

# Relation between soil age and silicate weathering rates determined from the chemical evolution of a glacial chronosequence

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## ABSTRACT

Long-term weathering rates ( $R_{LT}$ ) were determined from base cation depletion in soil profiles developed on six granitic glacial moraines varying in age from 0.4 to  $\geq 297$  ka in the Wind River Mountains, Wyoming. Weathering rates were found to decrease with soil age ( $t$ ) according to the power-law equation  $R_{LT} = 215 \cdot t^{(-0.71)}$ , where  $R_{LT}$  is in  $\text{meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ , and  $t$  is in ka. Comparable data from the literature are consistent with this function, and it is similar to power-law equations describing changes in laboratory weathering rates with time. On the basis of our study, we predict that for a catchment unaffected by anthropogenic inputs and in a steady state with respect to the organic and cation exchange pools,  $R_{LT}$  should be higher than present-day weathering rates derived from stream fluxes ( $R_{PD}$ ) by a factor of about 3.4.

## INTRODUCTION

Studies of base cation depletion from soil profiles of known age have allowed quantification of long-term weathering rates, which are an important factor in understanding soil nutrient availability, the acid neutralizing capacity of soils, marine geochemical cycles, and atmospheric  $\text{CO}_2$  consumption by silicate weathering. Many factors, including climate, vegetation, mechanical erosion, parent material composition, and soil age, affect rates of chemical weathering. Previous studies have investigated soils developed on glacial moraines deposited by continental ice sheets, which provide weathering rates at a single time interval (April et al., 1986; Kirkwood and Nesbitt, 1991), or soils developed on fluvial or marine terraces, which can be problematic because sedimentary deposits are commonly density sorted and do not represent pristine parent material (Bain et al., 1993; Harden, 1987; Merritts et al., 1992). Present-day weathering rates have also been measured from catchment solute fluxes but do not provide information on changes in rates with time (e.g., Mast et al., 1990; Sharp et al., 1995). Our goal in this study was to isolate the effects of soil age on weathering rates by holding other factors as constant as possible to document changes in weathering rates that may have occurred over a wide area on

the North American and Eurasian shields immediately following global glaciations.

We measured base cation release from six soil profiles developed on alpine glacial moraines with ages varying from 0.4 to  $\geq 297$  ka, which form a soil chronosequence (Jenny, 1980) in the Fremont Creek drainage basin in the northern Wind River Mountains, Wyoming. Bedrock and glacial deposits in the drainage consist entirely of Archean granite and gneiss typical of the continental shield rocks, and the area has glacial deposits and soils that have previously been described, mapped, and dated (Richmond, 1973; Mahaney and Halvorson, 1986; Sorenson, 1986; Gosse et al., 1994; Blum and Erel, 1995).

## STUDY AREA AND METHODS

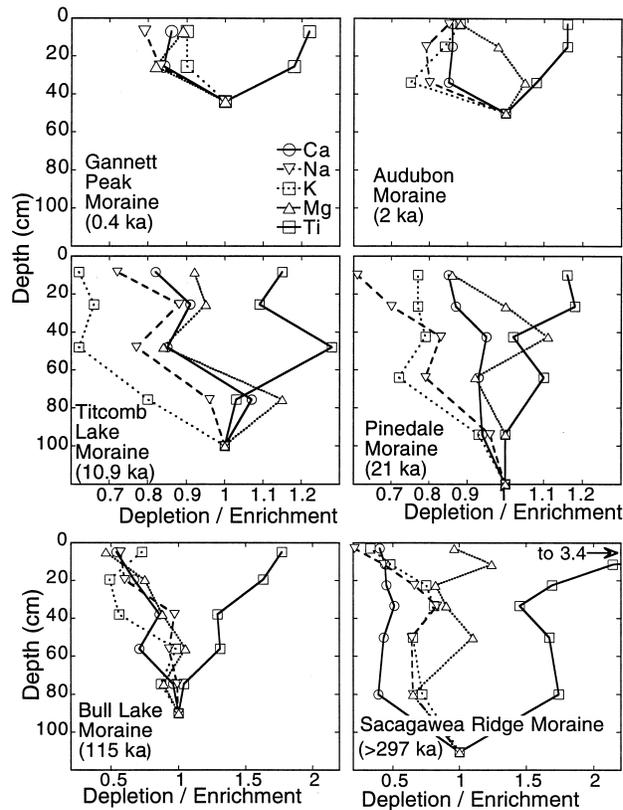
Soil profiles from the Gannett Peak, Audubon, and Titcomb Lake moraines were sampled in the Titcomb basin at elevations of 3440 to 3230 m. These moraines were mapped by Mahaney and Halvorson (1986), who correlated the Gannett Peak till with the "Little Ice Age," for which the global historic record indicates maximum glacial advances between 0.3 and 0.5 ka (Imbrie and Imbrie, 1979), and the Audubon till with the Audubon glacial advance, which is dated by  $^{14}\text{C}$  at 1.5–2.5 ka (Mahaney and Halvorson, 1986). The Titcomb Lake till was dated by  $^{10}\text{Be}$  at 10.4–11.4 ka (Gosse et al., 1994). Soil profiles from the Pinedale and Bull Lake moraines were sampled near Fremont Lake at elevations of 2315 and 2285 m. These moraines were mapped by Richmond (1973) and dated by  $^{10}\text{Be}$  at 19.5–22.5 and

