

# Biogeochemistry of Glacial Landscape Systems

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## Key Words

glaciers, silicate weathering, carbonate weathering, loess,  
continental margin, paraglacial, erosion, carbon cycle

## Abstract

Glaciers affect biogeochemistry of landscapes through their sediments. Glacial erosion rates are high and the sediments produced are distinctively fine grained, hence glaciers can be thought of as producers of mineral surface area. Although this mineral surface area is highly reactive, temperature limits chemical weathering fluxes from glaciers and their surroundings. More significant effects may be associated with silt deposited in loess and on continental margins. Thick deposits in both settings contribute to carbon cycling through both silicate weathering and organic carbon burial. The impact of glaciers on biogeochemical cycles will be long-lasting, as the legacy of glacial erosion processes continues as long as sediment yields are elevated.

## 1. INTRODUCTION

Glaciers profoundly impact the landscapes they override. U-shaped valleys, paternoster lakes, and striated bedrock are familiar signatures of glacial occupation. The sediments formed by glacial abrasion and plucking reside in till and moraines or are strewn far beyond the most advanced glacier positions in fluvial outwash and eolian loess deposits. Although glacial landforms, both erosional and depositional, are featured prominently in physical geography and geology textbooks, the geochemical impact of the wholesale rearrangement of landscapes by glaciers is not well known. We might expect the chemical impacts of glaciers to be as profound as their physical manifestations, given that glaciation affects all of the parameters that control chemical weathering rates: temperature, biological activity, physical erosion rates, and the amount and freshness of substrates undergoing weathering. The purpose of this review is to assemble our current understanding of weathering in broadly defined glacial landscapes—those regions affected by glaciers and glacial sediments—with the goal of inspiring an integrated view of the biogeochemical role of glaciers. The focus is particularly on the geochemical carbon cycle, and therefore on the role of glaciers in changing the global rate of CO<sub>2</sub> consumption by silicate weathering and in sequestration of organic carbon.

Glaciers play a key role in the linkages between uplift, weathering, and climate. Chemical weathering of silicate minerals is one important control on atmospheric CO<sub>2</sub> levels (Kump et al. 2000). The idea that uplift increases silicate chemical weathering fluxes (see sidebar) and draws down atmospheric CO<sub>2</sub> inspired a search for the tectonic stimulant that led to onset of late Cenozoic glaciation (see Ruddiman 1997). The uplift-weathering-climate change hypothesis (Raymo & Ruddiman 1992) raises the question of identifying tectonic events that precede climate deterioration, but also highlights the need to show how uplift impacts silicate weathering fluxes. Uplift of land surfaces to elevations above the snowline produces a mode-shift in erosion processes and rates from fluvial to glacial processes (Brozović et al. 1997) that can provide the means to change CO<sub>2</sub> consumption and carbon storage.

### WEATHERING FLUX

The weathering flux is the rate of mass loss in solution owing to chemical weathering reactions from a landscape or weathering profile. Weathering flux is controlled by landscape attributes such as the suite of minerals present, the mineral surface area exposed, depth and nature of surface water flow paths, vegetation, and climatic parameters such as temperature and water flux. Weathering flux differs from weathering rate, a term best reserved to describe the rate at which particular rocks or minerals dissolve or alter, normalized to the surface area of the mineral. The weathering flux is an appropriate measure from which to determine the CO<sub>2</sub> drawdown from the atmosphere associated with silicate weathering.

The weathering flux from a landscape can be viewed as resulting from the intrinsic weathering rate of minerals as tempered by external parameters. The term intrinsic weathering rate here refers to kinetics of particular mineral weathering reactions that can be considered an immutable material property, and whose control by mineralogy, temperature, pH, and solution saturation state are to some extent understood (White & Brantley 1995). In contrast, a landscape weathering flux, while at a fundamental level reflecting intrinsic mineral weathering rates, is a product of the geomorphic, geologic, and ecologic attributes of that landscape, such as access of water to mineral surfaces, water contact time, presence of organic acids or chelating agents, or mineral surface age. For this reason, weathering fluxes have been viewed as controlled by the supply of weatherable material and by weathering kinetics. The supply term primarily controls the length of time rock spends within the weathering zone (Waldbauer & Chamberlain 2005), and indirectly controls water access and its saturation state, whereas kinetic parameters such as temperature control intrinsic weathering rates (Kump et al. 2000). In this context, uplift is characterized in climate models as increasing the weatherability of landscapes (e.g., Kump & Arthur 1997), where weatherability is a measure of all effects other than temperature and rainfall on chemical weathering fluxes.

River water chemistry shows silicate weathering fluxes are high in tectonically active regions (West et al. 2005), an association attributed to the linkage between physical erosion rates and chemical weathering fluxes (Gaillardet et al. 1999, Millot et al. 2002, Jacobson et al. 2003, Riebe et al. 2004). The reasons that physical erosion rates are correlated with chemical weathering fluxes are less well understood. Most argue that high rates of physical erosion supply fresh rock to the weathering environment (Riebe et al. 2001, Waldbauer & Chamberlain 2005) and remove highly weathered material that isolates fresh rock from the weathering environment (Braun et al. 2005). Our understanding of how weathering and erosion are linked is largely based on empirical correlations rather than on predictive process-based models.

This review will focus on temperate glaciers (see Temperate versus Polar Glaciers sidebar). Glacial weathering systems of this sort are of interest because

## TEMPERATE VERSUS POLAR GLACIERS

Glaciers can be categorized by their thermal structures. Temperate glaciers are at the melting point throughout the ice mass, in contrast to polar glaciers in which the ice is below the melting point at the bed (Paterson 2003). Polythermal glaciers contain both temperate and polar ice. The presence of water at the bed of temperate glaciers allows basal sliding (see Clarke 2005), a much more efficient mode of ice motion than internal deformation, and a requirement for physical erosion of the glacier bed (e.g., Iverson 1990, 1991). Abrasion during sliding pulverizes rock, producing the rock flour characteristic of glacial erosion (Hooke & Iverson 1995). Polar glaciers perform insignificant erosion of the bed, and consequently do little geochemical work (Kump & Alley 1994).

**Paraglacial geomorphology:** the study of surface processes and landscapes directly conditioned by former glaciation and deglaciation

they are the high physical erosion rate landscape end-member and thus provide insight into the mechanisms that couple physical and chemical weathering processes. Alpine, temperate glaciers are the style of glaciation that will be instigated by tectonic uplift as growing mountain ranges intersect the snowline. Therefore, understanding the geochemical effects of this switch in surface processes associated with orogeny is important to evaluate the uplift-weathering-climate change hypothesis.

