

## **Chemical weathering in the South Cascade Glacier basin, comparison of subglacial and extra-glacial weathering**

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**Abstract** The cationic denudation for South Cascade Lake drainage basin was calculated to be  $676 \text{ meq m}^{-2} \text{ year}^{-1}$ , somewhat less than previous estimates. The denudation rate was estimated for both the subglacial and extra-glacial waters that comprise the total basin runoff. Subglacial waters have a significantly higher yield than extra-glacial waters (between approximately  $800$  and  $2380 \text{ meq m}^{-2} \text{ year}^{-1}$  for subglacial waters, and  $580 \text{ meq m}^{-2} \text{ year}^{-1}$  for extra-glacial waters). All yields for the basin are higher than the reported world average of  $190 \text{ meq m}^{-2} \text{ year}^{-1}$  for chemical erosion (Meybeck, 1979). Although total cation yields are similar for South Cascade Glacier basin and a tropical watershed with similar area, runoff, and geology, the proportions of dissolved constituents are markedly different. Subglacial waters have unusually high K/Na and Ca/Na ratios, and very low dissolved Si. This appears to be typical of waters draining warm-based glaciers.

### **INTRODUCTION**

During the past 30 million years the Earth's climate has undergone a gradual cooling. Models such as that presented by Berner *et al.* (1983) indicate that this cooling is linked to a reduction in atmospheric  $\text{CO}_2$ . Raymo *et al.* (1988) have argued that enhanced chemical weathering in tectonically active areas may have lowered atmospheric  $\text{CO}_2$  over the past few million years.

Atmospheric  $\text{CO}_2$  has typically been even lower during periods of widespread glaciation (Barnola *et al.*, 1987). Although it is generally accepted that the amount of physical erosion during continental glaciations is extensive (up to 200 m physically eroded from the Laurentide region in the last 2 ma [Bell & Laine, 1985]), the extent of chemical denudation due to glaciation is harder to characterize. Recent work by Gibbs & Kump (1994) tries to quantify the effect of this chemical erosion, and its influence on the  $\text{CO}_2$  budget.

The basal temperature regime of glaciers and ice sheets determines the degree of glacial erosion (Sugden, 1978; Kump & Alley, 1994). Little or no physical erosion is associated with cold-based ice, whereas warm-based ice is associated with significant scouring. Approximately 30% of the present land area was glaciated during the height of the last glaciation (Kump & Alley, 1994). During this maximum, the area of warm-based ice was probably extensive (Sugden, 1978).

There have been at least three studies of chemical denudation in alpine catchments with warm-based glaciers (Reynolds & Johnson, 1972; Eyles *et al.*, 1982; Sharp *et al.*, 1995). All three studies found accelerated rates of cationic denudation relative to world average (930, 947, and between 640 and 845 meq m<sup>-2</sup> year<sup>-1</sup>, respectively, as compared to 190 meq m<sup>-2</sup> year<sup>-1</sup> (Meybeck, 1979, Tables 1 and 8) for the world average). At least the first two studies, however, included in their denudation calculations the chemistry of streams draining both glacierized and nonglacierized portions of the catchments and therefore may not be indicative of strictly subglacial processes.

In this paper we estimate solute yields for South Cascade Glacier basin, the same basin studied by Reynolds & Johnson (1972). The denudation rate calculated by Reynolds & Johnson (1972) was based on the chemistry and discharge of South Cascade Lake, which is a composite of both glacial (streams draining the glacier directly) and extra-glacial (marginal stream draining non-ice-covered portions of the catchment) waters. In the last 30 years, South Cascade Glacier has receded about 450 m (see Fig. 15 in Krimmel, 1994), exposing streams that drain the glacier. Because glacial waters can now be sampled directly, it is possible to estimate the fractional contribution of glacial and extra-glacial waters that comprise South Cascade Lake. This approach provides a technique for estimating solute yields directly attributable to subglacial chemical weathering. This is an essential step if the marine geochemical record is to be used to characterize the extent and environmental effect of glaciations in the past.

