Weathering reactions and hyporheic exchange controls on stream water chemistry in a glacial meltwater stream in the McMurdo Dry Valleys

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[1]   In the McMurdo Dry Valleys, Antarctica, dilute glacial meltwater flows down well-established streambeds to closed basin lakes during the austral summer. During the 6–12 week flow season, a hyporheic zone develops in the saturated sediment adjacent to the streams. Longer Dry Valley streams have higher concentrations of major ions than shorter streams. The longitudinal increases in Si and K suggest that primary weathering contributes to the downstream solute increase. The hypothesis that weathering reactions in the hyporheic zone control stream chemistry was tested by modeling the downstream increase in solute concentration in von Guerard Stream in Taylor Valley. The average rates of solute supplied from these sources over the 5.2 km length of the stream were 6.1×10^{-9} mol Si L^{-1} m^{-1} and 3.7×10^{-9} mol K L^{-1} m^{-1}, yielding annual dissolved Si loads of $0.02–1.30$ mol Si m^{-2} of watershed land surface. Silicate minerals in streambed sediment were analyzed to determine the representative surface area of minerals in the hyporheic zone subject to primary weathering. Two strategies were evaluated to compute sediment surface area normalized weathering rates. The first applies a best linear fit to synoptic data in order to calculate a constant downstream solute concentration gradient, dC/dx (constant weathering rate contribution, CRC method); the second uses a transient storage model to simulate dC/dx, representing both hyporheic exchange and chemical weathering (hydrologic exchange, HE method). Geometric surface area normalized dissolution rates of the silicate minerals in the stream ranged from 0.6×10^{-12} mol Si m^{-2} s^{-1} to 4.5×10^{-12} mol Si m^{-2} s^{-1} and 0.4×10^{-12} mol K m^{-2} s^{-1} to 1.9×10^{-12} mol K m^{-2} s^{-1}. These values are an order of magnitude lower than geometric surface area normalized weathering rates determined in laboratory studies and are an order of magnitude greater than geometric surface area normalized weathering rates determined in a warmer, wetter setting in temperate basins, despite the cold temperatures, lack of precipitation and lack of organic material. These results suggest that the continuous saturation and rapid flushing of the sediment due to hyporheic exchange facilitates weathering in Dry Valley streams.   *INDEX TERMS:* 1045 Geochemistry: Low-temperature geochemistry; 1806 Hydrology: Chemistry of fresh water; 1625 Global Change: Geomorphology and weathering (1824, 1886); 1890 Hydrology: Wetlands; *KEYWORDS:* hyporheic zone, chemical weathering, flow path, Antarctica, stream

Citation: Gooseff, M. N., D. M. McKnight, W. B. Lyons, and A. E. Blum, Weathering reactions and hyporheic exchange controls on stream water chemistry in a glacial meltwater stream in the McMurdo Dry Valleys, *Water Resour. Res.*, *38*(12), 1279, doi:10.1029/2001WR000834, 2002.

1.   Introduction

[2]   The physical hydrology of catchments and the definition of hydrologic flow paths have received increasing attention. Better characterization of sources, sinks and movement of solutes through catchments is accomplished by employing quantitative hydrologic approaches. Studies have shown that water exchange between streams and their hyporheic zones, defined as the sediment (and pore space) adjacent to the stream through which stream water exchanges, is important to understanding the chemical composition of stream water for both nutrients [*Grimm*, 1987; *Kim et al.*, 1990, 1992; *Findlay et al.*, 1993;

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Wondzell and Swanson, 1996; *Mulholland and DeAngelis*, 2000] and metals [*McKnight and Bencala*, 1989; *Benner et al.*, 1995; *Harvey and Fuller*, 1998; *Runkel et al.*, 1999; *Fuller and Harvey*, 2000]. Studies of nutrient dynamics in streams have found the hyporheic zone to be a sink for nutrients due to biologic uptake [*Hill et al.*, 1998; D. M. McKnight et al., Inorganic nitrogen and phosphorous dynamics of Antarctic glacial meltwater streams as controlled by hyporheic exchange and benthic autotrophic communities, submitted to *Journal of North American Benthological Society*, 2002 (hereinafter referred to as McKnight et al., submitted manuscript, 2002)], and microbially mediated denitrification [*Duff and Triska*, 1990]. The hyporheic zone also represents a potential zone of chemical weathering, acting as a source of inorganic solutes (e.g., Si, K). Previous hyporheic zone studies have addressed differences in dissolved Si concentrations among stream water, groundwater, and hyporheic water. *Ford and Naiman* [1989] postulate that dissolved Si in groundwater inputs could be an important source of Si to diatom communities. *Boissier et al.* [1996] suggest that decreases in dissolved Si downstream could be due to biotic assimilation. *Hendricks and White* [1991, 1995] found that SiO_2 could be used as a conservative tracer indicating trends in vertical hyporheic gradients. However, in-stream weathering fluxes due to interaction of stream water with hyporheic zones has not been a focus of previous studies.

[3] Previous studies [e.g., *Kennedy*, 1971; *Smith and Dunne*, 1977] have shown direct contribution to stream solute loads from weathering of catchment sediments and soils. One approach to quantifying weathering solute fluxes is to calculate weathering rate normalized to catchment surface area. To calculate this land-surface normalized weathering flux (LWF) value, an annual solute flux in a stream is computed and normalized to the area of the catchment [*Ming-hui et al*, 1982; *Lyons et al.*, 1997a; *Nezat et al.*, 2001]. A second approach normalizes solute flux to the surface area of weathering materials in soil or sediment [*Swoboda-Colberg and Drever*, 1993; *Drever and Clow*, 1995]. When calculating sediment surface-normalized rates, challenges include identifying the appropriate volume of weathering substrate and determining the actively weathering grain surface area [*White and Peterson*, 1990]. As pointed out by *Velbel* [1990], *Swoboda-Colberg and Drever* [1993], *White* [1995], *White et al.* [1996], and *Dahlgren et al.* [1999], mineral surface area-normalized rates from field studies are as much as 5 orders of magnitude slower than rates determined by laboratory experiments under controlled conditions. Discrepancies may be due to temperature differences and/or inhomogeneous contact of interstitial waters to mineral surfaces [*Velbel*, 1990; *Swoboda-Colberg and Drever*, 1993]. Although the LWF calculation is more straightforward and commonly reported, it does not include information about specific catchment flow paths. A few studies have discerned flow paths in relation to chemical weathering processes in the context of hydrograph separation [*Hooper and Shoemaker*, 1986; *Anderson et al.*, 1997a].