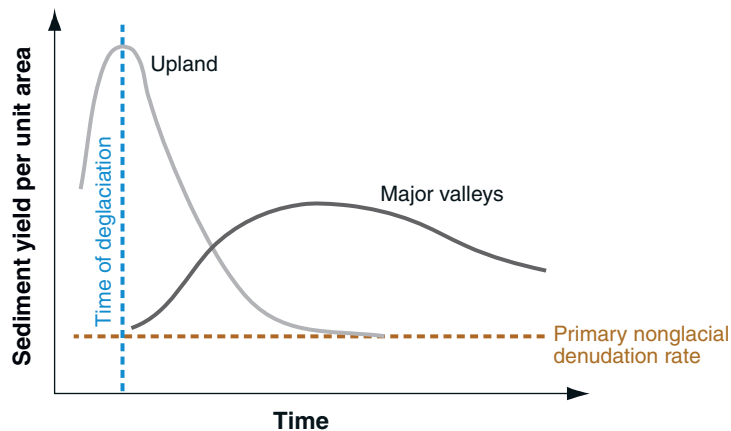
## 2. GLACIAL LANDSCAPE SYSTEMS

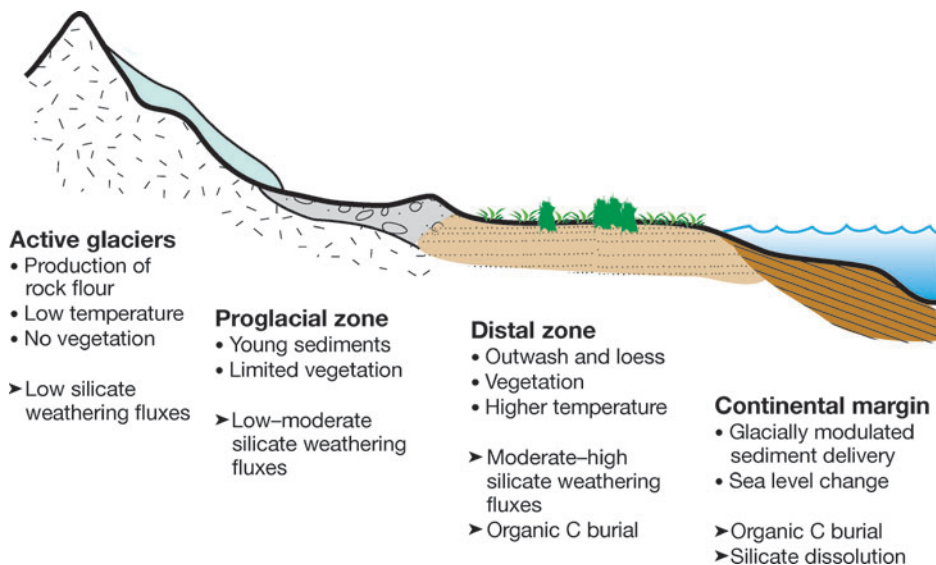
The glacial environment is one in which the supply of freshly eroded rock can be substantial. Sediment yields from temperate glaciers are up to an order of magnitude greater than from steep, mountainous catchments without glaciers (Hallet et al. 1996). Further, because glaciers erode by a combination of plucking and abrading bedrock, the sediment produced is poorly sorted, but it encompasses grain sizes ranging from clay to boulders (e.g., Hooke & Iverson 1995, Lee & Rutter 2004). Sediments produced by glacial erosion are deposited widely in environments from underneath the glacier itself to continental shelves. The range of depositional settings includes subglacial lodgement till, moraines at glacier margins, outwash beyond glacial limits, and deltas and glacialmarine deposits offshore.

Withdrawal of glaciers begins a new phase of landscape evolution in which steepened slopes relax, and glacial sediments and hillslope debris are reworked and move through valley systems. This evolution of landscapes following deglaciation is the purview of paraglacial geomorphology (Ballantyne 2002), which considers impacts of past glaciation on landforms and sediment yields. In general, the adjustment of hillslopes to withdrawal of glaciers occurs relatively rapidly (hundreds to thousands of years), whereas fluvial sediment loads are elevated for periods of as great as  $10^4$  years (Church & Slaymaker 1989, Dadson & Church 2005), a timescale that increases with basin size (**Figure 1**). Two important notions emerge from paraglacial geomorphology: Sediment yields in rivers reflect reworking of sediment rather than primary

**Figure 1**

Sediment yields during paraglacial time in different size basins. After Church & Ryder 1972, Ballantyne 2002.





**Figure 2**

Schematic overview of glacier-influenced landscapes, emphasizing broad depositional zones found between the glacial sediment source and its ultimate sink offshore.

physical erosion of bedrock and the influence of glaciers on landscapes extends for long periods after the glaciers have retreated. In summary, glacial influences on landscapes extend throughout the sedimentary system to which glaciers contribute and for periods of time well beyond the period of glaciation.

I use a highly simplified model of glacially conditioned landscapes as a framework for discussing biogeochemistry of glacial weathering systems (**Figure 2**). The sediment system is broken into four zones: the region underneath an active glacier, the formerly glacier-covered proglacial zone, the distal zone where terrestrial processes redistribute glacially produced sediment, and continental margin sediments. Weathering processes and rates are expected to differ within each of these settings owing to differences in environmental conditions, but the sediments that move through the system link the environments. I have kept to a highly simplified characterization of glacial landscapes relative to the highly developed “land systems” sedimentological models in existence (Evans 2003) because our understanding of chemical weathering and carbon storage in these settings does not merit greater refinement.

### 3. ACTIVE GLACIERS

Glaciers erode bedrock through a combination of abrasion and plucking, producing the sediment that feeds the glacial sediment system. Because of high erosion rate and fine-textured sediment, glacial erosion is a veritable mineral surface area production factory. The rate of surface area production,  $\dot{S}_{geo}$ , can be estimated for spheres or

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**Glacierized:** a landscape that contains one or more active glaciers

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cubes from erosion rate,  $\dot{E}$ , and grain size,  $D$ , as