96–133 ka, respectively (Gosse et al., 1994). A soil of pre-Bull Lake age was sampled at an elevation of 2555 m in Surveyor Park near Fremont Lake. This area was mapped as Sacagawea Ridge till by Richmond (1973); we consider its origin and age to be uncertain, constrained only to  $\geq 297$  ka by  $^{10}\text{Be}$  (Gosse et al., 1994). Average annual temperature and precipitation are 1.8 °C and 230 mm at Fremont Lake and are estimated to be  $-3.5$  °C and 500–700 mm at the Titcomb basin (Mahaney and Sanmugadas, 1983; Mahaney and Halvorson, 1986). The three high-elevation profiles are above timberline and vegetation is dominated by perennial sedges and grasses; the three low-elevation profiles are from vegetation zones dominated by sagebrush.

The soil parent material (i.e., tills) for each of the profiles is a mixture of Archean granite, granodiorite, and diorite gneiss that crop out throughout the drainage basin (Worl et al., 1984). The primary minerals observed in optical and scanning electron microscope (SEM) analysis of the deepest (unweathered) sample from each soil profile are (in order of decreasing abundance): plagioclase ( $\text{An}_{7-36}$ ), quartz, biotite, K-feldspar, hornblende, and magnetite. Minor amounts ( $<1\%$ ) of pyroxene, garnet, apatite, titanite, muscovite, and chlorite were also found in some samples. Secondary clay minerals in the  $<2$   $\mu\text{m}$  size fraction include kaolinite, vermiculite, illite, and smectite (Mahaney and Halvorson, 1986). All six soil profiles sampled were collected adjacent to profiles described in detail by Mahaney and Sanmugadas (1983), Mahaney and Halvor-

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**Figure 1. Enrichment and depletion factors for base cations in six soil profiles plotted vs. depth in each profile.**



son (1986), Sorenson (1986), and/or Shroba (1989), and therefore descriptions will not be repeated here.

Soil pits were dug to 60–120 cm depth until till material that was visibly unweathered and contained clasts without weathering rinds was reached. Within each soil pit, ~2 kg samples were taken over ~10 cm intervals. Samples were dried at 50 °C, sieved through a 2 mm mesh, and weighed. A ~100 g aliquot of each <2 mm sample was powdered, and ~50 mg was fused for 1 min on a molybdenum-filament strip heater under 275 KPa of argon (e.g., Fedorowich et al., 1993) and then quenched to a glass, and polished for analysis. The major element composition of the glass was determined by energy dispersive X-ray analysis (EDX) using a Zeiss DSM-962 SEM. Pure oxide standards were used for all elements except sodium, for which albite was used. For each sample, three 1 mm<sup>2</sup> areas were analyzed by rastering the electron beam for 200 s, corrected using a ZAF procedure, normalized to 100% total oxides, and then averaged. To test the accuracy and precision of the analytical method, we fused and analyzed a granodiorite standard KQM nine times during our analysis of the soil samples and compared the results with the accepted composition of KQM. Both the standard deviation of the replicate analyses and the variation between the EDX values and the KQM

standard values are less than 6%. Na<sub>2</sub>O agreed within 0.6%, indicating that there was no significant sodium volatilization during the fusion.