## STUDY AREA

South Cascade Glacier is a small temperate glacier located in the North Cascade Mountains of Washington. The glacier basin is 6.142 km<sup>2</sup> in area, and in 1992, 2.089 km<sup>2</sup> of the basin was occupied by glacier, and another 0.4 km<sup>2</sup> by nonglacier ice (Krimmel, 1993). The topography of the basin is steep, ranging from 1615 to 2518 m in elevation, and vegetation is sparse. The bedrock consists of banded magmatite, hornblende-biotite-quartz diorite, hornblende-quartz-plagioclase gneiss, biotite-quartz schist, and amphibolite (Tabor, 1961).

South Cascade Glacier has been the focus of on-going glaciological studies by the U.S. Geological Survey and others since 1957. Numerous studies of glacier hydrology have been published (see Fountain, 1992, 1993, 1994; Vaughn, 1994; and others), and water budgets and mass balances for the glacier dating back to 1958 have been documented (Tangborn *et al.*, 1975; Krimmel, 1989). The U.S. Geological Survey has maintained a gage at the outlet of South Cascade Lake since 1957, and on Middle Tarn since June 1992 (Fig. 1). The average temperature in the basin is 1.3°C, and precipitation commonly reaches 4.5 m year<sup>-1</sup> (mean water equivalent), and falls mainly as snow during the winter months (Meier *et al.*, 1971). For the water year of the present study, 1992, the glacier had a mass balance of -2.01 m (water equivalent) averaged over the surface of the glacier, and the combination of precipitation and ablation resulted in approximately 3.9 m of runoff (Krimmel, 1993).

In 1992, three streams (Streams 2, 3, and 4) drained the terminus of the glacier (Fig. 1). Streams 3 and 4 issued out of adjacent ice caves at the glacier snout and flowed for several hundred meters through glacial debris before entering Middle Tarn. Stream 2 was exposed for several hundred meters along the east margin of the terminus and then re-emerged at the snout and discharged directly into Middle Tarn.

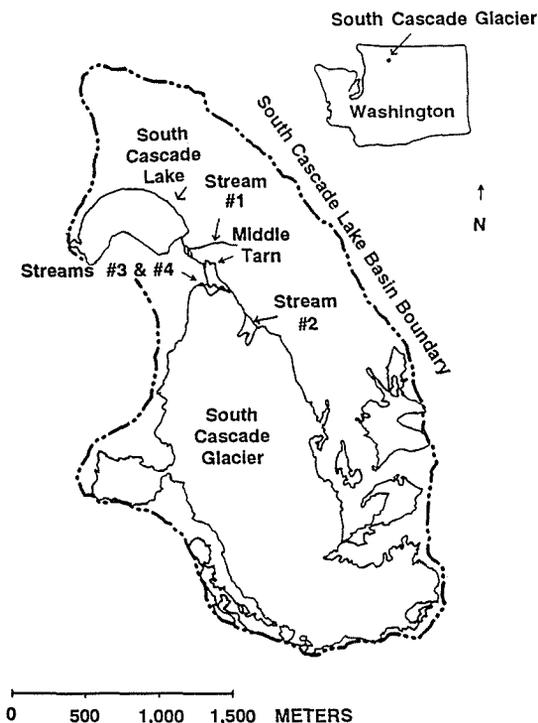


Fig. 1 Map of South Cascade Glacier basin (after Krimmel, 1993). Locations of subglacial Streams 2, 3, and 4, as well as extra-glacial Stream 1 are noted.

## METHODS

In August 1992, approximately 100 water samples were collected from within South Cascade basin. These included hourly samples taken over a 24-h period from the three glacial streams (2, 3, and 4, Fig. 1), grab samples from those three streams taken at very low flow, as well as grab samples from the outlet of South Cascade Lake and from extra-glacial marginal streams on both the east and west flanks of the basin (Fig. 1). Samples of firn, snow, glacier ice, and precipitation were also collected.

