4^{2-} derived from atmospheric deposition and mineral weathering may preclude the ability to detect S weathering products isotopically at HBEF.

The SRW stream samples had relatively high concentrations of SO_4^{2-} (111–133 $\mu eq\ L^{-1}$), high $\delta^{34}S_{sulphate}$ values (7·3 to 10·5‰; Table IV), and mean $\delta^{18}O_{sulphate}$ values of 2·9 ± 1·9‰ ($n = 3$). In comparison, total and reduced inorganic S of the Waits River Formation bedrock sample collected from the vicinity had $\delta^{34}S$ values similar to that of stream-water SO_4^{2-} (7·7 to 8·5‰; Table I), although two soil samples had relatively low $\delta^{34}S_{total}$ values (−22·5 and −9·8‰; Table II). The comparatively high $\delta^{34}S$ values of streamwater SO_4^{2-} can be explained by a watershed-internal S source with positive $\delta^{34}S$ values, such as the sulphide minerals in the bedrock (Table I). Hence, mineral weathering appears to be a significant internal S source in this catchment. Unlike the HBEF experimental catchments, the SRW experimental catchment includes several wetland areas with poorly drained soils, where anaerobic conditions may have a strong influence on S cycling. Bacterial (dissimilatory) SO_4^{2-} reduction could also explain high $\delta^{34}S_{sulphate}$ values. However, the high concentrations

Table IV. Concentration and isotopic composition of SO_4^{2-} from stream-water samples from experimental catchments. Samples were collected during baseflow conditions during later summer, 1998

Catchments	Location	SO_4^{2-} ($\mu eq\ L^{-1}$)	$\delta^{34}S_{sulphate}$ (‰)	$\delta^{18}O_{sulphate}$ (‰)
CPW	At weir	78	7·2	5·5
HBEF	W1 at weir	97	4·8	2·2
	W2 at weir	81	4·3	2·5
	W3 at weir	97	4·8	2·6
	W4 at weir	102	5·2	3·7
	W5 at weir	108	2·1	3·4
	W6 above weir	94	4·2	2·6
	W6 below weir	97	4·2	2·4
	W6 below weir	94	2·9	4·0
	W7 at weir	89	3·7	2·5
	W8 at weir	80	4·3	2·5
	W9 at weir	80	5·0	4·2
	W9 tributary	76	5·3	4·6
	W9 tributary	94	3·5	4·7
	Lost Brook, T33	97	5·1	4·2
	Hubbard Brook, H33	60	5·3	2·3
	Cushman Brook, T31	101	4·0	3·9
	Hubbard Brook, H31	79	5·4	2·4
	Beaver Brook, T22	40	5·5	—
	Hubbard Brook, H22	79	4·6	3·5
	Cascade Brook, T19	80	5·6	4·1
	Hubbard Brook, H19	77	5·1	4·5
	Bagley Trail Brook T15	81	3·6	3·3
	Bear Brook, T10	80	1·4	5·0
	Paradise Brook, T9	90	2·8	—
	Hubbard Brook, H9	80	3·9	3·3
	Unamed brook T7	119	1·6	6·9
	Hubbard Brook, H5	84	3·7	3·7
SRW	W-9 east tributary	111	10·5	2·3
	W-9 west tributary	115	7·3	1·4
	W-9 at weir	133	9·1	5·0

–, quantity insufficient for analysis.

and relatively low $\delta^{18}O$ values of stream-water SO_4^{2-} suggest that bacterial (dissimilatory) SO_4^{2-} reduction cannot fully explain the chemical and isotopic composition of stream-water SO_4^{2-} at SRW.

Based on the high SO_4^{2-} concentrations in stream water, high S concentrations in bedrock and isotopic values distinct from those of atmospheric SO_4^{2-} deposition, it seems likely that mineral weathering does contribute to SO_4^{2-} in stream water at SRW and thus partially explains the high net S loss in this watershed (Table V). However, given the variations noted in the S isotopic composition of stream water, bedrock and soil samples, and the uncertainties associated with spatial variability in these values, it is not possible at present to quantify the S mineral weathering flux for SRW without further analyses.