$$\dot{S}_{geo} = 6\dot{E}A \sum_{i=1}^n \frac{f_i}{D_i}, \quad (1)$$

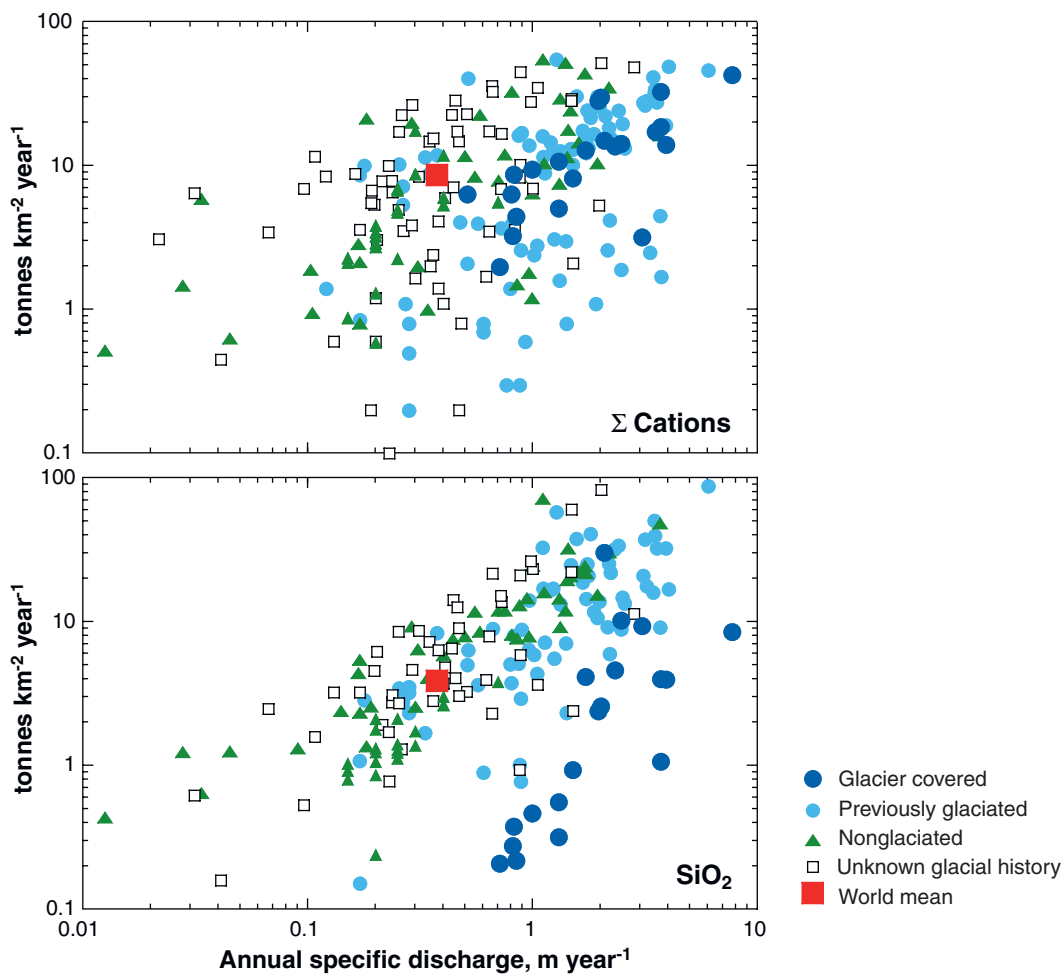
where  $A$  is the basin area and  $f_i$  is the volume fraction of each grain size class. For an erosion rate of  $1 \text{ mm year}^{-1}$ , and a grain size distribution of 25% coarse silt ( $62 \mu\text{m}$ ), 25% coarse clay ( $2 \mu\text{m}$ ), and 50% coarser than silt and therefore an insignificant contributor to mineral surface area, the surface area production rate is  $775 \text{ km}^2$  of mineral surface area per year per square kilometer of glacier area. Surface roughness, which can increase surface area by an order of magnitude or more above the geometric surface area calculated in Equation 1, is expected to be high for the indented and fractured grains produced by glacial abrasion (Mahaney & Kalm 2000).

The silt and clay produced by glacial abrasion contains primary minerals in near bedrock proportions, hence the high surface area associated with the finer grain size categories is weatherable surface area. Softer minerals are probably slightly enriched in the finest size fractions (Dreimanis 1976, Mahaney & Milner 1998, Fairchild et al. 1999a), but mineral fractionation by grain size is not always noted (e.g., Nesbitt & Young 1996). The substantial primary mineral surface area exposed by glacial erosion is the reason that subglacial chemical weathering rates have been fingered as significant players in global geochemical cycles (e.g., Armstrong 1971).

The first assessment of glacial chemical weathering fluxes was made for South Cascade Glacier, Washington. Reynolds & Johnson (1972) found cationic denudation rates “substantially higher than the world average” and concluded “low temperatures generally associated with an active glacier do not inhibit chemical weathering reactions.” Weathering fluxes have been measured at many other glaciers in the intervening years. Compilations of these studies show total cation fluxes generally in excess of the global mean, but dissolved silica fluxes are commonly lower than the global mean. Because the amount of water discharge exerts important control on dissolved flux (Collins & MacDonald 2004), it is most instructive to consider weathering fluxes as a function of water discharge (**Figure 3**). Plotted in this way, glacierized catchments are indistinguishable from nonglacierized catchments with respect to cation flux, but are distinctly lower in dissolved silica flux.

Several patterns emerge from studies of solute fluxes from glaciers (Tranter 2003): (a) carbonate dissolution dominates solute fluxes, (b) sulfide oxidation reactions are often significant contributors to solute fluxes, (c) silicate weathering fluxes are depressed, and (d) radiogenic strontium is released from glaciers.

Carbonate dissolution contributes more than half (in some cases substantially more than half) of the total solute flux from glaciers underlain by a variety of non-carbonate crystalline and sedimentary rocks, including gneiss and quartz diorite in the Cascade Mountains (Drever & Hurcomb 1986), schistose granite in the Alps (Sharp et al. 1995, Tranter et al. 2002), metasedimentary rocks in Alaska and New Zealand (Anderson et al. 2000, Jacobson et al. 2003), slate-dolomite-granodiorite in the Karakoram (Hodson et al. 2002), and granite and gneiss in the Alps (Hosein et al. 2004). In most of these examples, carbonate minerals comprise only a few percent of the bedrock. Although the dominance of carbonate dissolution on glacial solute



**Figure 3**

Flux of dissolved cations and dissolved silica versus annual specific discharge for a variety of catchment types. Plot based on Anderson et al. (1997), with additional data from Huh & Edmond (1999), Hodson et al. (2000, 2002), Anderson et al. (2003), and Hosein et al. (2004). World means based on Meybeck (1979).

fluxes can be linked in part to the roughly five orders of magnitude difference in rate constants between carbonate and silicate minerals, some aspects of the glacial environment are important as well. A disproportionate representation of calcite (hardness 3) in the finest size fraction of glacial sediment may contribute to the high carbonate dissolution fluxes from active glaciers. Although dissolution of carbonate can be limited by the availability of protons, particularly exhaustion of carbonic acid and its slow replenishment from dissolution of atmospheric CO<sub>2</sub>, this limit is not met where carbonate is a minor component (Fairchild et al. 1999a). Finally, calcite dissolution

is less sensitive to temperature effects than silicates. The activation energy for calcite dissolution of approximately 9 kJ/mol (Morse & Arvidson 2002) is two to six times lower than for silicate minerals; the slight reduction in rate constant may be offset by the increased solubility of CO<sub>2</sub> in colder water.

After carbonate dissolution, sulfide oxidation is the next most important process in subglacial environments. As was the case for carbonates, sulfide oxidation contributes to solute fluxes from glaciers to an extent greater than might be expected from mineral abundance. For instance, at Haut Glacier d'Arolla (Switzerland) on metamorphic silicate rocks, sulfate from sulfide oxidation comprises 14% of the solute flux (Sharp et al. 1995). Trace sulfides in metasediments at Bench Glacier (Alaska) were the source of 23% of the measured solute flux (Anderson et al. 2000). Trace sulfides in mixed volcanic, sedimentary, and metavolcanics at Kennicott Glacier (Alaska) were responsible for 10%–15% of the total solute flux (Anderson et al. 2003). The concentration of sulfate produced from sulfide oxidation at times exceeds the amount predicted from dissolved oxygen concentrations (Tranter et al. 2002, Anderson et al. 2003). It is likely that microbial populations at glacier beds (see Subglacial Microbiology sidebar) mediate this reaction (Bottrell & Tranter 2002, Skidmore et al. 2005), utilizing Fe(III) under anoxic conditions. Sulfide oxidation provides protons that drive additional carbonate dissolution, or in the absence of carbonates, silicate weathering. The global carbon role of weathering reactions driven by protons produced by sulfide oxidation rather than from carbonic acid produced by dissolution of atmospheric CO<sub>2</sub> is uncertain. At face value, sulfuric acid-driven weathering reactions do not contribute to carbon cycling. However, if Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions produced by coupled sulfide