All water, ice, and snow samples were filtered on site through 0.22- $\mu\text{m}$  cellulose acetate filters. Samples for trace and major element analysis were preserved by acidifying to 1% with ultrapure  $\text{HNO}_3$ . Samples for nutrient analysis were preserved with chloroform, and samples for anion analysis were kept cold. All samples were transported on ice to the laboratory for chemical analysis. Conductivity, temperature, and pH were all measured in the field.

$\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$  were analyzed by ion chromatography. Silica was analyzed colorimetrically.  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{Mg}^{2+}$  were analyzed by Inductively Coupled Plasma Emission Spectrometry, and  $\text{K}^+$  by flame Atomic Absorption Spectrometry. Alkalinity was measured using the Gran plot method on an autotitrator. Charge balance errors for the water analyses averaged approximately 3% (the difference between the sum of the positive and negative charges, divided by the mean of the positive and negative charges).

A continuous record of stage is available for the period of this study for Middle Tarn, at 15-min intervals, and from the outlet of South Cascade Lake, at 60-min intervals (Krimmel, 1993). Stage measurements were also made during our field study on Streams 2, 3, and 4 using stilling wells with float and counterweight pulley systems recorded on a data logger (data in Vaughn, 1994). In addition to stage, conductivity was recorded continually in all three streams during the study period.

A complete record of discharge is available only for South Cascade Lake for the entire 1992 water year. In order to estimate solute yields for both the extra- and subglacial components of the basin, it is necessary to calculate a best estimate fractional contribution of the various waters that comprise South Cascade Lake based on solute chemistry. Linear least squares analysis (after Stallard, 1987) was used to obtain these best estimates.

End-member components were selected by choosing representative waters from around the basin that were chemically dissimilar. Because there is a clear diel trend in both chemistry and discharge related to the daily melt cycle of the glacier, discharge weighted mean concentrations were calculated for the 24-h sampling of the three glacial streams.

Various combinations of possible end-members were tried. The selected end-members could also be combined to create historical lake chemistry published in Reynolds & Johnson (1972) and Hurcomb (1984). Stream 3 was not used as an end-member because its chemistry could be calculated as a mixture of waters from Streams 2 and 4. The chemistry of Stream 1 was chosen as representative of extra-glacial waters, and the average chemistry of several headwall streams (fed by perennial ice and snow fields) was taken as representative of that part of the basin.

The calculation of solute yields is summarized in the Appendix, and the results are presented in Table 1. For comparison, runoff and constituent yields from the Icacos River basin (a tropical watershed in Puerto Rico of similar size, bedrock, and runoff) are included (from McDowell & Asbury, 1994). The tropical stream appears to be typical of streams from high-runoff areas on silicate rocks (Stallard, 1995).

## RESULTS

The results of the linear-least-squares analysis indicate that the chemistry of South Cascade Lake can be produced by mixing 17% extra-glacial water (Stream 1), 71% Stream 2 water, and 12% Stream 4 water. The cationic denudation rate calculated for the entire South Cascade Glacier basin was  $676 \text{ meq m}^{-2} \text{ year}^{-1}$  (Table 1).

