

Chemical weathering of phosphate and germanium in glacial meltwater streams: Effects of subglacial pyrite oxidation

S. N. Chillrud

Department of Geosciences, Columbia University, Lamont-Doherty Earth Observatory, Palisades, New York 10964

F. L. Pedrozo, P. F. Temporetti, and H. F. Planas

Department of Aquatic Resources, Centro Regional Universitario Bariloche, Univ. Nacional Comahue, C.C. 1336, (8400) Bariloche, Argentina

P. N. Froelich

Department of Geosciences, Columbia University, Lamont-Doherty Earth Observatory

Abstract

Data from three glacial meltwater streams draining Mt. Tronador in the southern Argentine Andes (72°W, 41°S) show that subglacial pyrite oxidation and the subsequent precipitation of iron oxides strongly influence dissolved phosphate concentrations but do not appear to affect dissolved germanium concentrations. Total-Fe (TFe) and total-P (TP) concentrations are high in all three glacial streams, but the ratios of soluble reactive phosphate (SRP) to TP are very different. The Upper Manso Stream that drains the Manso Glacier has relatively low SRP (0.01–0.23 μM), representing a small fraction of its TP (0.1–5%). The SRP of the two streams draining smaller side glaciers (0.12–0.69 μM) represents a much larger portion of their TP (20–32%). TFe, dissolved sulfate, and $\delta^{34}\text{S}$ data suggest that pyrite oxidation is the most likely weathering reaction contributing sulfate to the Upper Manso Stream but not to the two smaller glacial-fed streams, in which atmospheric inputs can account for all of the sulfate. Dissolved Ge appears to show no preferential sorption relative to dissolved silica, in contrast to the speculation that Ge preferentially sorbs on fresh iron hydroxyoxide surfaces.

Rock–water interactions are an important part of the geochemical cycles of the earth, ultimately controlling the compositions of rivers, streams, and lakes—both dissolved and suspended solids—and thus the fluxes of chemicals to the sea. Sorption-desorption reactions with surfaces of suspended solids strongly affect the dissolved composition of waters, and the riverine fluxes of most elements are dominated by the suspended solids load (Martin and Meybeck 1979).

Two driving forces of rock–water reactions are acid hydrolysis reactions and the formation of fresh solid surfaces for sorption reactions. Pyrite oxidation provides both. Its oxidation produces sulfuric acid, and iron hydroxyoxides are precipitated as a by-product. Whereas a

region can have sulfide oxidation as its main acid source for weathering (e.g. natural mine drainage streams), globally, sulfide oxidation is estimated to produce 10% of the acid source (Berner et al. 1983) for chemical weathering, with CO_2 providing the other 90%.

This study is unique in that we examine pyrite oxidation as a stoichiometric control on P and Ge in a glacial meltwater setting where strong redox gradients are absent. Studies of chemical weathering often suffer from interferences due to atmospheric and aquatic pollution (acid rain, fertilizer application, deforestation, etc.). In the Upper Manso catchment, these complications are avoided because of its relatively remote location in the Andes Mountains. Furthermore, glaciated catchments offer environments in which the relationships between physical and chemical denudation and the chemical evolution of natural waters can be studied. Glacier grinding provides an extreme end-member of the physical denudation process, resulting in relatively high suspended solid loads. Although it was first thought that chemical weathering in glacial settings might be unimportant due to their low temperatures and abiotic nature (and hence low $p\text{CO}_2$), it

Acknowledgments

We thank the following for their work, encouragement, and help: Lucia Roselli, Tim Lyons, Maddy Scheiber, Danny Rye, Rick Mortlock, Jordan Clark, and Kevin Harrison. The manuscript was greatly improved by the anonymous review process—the reviewers' time and input are much appreciated.

This work was supported by the Lamont-Doherty Climate Center of Columbia University and represents a contribution from Lamont-Doherty Earth Observatory.

Subglacial chemical weathering

has been shown that glaciated catchments can be areas of intense chemical weathering (Reynolds and Johnson 1972). Finally, a glacial setting provides an environment where weathering and the effects of inorganic suspended solids proceed in the near absence of biological activity and organic matter. Organic acids, present in some soils at high concentrations, are at very low concentrations in subglacial environments (Raiswell 1984).

Proglacial stream water is a mixture of supraglacial and subglacial meltwater with groundwater inputs (Raiswell 1984). The term *supraglacial* is used for both superglacial (surface melt) and englacial (throughput) meltwaters that do not come into contact with subglacial water until just before or after the portal of the glacial stream. Subglacial meltwaters are characterized by high suspended and dissolved solids and residence times on the order of several days, while supraglacial meltwaters are typically characterized by very low dissolved and suspended solids, atmospheric $p\text{CO}_2$ levels ($10^{-3.5}$ atm), and residence times of <24 h (Raiswell 1984). Collins (1979) found that supraglacial meltwater accounted for a large percentage (50–80%) of the total meltwater discharge of two alpine glaciers during warm summer months. Mixing of very dilute supraglacial meltwaters with subglacial water rich in finely ground glacial flour creates a reactive environment for ion exchange (Lemmens and Roger 1978) and mineral dissolution (Raiswell 1984). An enhanced reactivity of minerals in glacial flour due to small particle size has been proposed frequently (e.g. Reynolds and Johnson 1972; Raiswell 1984) and has been qualitatively simulated in the laboratory (Keller and Reesman 1963).

The objectives of this paper are to demonstrate that pyrite oxidation is an important weathering reaction beneath only one of the three glaciers; that chemical weathering of pyrite strongly influences the geochemistry of soluble reactive phosphorus (SRP); and that precipitation of iron hydroxides following oxidation of pyrite does not appear to have any effect on ratios of dissolved germanium to silicon.

Study area

The Upper Manso catchment, in the southern Argentine Andes Mountains (72°W, 41°S)

(Fig. 1), is 23 km long with a surface area of 250 km². The stream begins at the glaciated Mt. Tronador (3,554 m), ~70 km from the Pacific Ocean on the Argentine–Chilean border. The dominant westerlies and the rain shadow effect of the Andes provide a strong west-to-east precipitation gradient within the catchment. The precipitation has very low solute concentrations (e.g. $[\text{Cl}^-] = 6 \pm 3 \mu\text{M}$), as would be predicted from previous studies (Junge and Gustafson 1957; Stallard and Edmond 1981), because the orographic effect of the Andean Cordillera strips out most of the marine cyclic inputs on the windward (Chilean) side.