Cone Pond Watershed, with relatively low SO_4^{2-} stream-water concentrations (Table V), had a stream-water $\delta^{34}S_{sulphate}$ value (7·2‰; Table IV) somewhat higher compared with those of SO_4^{2-} in atmospheric deposition and the regional streams draining low-S substrates (Figure 2). Also, the $\delta^{18}O_{sulphate}$ value was 5·5‰, approximately 2‰ higher than the mean $\delta^{18}O_{sulphate}$ values in streams at HBEF and SRW. Note that bedrock analyses were not undertaken as the geological literature on the Perry Mountain Formation bedrock is in agreement with our petrographic inspections of bedrock samples and weathering rinds in suggesting

Table V. Comparison of sulphur mass balance, stream-water SO_4^{2-} concentration and isotopic composition, and bedrock S concentration and isotopic composition at three reference catchments. Mass balance was computed for the period 1991–1994 (Hornbeck *et al.*, 1997)

	Hubbard Brook[a]	Cone Pond[b]	Sleepers River[c]
Input (kg S ha^{-1})	9·3	7·8	7·2
Output (kg S ha^{-1})	13·8	13·4	17·1
Net (kg S ha^{-1})	4·4	5·6	9·9
Stream SO_4^{2-} (μeq L^{-1})	100	135	160
Stream $\delta^{34}S$	1·4 to 5·6	7·2	7·2 to 10·5
Bedrock S (mg g^{-1})	1·920–8·340	—	7·810
Bedrock $\delta^{34}S$(‰)	−11·5 to 6·0	—	8·5

[a] Bedrock at Hubbard Brook comprises the Rangeley Formation.
[b] Bedrock at Cone Pond was not sampled but comprises Perry Mountain Formation.
[c] Bedrock at Sleepers River comprises the Waits River Formation.

a low S content in CPW bedrock. Like SRW, CPW also contains several wetland areas, where bacterial (dissimilatory) SO_4^{2-} reduction might occur. This would result in a reduction of S exports accompanied by elevated $\delta^{34}S$ and $\delta^{18}O$ values in the remaining SO_4^{2-}. However, as this process would also result in lower S export than input, an unidentified S source is still required to explain the net S loss in CPW (Table V). Mineralization of carbon-bonded S remains a possibility, as does an unidentified geological source in CPW.

Stream water in catchments with a range of geological influences

Streams chosen to represent distinct geological influences exhibited a broad range of SO_4^{2-} concentrations and $\delta^{34}S$ values (Figure 2 and Table III). Streams draining catchments with low S concentration in geological substrates all had <100 μeq L^{-1} SO_4^{2-} and $\delta^{34}S$ values ranging from 4·5 to 6·3‰ (Table III). This indicates minimal contribution of S from mineral weathering, because bedrock $\delta^{34}S$ values were lower than 0 or higher than +10‰ in these catchments (Table I). Hence, atmospheric input of S is presumably the dominant S source

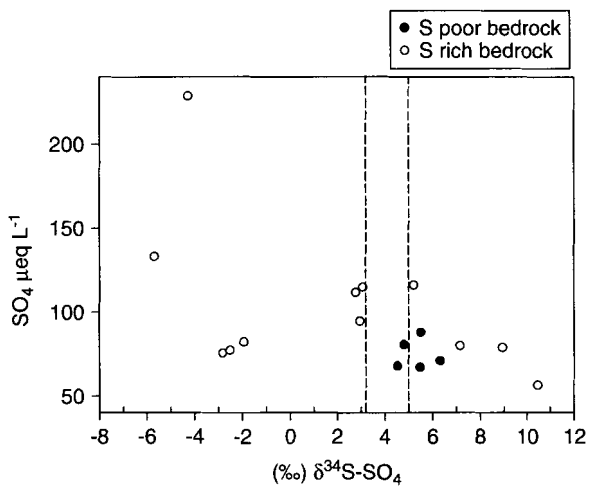

Figure 2. Concentration (μeq L^{-1}) and sulphur isotope ratios ($\delta^{34}S$‰) of SO_4^{2-} in streams draining geological materials of contrasting S concentration. The dashed lines indicate the range of $\delta^{34}S$ values for sulphur of atmospheric origin. Streams draining catchments with S-poor bedrock are denoted by solid circles. Streams draining catchments with S-rich bedrock are represented by open circles

in these catchments. However, the $\delta^{18}O_{sulphate}$ values <6‰ (Figure 3 and Table III) suggest that originally atmospherically deposited SO_4^{2-} (with $\delta^{18}O_{sulphate}$ values >6‰) has cycled through the organic soil S pool before reaching the stream, consistent with the results of Mayer *et al.* (1995b) and Alewell (2001).