Chemical weathering yields were calculated for each of the end-member waters. The cationic denudation rate calculated for extra-glacial streams (Stream #1 end-member) was  $579 \text{ meq m}^{-2} \text{ year}^{-1}$ . Dethier (1975) calculated a rate of  $600 \text{ meq m}^{-2} \text{ year}^{-1}$  for a nearby subalpine catchment (not glacierized) in the Cascades. Denudation rates were also calculated for the two subglacial streams (Streams 2 and 4). Stream 2 had a rate of  $799 \text{ meq m}^{-2} \text{ year}^{-1}$ , close to but less than the rate calculated by Reynolds & Johnson (1972) for the whole catchment ( $930 \text{ meq m}^{-2} \text{ year}^{-1}$ ). The cationic denudation rate for Stream 4 was calculated as  $2381 \text{ meq m}^{-2} \text{ year}^{-1}$ , a rate over twice as high as those reported by Reynolds & Johnson (1972), Eyles *et al.* (1982), and Sharp *et al.* (1995). It is important to note that our denudation rates are based on stream chemistry sampled

**Table 1** Concentrations and yields of sub-basins within the South Cascade Lake basin compared to the Icaos River of Puerto Rico.

		South Cascade Lake	Stream 1, extra- glacial	Headwall Streams	Stream 2, subglacial	Stream 4, subglacial	Icaos River
Concentrations:							
Sodium	$\mu\text{eq l}^{-1}$	6.3	16.0	5.2	2.5	16.6	44.7
Potassium	$\mu\text{eq l}^{-1}$	18.2	17.7	13.9	9.7	36.7	8.8
Magnesium	$\mu\text{eq l}^{-1}$	13.7	19.0	15.0	8.3	12.7	21.4
Calcium	$\mu\text{eq l}^{-1}$	60.5	130.8	61.3	35.0	107.8	59.8
Alkalinity	$\mu\text{eq l}^{-1}$	130	243	98	83	274	240
Sulfate	$\mu\text{eq l}^{-1}$	16.3	41.0	32.9	7.9	8.2	-0.5
Silica	$\mu\text{mol l}^{-1}$	17.1	62.7	16.0	4.3	6.1	219.7
Nitrate	$\mu\text{eq l}^{-1}$	0.9	5.1	1.4	1.4	-0.2	4.9
Cations	$\mu\text{eq l}^{-1}$	173	333	172	99	294	216
Yields:							
Runoff	$\text{meq m}^{-2} \text{ year}^{-1}$	3.90	1.74	1.74	8.09	8.09	3.68
Basin Area	$\text{meq m}^{-2} \text{ year}^{-1}$	6.1	2.3	1.7	1.8	0.3	3.3
Sodium	$\text{meq m}^{-2} \text{ year}^{-1}$	27	28	9	20	135	164
Potassium	$\text{meq m}^{-2} \text{ year}^{-1}$	71	31	24	78	297	33
Magnesium	$\text{meq m}^{-2} \text{ year}^{-1}$	53	33	26	67	102	82
Calcium	$\text{meq m}^{-2} \text{ year}^{-1}$	236	227	107	283	872	220
Alkalinity	$\text{meq m}^{-2} \text{ year}^{-1}$	507	423	171	674	2221	883
Sulfate	$\text{meq m}^{-2} \text{ year}^{-1}$	64	71	57	64	67	-2
Silica	$\text{mM m}^{-2} \text{ year}^{-1}$	67	109	28	35	49	809
Nitrate	$\text{meq m}^{-2} \text{ year}^{-1}$	4	9	2	11	-2	18
Cations	$\text{meq m}^{-2} \text{ year}^{-1}$	676	579	299	799	2381	801

Cyclic salt corrections utilized the ratio of the constituent to  $\text{Cl}^-$ . For South Cascade Glacier the ratios are,  $\text{Na}^+ = 0.852$ ;  $\text{K}^+ = 0.165$ ;  $\text{Mg}^{2+} = 0.101$ ;  $\text{Ca}^{2+} = 0.166$ ; alkalinity =  $-1.376$ ;  $\text{Cl}^- = 1.000$ ;  $\text{SO}_4^{2-} = 0.964$ ;  $\text{Si}(\text{OH})_4 = 0.000$ ;  $\text{NO}_3^- = 0.000$ . For the Icaos River of Puerto Rico,  $\text{Na}^+ = 0.852$ ;  $\text{K}^+ = 0.018$ ;  $\text{Mg}^{2+} = 0.101$ ;  $\text{Ca}^{2+} = 0.019$ ; alkalinity =  $-0.144$ ;  $\text{Cl}^- = 1.000$ ;  $\text{SO}_4^{2-} = 0.127$ ;  $\text{Si}(\text{OH})_4 = 0.000$ ;  $\text{NO}_3^- = 0.000$ .