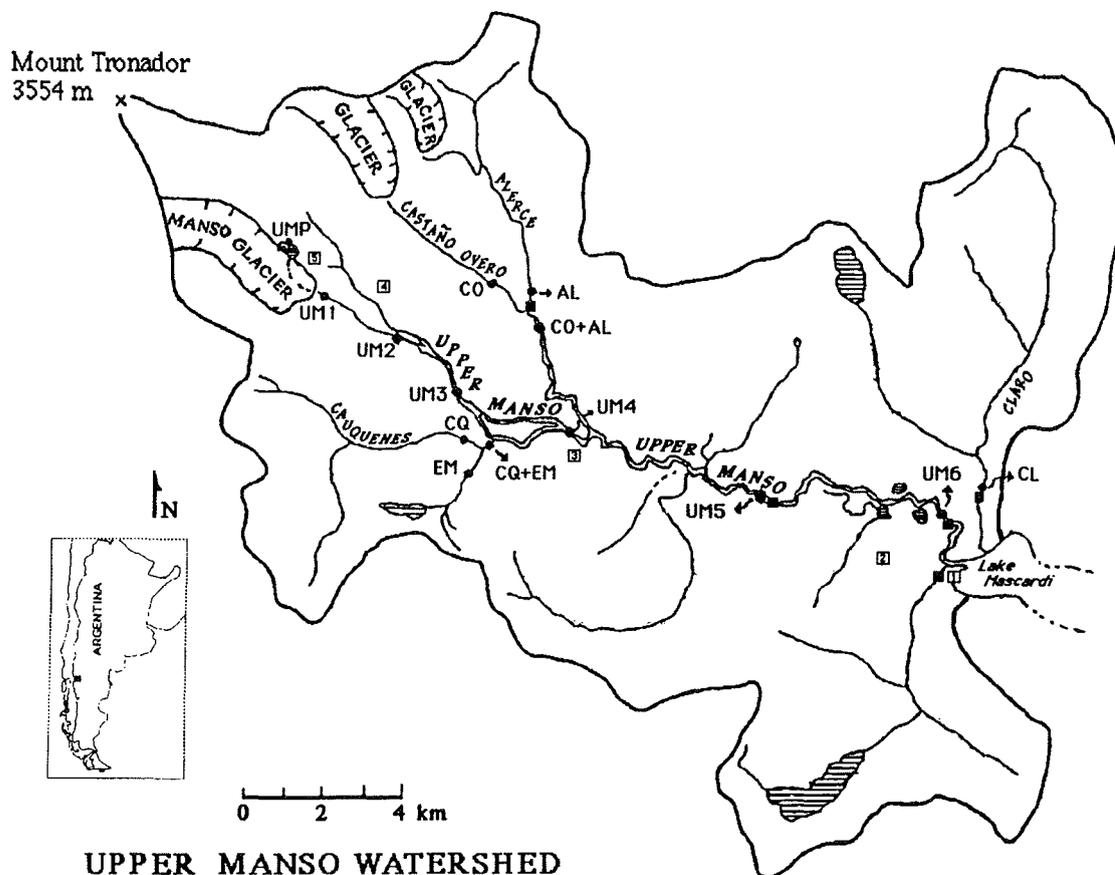
Three glaciers cap the western end of the catchment. The meltwaters from the largest glacier (Manso Glacier) form the source of the mainstem of the Upper Manso Stream. Two smaller glaciers are located at the headwaters of the Castaño Overo Stream and the Alerce Stream, which join to form the Castaño Overo + Alerce Stream. Sample sites on these streams (CO, AL, CO + AL) are a few kilometers below their meltwater portals, whereas the sample sites on the Upper Manso Stream include two sites at the glacial meltwater outlets of the Manso Glacier (UMP—Manso proglacial pond; UM1—bottommost meltwater outlet of the Manso Glacier) and four sites along the course of the Upper Manso Stream (UM2–UM6; Fig. 1). During the warm months, all three glaciers discharge large amounts of glacial flour and are classified as white-water streams. The concentration of suspended solids in the three meltwater streams roughly correlates with the size of their glaciers (Manso > Castaño Overo >> Alerce).

The dominant bedrock units in the three glaciated subdrainages include volcanics (basalts, base andesites, tuffs, and pyroclastic breccias), granites, and pyritized, silicic metamorphic rocks (Gallopín 1978). Pleistocene volcanic ash beds are prevalent throughout most of the area. The lithologic units are similar in the three glaciated subdrainages, except that granitic intrusions are much more common in the subdrainage of the Alerce Stream.

Methods

Samples were collected during austral summers (January and February) 1990 and 1991. Water temperature (thermistors) and pH (po-

Chillrud et al.



UPPER MANSO WATERSHED

Fig. 1. The Manso catchment. Sample sites are identified by a 2-4 character abbreviation of the name of the stream(s). Also shown are the five precipitation stations (□) and five water gauging stations (■). Hatched areas indicate small lakes. (Adapted from Gallopin 1978.)

tentiometric) were measured in situ. Water samples were collected below the water surface in plastic jugs which were thoroughly rinsed with sample water. In January 1991, unfiltered samples pipetted directly from the streams and also from the sampling jugs were placed into reaction flasks for total Fe (TFe) (hydroxylamine-HCl digest; phenanthroline; Am. Public Health Assoc. 1985) and total P (TP) (acid-persulfate autoclave digestion, modified by filtering the solution immediately after the digest step to avoid any possible reabsorption of SRP onto remaining particulate surfaces and interferences from the particles in reading the transmittance of the samples; molybdate blue; Koroletff 1983). (TP samples collected in 1990 were frozen in plastic bottles until time of the analyses.) The remaining sample was imme-

diately passed through sequential 1.0- and then 0.45- μm Nuclepore filters. In the field, filtered aliquots for the SRP analyses (molybdate blue; Murphy and Riley 1962) were pipetted into phosphate reaction vessels and stored in a darkened cooler. Total particulate P (TPP) was calculated as the difference between TP and SRP, since dissolved organic P is assumed to be unimportant in glacial meltwater streams. Major cations (Ca^{2+} , Na^+ , K^+ , Mg^{2+}) were analyzed by flame atomic absorption spectrophotometry (AAS). Sulfates were determined by BaSO_4 turbidimetry (Tabatabai 1974). Chloride was determined with a chloridometer (automated AgCl) (Ewing 1981) and a DI-ONEX system. Silica analyses were carried out by the molybdate-blue method (Mortlock and Froelich 1989). Ge analyses were done by the

Subglacial chemical weathering

hydride generation technique (graphite furnace AAS) of Hambrick et al. (1984). Suspended sediment concentrations ($>0.45 \mu\text{m}$) were estimated via the mass retained on the Nucleopore filters.