[4] Numerous authors have made the case that chemical weathering (e.g. silicate hydrolysis, salt dissolution) occurs in glacial meltwater streams of the McMurdo Dry Valleys of Antarctica [e.g., *Keys and Williams*, 1981; *Green and Canfield*, 1984; *Green et al.*, 1988; *de Mora et al.*, 1991; *Lyons and Mayewski*, 1993; *Lyons and Welch*, 1997; *Nezat et al.*, 2001] and is important to solute budgets of the closed basin lakes. Occurrence of chemical weathering in the Dry Valleys landscape is limited to locations of liquid water, specifically lakes, stream channels and in the hyporheic zones of the streams. Dissolved K:Cl and Ca:Cl ratios in Dry Valley surface waters are elevated relative to seawater ratios, suggesting input of these cations from chemical weathering [*Lyons et al.*, 1998]. This preferential enrichment of K and Ca is similar to that in streams from glaciated catchments around the world, which may result from preferential release of K from biotite and Ca from carbonates in freshly exposed bedrock [*Anderson et al.*, 1997b]. Furthermore, Dry Valley stream waters tend to have higher ratios of lighter:heavier alkali metals or alkaline earths than the sediments being weathered, due to the preferential removal of the lighter, more mobile cations by water during chemical weathering, while the heavier, less mobile cations are retained in the weathering products [*Hinkley*, 1974; *Nesbitt et al.*, 1980]. The Ca:Sr and K:Rb ratios in Taylor Valley streams are similar to streams draining basalt, diorite, or high-grade metamorphic rocks in monolithologic watersheds [*Nezat et al.*, 2001]. At the reach scale, *Green et al.* [1989] found that longer streams generally had higher solute concentrations, and *Lyons et al.* [1997a] have shown that Dry Valley stream dissolved Si fluxes (LWF) can be comparable in magnitude to weathering fluxes determined in studies of temperate catchments.

[5] At the sediment matrix scale, *Maurice et al.* [2002] have shown direct evidence of weathering in the hyporheic zone of Green Creek, at a rate of 8.3×10^{-14} mol muscovite m^{-2} s^{-1}, based on geometric surface area. Further, *Maurice et al.* [2002] observed bacteria on mineral surfaces, which may influence chemical denudation rates, but such an effect is not yet known. *Huh et al.* [1998a, 1998b] have argued that freeze/thaw cycles and other related physical weathering processes control chemical weathering in northern polar environments. Although mechanical processes may be important and bacterial influence is unknown in the Dry Valleys, we hypothesize that water residence time and variations in rock-water ratios in the streams themselves also control chemical weathering rates.

[6] Unlike temperate streams, the extent of the hyporheic zone in the Dry Valleys can be constrained by direct observations. The streams flow for 4–10 weeks per year down well-defined channels that cut through a barren landscape of unconsolidated sediment. Stream water carries little to no suspended material (except at very high flows), and continuously exchanges with the sediment underneath and adjacent to the stream, which comprises a hyporheic zone [*Runkel et al.*, 1998; *Conovitz*, 2000]. Sediment adjacent to the stream becomes fully saturated at a depth of a few cm and is wetted at the surface. Deep permafrost excludes the possibility of groundwater contribution to streamflow [*Chinn*, 1993]. Thus the hyporheic zone is bounded underneath by permafrost at depths ranging from 40–70 cm [*Conovitz*, 2000], depending on location and the time within the flow season. The maximum lateral extent can be directly measured as the boundary between wet and dry alluvium,

which can occur several meters from the edge of the stream. The portion of the hyporheic zone cross sectional area that is rapidly exchanging with the stream is considered to be the hyporheic storage zone area (later defined as A_S), which can be assessed by stream tracer studies and subsequent inverse modeling. *Gooseff et al.* [2002] have found that the lateral extents of Dry Valley hyporheic zones, beyond the rapidly exchanging hyporheic zone areas (A_S), exchange stream water on the order of weeks to months. One assessment of hyporheic exchange potential is to compare A_S with A, the cross sectional area of the water flowing in the stream. Typical values of A_S/A range from 10^{-3} to 5 [*Harvey and Wagner*, 2000]. Exchange rates between the hyporheic zone and the main channel and A_S/A ratios have been determined by previous tracer experiments in Dry Valley streams, and are high compared to those in temperate streams because of the high porosity of the alluvium [*Runkel et al.*, 1998; McKnight et al., submitted manuscript, 2002]. During cold summers when the flows are low, the volume of water stored in the hyporheic zone can be several times greater than the volume of annual discharge of the particular stream [*Bomblies*, 1999; *Conovitz*, 2000].

[7] In addition to defined hyporheic zone extent, Dry Valley streams contain little organic material. The streams contain perennial benthic mats of cyanobacteria, which grow slowly during periods of flow [*Vincent and Howard-Williams*, 1986, 1989; *Alger et al.*, 1997]. Except for an initial pulse when the streams are first wetted, the dissolved organic carbon (DOC) concentration in the streams is low, less than 50 μM-C, and the percentage of this DOC that is humic material (primarily fulvic acid), which may influence weathering rates is also low, about 20% [*Aiken et al.*, 1996]. The organic content of hyporheic sediments is also low [*Treonis et al.*, 1999]. Thus the defined hydrology and the minimal amount of organic material make the Dry Valley streams a natural environment that is intermediate between a simple laboratory system for measurement of weathering rates and a temperate stream system.

[8] In this study, we hypothesize that the interaction of water with sediments in the hyporheic zone influences the weathering rates of minerals that make up fine to sand grained materials of the hyporheic zone. The exchange of water between the stream and the hyporheic zone has the effect of flushing out weathering products from the locality of the mineral surface, as well as providing dilute water, which will enhance dissolution and minimize effects of inhomogeneous access of mobile interstitial water to mineral surfaces. We evaluated this hypothesis by examining the downstream changes in solutes in von Guerard Stream. In order to characterize primary weathering, we modeled downstream changes in Si and K concentrations from sediment matrix scale weathering reactions. We characterized weathering products in streambed sediment through X-ray diffraction (XRD) analyses. We then evaluated the weathering rate of von Guerard Stream sediments by calculating the land surface normalized weathering flux and the supply of solutes from the hyporheic zone to the stream using a static mineral surface approach. Finally, we calculated weathering rates by using a transient storage model in a hyporheic exchange-mineral surface reaction approach. From these results, we can quantify the extent to which geochemical processes control stream chemistry through dissolution of marine aerosols, calcium carbonate, and rapid weathering of silicate minerals in the hyporheic zone.