## SUBGLACIAL MICROBIOLOGY

Viable microbial populations are found in glacial outlet streams (Sharp et al. 1999) and debris-rich basal ice (Skidmore et al. 2000) at cell densities comparable to that found in permafrost. Microbes are also found in ice cores (Campen et al. 2003), probably living in narrow water-filled veins rich in solutes found at ice crystal boundaries (Mader et al. 2006). Numbers of cells are correlated with sediment concentration in ice and stream water samples, suggesting that mineral grains provide metabolic substrates for microbes. Evidence that microbes mediate subglacial weathering reactions comes from a variety of observations. Reactions normally mediated by microbes, including production of sulfate under anoxic conditions (Bottrell & Tranter 2002, Tranter et al. 2002), oxidation of organic carbon (Fairchild et al. 1993) and denitrification, occur at glacier beds (Hodson et al. 2005). Isotopic evidence suggests that microbes also reduce sulfate in anoxic subglacial conditions (Wadham et al. 2004). The composition of subglacial microbial populations at two glaciers characterized with 16S rRNA genetic clone libraries showed a correlation between the metabolic pathways employed by phylogenetic groups and runoff geochemistry (Skidmore et al. 2005), which suggests that microbes control some glacial weathering fluxes.



oxidation-carbonate dissolution precipitate as gypsum (e.g., Darmody et al. 2000), then the  $\text{HCO}_3^-$  may return to the atmosphere, providing a source of atmospheric  $\text{CO}_2$ .

The low silica fluxes from glaciers (**Figure 3**) can be attributed to low temperature at glacier beds. Anderson (2005) revisited the apparent paradox of high mineral surface area production and low silicate mineral-derived weathering fluxes from glaciers. For Bench Glacier, a small temperate glacier on metagraywacke in Alaska, the measured dissolved silica flux and cation flux from silicate weathering reactions could be predicted from the physical erosion rate, grain size distribution, and mineral dissolution rate constants adjusted for the  $0^\circ\text{C}$  conditions at the glacier bed. The measured  $\text{K}^+$  flux was not matched in the model, presumably owing to nonstoichiometric potassium release from biotite under conditions of grinding found in the glacier bed. Strontium isotope data, discussed below, also points to subglacial grinding leading to preferential release of interlayer cations from biotite, which could explain why lab-based dissolution kinetic rate constants underpredicted K flux from Bench Glacier.

Few studies have looked at strontium isotopic composition of glacial runoff, despite long-standing interest in links between the marine strontium isotope record and glaciation (e.g., Armstrong 1971). K-bearing silicate minerals release radiogenic strontium during weathering because  $^{87}\text{Rb}$ , the parent for  $^{87}\text{Sr}$ , substitutes for K in silicate mineral lattices. The most distinctive characteristic of glacial runoff is that after calcium, potassium is the most abundant cation in glacial runoff (Anderson et al. 1997). The unusually high proportion of potassium is believed to be due to enhanced release of interlayer cations under conditions of glacial grinding (Stallard 1995, Anderson et al. 1997). At Bench Glacier, the  $^{87}\text{Sr}/^{86}\text{Sr}$  of runoff was higher than the metasedimentary bedrock, but was less radiogenic than leachate produced from river sediment after 1 h in 6N HCl (Anderson et al. 2000). The radiogenic character of Bench Glacier runoff was attributed to grinding of biotite in the subglacial environment. At Robertson Glacier, Alberta, Sharp et al. (2002) found that the flux-weighted mean  $^{87}\text{Sr}/^{86}\text{Sr}$  in runoff was similar to the carbonate bedrock composition. However, even in this carbonate terrain,  $^{87}\text{Sr}/^{86}\text{Sr}$  released from radiogenic muscovite was detectable at low flow in a stream issuing from a side of the glacier with a band of silicate rocks and controlled the  $^{87}\text{Sr}/^{86}\text{Sr}$  of low flow runoff. Strontium appeared to be released preferentially over potassium, suggesting that the flux of radiogenic strontium may exceed the flux expected from mineral abundance and rate constants. At Mittivakkat Gletscher, Greenland, on mafic intrusives and garnet-granite gneiss, Hagedorn & Hasholt (2004) found  $^{87}\text{Sr}/^{86}\text{Sr}$  was greater in runoff than in suspended sediment, indicating preferential release of radiogenic strontium from both biotite and K-feldspar. These few studies demonstrate that runoff from active glaciers in silicate terrain is more radiogenic than underlying whole rock. The implications of this observation on global fluxes of strontium to the oceans during glaciations remain to be explored.

#### 4. PROGLACIAL ZONE

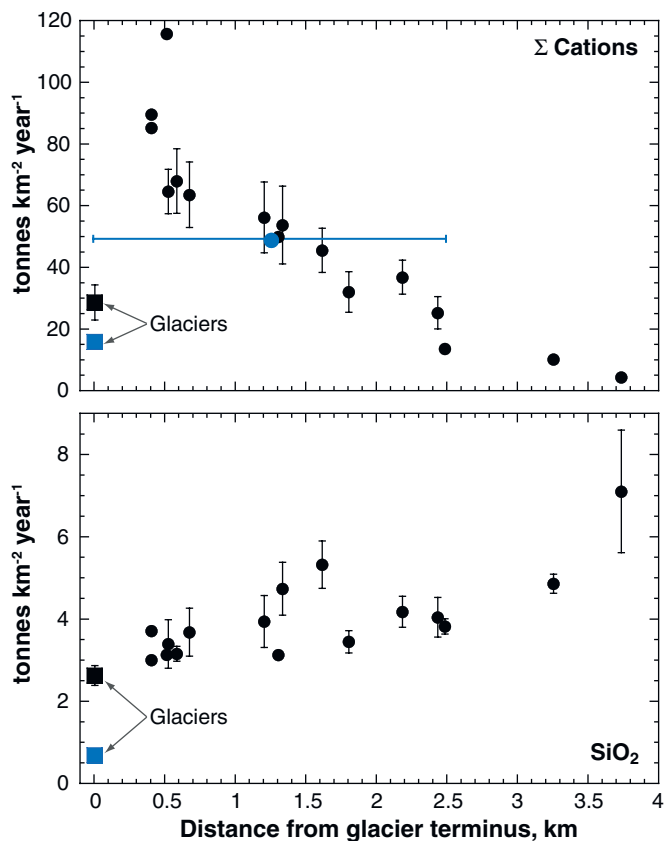
The deglaciated landscapes found between outermost glacial moraines and either the present glacier terminus or the valley headwall in completely deglaciated terrain are

dynamic regions in which vegetation and soils vary spatially owing to gradients in surface age. These landscapes newly emergent from ice evolve rapidly as recently unbuttressed slopes fail (Ballantyne 2002), vegetation encroaches (Matthews 1992), and weathering processes proceed. While considerable study has addressed questions of succession and soil development in glacier forelands, little attention has been placed on quantifying chemical weathering fluxes from these regions. Matthews (1992) defined proglacial forelands as the terrain deglaciated since the Little Ice Age, but here the proglacial area will be taken to include any region with sediments deposited by ice, regardless of age.

Contrasting conclusions on weathering in proglacial forelands emerge from studies at two glaciers on carbonate-dominated lithology, Glacier de Tsanfleuron, Switzerland, and Finsterwalderbreen, Svalbard. The solute concentrations and solute fluxes in the outlet streams of these glaciers increase downstream by 30%–47% as they traverse the 1.5–2.5-km-wide, recently deglaciated proglacial zone. In both cases, the downstream increase in solute flux is due to sulfide oxidation and carbonate dissolution (silica fluxes did not change). The increase in fluxes reflects an increase in solute concentrations, as discharge does not increase measurably in the proglacial reaches. Here the similarities end. Fairchild et al. (1999b) attributed the downstream increase in solute flux at Tsanfleuron to dissolution of suspended sediment in stream, whereas Wadham et al. (2001) conclude that small fluxes of highly mineralized shallow groundwater from the proglacial zone account for the downstream increase in solute flux at Finsterwalderbreen.