Water and rock samples were analyzed for $\delta^{34}\text{S}$. Analyses were performed on SO_2 gas quantitatively converted from either BaSO_4 or Ag_2S in D. Rye's lab on a Nuclide 611 RMS with dual viscous inlet system (Rye and Williams 1981). Chrome reduction was used on both the pyritic and native sulfur rock samples collected in the catchment to produce Ag_2S that was subsequently burned with copper oxide at $1,150^\circ\text{C}$ to produce SO_2 (Zhabina and Volkov 1978; Canfield et al. 1986). BaSO_4 was precipitated from acidified water samples ($\text{pH} \sim 1.8$) to which a concentrated BaCl_2 solution was added after boiling for a few minutes. After allowing the solutions to cool overnight, the BaSO_4 was collected on $0.45\text{-}\mu\text{m}$ Millipore filters, dried, and finally fused in quartz (Westridge 1983). The gas emissions of the fusion were passed over Cu at 550°C and collected as SO_2 . H_2O and CO_2 were removed before isotopic analysis of the SO_2 . All $\delta^{34}\text{S}$ values are reported on the per mil scale relative to the Diablo Canyon Troilite standard. The final $\delta^{34}\text{S}$ values for the sulfides were determined with the NBS-123 sphalerite standard with a value of $+17.3\text{‰}$. The final $\delta^{34}\text{S}$ values for the dissolved sulfates were determined with the NBS-127 BaSO_4 (seawater) standard with a value of $+20.9\text{‰}$.

Results and discussion

Pyrite oxidation—The major ion composition of the stream waters provides the first evidence for the oxidation of pyrite as an important weathering reaction in the Upper Manso Stream. The streams of the Andean-Patagonian region are, in general, very dilute solutions, dominated by calcium (avg, $153 \mu\text{M}$), bicarbonate (avg, $369 \mu\text{eq liter}^{-1}$), and dissolved silica (avg, $193 \mu\text{M}$) (Pedrozo et al. 1993). However, the Upper Manso Stream, which drains the Manso Glacier, has relatively high levels of dissolved calcium (avg for January 1991, $217 \mu\text{M}$) and sulfate (avg for January 1991, $222 \mu\text{M}$). One-to-one dissolved calcium:sulfate molar ratios exist for the samples taken from the Upper Manso Stream (at sites UM1 and UM2) (Fig. 2). The $\text{Ca}:\text{SO}_4$ ratio

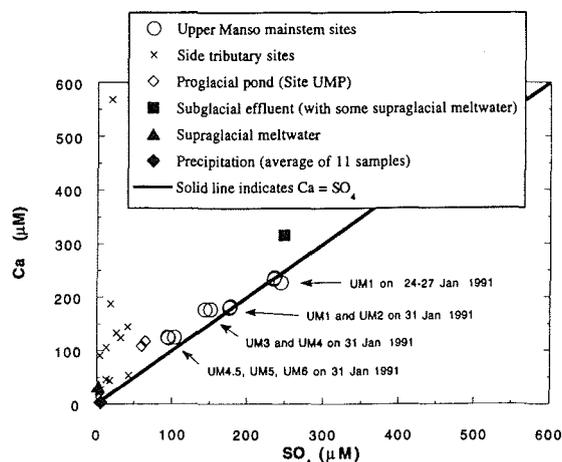


Fig. 2. Ca^{2+} vs. SO_4^{2-} for the Manso Watershed, January 1991. The Upper Manso Stream begins with a 1:1 $\text{Ca}:\text{SO}_4$ ratio at site UM1. As the Upper Manso Stream mixes with the sulfate-poor side tributaries the $\text{Ca}:\text{SO}_4$ ratio increases slightly. Also plotted are average rain water and both surface and subglacial meltwater samples from the Manso Glacier.

increases slightly downstream in the Upper Manso Stream due to mixing with sulfate-poor side tributaries. Site UMP, although next to the Manso Glacier, has much lower SO_4 levels than the Upper Manso Stream and a $\text{Ca}:\text{SO}_4$ ratio significantly greater than unity. We attribute these differences to the proglacial pond receiving more supraglacial meltwater and less subglacial meltwater at the time of sampling. The supraglacial meltwater has dissolved Ca and almost no SO_4 (Fig. 2). The mixing of these two water masses can change with time, often resulting in the proglacial pond having elevated concentrations of Ca and SO_4 , with $\text{Ca}:\text{SO}_4$ ratios = 1 (e.g. on 17 February 1990, site UMP: $[\text{Ca}] = 240 \mu\text{M}$ and $[\text{SO}_4] = 242 \mu\text{M}$).

The dissolved sulfate in the stream derives mostly from weathering of sulfur-containing minerals plus trace amounts of atmospheric cyclic salts. Precipitation in the region comes from the Pacific Ocean via the persistent westerlies; the moisture and cyclic salts are stripped out on the Chilean side of the Andes, resulting in very dilute rainwater on the Argentine side and a strong precipitation gradient in the catchment. The average sulfate content of one snow and 10 rain samples, corrected for evaporation (factor of two based on pan evaporation data from the catchment—Rubulis 1978),

Chillrud et al.

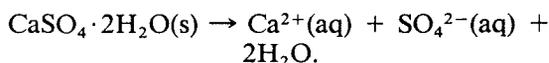
Table 1. Chemistry of precipitation samples from the Manso Watershed. The cyclic salt correction term for each element is calculated by multiplying the average precipitation concentration by the average evaporation factor ($f = 2$), determined through pan evaporation measurements in the watershed (Rubulis 1978). This cyclic salt term gives the atmospheric input to which chemical weathering products are added. (na—not analyzed.)