2. Site Description

[9] The McMurdo Dry Valleys region is an ice-free polar desert on the western edge of McMurdo Sound, Antarctica (Figure 1). The climate is dry and cold, with less than 10 cm water equivalent of precipitation per year (all snow) and mean annual air temperature of $-20°C$ [*Clow et al.*, 1988]. The landscape is dominated by barren soils, exposed bedrock, well-established streambeds, permanently ice-covered lakes, and alpine, piedmont, and terminal glaciers. The soils are inhabited by nematodes, rotifers, and bacteria, and benthic algal mats and mosses exist in the streambeds. There are no higher order plants in Dry Valley streams. Taylor Valley contains three major lake basins (Bonney, Hoare, and Fryxell). Each of the Taylor Valley lakes is fed by 4 to 11 streams.

[10] Lake Fryxell (Figure 1) is the easternmost lake in Taylor Valley, located roughly 7 km from McMurdo Sound. The numerous streams in the basin range in gradient from 0.02 to 0.55 m m^{-1}, and stream lengths range from 1.0 km to 11.2 km [*Conovitz et al.*, 1998]. von Guerard Stream drains an alpine glacier in the Kukri Hills, and flows into the east end of the lake (Figure 1). Based on close inspection of the active portion of the channel, the sinuosity of the stream, and the distances between stream locations determined by GPS from a helicopter, we estimated the active length of von Guerard Stream to be 5.2 km. The von Guerard Stream gauge at F6 is located about 100 m from the mouth of the stream and has been operated since 1990 [*von Guerard et al.*, 1995]. This gauge records water stage, temperature, and conductivity at a natural control site on a 15-minute interval during the flow season. The discharge for the two years of the study is shown in Figure 2. All sampling dates occurred during the main flow period (Figure 2), when the hyporheic zone was fully developed. These years had high flows compared to the subsequent 5 years [*Bomblies et al.*, 2001]. Discharge exhibits diel variation, which is controlled by the solar trajectory and the orientation of the face of the source glacier [*Conovitz et al.*, 1998]. As a result of multiple lithologic sources, the minerals in the sediment comprising the hyporheic zone have a heterogeneous composition of granite, gneiss, dolerite, Beacon sandstone [*Péwé*, 1960; *Doran et al.*, 1994], and carbonate deposits [*Hendy et al.*, 1979]. *Angino et al.* [1962] reported the presence of thenardite (Na_2SO_4) and suggested that its dissolution contributes to stream water chemistry. *Claridge and Campbell* [1977] attributed dissolved K concentrations to dissolution of muscovite micas. *Conovitz* [2000] reports porosity values ranging from 0.29 to 0.47 for streambed sediments from von Guerard Stream.

[11] The physical and ecological conditions of von Guerard Stream change significantly from the glacier source to the lake. Sampling sites were distributed to characterize the stream chemistry in reaches with different characteristics (Figure 1). The site location was determined using the GPS unit of the helicopter providing logistical support. Near the glacier face, the meltwater is carried in 3 small channels (sites 9 A, B, and C) which then join into one main channel (site 8). Below this confluence, the gradient is steep, the channel is cut 20 m wide at the bottom (though the active stream only wets a portion of this) with large jumbled rocks,
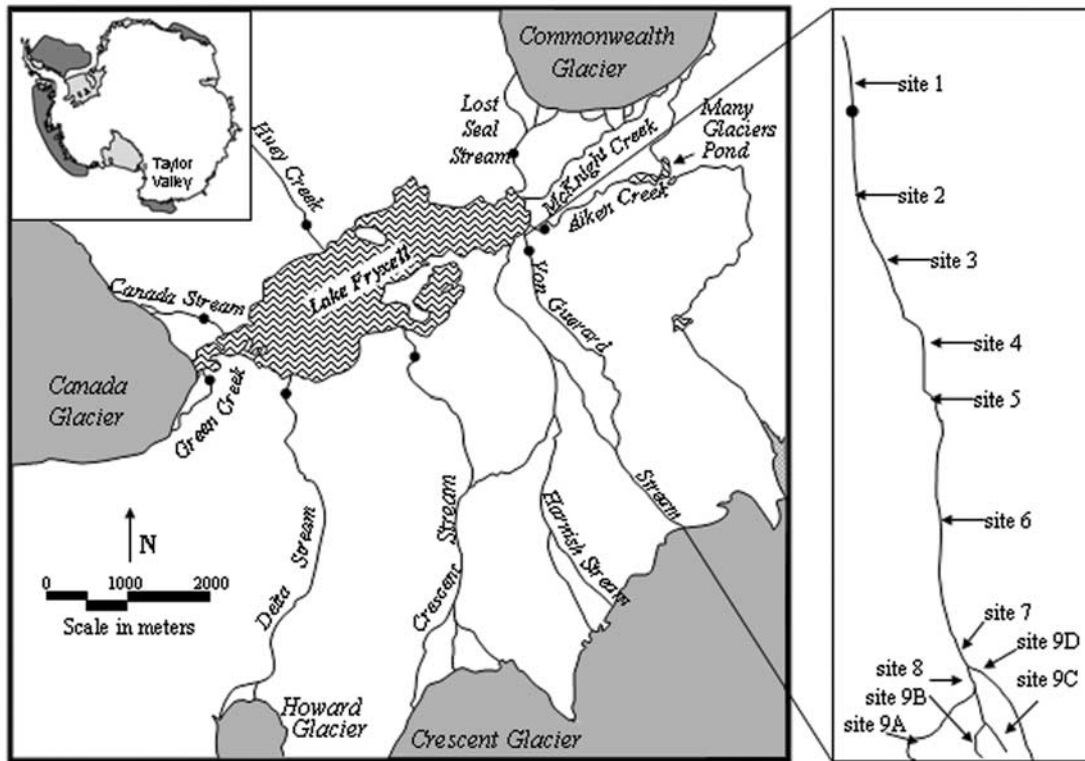
Figure 1. Location map of Taylor Valley, the Lake Fryxell basin, and von Guerard Stream showing location of inflows and sampling sites. Stream gauges are represented by solid dots. Map of von Guerard Stream is not to scale.

and the banks are steeply sloped and 5–8 m high (site 7). A final small tributary enters just above this point (site 9D). At the base of the steep reach, the flow divides and, at the time of the study, the main portion flowed to the east through a shallow gradient sandy reach (site 6). In this reach the banks are low and shallow pools may form during high flow. The stream then flows through a long reach with a moderate gradient, a wide active channel (about 15–20 m) containing stones wedged together in a stone pavement, and steep banks 3–6 m high (sites 5-2). About 1.5 km from the lake outlet, the stream gradient is more gradual and streambed is sandy (site 1). The stone pavement habitat of the moderate gradient reach supports abundant perennial algal mats

[*Alger et al.*, 1997]. However, algal mats are sparse in both the upper and lower reaches.