Fairchild et al. (1999b) demonstrated that the limestone bedrock at Tsanfleuron released solutes rapidly (8–10 ppm Ca within minutes) when milled and suspended in water. This experimental evidence, along with the lack of tributary streams and presence of karst features in the proglacial zone, which preclude groundwater flow out of the proglacial region, support the interpretation that dissolution of suspended sediment far exceeds proglacial zone weathering fluxes. Wadham et al. (2001) dismiss in-stream dissolution of suspended sediment as a significant process because the experiments that show rapid dissolution of suspended sediment do not replicate field conditions. Their experiments showed that solute release is most rapid when dry rock powder is mixed with deionized water, conditions quite different from the emergence of sediment-laden water at the glacier terminus. Wadham et al. (2001) and Cooper et al. (2002) explored groundwater in the proglacial zone of Finsterwalderbreen, and found it highly mineralized compared with glacial runoff and commonly saturated with respect to calcite. Head gradients in the active layer (seasonally thawed surface layer) of the proglacial area drove water seasonally into the stream channel, and surface runoff from small ponds in the proglacial area was observed (Cooper et al. 2002). The cation and total chemical denudation rates Wadham et al. (2001) compute for the proglacial zone are greater than underneath Finsterwalderbreen itself by a factor of approximately three. The increased weathering flux was due to sulfide oxidation and carbonate dissolution; no change in silica flux was observed as the stream crossed the proglacial area.

Bench Glacier, Alaska, presented an unusual opportunity to study proglacial weathering (Anderson et al. 2000). The glacier has retreated up a steep-walled



**Figure 4**

Fluxes of dissolved cations and dissolved silica from subglacial (*squares*) and proglacial (*circles*) environments at Bench Glacier (*black*) and Finsterwalderbreen (*blue*). Bench proglacial fluxes are estimated for individual streams located at various distance from the active glacier (Anderson et al. 2000). Finsterwalderbreen proglacial flux is an average for the 2.5-km-wide proglacial area; no silica flux from the proglacial area was detected (Wadham et al. 2001).

till-mantled valley. A number of small streams drain the valley walls, allowing a comparative watershed approach to be used to look at spatial variation in proglacial weathering. Although no downstream change in Bench Glacier outlet stream chemistry was observed in a 4-km-wide proglacial zone, these small tributaries showed significant spatial variations in solute concentration within the proglacial area (**Figure 4**). Dissolved cation concentrations were high near the glacier, and they fell with increasing distance (and age of sediments) away from the glacier. Dissolved silica concentrations showed the opposite trend. Although the bedrock is metagraywacke with only trace carbonate and sulfide minerals, carbonate dissolution and sulfide oxidation accounted for 80% of the solute from the glacier and 90% of the solute in the streams draining the youngest proglacial sediments. The streams draining sediments deposited at the Last Glacial Maximum (ca. 10,000 year ago) had the highest dissolved silica concentrations measured anywhere in the proglacial zone. In the most distal stream, silicate-weathering fluxes actually exceeded fluxes from carbonate dissolution and sulfide oxidation. Anderson et al. (2000) suggested that the change in weathering process with sediment age in the proglacial zone resulted from progressive leaching of the highly soluble carbonate and sulfide minerals from the sediments, and

that establishment of vegetation was the likely explanation of the increase in silicate mineral weathering fluxes. Both of these explanations need further observational and experimental support.

Anderson et al. (2000) noted that the youngest parts of the Bench proglacial area were similar to carbonate terrains in cation denudation rates, but were much lower in silica denudation rates. This observation was based on comparison with a large, nonglacial data set compiled by Bluth & Kump (1994). In **Figure 4**, the Bench data are compared with the Finsterwalderbreen glacial carbonate terrain (Wadham et al. 2001). Bench Glacier cation flux is nearly a factor of two greater than the glacial flux from the carbonate bedrock, but partially cold-based (frozen to its bed), Finsterwalderbreen. Total weathering fluxes from the proglacial areas of the two glaciers, one on silicate bedrock and one on carbonate bedrock, are effectively identical. Both sites show higher fluxes of cations derived from carbonate dissolution in recently exposed glacial sediment than from the erosive subglacial environment. Silica fluxes at Bench Glacier exceed those at Finsterwalderbreen in both the subglacial environment (Bench is three times higher), and in the proglacial environment (silica fluxes were too low to be measured in the proglacial zone at Finsterwalderbreen). The higher silica fluxes at Bench from both the glacier and its foreland are probably due to the silicate bedrock, and perhaps to the presence of vegetation.

Strontium isotopic ratios and concentrations in Bench proglacial streams are consistent with a dominant carbonate source in this region (Anderson et al. 2000). With increasing sediment age, the streams show declining  $^{87}\text{Sr}/^{86}\text{Sr}$  and strontium concentration, probably reflecting the loss of carbonate over time, and switch to silicate weathering sources. The Bench Glacier data suggests that runoff from active glaciers will have a high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio owing to abrasion-enhanced leaching of biotite. Deglaciation will lead to a short-lived increase in strontium flux as carbonates are leached, but the  $^{87}\text{Sr}/^{86}\text{Sr}$  from deglaciated terrain is lower than that from active glaciers because stripping of cations from biotite does not occur after abrasion ceases. Similar conclusions were drawn from a 55 ka chronosequence in the Himalayas (Jacobson et al. 2002). These authors found that dissolution of carbonate found at 1 wt% in fresh till dominates weathering in moraines in the Raikhot watershed on Nanga Parbat, Pakistan, influencing both the weathering flux and its strontium isotopic ratio. The drier climate and the deposition of carbonate-bearing dust may explain why dissolution of trace carbonates remains the dominant weathering process after 55 ka in Pakistan, whereas carbonate fluxes diminish within 10 ka at Bench Glacier in Alaska.

Weathering within proglacial sediments appears to evolve over timescales of hundreds to thousands of years after the glaciers retreat. Weathering fluxes from recently deglaciated terrain are higher than from glaciers, although the dominance of weathering of reactive phases (carbonate and sulfide) over weathering of silicates persists. Over time, loss of carbonates and sulfides leads to lower overall weathering fluxes. There may be a gradual increase in silicate weathering fluxes with age.

## 5. DISTAL SEDIMENTS

Beyond the limits of former ice margins, glacial sediments are distributed by fluvial and eolian transport systems in distal deposits (**Figure 2**). In this environment, carbon sequestration becomes an important consideration, as vegetation is found in greater abundance and may be present throughout a glacial cycle. Two broad classes of distal deposits are fluvial glacial outwash and eolian loess deposits (Benn et al. 2003). The predominantly gravel outwash deposits are not likely to be a significant site of weathering or carbon sequestration. Water contact time is expected to be low in porous gravel outwash, and available mineral surface area per unit volume is low in coarse sediment. Fine-grained sediments produced by glaciers are either trapped in lakes, transported further downstream in suspension, or are winnowed off braid plains by wind and deposited in loess. Of all terrestrial distal glacial sediment, loess has the greatest potential to impact global geochemical cycles.