Sample-type	Sample site	1989	pH	Si(OH) ₄	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	Cl ⁻
				(μM)						
L1A-rain	2	25 Jul	na	1.2	3.8	0.9	3.9	0.8	7.9	10
L2C-rain	1	25 Jul	na	0.8	2.1	0.6	2.0	0.6	7.9	6
L3A-rain	3	25 Jul	4.38	0.8	2.4	0.3	2.7	0.5	6.8	11
L4B-rain	2	27 Jul	na	0.9	1.9	0.4	4.2	0.5	6.8	7
L5B-rain	3	27 Jul	4.51	0.8	3.7	0.4	1.2	0.6	5.8	5
L6B-rain	1	27 Jul	4.56	0.8	2.1	0.3	2.3	0.5	7.9	19*
L7A-snow	4	28 Jul	5.00	0.9	0.0	0.3	0.2	0.1	11.0	0
L9A-rain	1	8 Aug	6.00	0.7	2.5	1.0	1.8	0.3	7.0	8
L10A-rain	2	8 Aug	5.90	0.8	3.4	0.4	1.2	0.2	7.0	5
L11A-rain	3	8 Aug	5.90	0.8	4.3	0.3	1.2	0.2	1.1	3
L30-rain	5	28 Feb	4.56	2.9	4.7	1.8	11.8	1.7	3.7	3
Avg evap. correction = 2 (avg)					2.8	0.6	3.0	0.5	6.6	5.8
					5.6	1.2	5.9	1.1	13.2	11.6

* Not included in average.

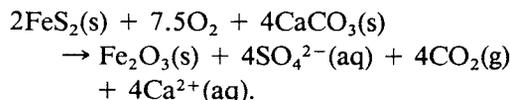
is 13 ± 5 μM, which we take as our cyclic salt correction for sulfate (Table 1).

There are two possible weathering scenarios that could produce a 1:1 Ca to SO₄ signal in the Upper Manso Stream. The simplest is congruent dissolution of gypsum or anhydrite:



Gypsum and anhydrite could be hidden in marine evaporite deposits beneath the glacier.

The second possibility is the oxidation of pyrite to produce sulfuric acid, which can then act as an acid source for weathering other minerals such as calcite. The net reaction for this is



If we adopt this second reaction as the source of the sulfate, mass balances on the stream-water chemistry indicate that 70–80% of the acid source in the Upper Manso Stream is derived from pyrite oxidation, with the remaining protons coming from carbonic acid (CO₂ + H₂O) (Chillrud et al. unpubl. data). The pyrite could be part of a porphyry base metal deposit within the volcanic Tronador Formation—the main lithologic unit that the Manso Glacier cuts. Although carbonate deposits are not known in the Tronador Formation, the persistence of the 1:1 ratio re-

quires their presence. If the Ca²⁺ were solely a product of weathering relatively resistant silicates, then sulfuric acid attack on Mg-, Na-, and K-containing silicates would result in Ca:SO₄ < 1:1. Other studies of glaciated catchments have found that microdeposits of CaCO₃ dominate weathering (Reynolds and Johnson 1972; Drever and Hurcomb 1986). The CaCO₃ precipitates secondarily from the concentrated subglacial solutions into microfractures of the volcanic deposit during pressure release caused by the retreat of the glacier over time (Hallet 1976; Drever and Hurcomb 1986).

Because both scenarios (gypsum vs. pyrite + calcite) produce Ca and SO₄ in equal molar ratios without adding alkalinity, there is no way to differentiate between the two from dissolved major ion chemistry alone. Evidence for the presence of pyrite oxidation beneath the Manso Glacier can be seen in the relationship between dissolved SO₄ and TFe data. Pyrite oxidation produces a mole ratio of 2 for dissolved SO₄ to particulate Fe. The Upper Manso Stream data, corrected for atmospheric sulfate inputs, fall reasonably close to the line in Fig. 3 with a slope of 2. The source of the Fe in the two smaller meltwater streams could be Fe weathered from primary silicate minerals and then reprecipitated as iron hydroxides on the surfaces of the suspended sediments.

Sulfur isotopes provide evidence that pyrite oxidation is the main source of sulfur to the

Subglacial chemical weathering

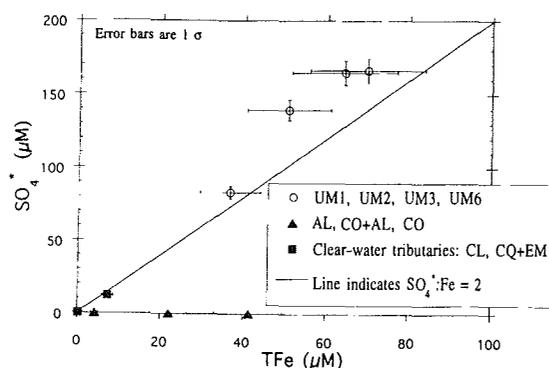


Fig. 3. Relationship of SO_4^* (dissolved SO_4 corrected for atmospheric inputs): TFe concentrations in the Upper Manso catchment. Line shows ratio = 2, as expected if pyrite oxidation is the primary source of these species. The Upper Manso Stream plots close to the line while the other two glacial streams appear to receive all their SO_4 from atmospheric input. Two clear-water streams with no glacial meltwater input (CL and CQ + EM) are also shown for comparison. The CQ + EM stream which drains the same type of lithology as the Manso Glacier also appears to have some minor amount of pyrite oxidation. TFe concentrations in UM1 are two orders of magnitude higher than the world average for riverine dissolved Fe ($0.72 \mu\text{M}$, Martin and Meybeck 1979); consequently we assume that the TFe analyses reflect the particulate-Fe concentrations in the stream. This assumption is substantiated by TFe analyses on two of the clear-water (i.e. low suspended sediments loads) tributaries in the watershed; the CL stream with $0.2 \text{ mg liter}^{-1}$ suspended sediments has a TFe concentration of $0.2 \mu\text{M}$, and the CQ + EM stream with $5.4 \text{ mg liter}^{-1}$ suspended sediments has a TFe concentration of $7.2 \mu\text{M}$. The $1-\sigma$ error bars for TFe are calculated from the reproducibility of triplicates and duplicates of stream samples pipetted directly from the stream or from a sampling jug; the relatively large errors are due to the variation of the suspended solids in a 50-ml pipetted sample and not the analytical precision of the phenanthroline technique.

Upper Manso Stream. Table 2 shows the $\delta^{34}\text{S}$ values of sulfur-bearing minerals collected within the catchment and for one water sample (AF183) taken on 24 January 1991 from the proglacial pond along the side of the terminal moraine of the Manso Glacier (site UMP). The measured SO_4 concentration of this sample is $64 \mu\text{M}$. This concentration is considerably lower than that measured at the outlet of the glacier because the pond receives a much larger proportion of its water from the dilute supraglacial meltwaters than from the concentrated subglacial meltwaters. Our cyclic salt sulfate correction would represent 20% of the sulfate in sample AF183.