3. Methods

3.1. Analytical Methods

[12] Three synoptic samplings were made on von Guerard Stream, and at least 6 sites along the length of the stream were sampled (Figure 1). Samples were collected on two occasions (12 December 1990 and 16 January 1992) during moderate flows (11.83 L s^{-1} and 7.59 L s^{-1}, respectively) and once during low flow (9 January 1992, 1.42 L s^{-1}). Sample collection began in early after-
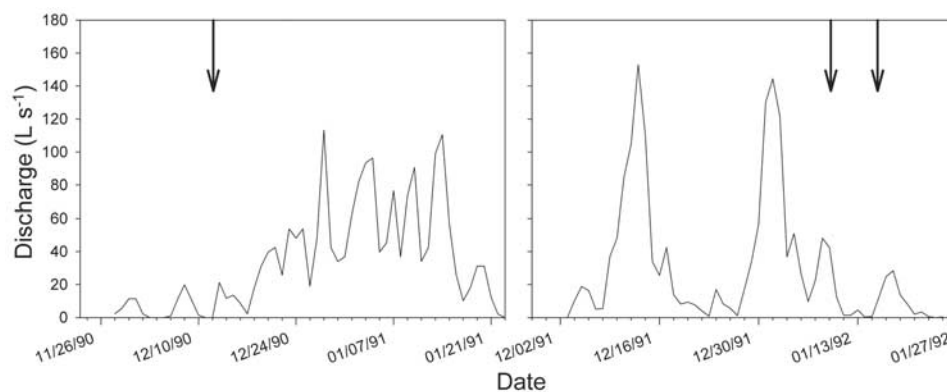
Figure 2. Hydrograph of mean daily flows at von Guerard Stream gauge for 1990/1991 and 1991/1992 flow seasons. Arrows denote days of synoptic sampling.

noon and was completed in 3 hours. Samples for major ion analysis were collected in 1 L polyethylene bottles and filtered through 0.4 μm Nuclepore filters using an Antlia filtration unit within 4–6 hours. Temperature, pH, and conductivity were measured in the field as described by *von Guerard et al.* [1995]. Filtered samples were transported to Boulder, Colorado for analysis. Analysis for Cl, Na, Ca, Mg, and Si was done with a Jarrel-Ash model 975 inductively coupled plasma (ICP) spectrometer using standard methods. K analyses were done by flame atomic absorption spectroscopy on a Perkin Elmer model 5000 spectrometer.

[13] No sediment sample was collected from von Guerard Stream, but the entire Lake Fryxell basin lithology is a homogeneous mix of very heterogeneous minerals. A qualitative evaluation of the lithology of the 1.6 to 3.15 cm size fraction of a representative sample of the stream sediments of Huey Creek and Green Creek, also in the Fryxell basin, was made. Geometric surface areas were estimated using the geometric mean of a uniform size distribution of a 19.7 kg representative sediment sample (sieved) from Huey Creek, assumed to be idealized spheres. Surface areas were also measured on a Micromeritics Flowsorb II 2300 using a three point BET (Brunauer-Emmett-Teller) adsorption isotherm with N_2 as the adsorbate. The makeup of the clay minerals were determined by X-ray diffraction (XRD) analysis using oriented samples mounted on the (010) surface of a silicon wafer. Mineralogy of the samples was determined by XRD using the techniques of *Srodon et al.* [2001]. This technique uses randomly oriented samples with a ZnO internal standard, and individual mineral abundances are determined by simultaneously fitting patterns from reference mineralogical standards and ZnO over peak regions diagnostic of the various mineral abundances. Based on sediment analyses and hyporheic water samples from Green Creek, chemical saturation state was computed using PHREEQC software [*Parkhurst and Appelo*, 1999].

3.2. Weathering Calculations

3.2.1. LWF Calculations

[14] A simple method of assessing watershed contribution to stream solute load is to periodically measure streamflow and stream water chemistry at a single location. Any location on a stream has a contributing watershed area associated with it, and a land surface area normalized weathering flux (LWF) for a solute can be computed for that location. As shown by *Ming-hui et al.* [1982], *Maybeck* [1987], and *Lyons et al.* [1997a], LWF values can be computed using the following formulation:

$$ LWF = \frac{C_{AVG}Q_{ANN}}{A_W} \qquad (1) $$

where C_{AVG} is average solute concentration measured at the stream site (μM), Q_{ANN} is cumulative annual streamflow (L yr^{-1}), and A_W is watershed area (m^2). With no streamflow contribution from precipitation and no hillslope weathering contributions in the Dry Valleys Streams, we assume that watershed area is defined as the length of the stream, multiplied by a 4 m wide buffer, a reasonable width of the active stream channel, similar to the approach of *Lyons et al.* [1997a] and *Nezat et al.* [2001].

3.2.2. Constant Weathering Rate Contribution (CRC) Modeling

[15] Another simple conceptual model is represented by a constant flux of solute to the stream from the streambed, analogous to a one-pass column experiment. This model is similar to the approach of *Kenoyer and Bowser* [1992a, 1992b] who studied increased Si concentrations in groundwater along a flow path between two lakes in Wisconsin, USA. An important issue is whether the evolution in water chemistry will retard the kinetics of the reactions further downstream. There are two end-member cases; (1) if the reactions are fast relative to the transport rate, the solution will approach equilibrium with the weathering phases, and further reaction will cease, and (2) the reaction kinetics are slow relative to the transport rate, and solutes never accumulate at concentrations high enough to significantly effect the reaction kinetics. Generally, silicate reaction kinetics are considered slow relative to hydrologic transport in near-surface systems.

[16] For the second case, simple linear best-fit regression lines to synoptic data can be used to calculate a constant solute supply rates for each data set. Assuming a known extent of the active, exchanging hyporheic zone, a weathering rate can be calculated as follows:

$$ \Gamma = \frac{dC}{dx} \frac{Q\Delta x}{m_{sed}S} \qquad (2) $$

where Γ is the net rate of solute contributed to solution from weathering reactions normalized to mineral surface area (mol m^{-2} s^{-1}), dC/dx is the change in solute concentration down stream (mol L^{-1} m^{-1}), Q is the streamflow rate (L s^{-1}), S is the surface area per grain mass (m^2 g^{-1}), and Δx is a finite difference spatial step (m), and m_{sed} is the mass of the sediment (g), given by:

$$ m_{sed} = (1-\phi)\rho_s \Delta x A_C \qquad (3) $$

where ϕ is the porosity of the sediment (cm^3 cm^{-3}), ρ_S is the solid density of the sediment (g m^{-3}), and A_C is the cross-sectional area of the active, weathering hyporheic zone sediment (m^2). von Guerard Stream is a good candidate for an initial rate assumption. The input waters are very dilute, the hyporheic zone remains fully saturated during the active period and is never desiccated, and the average residence time of the water during high flows is short, on the order of hours to days, which does not allow significant time for solutes to accumulate.