Loess and loess-like deposits cover 5%–10% of the global land surface (Pye 1987), with the most extensive deposits formed near glaciers (periglacial loess) or tectonically active mountains (perimontane loess). In Alaska, loess is “the most widely distributed sediment of Quaternary age” (Péwé 1975), and is found in deposits ranging from a few millimeters to tens of meters thick. Loess is silty; grain sizes range from 10–50  $\mu\text{m}$ , with a prominent mode at 20–30  $\mu\text{m}$ . Winds entrain silt from braid plains and exposed bars of glacial rivers; the dust is preferentially deposited in vegetated areas, which offer aerodynamic resistance to the wind and are efficient sediment traps (Pye 1995). The thickest accumulations are found in forests near rivers (Begét 2001). In Alaska and the Yukon, loess often is a mixture of organic matter and mineral sediment, sometimes known as muck (Fraser & Burn 1997, Péwé 1975), a good combination for enhancement of chemical weathering rates.

Most loess shows signs of syn- or postdepositional chemical alteration. Consequently, deep loess profiles around the world, such as those in western China (Heller & Liu 1982, Kukla et al. 1988) and central Alaska (Begét 2001), contain valuable records of paleoclimate, most prominently seen in the correlation between climate proxy records and magnetic susceptibility. In Chinese loess, magnetic susceptibility is higher during interglacial periods and lower during glacial episodes, whereas in Alaskan loess, this pattern appears to be reversed. Weathering and oxidation of iron-bearing minerals under well-drained conditions is the prevailing explanation for higher magnetic susceptibility during interglacial periods in Chinese loess records (Heller et al. 1993, Maher et al. 2003). In contrast, weathering in poorly drained conditions during interglacial periods in Alaska may reduce magnetic susceptibility (Liu 1999). Recently, illite/chlorite ratios have been shown to vary with monsoon conditions in Chinese loess-derived soils, with stronger silicate weathering (chlorite loss) in warm, wet conditions (Zhao et al. 2005).

### 5.1. Loess Weathering

Studies of loess weathering have focused on understanding the paleoclimate records in loess deposits, rather than on documenting chemical weathering fluxes. The following

discussion, therefore, is theoretical consideration of the potential impact of loess deposition on silicate weathering fluxes.

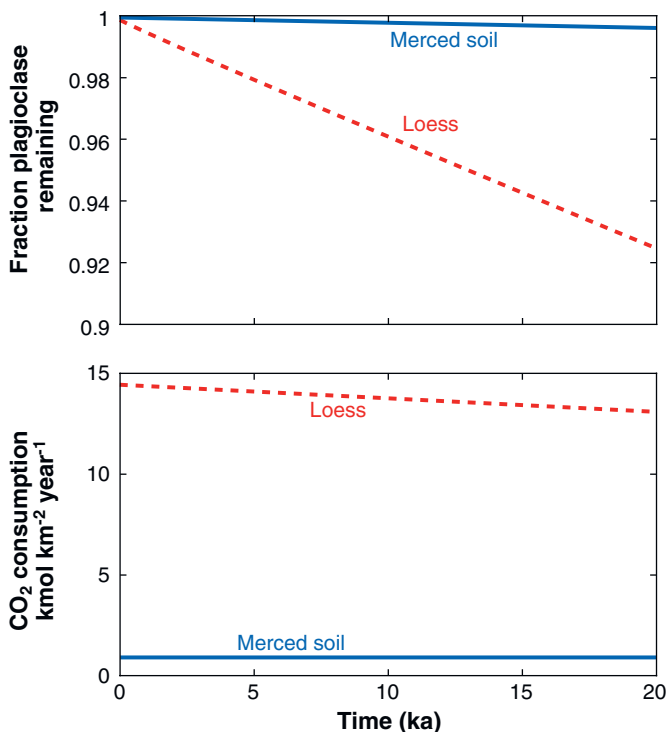
The weathering flux,  $Q_w$ , from a soil profile can be modeled as the product of mineral surface area,  $S_{total}$ , weathering rate constant,  $r_j$ , and water content,  $\theta$ :

$$Q_w = \sum_{j=1}^{minerals} r_j S_{total} x_j \theta Z, \quad (2)$$

where  $x_j$  is the fraction of the soil mineral surface area represented by mineral  $j$ , and  $Z$  is the thickness of the profile undergoing weathering. Equation 2 is based on the PROFILE model (Sverdrup & Warfvinge 1988), which was developed to estimate base cation release in soils subjected to acid deposition. This expression highlights four parameters that control landscape chemical weathering fluxes: (a) mineral surface area, which to first order varies with grain size, (b) mineral weathering rate constants, understood to depend on the mineral surface age, the solution saturation state, and the pH of the weathering solution; (c) soil moisture, which not only controls the fraction of the mineral surface wetted, but also the fraction of time that the surface is wetted, and therefore that weathering can proceed, and also influences mineral weathering rate constants because water contact time controls the solution saturation state; and (d) the thickness of the profile undergoing weathering.

The importance of grain size on chemical weathering fluxes from a soil can be demonstrated by applying Equation 2 to a pair of hypothetical soils that differ only in grain size distribution. In this example, the soil grain size distribution, mineralogy, and field-based weathering rate constants for a nonloess soil are drawn from the work of White et al. (1996) on a soil chronosequence developed in Sierran alluvium near Merced, California. The hydrologic component has been folded into the rate constant, so a single field-determined  $r_j$  replaces  $r_j \theta$  in Equation 2 for this calculation. This effectively makes the hydrology uniform between the two soils, at soil wetness comparable to the conditions in the Merced chronosequence. **Figure 5** compares the weathering of anorthite in a 1-m-deep soil with characteristics of the 40 ka soil in the Merced chronosequence to weathering in a hypothetical 1-m-deep loess soil, which differs only in having a finer grain size distribution (**Table 1**). The finer grain size of the loess results in a substantially greater weathering flux through time. In the 20 ka model run, 7.5% of the plagioclase is lost from the loess compared to a loss of ~0.5% in the soil, which translates into an order of magnitude greater CO<sub>2</sub> consumption rate in the loess. The CO<sub>2</sub> consumption rate declines through time as the plagioclase is slowly removed from the soil.

A second calculation explores the effect of loess deposition on the weathering flux from the alluvial soil (**Figure 6**). In this calculation, weathering is again assumed to be confined to a 1-m-thick layer, the portion of which is loess increases steadily from 0 to 1 m. High deposition rates (e.g., 1 mm year<sup>-1</sup>) result in the loess quickly overwhelming the background soil weathering. In 10<sup>3</sup> years, the soil is completely buried by loess, and the weathering fluxes stabilize to that of the loess at time 0 in **Figure 5**. The slow decline in flux of **Figure 5** does not occur in this calculation owing to the loess inputs replenishing plagioclase content in the profile. At low deposition rates



**Figure 5**

Soil weathering model results. Top panel: plagioclase remaining over time. Bottom panel: CO<sub>2</sub> consumption by plagioclase weathering.

(e.g., 0.01 mm year<sup>-1</sup>, or one 10 μm grain per year), a steady weathering flux is reached only after 10<sup>5</sup> years. Even in this case, however, weathering fluxes are two times greater than the background nonloess soil after 6000 years of deposition. Loess deposition rates in Alaska range from 0.05–1 mm year<sup>-1</sup> (Muhs et al. 2003), and so are within the limits explored in this calculation. This preliminary analysis, based only on grain size, suggests that modest loess accumulation rates can substantially enhance weathering fluxes.