Table 2. $\delta^{34}\text{S}$ values of NBS standards together with water and rock samples collected in the Upper Manso Watershed in January and February 1991. All $\delta^{34}\text{S}$ values relative to the Canyon Diablo troilite.

	$\delta^{34}\text{S}$ (‰)
Sulfide samples	
NBS-123 sphalerite standard	17.3
Surficial pyrite coating on metamorphic rock	2.53
Pyrite vein	2.60
Dispersed pyrite crystals in metamorphic rock	1.41
Elemental sulfur samples	
Crystalline sample No. 1	-4.80
Duplicate	-4.71
Amorphous sample No. 2	-4.31
Replicate	-4.27
Replicate	-4.55
Water samples precipitated as BaSO_4	
Upper Manso Stream, site UMP, AF183	4.7
NBS-127 seawater BaSO_4 standard	20.9

Precipitation and side tributaries were not isotopically analyzed due to the very low SO_4 concentrations. However, the Pacific Ocean, which is only $\sim 70 \text{ km}$ away, is the source for practically all the moisture, and presumably SO_4 , falling in the catchment. Oceanic inputs of sulfur into the atmosphere are believed to be mainly from sea-salt aerosols and biogenically produced dimethyl sulfide gas (DMS) (Charlsson et al. 1987). The $\delta^{34}\text{S}$ value of sea-salt aerosols can be assumed equivalent to seawater (20–22‰) (Chukhrov et al. 1980). However, the $\text{SO}_4 : \text{Cl}$ molar ratio in the local precipitation is between 1 and 3, indicating that all the SO_4 is nonsea-salt sulfur (Table 1). Sea-salt $\text{SO}_4 : \text{Cl}$ ratios are $\ll 1$. Nonsea-salt sulfur (nss- SO_4) is composed of oceanic DMS and terrestrial sulfur inputs. Some fractionation is believed to occur during biogenic formation of DMS in the ocean, which has led to estimates of the $\delta^{34}\text{S}$ value of marine DMS between 16 and 20‰ (Wadleigh 1989). These estimates have been confirmed by recent measurements by Calhoun et al. (1991) of $\delta^{34}\text{S}$ of marine nss- SO_4 (15.6 ± 3.1 ‰) from the South Pacific Ocean which they attributed to marine DMS. Although terrestrial biogenic inputs to the atmosphere can have very negative $\delta^{34}\text{S}$ values (-32 to -6 ‰) (Nielsen 1974), there should be little terrestrial biogenic input, since the distance over which the marine moisture has to travel before it gets to the Manso catchment

Chillrud et al.

Table 3. Simple mass balance of sulfate sources to the Upper Manso Stream. A rainwater $\delta^{34}\text{S}$ value of 15‰ was assumed. All the water comes from precipitation—pyrite oxidation adds sulfate to the water that is already present.

Inputs	$\delta^{34}\text{S}$ (‰)	Water added (%)	μmol SO_4 added liter^{-1}	Sulfate mixture (%)
Atmospheric input	15	100	12.5	19.5
+ pyrite oxidation	2.2	0	51.5	80.5
= Stream SO_4	4.7	100	64	100

is only 70 km. Furthermore, marine moisture is thought to be more important in high mountain areas; this is reflected in the more positive $\delta^{34}\text{S}$ values (up to values $\sim +16\text{‰}$) compared to surrounding lowlands (Chukhrov et al. 1980). Continental lowland-type precipitation typically has less positive $\delta^{34}\text{S}$ values (i.e. between +1 and +5‰) (Chukhrov et al. 1980).

The Upper Manso $\delta^{34}\text{S}$ value of 4.7‰ rules out evaporite deposits as the source of SO_4 because seawater values throughout all of geologic time range from +10 to +30‰ (Holser and Kaplan 1966). Likewise, local native sulfur (avg, -4.6‰) can be ruled out as the source of the SO_4 because too much rainwater sulfate would be required to balance the light signal of the elemental sulfur. The most reasonable source of the SO_4 is the oxidation of pyrite plus some atmospheric inputs. Table 3 displays the results of mixing rainwater sulfate

with the oxidation products of pyrite. Mixing would require that 20% of the sulfate (12.5 μM) of water sample AF183 came from the atmosphere and the rest from the oxidation of pyrite (avg $\delta^{34}\text{S}$, 2.2‰). This result agrees well with our sulfate cyclic salt correction of $13 \pm 5 \mu\text{M}$ SO_4 .

Pyrite oxidation is apparently absent in the Castaño Overo and Alerce subdrainages; atmospheric cyclic salt inputs can account for all of their sulfate. The average SO_4 concentrations at sites CO and AL from samples taken over a 30-month period are $13 \pm 8 \mu\text{M}$ ($n = 10$) and $9 \pm 6 \mu\text{M}$ ($n = 5$). These stream waters have $\text{SO}_4:\text{Cl}$ ratios between one and three, which is very similar to the precipitation samples.

Phosphorus and iron hydroxides—P, located in accessory minerals, is ubiquitously found in continental rocks at concentrations of $\sim 0.2\%$ (Henderson 1982). The factors that control the levels of dissolved phosphate in natural waters have been of interest to scientists for years because of the role of P as an essential nutrient. Interactions of P with surfaces of naturally occurring Fe and Al oxides are thought to be important because these surfaces are particularly reactive toward phosphate. The release and capture of P has been investigated in freshwater systems that have strong redox gradients (i.e. lakes and rivers—Caraco et al. 1989; Elser et al. 1990 and references therein).

Table 4. Phosphorus data during austral summer months from the Upper Manso catchment. Sample sites are shown on Fig. 1. (na = not analyzed.) The February 1990 SRP data points (in parentheses) for sites CO+AL and AL (where SRP represents only 3.3–6.7% of the TP) are poor data for the following reason. In February 1990, the major ions indicate that 70% of CO+AL is from CO, but the SRP data, if valid, indicate that CO+AL either did not mix conservatively or was totally dominated by AL. At other sampling times, the assumption of conservative mixing of streams CO and AL to form CO+AL usually results in the SRP and the major ion data giving very similar mixtures, with the flow from CO accounting for anywhere from 40 to 70% of the CO+AL.