[17] Parameterization of the CRC model was based on field measurements. The cross-sectional area of the hyporheic zone was estimated based upon width of the active channel and the depth to permafrost. *Conovitz* [2000] measured large subsurface wetted zone areas (sediment and porous area) ranging from 3.5 to 6.4 m^2 ($n = 6$) in von Guerard Stream during the 1997–1998 austral summer. From these values, we constrain our model with an average area (5.3 m^2). We assumed that only half of that area was rapidly exchanging with the stream (A_C). For the moderate flow dates, A_C values were 2.67 m^2, a reasonable value on the order of previously published A_S values [*Runkel et al.*, 1998; McKnight et al., submitted manuscript, 2002]. Because hyporheic exchange is driven by head gradients between the stream and the storage zone, we assumed A_C to be 1.34 m^2
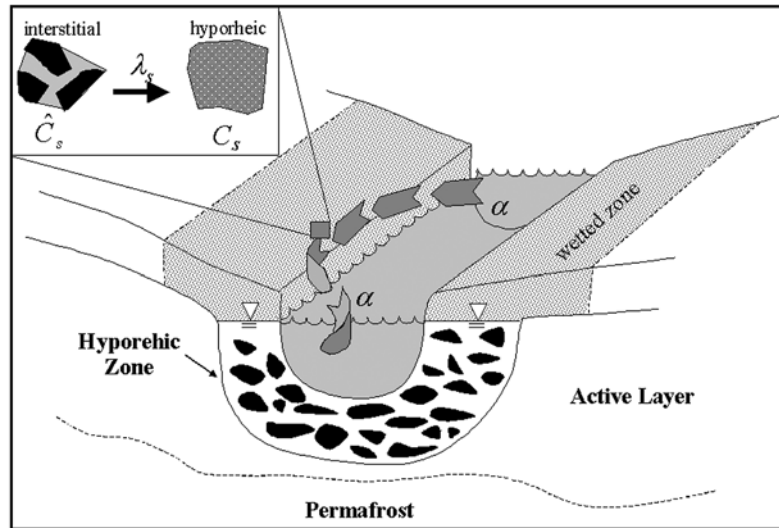
Figure 3. Hyporheic zone weathering concept. Exchange of water between the stream and the hyporheic zone is controlled by α, but solute flux into the hyporheic zone from weathering substrate is controlled by λ_S.

for the very low flow date. Porosity was assumed to be 0.33, based on measurements reported by *Conovitz* [2000]. Flow rate was measured at the gauge near the mouth of the stream.

[18] Sources of solutes to stream water are marine aerosol dissolution, and mineral weathering. The solute inputs along the stream length were partitioned among four major sources: (1) dissolution of atmospherically deposited marine aerosols, (2) dissolution of thenardite (Na_2SO_4), as suggested by *Green et al.* [1989], (3) the dissolution of calcite, and (4) the chemical denudation of primary silicate minerals. Solute source partitioning was computed given two key assumptions: (1) all Cl and some proportion of Na, SO_4, K, and Ca come from marine aerosol deposition and (2) SO_4 that does not come from marine aerosol deposition comes from dissolution of thenardite, as proposed by *Green et al.* [1989].

3.2.3. Hydrologic Exchange (HE) Modeling

[19] Given the importance of hyporheic exchange in Dry Valley stream systems [*Runkel et al.*, 1998; McKnight et al., submitted manuscript, 2002] and the direct weathering results from *Maurice et al.* [2002], a hydrologic exchange (HE) model that includes transient storage [*Bencala and Walters*, 1983] and chemical weathering was developed, based on OTIS-P (One-dimensional Transport with Inflow and Storage and Parameter estimation, http://webserver. cr.usgs.gov/otis) [*Runkel*, 1998]. Both hydrologic exchange and chemical reaction rates were modeled to simulate the field results. The transient storage model is governed by the following equations:

In stream

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \alpha(C_S - C) \qquad (4)$$

In storage zone

$$\frac{\partial C_S}{\partial t} = \alpha\frac{A}{A_S}(C - C_S) + \lambda_S(\hat{C}_S - C_S) \qquad (5)$$

where A is the cross sectional area of stream (m^2), A_S is the cross sectional area of storage zone (m^2), α is the storage

zone exchange coefficient (s^{-1}), C is the main channel solute concentration (μM), C_S is the storage zone solute concentration (μM), $\hat{C}_S$ is the storage zone source concentration (μM), D is the dispersion coefficient (m^2 s^{-1}), λ_S is the weathering rate coefficient (s^{-1}), x is the distance downstream (m), and t is time (s). This model assumes no precipitation reactions, and considers only the net release of solute from weathering reactions. Here we assume that the $\lambda_S(\hat{C}_S - C_S)$ term in equation (5) represents the weathering flux from sediment into solution in the hyporheic zone, while $\alpha(C_S - C)$ in equation (4) (and the $\alpha(A/A_S)(C - C_S)$ term in equation (5)) represents the hydrologic flux between the hyporheic zone and the stream (Figure 3). While the weathering flux term may not be an accurate representation of dissolution kinetics for the hyporheic zone minerals, it is a simplified representation of the dissolution reactions. The $\hat{C}_S$ value is assumed to be a hyporheic water solute concentration, representative of water that has been in contact with sediment for a long period of time. This is not necessarily an equilibrium concentration. Assuming steady state conditions, the weathering flux must be equal in magnitude to the hyporheic exchange flux, $\alpha(A/A_S)(C - C_S)$. A bulk-weathering rate for a specific solute (Si and K in this case) can then be formulated, based on hyporheic sediment specific surface area and the stream dC/dx computed as a function of transient storage parameters using equation (2). Solving equation (4) for dC/dx,

$$\frac{dC}{dx} = \alpha(C_S - C)\frac{A}{Q} \qquad (6)$$

assuming steady state conditions, the dispersion term of equation (4) has no effect on the model output. At steady state, equation (5) is solved for C_S,

$$C_S = \frac{\alpha A C + \lambda_S A_S \hat{C}_S}{\alpha A + \lambda_S A_S} \qquad (7)$$