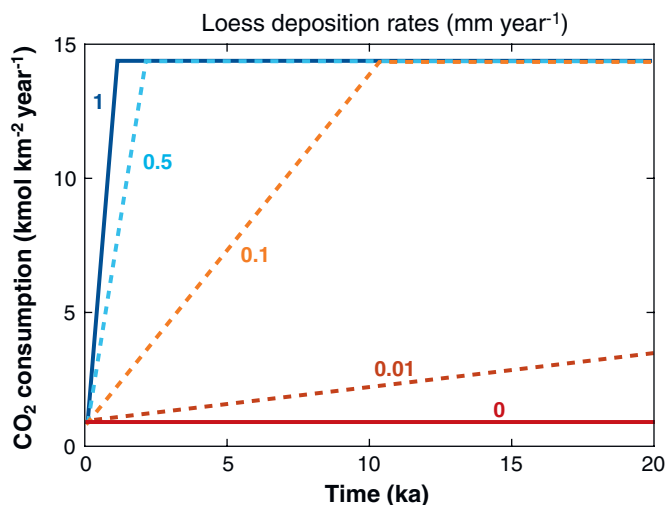
The models shown in **Figure 5** and **6** do not include the important real effects of hydrology and profile thickness. The rate of water flow through a profile will control the chemical saturation state of the water. Over time, water approaches saturation with respect to minerals weathering, and consequently the weathering rate constant approaches zero (Lasaga et al. 2004). Greater amounts of water flowing through the

**Table 1** Hypothetical soil weathering flux calculation parameters

Parameter	Alluvial soil	Loess soil
Mean grain size	320 μm	25 μm
Mineralogy	33 wt% anorthite	33 wt% anorthite
Bulk density	1500 kg m <sup>3</sup>	1500 kg m <sup>3</sup>
log <i>r</i> <sub>anorthite</sub>	-19.5 mol cm <sup>-2</sup> s <sup>-1</sup>	-19.5 mol cm <sup>-2</sup> s <sup>-1</sup>
Time step	200 years	200 years

**Figure 6**

Rate of CO<sub>2</sub> consumption over time in a 1-m-deep weathering zone at loess deposition rates ranging from 0 to 1 mm/year. The starting sandy alluvium is slowly replaced by silt at varying deposition rates.



profile (higher effective rainfall) will allow water penetration to greater depths before weathering rates decline. Thus, the amount and rate of delivery of water to the profile will set the depth to which weathering can proceed in the profile.

Continued deposition of loess will maintain the concentrations of reactive minerals high in the soil profile, where water is most aggressively reactive because it is furthest from limitation by saturation. Deposition also has the effect of moving soil down in the profile; if the deposition rate is high, burial will move relatively unweathered material out of the “weathering zone”—the depth interval where soil solutions are most reactive. The tradeoffs in deposition rate and weathering have been recognized in loess soils. Almond & Tonkin (1999) note complete alteration of P minerals in subsoils of slowly accreting soils that occurred in the near surface and subsurface horizons. Similarly, the lack of carbonate in central Alaskan Quaternary loess, despite its abundance in source regions, led Muhs & Budahn (2006) to infer that deposition rates were slow enough for leaching to remove all incoming carbonate. There is likely to be a combination of loess deposition rate and rainfall rate that maximizes the silicate weathering flux from a particular loess profile.

A field-based estimation of weathering fluxes from loess has been undertaken in the Matanuska-Susitna lowlands in central Alaska. Muhs et al. (2004) showed that loess deposition began in this region after 6500 <sup>14</sup>C year BP, following retreat of glaciers into the surrounding mountain ranges. Buried soils in the thinner parts of the loess cover in the lowlands imply that loess deposition competes with weathering to control soil formation. Cacy (2006) estimated weathering fluxes in the same profiles, based on mass balance relative to an immobile trace element. Silicate weathering was slightly more intensive in the thinner distal parts of the loess sheet than in thicker deposits near the source. The total weathering flux, i.e., the weathering integrated over the soil thickness, was greatest in the thickest, most rapidly accreting deposits. The silicate weathering fluxes Cacy (2006) computed were about a factor of two greater than the



highest proglacial fluxes measured in till derived from similar rock types (Anderson et al. 2000). More weathering flux measurements from loess deposits are needed to fully test the impact of loess on silicate weathering fluxes.

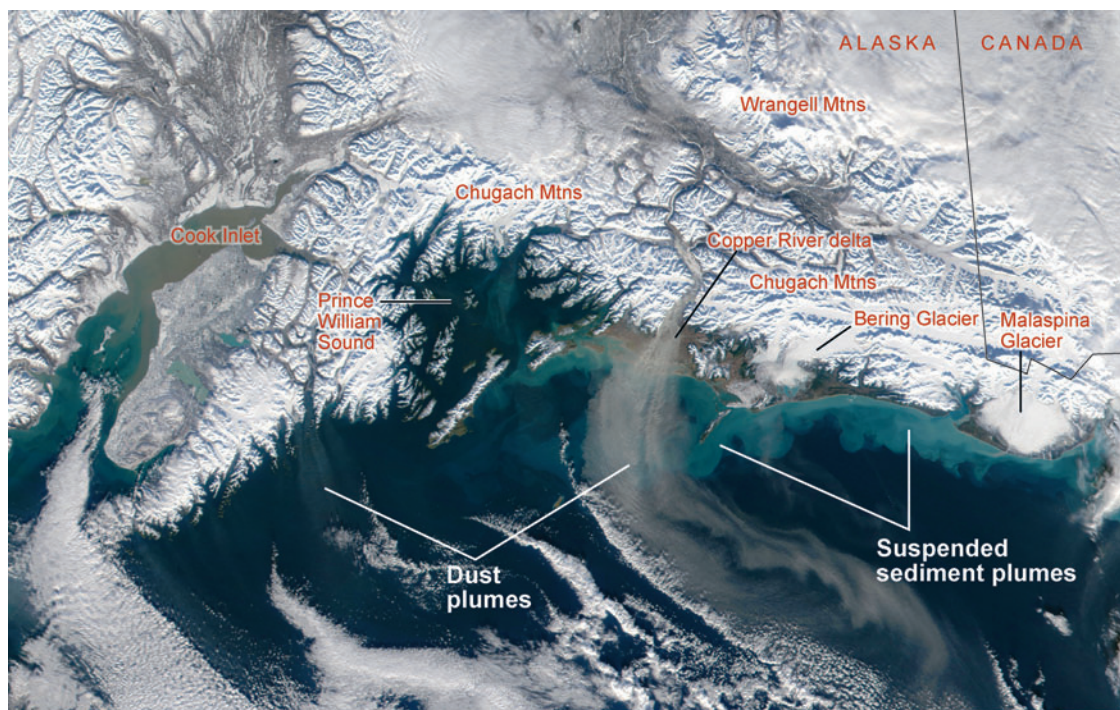
## 5.2. Organic Carbon

Soils are the largest terrestrial reservoir of organic carbon on Earth's surface, and boreal soils are the largest soil carbon store (Schlesinger 1991). Organic carbon storage is the result of a difference between primary production of organic matter and its decomposition, integrated over time. Both primary production and decomposition respond to climatic parameters of temperature and rainfall, and they vary with ecosystem type and landscape properties. Loess deposition may affect the storage of soil organic carbon in a variety of ways. Burial of surfaces and their organic carbon content may lead to storage if the organic carbon is not oxidized. Poorly drained loess soils in New Zealand contained more organic carbon in the subsoil than well-drained sites (Almond & Tonkin 1999). In these sites, carbon accumulated in O and A horizons and persisted after burial. Surface rejuvenation by loess accretion may impact carbon storage. Because organic matter accumulation rates are greatest in young soils (Amundson 2001), dust deposition keeps the soil in a state of maximum organic matter accumulation rate. In a 140 km transect of Holocene loess in Nebraska, the organic matter storage was greatest in the thickest deposits and was unrelated to grain size variations (Jacobs & Mason 2005). This last observation suggests that association of organic matter with mineral surfaces, often cited as an important control on carbon storage (Kahle et al. 2003), was less important than thickness of the deposit.