Of the 12 streams sampled that drain catchments with intermediate to high S concentrations in the geological substrate, seven had <100 μeq L^{-1} SO_4^{2-} whereas the remaining five streams had 100–230 μeq L^{-1} SO_4^{2-} (Figure 2 and Table III). Only one stream underlain by S-rich bedrock had a $\delta^{34}S_{sulphate}$ value in the range exhibited by the streams underlain by S-poor bedrock with the other 11 streams having either higher (>7·0‰) or lower (<3·2‰) $\delta^{34}S_{sulphate}$ values. The $\delta^{18}O$ values of stream SO_4^{2-} ranged between 0·9 and 5·6‰ with a mean value of 2·9 ± 1·8‰ ($n = 10$). These values indicate that stream SO_4^{2-} was derived either from mineralization of soil organic (carbon-bonded) S and/or from sulphide oxidation, but not directly from atmospheric SO_4^{2-} deposition (Figure 3).

Four streams draining intermediate to high S concentration substrate had elevated SO_4^{2-} concentrations and $\delta^{34}S$ values between 2·8‰ and 5·2‰. The majority of the SO_4^{2-} presumably derived from atmospheric SO_4^{2-} that has cycled through the soil organic pool. However, some SO_4^{2-} also may have been contributed by mineral weathering, particularly in the two streams with $\delta^{34}S_{sulphate}$ values near 3‰ underlain by Ammonoosuc Volcanics, which are characterized by high S concentrations with negative $\delta^{34}S$ values (Table I). Thus, mineral weathering is a potential SO_4^{2-} source for these streams but quantification of its relative importance is difficult based on available data. More sampling would be necessary in each catchment to determine spatial variability in mineral $\delta^{34}S$ values and temporal variability in stream-water $\delta^{34}S$ values to support such quantification. The remaining eight streams draining intermediate to high S concentration substrate had variable concentrations of SO_4^{2-}, $\delta^{34}S$ values <2‰ or >7‰ (Figure 2), and $\delta^{18}O_{sulphate}$ values <5·6‰ (Figure 3). The $\delta^{34}S_{sulphate}$ values <2‰ provide clear evidence for contributions from weathering of S minerals with negative sulphur isotope ratios. The $\delta^{34}S_{sulphate}$ values >7‰ could be caused either by weathering of S minerals with high sulphur isotope ratios or by bacterial (dissimilatory) reduction of SO_4^{2-} derived from atmospheric or pedogenic sources.

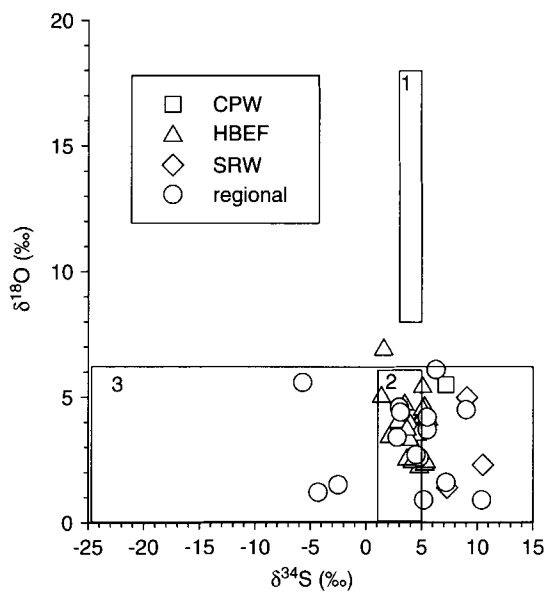

Figure 3. $\delta^{34}S$ versus $\delta^{18}O$ values (‰) of streamwater SO_4^{2-} in both experimental catchments and streams chosen to represent the range of S in bedrock in the region. The numbered rectangles indicate the range of isotopic composition of SO_4^{2-} in (1) atmospheric deposition, (2) derived from mineralization of soil organic S and (3) derived from weathering of sulphide minerals