Equation (7) can be substituted into equation (6) to determine the dependence of stream spatial concentration gradients on transient storage parameters as

$$\frac{dC}{dx} = \left(\frac{\alpha^2 AC + \alpha\lambda_S A_S \hat{C}_S}{\alpha A + \alpha\lambda_S A_S} - \alpha C \right) \frac{A}{Q} \qquad (8)$$

Combining (2) and (8) yields a transient storage-dependent weathering rate:

$$\Gamma = \left(\frac{\alpha^2 AC + \alpha\lambda_S A_S \hat{C}_S}{\alpha A + \alpha\lambda_S A_S} - \alpha C \right) \frac{A\Delta x}{m_{sed}S} \qquad (9)$$

4. Results

4.1. Stream Water and Sediment Analyses

[20] Synoptic sample analysis shows that von Guerard Stream became more enriched in solutes downstream (Figure 4). Increases in major ion concentrations at the furthest downstream site ranged from 12 to 66% compared to the furthest upstream site. On the two moderate flow dates, consistent increases occurred in solute concentrations downstream. On the lowest flow synoptic date (9 January 1992), specific conductance did not increase greatly downstream, yet solute concentrations generally increased. At such a low flow, the water in the stream channel at the downstream sites has likely exchanged many times with the hyporheic zone water, and it more closely represents the actual hyporheic zone chemistry.

[21] Based on the lithology (Table 1) and mineralogy (Table 2) the density of the solids in the sediment samples was estimated to be 2.7 g cm^{-3}. A geometric surface area of 3.79×10^{-3} m^2 g^{-1} was calculated for the bulk sediment, based on the size distribution from 21 size fractions of the <3.2 cm sediment, and assuming a spherical particle geometry. The N$_2$ BET surface area of the bulk sediment was computed to be 1.23 m^2 g^{-1} of sediment. This is based on the BET measurements of 10 different size fractions of the <1 mm material, which account for >90 % of the geometric surface area, and extrapolation to larger size fractions. The ratio of the BET to geometric surface area is about 320, typical for natural material.

[22] The lithology of the sediment was varied, but dominated by igneous and high-grade metamorphic rocks, with roughly equal amount of felsic, intermediate and basic compositions, and no evidence of volcanics (Table 1). The variability of the sediment lithology is expected, given the diverse geology and history of the Fryxell basin [*Doran et al.*, 1994; *Denton et al.*, 1989]. There were a few sedimentary rocks observed (<1%), and these are probably exotics, rafted into the valley bottom during an incursion of sea ice during the Pleistocene [*Denton et al.*, 1989]. Mineralogy of the fine fraction of the sediment from Huey Creek and Green Creek, based on XRD analysis are shown in Table 2. The 1.4−2 mm size fraction should be fairly representative of the course sediment, and has mineralogy generally consistent with the lithologies in Table 1. The 2−63 μm fraction has a mineralogy similar to the course fraction, except that it is somewhat enriched in amphibole and plagioclase. This may be a result of the tendency of amphiboles and plagioclase to form etch pits, developing a spongy texture that allows subsequent disaggregation and the generation of fine particles [*Berner and Holdren*, 1979; *Berner and Schott*, 1982; *Hall and Martin*, 1986]. The courser fraction was mostly primary silicate minerals with some kaolinite and muscovite/illite/smectite (which can not be quantitatively differentiated by the XRD technique) and the analyses totals near 100%, indicating primarily crystalline material. The <2 μm fraction from both Huey Creek and Green Creek contained more muscovite/illite/smectite and kaolinite, but much lower amounts of primary minerals. Glycolated, oriented samples indicate smectite is present in the <2 μm fraction, and a 10 Å peak indicates that illite and/or muscovite are also present. The very low totals for the crystalline material in Table 2 suggests the presence of considerable amorphous weathering products, on the order of 40–65% by weight of the <2 μm size fraction (Table 2), although this would only be ∼0.3 wt% of the bulk sediment. Saturation state analysis, assuming equilibrium with gibbsite, suggested that hyporheic waters are undersaturated with respect to albite, Ca-montmorillonite, chlorite, illite, K-feldspar, quartz, and SiO$_2$ (saturation index values of −5.2, −2.4, −14.9, −3.2, −3.0, −0.1, −1.5, respectively) and oversaturated with respect to kaolinite (saturation index of 0.6).

4.2. LWF Modeling

[23] Equation (1) was applied to the von Guerard Stream hydrologic and solute data collected from the 1990–1991 and 1991–1992 austral summer seasons. In the 1990–1991 flow season, Si C_{AVG} was 168 μM, and Q_{ANN} was 1.60×10^8 L yr^{-1}. For the 1991–92 flow season, Si C_{AVG} was 167 μM, and Q_{ANN} was 1.40×10^8 L yr^{-1}. Assuming a watershed width of 4 m, the LWF values are computed to be 1.3 mol Si m^{-2} yr^{-1} for 1990–1991 and 1.1 mol Si m^{-2} yr^{-1} for 1991–1992. The LWF value for the 1994–1995 season from *Lyons et al.* [1997a] was recomputed to include the longer stream length estimate and was found to be 2.4×10^{-2} mol Si m^{-2} yr^{-1} (Figure 5).

4.3. CRC Modeling

[24] On the two moderate-flow sampling dates, all major cations, anions and Si increased in concentration downstream (Figure 4). A linear regression of solute concentration with distance below the glacier had R^2 values of 0.42 and 0.96 for Ca, 0.96 and 0.99 for Mg, and 0.92 and 0.95 for Cl on 12 December 1990 and 16 January 1992, respectively. The calculated *dC/dx* values based on linear regression are presented in Figure 4 for Si and K. The simplified solute increase derived from the observations resulted in spatially constant weathering rates of 1.6×10^{-15} to 1.1×10^{-14} mol Si m^{-2} s^{-1} for BET computed sediment surface areas, and 5.3×10^{-13} to 3.4×10^{-12} mol Si m^{-2} s^{-1} for geometric sediment surface areas (Table 3). In all cases, CRC weathering rates for K were lower, generally about one-half the Si weathering rate values.