Long-term chemical weathering rates ( $R_{LT}$ ) were calculated for each soil profile by comparing soil analyses with the deepest (unweathered) sample for each profile; Ti was used as the immobile index element (e.g., April et al., 1986; Merritts et al., 1992; Bain et al., 1993). First, we calculated the depletion factor ( $x_{i,j}$ ) for the <2 mm fraction of each soil sample based on the equation  $x_{i,j} = (C_{i,j}/C_{i,p})/(T_i/T_p)$ , where  $C_{i,j}$  is the concentration of element  $i$  in soil slice  $j$ , and  $T_i$  and  $T_p$  are the concentrations of Ti in the weathered and parent materials, respectively. Second, we calculated the chemical inventory of each element in the <2 mm fraction of each soil slice that would have been in a 1 m<sup>2</sup> column prior to any weathering ( $S_{i,j}$ ) on the basis of the equation  $S_{i,j} = (C_{i,p})(\rho)(F_j)(T_j)$ , where  $C_{i,p}$  is the concentration in the parent material,  $\rho$  is the parent material density (we used the average measured  $\rho$  of 2.0 g·cm<sup>-3</sup>),  $F_j$  is the weight fraction of <2 mm material, and  $T_j$  is the thickness of the soil slice. Third, values for  $S_{i,j}$  were summed over each soil pit to get a total initial inventory for each element ( $I_i$ ). Fourth, we calculated the present-day inventory of each element from each soil slice ( $L_{i,j}$ ) on the basis of the equation  $L_{i,j} = (x_{i,j})$

( $S_{i,j}$ ), and summed  $L_{i,j}$  over each soil profile to get the total amount of each element present in each soil profile ( $P_i$ ). Fifth, the amount weathered ( $W_i$ ) was calculated for each element in each profile on the basis of the equation  $W_i = I_i - P_i$ , and  $W_i$  was divided by the age of the soil profile to yield  $R_{LT}$  for each base cation. Our calculations are dependent on the assumptions that (1) the deepest sample from each profile and each of the >2 mm soil fractions are not significantly weathered; (2) Ti is immobile in granitic soils; (3) there have not been significant additions of eolian material; and (4) there has not been significant lateral transport or erosion of soil. The first assumption was verified by optical and SEM observations; the second has been generally documented in the literature (e.g., Gardner, 1980; April et al., 1986); the third has been verified by Dahms (1993), who observed that <5% of the heavy minerals in the 20–50  $\mu$ m size fraction of the B-horizons of these soils came from eolian sources; and the possibility of lateral transport or erosion was minimized by sampling only flat summit sites on moraine crests.

## RESULTS AND DISCUSSION

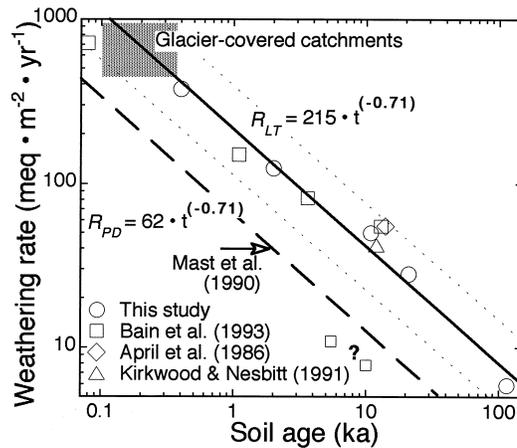
The average composition of the deepest (unweathered) samples in weight percent is SiO<sub>2</sub> (69.2), Al<sub>2</sub>O<sub>3</sub> (15.9), CaO (3.20), Na<sub>2</sub>O (3.52), K<sub>2</sub>O (2.55), MgO (1.15), FeO<sub>total</sub> (3.48), and TiO<sub>2</sub> (0.55). In profiles of the moraines (Fig. 1), Ca, Na, K, and Mg show a general decrease toward the surface; most depletion factors range from 1 to 0.5. Ti increases in concentration toward the top of each profile, consistent with the assumption that Ti is immobile (Fig. 1). In general, the overall amount of base cation depletion at the top of the profiles increases with increasing soil age. The present-day chemical inventories for the base cations in each soil profile are listed in Table 1, along with the amount lost by weathering, which increases with soil age.