It is, however, interesting to note that within bedrock map units, streams draining different catchments showed isotopic similarities to rock samples collected nearby. For example, the three streams draining catchments underlain by the Smalls Falls Formation in Dixville all had high $\delta^{34}S_{sulphate}$ values (7·2 to 10·4‰; Table III) as did all S fractions of the Smalls Falls Formation bedrock sample from Dixville (15·1 to 17·4‰; Table I). In contrast to the samples from Dixville, which is in northern New Hampshire, a stream draining a Smalls Falls Formation catchment in central (Hill) New Hampshire had a low $\delta^{34}S_{sulphate}$ value (−5·7‰; Table III), as did two Smalls Falls Formation rock samples collected in nearby Plymouth (−28·3 to −21·8‰; Table I). Three stream SO_4^{2-} samples from Rangeley Formation catchments all clustered around $\delta^{34}S$ values of −1·9 to −2·8‰ (Table III). Although no Rangeley Formation rock samples from these catchments were analysed, samples of Rangeley Formation bedrock from the HBEF had widely divergent values, ranging from −11·5 to 9·2‰ (Table I; Fuller *et al.*, 1986).

The sulphur isotope composition of stream-water SO_4^{2-} from a majority of the catchments with S-rich bedrock provided strong evidence for SO_4^{2-} contributions from mineral weathering. The contribution of bedrock weathering to stream-water SO_4^{2-} can be determined quantitatively if the $\delta^{34}S$ value of bedrock S is different from that of atmospheric SO_4^{2-}, uniform, and well known. The spatial variability in the $\delta^{34}S$ values of bedrock S in our study, and limited stream-water sampling prevented us from such a quantitative source apportionment. However, with further sampling to determine the scale and patterns of spatial variability of concentrations and isotope ratios in various bedrock sulphur compounds, it might be possible to use the isotope technique for quantification of SO_4^{2-} contributions from mineral weathering in individual catchments or subcatchments that meet the above criteria. Figure 4 shows hypothetical mixing lines, illustrating the method for determining the portion of stream-water SO_4^{2-} derived from mineral weathering. In cases (a) and (c) a determination via this method is possible, whereas in case (b), another approach would be necessary to detect S weathering. Based on the available data, case (a) may apply to SRW whereas, HBEF seems to fall into case (b).

SUMMARY AND CONCLUSIONS

Stream water draining catchments with S-poor substrates had relatively low SO_4^{2-} concentrations (<90 μeq L^{-1}) and S isotope values predominantly between 3 and 6‰, consistent with those of atmospheric SO_4^{2-}. Sulphur isotope values suggest that atmospheric deposition is the dominant SO_4^{2-} source in these catchments, but the $\delta^{18}O$ values of stream-water SO_4^{2-} indicate that this atmospheric SO_4^{2-} cycled through the soil organic S pools, and thus does not behave conservatively.

Stream water draining catchments with S-rich substrates had variable SO_4^{2-} concentrations. Whereas about half the streams had SO_4^{2-} concentrations in the same range as streams draining catchments with S-poor bedrock, the other half was characterized by elevated concentrations (SO_4^{2-} > 100 μeq L^{-1}), strongly suggesting an additional watershed internal S source. Sulphur isotope values of SO_4^{2-} in streams draining catchments with S-rich bedrock were generally distinct from those of atmospheric SO_4^{2-}, with surface water $\delta^{34}S_{sulphate}$ values higher than +7‰ or lower than 1‰. In these cases, we were able to conclusively demonstrate that lithogenic S sources contribute to SO_4^{2-} export with drainage waters.

Of the three experimental catchments, SRW showed the clearest evidence of a mineral weathering influence on S cycling. Further analysis to determine spatial variability in bedrock $\delta^{34}S$ values as well as investigations of the potential influence of microbially mediated oxidation/reduction processes in wetlands will enhance our ability to quantify the S flux from internal watershed sources.