Holocene loess deposits in Nebraska contain 8–17 kg C m<sup>-2</sup> in deposits ranging from 0.25–1.25 m thick (Jacobs & Mason 2005), whereas the Matanuska lowlands Holocene loess contains ~14–50 kg C m<sup>-2</sup> (assuming organic carbon is 50% of loss on ignition) in deposits ranging from 0.3–2 m thick (Cacy 2006). These soil carbon amounts rival, and in the thickest deposits in Matanuska lowlands exceed, the mean soil carbon content of tundra (21.8 kg m<sup>-2</sup>), wet boreal forest (19.3 kg m<sup>-2</sup>), and wet tropical forest (19.1 kg m<sup>-2</sup>) ecosystems, which globally have the highest soil carbon content (Amundson 2001). Mean annual precipitation and mean annual temperature both influence soil organic carbon through their influence on rates of productivity and decomposition. The mean annual precipitation in tundra, wet boreal forest, and wet tropical forest exceeds the 400 mm year<sup>-1</sup> of the Matanuska lowlands, and the 450–725 mm year<sup>-1</sup> in Nebraska, suggesting that factors other than climatic parameters are responsible for the high stored organic carbon in the loess deposits in these regions.

## 6. CONTINENTAL MARGINS

Continental margins impact atmospheric chemistry through the effects of sediment deposition and burial (Bernier 1982). Organic carbon burial in continental margin sediments is a sink of atmospheric CO<sub>2</sub>; the removal of fixed carbon from the biosphere contributes to accumulation of O<sub>2</sub> in the atmosphere. Most organic carbon burial occurs on continental shelf and slope sediments, and half occurs in deltas (Blair et al.



**Figure 7**

NASA true-color Terra MODIS image of a portion of the Gulf of Alaska along the coast of southern Alaska acquired on October 26, 2001. Plumes of suspended sediment from rivers and of eolian dust extend far offshore. The largest eolian dust plume in the center of the image emanates from the Copper River, which drains the heavily glacierized Chugach Mountains and Wrangell Mountains. Recent sediment deposition rates on the Copper River delta front exceed  $20 \text{ mm year}^{-1}$  (Jaeger et al. 1998).

2004). The amount of carbon preserved is closely tied to the surface area of sediment deposited (Hedges & Keil 1995). Thus, these important aspects of the global carbon cycle are strongly controlled by sediment deposition rate and grain size, both of which are impacted in glacial systems. Sedimentation on continental margins affected by glaciers can be extraordinarily high (**Figure 7**). Holocene sediments as thick as 200 m are found in the Gulf of Alaska (Jaeger et al. 1998), the depocenter for  $90,000 \text{ km}^2$  of glacierized coastal Alaska and neighboring Canada (Arendt et al. 2002). Recent deposition rates off the largest glacier in this region, the Bering Glacier, average  $16\text{--}18 \text{ mm year}^{-1}$  (Jaeger & Nittrouer 1999).

Organic carbon preservation in marine sediments appears to be related to a protective association between mineral surfaces and carbon (Keil et al. 1994), and hence organic matter burial is positively correlated with sedimentation rates. The Eel River is an example of low storage bypass system, with little transport of terrestrial carbon offshore. The high deposition rate preserves carbon from bedrock, terrestrial, and marine sources (Blair et al. 2004). To the extent that marine or terrestrial carbon is

available for loading on sediments in glaciated watersheds, the high deposition rates found offshore may lead to high carbon preservation rates on glaciated continental margins. The most dramatic example of the importance of organic carbon burial is the Bengal Fan, where organic carbon burial accounts for 2–3 times more CO<sub>2</sub> loss to the atmosphere than the silicate weathering in the Ganges-Brahmaputra headwaters in the Himalayas (France-Lanord & Derry 1997).

Chemical interactions between suspended sediments and seawater also affect atmospheric CO<sub>2</sub>. Ion exchange of calcium on clays for sodium in seawater releases calcium ions that can immediately precipitate into carbonates in seawater; this process accounts for as much as 40% of the dissolved calcium flux in rivers (Gislason et al. 2006). Silicate weathering in seawater can dissolve up to 0.05% of basaltic suspended sediment per day (Gislason et al. 2006). In high suspended sediment flux systems, the chemical transformations of suspended sediments offshore can produce CO<sub>2</sub> consumption as great as that due to terrestrial silicate weathering.

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**Glaciated:** a landscape that was occupied by glaciers in the past

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## 7. GLACIAL SYSTEMS

Glacial landscape systems include all the regions where glacially derived sediments are stored in their transit to continental margin depocenters. Because these landscapes are widespread and long-lasting, the biogeochemical impact of glaciers should also be long-lived. It is clear that while temperate glaciers may carry the geochemical punch to set off the uplift-climate change connection, they will continue to deliver that punch long after the glaciers retreat. Quantifying the biogeochemical effect of glaciers in the myriad environments and over the paraglacial timescales remains to be done.

### SUMMARY POINTS

1. Glaciers are mineral surface area factories, producing sediments that affect chemical weathering fluxes in every environment, from the sole of the glacier to continental margins. The influence persists as long as glacial sediments modulate sediment yields from a landscape.
2. Low temperatures suppress silicate weathering fluxes from glaciers and their immediate surroundings. Establishment of vegetation seems to be necessary to bring silicate weathering fluxes up.
3. Loess deposits have the potential to be significant contributors to silicate weathering fluxes. Limited data suggests that thicker deposits produce greater weathering fluxes.
4. Dissolution of silicates in seawater and ion exchange processes may consume more CO<sub>2</sub> than terrestrial weathering processes.
5. Organic carbon burial rates are correlated with deposit thickness in loess and with sediment surface area offshore. Organic carbon burial in loess and marine sediments may represent a greater sink of carbon than silicate weathering associated with glacial sediments.

## FUTURE DIRECTIONS

1. Glacial systems present an interesting challenge for models that link chemical weathering fluxes and physical erosion rates. Sediment age and residence time within an environment may be the more fundamental link to chemical weathering fluxes.
2. More fieldwork is needed. Chemical weathering fluxes and organic carbon burial rates should be quantified in additional glacially influenced environments, particularly those beyond glacial limits, so that a quantitative analysis of the effect of glaciers on carbon cycle dynamics can be undertaken.
3. Models linking uplift, erosion, and climate change should incorporate sediment storage to fully realize the effect of erosion processes on atmospheric CO<sub>2</sub>.

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