4.4. Partitioning Solute Sources

[25] Our assumption that longitudinally increasing concentrations of Si and K in the stream are evidence of primary weathering in the hyporheic zone can be evaluated by considering sources of solutes and elemental ratios. Considering the small amount of snow and its low ion
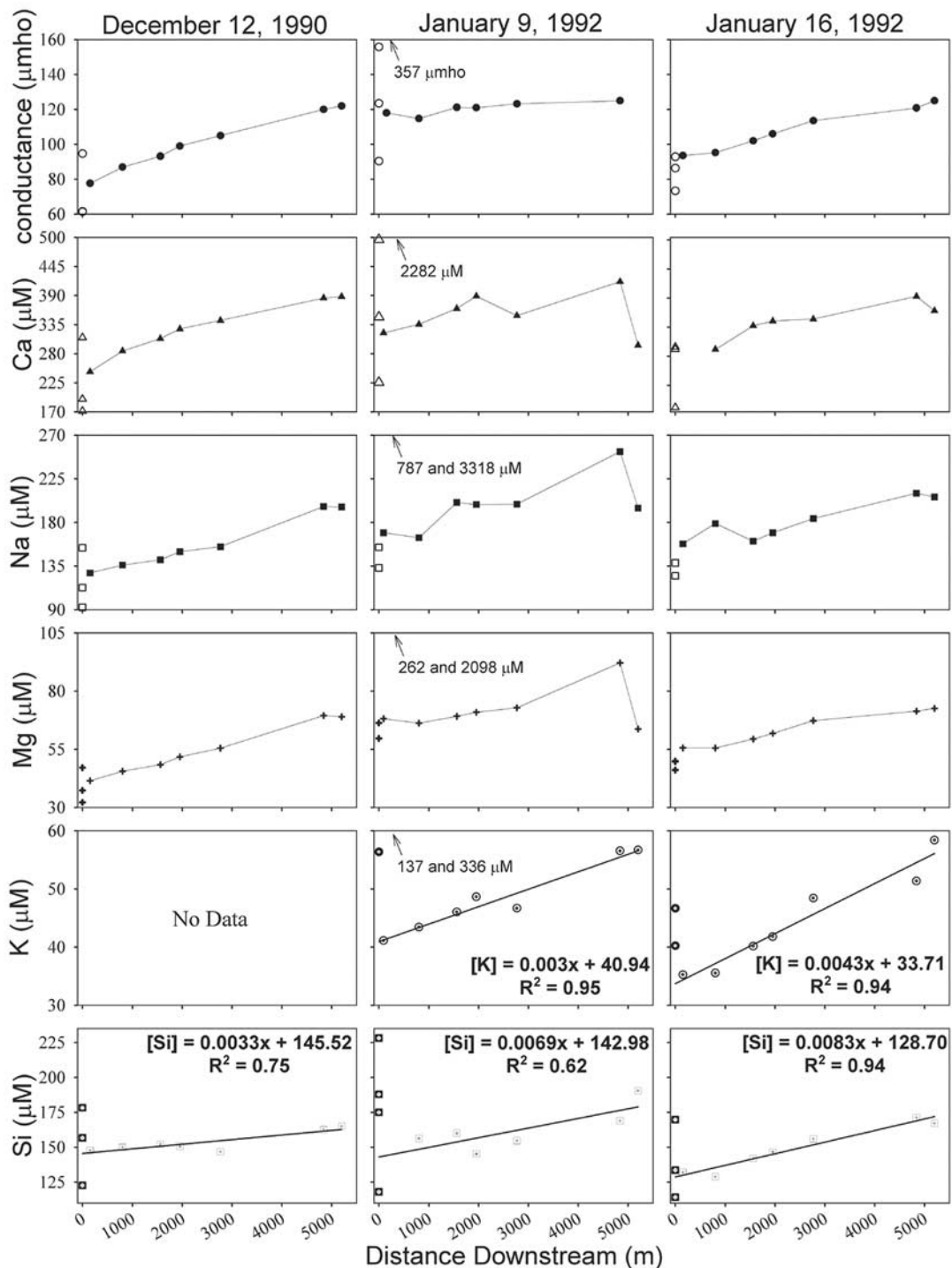
Figure 4. Synoptic solute data for von Guerard Stream for 12 December 1990, 9 January 1992, and 16 January 1992 conductance, Ca, Na, Mg, K, and Si. Data at 0 m represent solute concentrations from the headwater channels (sites 9A, B, C, and D). Note that some samples were not run for certain solutes (i.e., missing data).

concentrations [*Legrand and Mayewski*, 1997], atmospheric precipitation cannot be entirely responsible for the stream chemistry. Further, H_4SiO_4, which is derived from weathering of silicate minerals, is found in much lower concentrations in the glaciers than in the streams [*Lyons et al.*, 1998]. Although marine aerosol deposition is an important contribution to salt in the soils [*Keys and Williams*, 1981],

we can constrain the significance of this source because compared to Cl, Na, and Mg, seawater has very little K [*Stumm and Morgan*, 1981]. *Lyons et al.* [1997b] used the USGS inverse model computer code NETPATH, which essentially subtracts the "final" water from the "beginning" water and provides the net geochemical reactions to explain the difference between the two, and found that no

Table 1. Hyporheic Zone Alluvium Lithology Based on Samples From Huey Creek

Grain Size	Composition	Felsic	Intermediate	Basic	Sedimentary
Course	number	140[a]	74		1 carbonate
Course	%	33.7%	17.8%		2 sand/silt
Intermediate	number	17	64[b]	62[c]	
Intermediate	%	4.1%	15.4%	14.9%	
Fine	number			55[d]	
Fine	%			13.3%	
Percent of total		37.8%	33.3%	28.2%	0.7%

[a] "Granitic" rocks.
[b] Contains ∼30% metamorphic rocks.
[c] "Diabase."
[d] "Basaltic" rocks.

Table 2. Sediment Mineral Composition of Other Lake Fryxell Basin Streams

Mineral	Weight Percent			
	Huey Cr. 1.4–2 mm	Huey Cr. 2–63 μm	Huey Cr. <2 μm	Green Cr. <2 μm
Quartz	18	9	0.3	2
Kspar	8	6	2	3
Plagioclase	46	30	3	4
Amphibole	7	14	0.4	0.2
Pyroxene (augite)	4	8	0.3	3
Biotite + chlorite	1	3	6	11
Muscovite/illite/smectite	11	21	22	35
Disordered kaolinite	4	6	2	0
Total:	99	97	35	57

single solution provided by the NETPATH output involved only the dissolution of simple salts. The hydrolysis of primary silicate minerals was needed to satisfy the difference in stream chemistry.