Despite the relatively high S concentrations in HBEF bedrock, catchment mass balances (Likens and Bormann, 1995), prior isotopic studies (Alewell *et al.*, 1999) as well as our stream-water data all suggest that weathering of S minerals contributes little to SO_4^{2-} runoff. Weathering of pyrrhotite (iron monosulphide) in surface exposures of Rangeley Formation bedrock has left a thick rusty weathering rind characteristic of this bedrock unit (Moench *et al.*, 1995). These thick weathering rinds could serve to isolate outcrops from

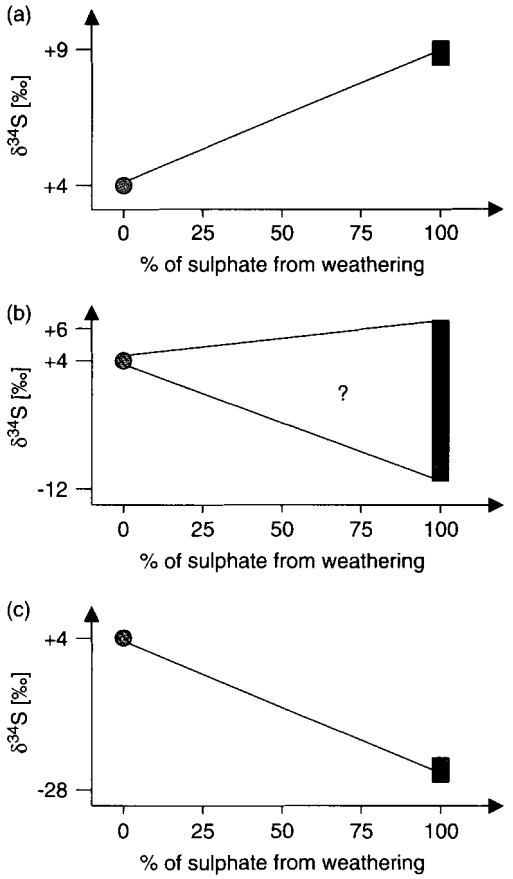

Figure 4. Mixing lines for computation of the portion of stream-water SO_4^{2-} derived from mineral weathering based on isotopic composition. The circles represent SO_4^{2-} derived from atmospheric deposition (no weathering contribution), whereas the rectangles represent bedrock isotopic compositions. In case (a) a narrow positive $\delta^{34}S$ value in bedrock allows calculation of the weathering contribution; in case (b) a calculation is not possible owing to a broad range in bedrock isotopic values that overlap with the atmospheric value, in case (c) a narrow negative $\delta^{34}S$ value in bedrock allows calculation of the weathering contribution

surface water contact, limiting further weathering. In areas where there was greater than 1·5 m thick glacial till, the bedrock surface was essentially unweathered, exhibiting fine glacial striations (Johnson *et al.*, 1968). Although the till parent material for HBEF soils is derived mostly from local bedrock, sulphide minerals have not been identified in till or soils, most probably owing to depletion by weathering over 14 000 years since glacial retreat.

However, there are other indications, including a few samples with relatively low $\delta^{34}S$ values and somewhat elevated SO_4^{2-} concentrations, that S weathering is occurring locally at HBEF, suggesting that further studies are warranted. Results from the samples of Rangeley Formation collected at HBEF suggest that the mean $\delta^{34}S_{total}$ value may not be distinct from $\delta^{34}S$ values in atmospheric SO_4^{2-} deposition. The spatial variability in $\delta^{34}S$ values of bedrock needs to be described to determine if S mineral weathering contributions to drainage waters might be detectible isotopically within portions of HBEF.

Secondary sulphate minerals have been identified in the weathering rinds of sulphidic schists in Massachusetts (Parnell, 1983) and their presence is suggested at HBEF and SRW as evidenced by the HCl-soluble S fraction analyses and the soluble bright yellow mineral coatings observed at HBEF. This evidence suggests

the potential for the weathering of sulphide minerals in shallow or exposed bedrock outcrops at HBEF. Further sampling is needed to determine the identity, occurrence and dissolution kinetics of secondary sulphate minerals in these catchments. Formation and dissolution of secondary S materials may represent an important process affecting the export of S in forested catchments.

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