Sample site	Jan 1990			Feb 1990			Jan 1991					
	TP (μM)	SRP (μM)	SRP:TP (%)	TP (μM)	SRP (μM)	SRP:TP (%)	TP (μM)	SRP (μM)	SRP:TP (%)	TFe (μM)	SO_4 (μM)	Susp. Sed. (mg liter^{-1})
UMP/UM1	5.29	0.18	3.4	8.92	0.01	0.1	4.39	0.23	5.2	64.2	177	92±6
UM2	3.99	0.13	3.3	10.6	0.04	0.4	4.21	0.20	4.8	69.8	178	102±7
UM3	3.43	0.16	4.7	10.1	0.05	0.5	3.77	0.21	5.6	50.8	151	68±11
UM4	na	na	na	8.45	0.14	1.7	3.59	0.16	4.5	na	144	55±9
UM5	na	0.31	na	6.44	0.01	0.2	2.44	0.18	7.4	na	103	43±14
UM6	9.32	0.14	1.5	4.75	0.08	1.7	3.06	0.13	4.2	36.7	95	na
CO	na	0.57	na	2.17	0.69	31.8	2.44	0.65	26.6	41.4	6.9	68±4
AL	0.45	0.13	28.9	0.75	(0.05)	(6.7)	0.47	0.12	25.5	4.19	2.9	11±8
CO+AL	1.28	0.33	25.8	1.52	(0.05)	(3.3)	1.73	0.34	19.7	22.1	3.7	36±1
CL	na	na	na	na	na	na	0.13	0.029	22.3	0.21	17	0.2
CQ+EM	na	na	na	na	na	na	0.42	0.28	66.7	7.25	31	5.4

Subglacial chemical weathering

Our study investigates the capture of P in glacial meltwater streams in which strong redox gradients are absent. Currently, we have TP data only from the 1990 and 1991 austral summers (Table 4). The difference between the Upper Manso Stream and the streams draining the two smaller glaciers is not so much in their absolute SRP or TP concentrations as in the SRP:TP ratio (i.e. what percentage of their TP is in the dissolved state). We interpret this ratio as indicating how much phosphate, after being released during weathering, has been sorbed. In this system, iron hydroxides appear to be the dominant species to which the phosphate is sorbed. Thus, a low SRP:TP ratio implies a high amount of sorption (and a relatively large concentration of iron hydroxides). The Upper Manso Stream (sites UMP, UM1, UM2), which drains the Manso Glacier, has relatively low SRP and a very low percentage of its TP in the dissolved state. The SRP:TP ratios of the streams draining the two smaller glaciers (sites CO, AL, and CO + AL) indicate that a lower percentage of the weathered phosphate is being sorbed in these streams, resulting in higher or slightly higher concentrations of SRP than in the Upper Manso Stream (sites UM1-UM6, UMP). The large differences in the SRP:TP ratios are not simply a function of the amount of suspended sediment in each stream, since there is a much smaller difference in suspended sediment concentrations than there is in SRP:TP (Table 4).

In January 1991, samples were collected for TFe analyses also (Fig. 4). The Upper Manso Stream has high TFe and SO_4 concentrations and a low percentage of P in the dissolved state (~5%). The smaller meltwater streams (Castaño Overo, Alerce, Castaño Overo + Alerce) have very low sulfate concentrations, lower TFe concentrations, and a much higher percentage of their P in the dissolved state (19–26%). These data are consistent with pyrite oxidation and subsequent precipitation of iron hydroxides controlling the SRP concentrations in these streams. High SO_4 concentrations indicate large amounts of pyrite oxidation and the subsequent precipitation of iron hydroxides which removes SRP from solution. Low sulfate levels indicate a relative lack of pyrite oxidation and iron hydroxide precipitation, thus allowing much higher percentages of the phosphorus to remain in the dissolved state. Particulate Fe:

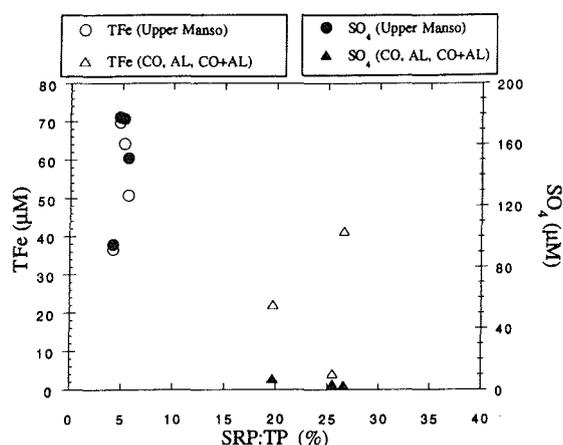


Fig. 4. TFe and SO_4 vs. SRP:TP in meltwater streams of Manso catchment for January 1991.

P ratios fall between 12 and 23—typical for P bound to iron hydroxide surfaces (Fox 1989).

Pyrite oxidation controlling riverine SRP is the reverse of a recently proposed mechanism for the control of SRP concentrations in lakes with strong redox gradients in their sediments (Caraco et al. 1989; Curtis 1989). In lakes with high SO_4 concentrations, Fe(III) hydroxide particles and dissolved SO_4 are reduced in anoxic sediments, allowing the resultant Fe(II) to be precipitated and trapped as FeS while the P, which was bound to iron hydroxides, is released from the sediments and diffuses into the overlying water column.

Ge:Si ratios and iron hydroxyoxides—Ge weathers from aluminosilicate minerals of continental rocks where it is “camouflaged” as a trace replacement for Si in mineral lattice sites (Goldschmidt 1958). In freshwaters, the dominant species of Ge and Si are the undissociated inorganic acids, $\text{Ge}(\text{OH})_4$ and $\text{Si}(\text{OH})_4$ (Froelich et al. 1985; Mortlock and Froelich 1987), hereafter referred to as dissolved Ge (Ge_D) and dissolved Si (Si_D). Froelich et al. (1992 and unpubl. data) estimated an average natural $\text{Ge}_D:\text{Si}_D$ continental weathering ratio of 0.54×10^{-6} , with a range from (0.1 to 1.7) $\times 10^{-6}$ in the dissolved loads of over 200 uncontaminated global rivers, significantly depleted below the average continental crustal ratio ($\text{Ge}:\text{Si} \sim 1.4 \times 10^{-6}$).

The $\text{Ge}_D:\text{Si}_D$ of rivers and groundwaters should be controlled by the ratio in the primary minerals undergoing dissolution plus any frac-

Chillrud et al.