Variables other than soil age that may influence weathering rates include temperature, precipitation, and vegetation. We contend that each of these factors is relatively constant among the three profiles in the Titcomb basin and among three profiles near Fremont Lake. However, the Fremont Lake profiles are in an area of lower precipitation and higher temperature than the Titcomb basin profiles. To assess the importance of this climate difference, we calculated the difference in predicted weathering rates between the two sites on the basis of the relation between modern-day granitic catchment weathering rates and climate (White and Blum, 1995), which suggests that the de-

TABLE 1. CATION INVENTORIES IN THE SOIL PROFILES

Moraine	Age (ka)	Present inventory (mol/m <sup>2</sup> )					Amount weathered (mol/m <sup>2</sup> )				
		Ca	Na	K	Mg	total(+)	Ca	Na	K	Mg	total(+)
Gannett Peak	0.4	138	233	118	84	795	25	55	13	15	148
Audubon	2.0	231	488	194	152	1448	40	122	46	1	250
Titcomb Lake	10.9	550	1150	459	244	3197	45	218	215	8	539
Pinedale	21.0	658	1499	645	247	3954	57	328	144	5	596
Bull Lake	115	404	680	328	281	2378	133	155	125	65	676
Sacagawea	>297	310	629	415	237	2138	431	425	227	32	1578

Figure 2. Log-log plot of base cation weathering rates vs. soil age. Data points are long-term weathering rates ( $R_{LT}$ ) from this study and literature. Dark solid line is curve fit to data from this study ( $R = 0.99$ ). Light dotted lines bracket curve fit to data and represent estimated maximum uncertainties of factor of two in weathering rates. Question mark indicates two points from Bain et al. (1993) that are suspect on basis of high Zr contents of parent materials. Dashed line represents present-day weathering rates ( $R_{PD}$ ) calculated from solid curve. Arrow represents  $R_{PD}$  measured by Mast et al. (1990); shaded area represents range of fluxes in glacier-covered catchments compiled by Sharp et al. (1995).



creased precipitation and increased temperature would approximately offset one another, and thus there would be no significant climatically induced difference in weathering rates.

The weathering rates for all of the base cations decrease with increasing soil age (by factors of 30–100), providing constraints on the relation between  $R_{LT}$  and soil ages over the age interval of 0.4 to 115 ka. We estimate that uncertainties in weathering rates (due to analytical error and soil heterogeneity) are less than a factor of two. Values for  $R_{LT}$  and soil age (Fig. 2) vary from 370  $\text{meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  for the 0.4 ka profile to 5.9  $\text{meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  for the 115 ka profile. Cation depletion studies of soils developed on granitic glacial moraines in the Adirondack Mountains (northeastern United States) yielded  $R_{LT}$  values of 45 to 62  $\text{meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  for 14 ka soils (April et al., 1986), and in Ontario (Canada) yielded a  $R_{LT}$  value of 42  $\text{meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  for 12 ka soils (Kirkwood and Nesbitt, 1991); all plot close to the trend established in this study (Fig. 2). A cation depletion study of soils developed on six fluvial terraces in Scotland ranging in age from 0.08 to 13 ka (Bain et al., 1993) yielded four values for  $R_{LT}$  close to the trend established by our data, but two terraces, which have anomalously high parent material Zr contents, yielded much lower  $R_{LT}$

values (Fig. 2), perhaps due to heterogeneity of zircon in the fluvial sediments.

The data presented here suggest that there is a power-law relation between  $R_{LT}$  and soil age over the 0.4 to 115 ka time scale described by the equation  $R_{LT} = 215 \cdot t^{(-0.71)}$ , where  $R_{LT}$  is in  $\text{meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ , and  $t$  is the age in ka. This relation is, however, specific to the precipitation-temperature regimes of the studied soils, which are estimated to vary by less than 50% and 5°C, respectively, among the four sites compared in Figure 2; these differences translate into a difference of less than a factor of two in predicted cation fluxes, on the basis of the model of White and Blum (1995). The data from the literature plotted in Figure 2 are consistent with this correlation within an uncertainty in the  $R_{LT}$  of less than a factor of two (Fig. 2). Harden (1987) observed a similar power-law relation between soil age and the clay content of soils in granitic fluvial deposits spanning the 10 to 3000 ka time scale. A power-law relation of the form  $R = k \cdot t^{(-0.5)}$ , where  $k$  is a constant, has also been used to describe the dependence of feldspar weathering with time in the initial stages of laboratory weathering experiments (e.g., Busenburg and Clemency, 1976). The explanation for the power-law relation is probably a combination of several mechanisms, including changes in mineral surface area, de-

pletion of reactive mineral surfaces, and exhaustion of rapidly weathered minerals. The function strictly applies only to the temperate climatic regime of the study areas from which it was derived; however, we believe it is likely that a power-law relation also exists in other climatic settings, but that the position of the curve would be shifted according to the relation between weathering rate and climate (White and Blum, 1995).