over a short period of time, late in the ablation season. Others (Brown & Tranter, 1990; Tranter *et al.*, 1993) have documented seasonal changes in the chemistry of glacial streams, and Reynolds & Johnson's (1972) work averaged lake chemistry over a year-long period. Clearly, our rates could be refined by including seasonal samples. Our analysis of Reynolds and Johnson's (1972) data indicates a somewhat greater contribution of Stream 1-type extra-glacial water (mean of 31%) in 1971 compared to in 1992 (17%).

The chemistry of the glacial waters draining South Cascade Glacier is quite distinct from the Icaos River, which drains a tropical watershed of similar size and bedrock lithology (Table 1). Although total cation yields, after cyclic salt correction, are similar for the South Cascade and the Icaos River, constituent proportions are very different (Fig. 2). In streams draining nonglacierized basins with high runoff, cation dominance is typically  $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$  with the  $\text{K}/\text{Na}$  ratio generally less than 1. In the extra-glacial streams in South Cascade Glacier basin we observe  $\text{Ca} \gg \text{Na}$ , and in subglacial waters the  $\text{K}/\text{Na}$  ratio is greater than 2. Waters draining South Cascade Glacier, like waters draining other warm-based glaciers (Keller & Reesman, 1963; Church, 1974; Eyles *et al.*, 1982), have an unusually high  $\text{K}/\text{Na}$  ratio that has been attributed to the

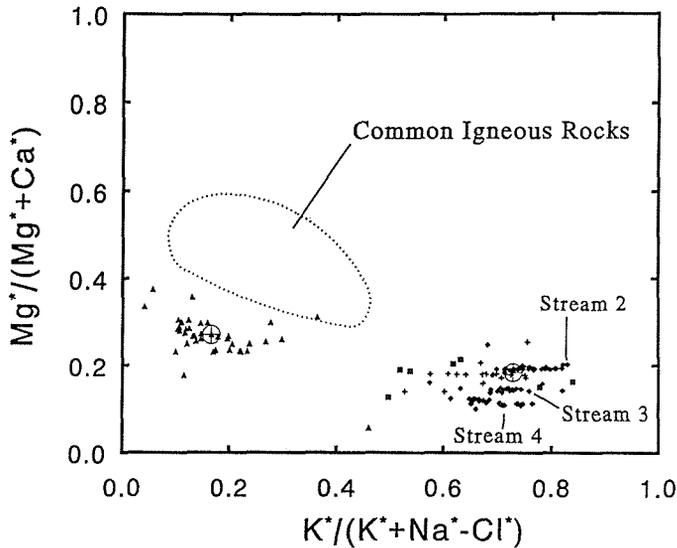


Fig. 2  $Mg^*/(Mg^* + Ca^*)$  compared to  $K^*/(K^* + Na^* - Cl^{1*})$  for glaciated and nonglaciated terrains in the South Cascade Glacier basin and warm-climate terrains of the Icosos River basin of Puerto Rico. The "\*" indicates cyclic-salt correction. The oval field represents complete cation leaching from common igneous rocks (Stallard, 1995). ■: extra-glacial streams in the South Cascade basin; ◆: glacial streams; ⊕: South Cascade Lake (data from Reynolds & Johnson, 1972; Hurcomb, 1984; and this study); ▲: Icosos River and tributaries (data from McDowell & Asbury, 1994, and Stallard & Axtmann, unpublished). The representative values for the Icosos River and South Cascade Lake used in calculations are indicated by ⊕. The three streams that drain the glacier form distinct clusters that are labeled.

weathering of biotite (Hurcomb, 1984; Drever & Hurcomb, 1986). The same authors note the high Ca/Na ratio and attribute it to the presence of calcite in the basin.