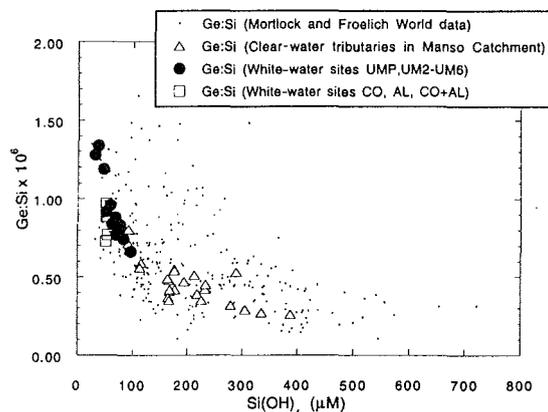


Fig. 5. $Ge_D:Si_D$ vs. Si_D for samples taken in austral summer 1990 from the Manso catchment, including all of its clear-water tributaries, and for uncontaminated river samples (Mortlock and Froelich 1987 and unpubl. data) of the world. Each site in the Manso catchment was sampled 1–2 times in summer 1990.

tionation effects occurring during formation of secondary aluminosilicate minerals and (or) any preferential sorption reactions to the surfaces of suspended solids. Mortlock and Froelich (1987) found a general lack of evidence for the predicted mineralogical control of fluvial $Ge_D:Si_D$ ratios and suggested the operation of an unidentified bulk fractionation process during weathering and transport of Ge and Si in rivers. They further conjectured that anomalously low $Ge_D:Si_D$ ratios could be due to sorption to iron hydroxide surfaces in the suspended solids because coprecipitation of Ge with iron hydroxides was an early analytical technique for analyzing Ge_D in seawater (Burton et al. 1959), and hematite deposits can be greatly enriched in Ge (Bernstein 1985). Murnane and Stallard (1990) analyzed Ge:Si in bedrock, suspended sediments, and the dissolved load of rivers in the Orinoco drainage basin, and found that only streams draining mafic lithologies display a distinctive $Ge_D:Si_D$ signature. Through use of a partition model, they related $Ge_D:Si_D$ in river waters to chemical weathering intensity of silicate rocks, defined as the fraction of Si that is removed from the bedrock (primary minerals) and stays in the dissolved state. Murnane and Stallard (1990) thus discovered the importance of the clay mineral fractionation effect which causes $Ge_D:Si_D < (Ge:Si)_{bedrock}$ since $(Ge:Si)_{clay} > (Ge:Si)_{bedrock}$.

Our $Ge_D:Si_D$ data from the entire Manso catchment (including all clear-water and white-water side tributaries) falls in the envelope of the data for uncontaminated rivers of the world (Mortlock and Froelich 1987 and unpubl. data) (Fig. 5). Even though the Upper Manso catchment is very small, these data display almost the same range in $Ge_D:Si_D$ ratios as the world data set. The samples from the meltwater stream of the Manso Glacier (UMP, UM1, UM2) have the highest $Ge_D:Si_D$ ratios in the catchment. The samples from the other two glacial meltwater streams (CO, CO + AL, AL) also have relatively elevated $Ge_D:Si_D$ ratios in comparison to the other tributaries (clear-water streams without glacial meltwater sources). Our $\delta^{34}S$, P, and TFe data all indicate that considerable concentrations of freshly precipitated iron hydroxides exist on the surfaces of the suspended sediments of the Upper Manso Stream. This circumstance together with the elevated $Ge_D:Si_D$ ratios provides strong evidence, albeit indirect, that Ge_D does not show a tendency to sorb preferentially to iron hydroxide surfaces in the neutral to slightly acidic pH ranges found in these waters. This impartiality of Ge_D is consistent with the findings of Mortlock and others (pers. comm.) that the oxidation of Fe in the oxic layer of the Black Sea has virtually no impact on $Ge_D:Si_D$ ratios and the current models of Murnane and Stallard (1990) and Froelich et al. (1992) in which weathering intensity controls $Ge_D:Si_D$ ratios.

Conclusions

The stable isotopes, TFe, and dissolved SO_4 data give strong evidence that pyrite oxidation occurs beneath only one of the three glaciers in the Upper Manso catchment, providing a natural setting in which to study the effects of iron hydroxides in the suspended solids material. Our data are consistent with pyrite oxidation and subsequent precipitation of iron hydroxides controlling the amount of TP as SRP within these streams. High SO_4 indicates large amounts of pyrite oxidation and subsequent precipitation of iron hydroxides which remove SRP from solution, resulting in low SRP:TP ratios. Low SO_4 levels indicate a relative lack of pyrite oxidation and iron hydroxide precipitation and so allow a much greater proportion of the TP to be in the dissolved

Subglacial chemical weathering

state. Contrary to previous arguments (Mortlock and Froelich 1987) that low $Ge_D:Si_D$ ratios in rivers could be due to preferential sorption of Ge_D to surfaces of iron hydroxides in the suspended and bedload sediments, $Ge_D:Si_D$ ratios are high in all three glacial meltwater streams and highest in the Upper Manso Stream where pyrite oxidation and a relatively large amount of subsequent iron hydroxide precipitation occur.