To proceed to a discussion of how present-day (or stream flux derived) weathering rates ( $R_{PD}$ ) compare with our empirically derived equation for long-term rates ( $R_{LT}$ ), we must transform the y axis of Figure 2 from  $R_{LT}$  to  $R_{PD}$ . Given that  $R_{LT} = k \cdot t^{-n}$ , and  $R_{PD} = (1/t) \int_0^t R_{PD}(t') dt'$ , by differentiation one can derive the relation  $R_{PD}/R_{LT} = 1 - n$ . Thus, for the data from this study we get:  $R_{PD} = 62 \cdot t^{(-0.71)}$  (Fig. 2). Mast et al. (1990) measured  $R_{PD}$  as 39  $\text{meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  in a granitic alpine catchment in the Rocky Mountains that is mostly active talus slopes and has temperature and rainfall similar to those of the Titcomb basin (Fig. 2). The average age of weathering surfaces in this active mechanical weathering regime is unknown, but it is younger than 15 ka, which is when the watershed was last deglaciated. The average surface age predicted by the curve in Figure 2 is 2 ka, which seems to us a reasonable estimate. We have also plotted estimates of values for the  $R_{PD}$  in partially glacier-covered catchments compiled by Sharp et al. (1995) which range from 450 to 950  $\text{meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ . The precipitation in these four catchments ranges from 2.5 to 8 times higher than in the Titcomb basin; therefore, on the basis of the relation between precipitation and the  $R_{PD}$  (White and Blum, 1995), we would expect the curve relating  $R_{PD}$  to soil age to be shifted toward higher values of  $R_{PD}$  by a factor of two to four. This coincidentally shifts the  $R_{PD}$  curve in Figure 2 to approximately the position of the  $R_{LT}$  curve. Accounting for this shift, the  $R_{PD}$  values from glacier-covered catchments would correspond to average surface ages of about 100 to 350 yr (Fig. 2), which seems to be a reasonable estimate in these actively glaciated regimes.

## IMPLICATIONS

The results of this study provide insight into the effect that global glaciations (e.g., Sharp et al., 1995) and variations in tectonic uplift rates (e.g., Raymo and Ruddiman, 1992) may have on the flux of dissolved cations to the oceans and rates of  $\text{CO}_2$  consumption by silicate weathering. On the basis of our work, we estimate that the  $R_{LT}$  over the past 15 ka (the period since the last major glaciation) was 3.4 times higher than

the  $R_{PD}$ , suggesting that rates of  $\text{CO}_2$  consumption by silicate weathering for glaciated shield areas based on riverine fluxes may be 3.4 times lower than the actual long-term average rate since glaciation. The strong dependence of the  $R_{LT}$  and  $R_{PD}$  on soil ages also suggests that increased uplift rates, which reduce the average age of weathering surfaces, should accelerate chemical weathering. For example, a tenfold decrease in the average surface age should translate into about a five-fold increase in weathering rates.

Several studies have suggested that acid deposition has accelerated the  $R_{PD}$  over values of the  $R_{LT}$  (Folster, 1985; April et al., 1986; Bain et al., 1993; Miller et al., 1993). We have shown that weathering rates are not constant with time as a soil develops, and we suggest that this should be considered when assessing the impacts of acid deposition. Even in a watershed unaffected by acid deposition and in a steady state with respect to the organic and exchangeable base cation pools, we calculate from the curve in Figure 2 that the  $R_{PD}$  should be lower than the  $R_{LT}$  by a factor of about 3.4, regardless of the soil age. Consideration of this factor in the interpretation of previously published data has the effect of enhancing the magnitude of the acceleration of weathering rates that has been proposed to have been caused by acid deposition.

Our results also support the hypothesis that global glaciations have the effect of increasing continental Sr fluxes to the oceans during periods of glacial-interglacial cycling, and may play a role in increasing the marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (Hodell et al., 1989). For example, one can compare the predicted values for the  $R_{LT}$  from a 1000 ka surface ( $1.6 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ ), which is an estimate of the average age of soils in continental areas unaffected by glaciations, with a 100 ka surface ( $8 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ ), which is an estimate of the maximum age of soils on the continental shields glaciated during Pleistocene time (assuming one major glacial advance and retreat per 100 ka). This fivefold difference suggests that the  $R_{LT}$  (and atmospheric  $\text{CO}_2$  consumption by silicate weathering) would be higher during periods of glacial-interglacial cycling than during nonglacial periods, but the magnitude of the change is difficult to estimate at the present time because of uncertainties in changes in global temperature and precipitation patterns during glacial periods and difficulties in estimating weathering fluxes from ice-covered continental shield areas.

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