In tropical streams, the Si/Ca ratio is quite high. In all South Cascade waters, this ratio was extremely low. Considering that overall Ca solute yields are similar for both watersheds, the dissolved Si yields are remarkably low in the South Cascade Glacier basin, especially in subglacial waters.

We conclude that chemical weathering under glaciers is as effective as for nonglacial watersheds with a similar runoff. Individual constituent yields are remarkably different, however. Especially notable are greatly diminished yields of Si and increased yields of K.

Future work will entail including trace elements and their isotopes, notably Sr and Ge, in this model (see Stallard, 1995), and refining the calculations presented in this paper to include historical South Cascade Lake data. We anticipate being able to more precisely characterize the chemical weathering processes in both subglacial and extra-glacial settings.

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## APPENDIX

The calculation of the fractional contribution of end-member waters to South Cascade Lake was based on solute chemistry. Linear least squares analysis was used to obtain these estimates (method is outlined in detail in Stallard, 1987). The regression requires that all fractional discharges total 1.0.

Having estimated the fractional contribution of water from extra-glacial (17%), Stream 2 (71%) and Stream 4 (12%) end-members, these proportions were used to calculate runoff and chemical yields associated with the end members.

The following variables are known; area of South Cascade Lake basin (6.142 km<sup>2</sup>) and runoff from the basin (3.9 m year<sup>-1</sup>), area of the glacier (2.089 km<sup>2</sup>) (values from Krimmel, 1993), area of Middle Tarn basin (including the glacier and headwalls above the glacier – 3.8 km<sup>2</sup>) (Vaughn, 1994), and by difference, the area of headwalls (1.711 km<sup>2</sup>), and area of South Cascade Lake basin that is not ice covered (2.342 km<sup>2</sup>).

The following assumptions have been made; the runoff of Streams 2 and 4 are equal (runoff is discharge per unit area, therefore the assumption is that discharge from the glacier is a function of basin area), the runoff from headwall streams is equal to runoff from the other ice-free portions of the basin.

### Calculation of the runoff for Streams 2, 4, and extra-glacial waters

- (i) The fractional contribution to South Cascade Lake *discharge* from each end member is calculated using the results of the linear least squares estimate, and dividing by the basin area of each end member:

*for extra-glacial waters:*

$$0.17 * (3.90 \text{ m year}^{-1} * 6.142 \text{ km}^2) \div 2.342 \text{ km}^2 = 1.739 \text{ m year}^{-1}$$

*for Streams 2 and 4:*

$$0.83 * (3.90 \text{ m year}^{-1} * 6.142 \text{ km}^2) \div 3.8 \text{ km}^2 = 5.232 \text{ m year}^{-1}$$

- (ii) Separate out marginal headwall streams from the discharge of Streams 2 and 4 (assuming that the runoff from headwall streams is equal to the runoff of extra-glacial waters in the basin as calculated in (i) above);

*discharge of headwall streams:*

$$1.739 \text{ m year}^{-1} * 1.711 \text{ km}^2 = 2.975 \text{ m km}^2 \text{ year}^{-1}$$

*discharge of combined glacial streams:*

$$5.23 \text{ m year}^{-1} * 3.8 \text{ km}^2 = 19.882 \text{ m km}^2 \text{ year}^{-1}$$

subtract the headwall streams component of discharge from the discharge of glacial streams to arrive at the strictly subglacial component, and calculate runoff by dividing by the glacier area;

$$(19.882 - 2.975) \div 2.089 \text{ km}^2 = 8.09 \text{ m year}^{-1}$$

The chemistry of Streams 2 and 4 was corrected for input from the headwall runoff. These corrected values are reported in Table 1.