References

- AMERICAN PUBLIC HEALTH ASSOCIATION. 1985. Standard methods for examination of water and wastewater, 16th ed. APHA.
- BERNER, R. A., A. C. LASAGA, AND R. M. GARRELS. 1983. The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.* **283**: 641-683.
- BERNSTEIN, L. R. 1985. Germanium geochemistry and mineralogy. *Geochim. Cosmochim. Acta* **49**: 2409-2422.
- BURTON, J. D., F. CULKIN, AND J. P. RILEY. 1959. The abundances of gallium and germanium in terrestrial materials. *Geochim. Cosmochim. Acta* **16**: 151-180.
- CALHOUN, J. A., T. S. BATES, AND R. J. CHARLSON. 1991. Sulfur isotope measurements of submicrometer sulfate aerosol particles over the Pacific Ocean. *Geophys. Res. Lett.* **18**: 1877-1880.
- CANFIELD, D. E., R. RAISWELL, J. T. WESTRICH, C. M. REAVES, AND R. A. BERNER. 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chem. Geol.* **54**: 149-155.
- CARACO, N. F., J. J. COLE, AND G. E. LIKENS. 1989. Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems. *Nature* **341**: 316-318.
- CHARLSSON, R. J., J. E. LOVELOCK, M. O. ANDREAEE, AND S. G. WARREN. 1987. Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. *Nature* **326**: 655-661.
- CHUKHROV, F. V., L. P. ERMILOVA, S. CHURIKOV, AND L. P. NOSIK. 1980. The isotopic composition of plant sulfur. *Org. Geochem.* **2**: 69-75.
- COLLINS, D. N. 1979. Quantitative determination of the subglacial hydrology of two Alpine glaciers. *J. Glaciol.* **23**: 347-362.
- CURTIS, P. J. 1989. Effects of hydrogen ion and sulphate on the phosphorus cycle of a Precambrian Shield lake. *Nature* **337**: 156-158.
- DREVER, J. I., AND D. R. HURCOMB. 1986. Neutralization of atmospheric acidity by chemical weathering in an alpine drainage basin in the North Cascade Mountains. *Geology* **14**: 221-224.
- ELSER, J. J., E. R. MARZOLF, AND C. R. GOLDMAN. 1990. Phosphorus and nitrogen limitation of phytoplankton growth in the freshwaters of North America: A review and critique of experimental enrichments. *Can. J. Fish. Aquat. Sci.* **47**: 1468-1477.
- EWING, G. W. 1981. Titrate with electrons. *Am. Lab.* **1981**(Jun): 16-22.
- FOX, L. E. 1989. A model for inorganic control of phosphate concentrations in river waters. *Geochim. Cosmochim. Acta* **55**: 1529-1538.
- FROELICH, P. N., AND OTHERS. 1992. River fluxes of dissolved silica to the ocean were higher during glacials: Ge/Si in diatoms, rivers, and oceans. *Paleoceanography* **7**: 739-767.
- , G. A. HAMBRICK, M. O. ANDREAEE, AND R. A. MORTLOCK. 1985. The geochemistry of inorganic germanium in natural waters. *J. Geophys. Res.* **90**: 1133-1141.
- GALLOPIN, G. C. 1978. Estudio ecológico integrado de la Cuenca del Río Manso Superior (Río Negro, Argentina) 1—Descripción general de la cuenca. *In An. Parques Nacl. Rep. Argent.* **14**: 161-230.
- GOLDSCHMIDT, V. M. 1958. *Geochemistry*. Oxford.
- HALLET, B. 1976. Deposits formed by subglacial precipitation of calcite. *Geol. Soc. Am. Bull.* **87**: 1003-1015.
- HAMBRICK, G. A., P. N. FROELICH, M. O. ANDREAEE, AND B. L. LEWIS. 1984. Determination of methylgermanium species in natural waters by graphite furnace atomic absorption spectrometry with hydride generation. *Anal. Chem.* **56**: 421-424.
- HENDERSON, P. 1982. *Inorganic geochemistry*. Pergamon.
- HOLSER, W. T., AND I. R. KAPLAN. 1966. Isotope geochemistry of sedimentary sulfates. *Chem. Geol.* **1**: 93-135.
- JUNGE, C. E., AND P. E. GUSTAFSON. 1957. On the distribution of sea salt over the United States and its removal by precipitation. *Tellus* **9**: 164-173.
- KELLER, W. D., AND A. L. REESMAN. 1963. Glacial milks and their laboratory-simulated counterparts. *Geol. Soc. Am. Bull.* **74**: 61-76.
- KOROLEFF, F. 1983. Determination of nutrients, p. 134-135. *In* K. Grasshoff et al. [eds.], *Methods of seawater analyses*. Verlag Chemie.
- LEMMENS, M., AND M. ROGER. 1978. Influence of ion exchange on dissolved load of alpine meltwaters. *Earth Surface Processes* **3**: 179-187.
- MARTIN, J. M., AND M. MEYBECK. 1979. Elemental mass-balance of material carried by major world rivers. *Mar. Chem.* **7**: 173-206.
- MORTLOCK, R. A., AND P. N. FROELICH. 1987. Continental weathering of germanium: Ge/Si in the global river discharge. *Geochim. Cosmochim. Acta* **51**: 2075-2082.
- , AND ———. 1989. A simple method for the rapid determination of biogenic opal in pelagic marine sediments. *Deep-Sea Res.* **36**: 1415-1426.
- MURNANE, R. J., AND R. F. STALLARD. 1990. Germanium and silicon in rivers of the Orinoco drainage basin. *Nature* **344**: 749-752.
- MURPHY, J., AND J. P. RILEY. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* **27**: 31-36.
- NIELSEN, H. 1974. Isotope comparison of major contributors to atmospheric sulfur. *Tellus* **26**: 213-218.
- PEDROZO, F., S. CHILLRUD, P. TEMPORETTI, AND M. DIAZ. 1993. Chemical composition and nutrient limitation in rivers and lakes of northern Patagonian Andes (39.5°-42°S; 71°W) (Rep. Argentina). *Int. Ver. Theor. Angew. Limnol. Verh.* **25**: 207-214.
- RAISWELL, R. 1984. Chemical models of solute acquisition in glacial melt waters. *J. Glaciol.* **30**: 49-57.

Chillrud et al.

- REYNOLDS, R. C., AND N. M. JOHNSON. 1972. Chemical weathering in the temperate glacial environment of Northern Cascade Mountains. *Geochim. Cosmochim. Acta* **36**: 537-544.
- RUBULIS, S. 1978. Una comparación de los valores de evaporación para tanque tipo "A" y tanque tipo "Young," en la estación hidrometeorológica "Lago Mascardi," Parque Nacional Nahuel Huapi, Rio Negro, Argentina. *An. Parques Nacl. Rep. Argent.* **14**: 333-336.
- RYE, D. M., AND N. WILLIAMS. 1981. Studies of the base metal sulfide deposits at McArthur River, Northern Territory, Australia: 3. The stable isotope geochemistry of the H. Y. C., Ridge, and Cooley deposits. *Econ. Geol.* **76**: 1-5.
- STALLARD, R. F., AND J. M. EDMOND. 1981. Geochemistry of the Amazon. 1. Precipitation chemistry and the marine contribution to the dissolved load at the time of peak discharge. *J. Geophys. Res.* **86**: 9844-9858.
- TABATABAI, M. A. 1974. A rapid method for determination of sulfate in water samples. *Environ. Lett.* **7**: 237-243.
- WADLEIGH, M. A. 1989. Geochemical characterization of coastal precipitation: Natural versus anthropogenic sources. Ph.D. thesis, McMaster Univ.
- WESTRIDGE, J. T. 1983. Consequences and controls of bacterial sulfide reduction in marine sediments. Ph.D. thesis, Yale Univ.
- ZHABINA, N. N., AND I. I. VOLKOV. 1978. A method of determination of various sulfur compounds in sea sediments and rocks, p. 735-745. *In* W. E. Krumbein [ed.], *Environmental biogeochemistry*. Ann Arbor Sci.

Submitted: 16 November 1992

Accepted: 10 August 1993

Amended: 22 September 1993