[26] Table 4 presents the results of partitioning the various stream solute sources. The remaining Na after accounting for the marine aerosol and thenardite sources is assumed to come from release of Na from weathering of sodium silicate minerals. There is very little contribution of K and Si from marine aerosol dissolution, thus the major source for these solutes is weathering of primary silicate materials. Strong biological cycling of K, which obscures K sources and sinks in most vegetated watersheds, is not a significant factor in Antarctica. Further, previous tracer experiments in Antarctic streams have shown minimal cation exchange for K (McKnight et al., submitted manuscript, 2002). Thus modeling K and Si weathering rates will provide weathering rates of primary silicate materials in Dry Valley stream systems.

4.5 Integrating Hyporheic Zone Circulation Into a Mineral Surface Weathering Modeling

4.5.1. Parameterization of the HE Model

[27] The parameter estimates for the transport simulation for HE model (Table 5) were based on physical measurements of von Guerard Stream and results of tracer experiments in two other Dry Valley streams. Stream cross-sectional area, A, was computed from discharge measurements at flows similar to those during the synoptic samplings. The same A_C values used in the CRC model were used for the HE model. To obtain the cross-sectional area of the hyporheic zone that contains water we multiplied A_C values by the porosity. A final value of A_S at the two moderate flows was calculated to be 0.88 m², and half of that value (0.44 m²) was used in the very low flow simulation, assumed to be representative of low flow conditions. OTIS-P was run to solve for λ_S for a matrix of reasonable values of A_S and α for each synoptic date. Upstream boundary condition concentration values for solutes in the stream (and therefore initial condition concentrations for the model runs) used in the hydrologic modeling were taken from the intercept values of the CRC modeling.

[28] The storage zone source concentration, $\hat{C}_S$, was set equal to concentrations observed in lateral hyporheic wells of Green Creek (Figure 1) in the 1999–2000 austral summer. Tracer injection experiments in Green Creek showed that there was little exchange between these lateral

well locations of the wetted zone, and the stream (Gooseff, unpublished data, 2000). Stable isotope transport modeling suggests that water in the Green Creek lateral wells exchanges slowly over several months [Gooseff et al., 2002], thus allowing weathering reactions to come to a state of relative equilibrium. Fully saturated sediment in the wetted zone that is not actively exchanging with the stream, or is exchanging on very long timescales, will likely yield weathered solutes to the interstitial water with concentrations that represent $\hat{C}_S$. The averages of three sample measurements from the farthest lateral well in Green Creek were 204 μM for Si and 192 μM for K, and we used these values for $\hat{C}_S$.

[29] An α value of 2.36×10^{-3} s⁻¹, which is an average of α values for the previous tracer experiments in Dry Valley streams [Runkel et al., 1998; McKnight et al., submitted manuscript, 2002] was used for the entire stream reach. Given this value of α and the A_S values of 0.88 m² for 12 December 1990 and 16 January 1992 and 0.44 m² for 9 January 1992, the estimated λ_S values used in the Si weathering using OTIS-P were 8.74×10^{-7} s⁻¹, 3.13×10^{-7} s⁻¹, and 1.27×10^{-6} s⁻¹ (chronologically), and for the K weathering, 1.75×10^{-7} s⁻¹ and 5.23×10^{-7} s⁻¹ (chronologically).

[30] To test the parameter sensitivity of α and A_S, several more model runs were made with OTIS-P to estimate λ_S values. The range of α (1.0×10^{-5} to 1.0×10^{-2} s⁻¹) and
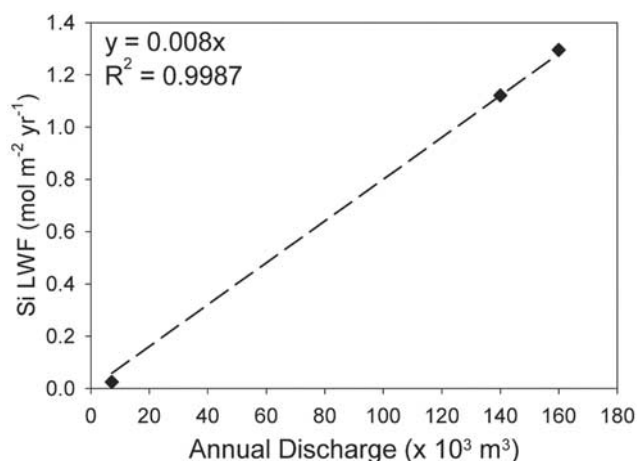
Figure 5. Si LWF calculations for von Guerard Stream for the 1990–1991, 1991–1992, and 1994–1995 flow seasons.

Table 3. Si and K Weathering Rates Calculated From Continuous Weathering Rate Contribution (CRC) Modeling Method

	12 December 1990		9 January 1992		16 January 1992	
	Si	K	Si	K	Si	K
dC/dx (mol L^{-1} m^{-1})	3.25×10^{-9}	N/A	6.87×10^{-9}	3.03×10^{-9}	8.26×10^{-9}	4.34×10^{-9}
Γ (mol m^{-2} s^{-1}), BET	6.5×10^{-15}	N/A	3.3×10^{-15}	1.5×10^{-15}	1.1×10^{-14}	5.6×10^{-15}
Γ (mol m^{-2} s^{-1}), geometric	2.1×10^{-12}	N/A	1.1×10^{-12}	4.7×10^{-13}	3.4×10^{-12}	1.8×10^{-12}

A_S (0.10 to 5.0 m^2) chosen bracket representative values for these parameters. An order of magnitude change in A_S produces an order of magnitude change in λ_S. But an order of magnitude change in α produces only a small change in λ_S. Given the range of α and A_S that have been found in previous studies of Antarctic streams, λ_S can range about two orders of magnitude. For 12 December 1990 the range of λ_S values for Si weathering is 1.54×10^{-7} to 1.11×10^{-5} s^{-1}, for 9 January 1992 it is 2.75×10^{-8} to 1.55×10^{-6} s^{-1}, and for 16 January 1992, it is 2.23×10^{-7} to 2.02×10^{-5} s^{-1}.

[31] Our approach is consistent with studies of hyporheic zone experiments in other streams. *Legrand-Marcq and Laudelout* [1985] found that for a series of tracer injection experiments in a stream in France, increasing flow reduced the ratio of A_S/A, because changes in flow had a greater affect on the cross sectional area of the stream and little affect on the cross-sectional area of the storage zone. That same study concluded that changes in flow had little affect on the hyporheic exchange rate, α, except that the lowest modeled exchange rates were found during the lowest flows and the largest exchange rates accompanied the highest flow rates. Similarly, *Morrice et al.* [1997] found that increased flow yielded decreased A_S/A ratios due to the compounding effects of decreasing A_S for increasing flow and increasing A. *D'Angelo et al.* [1993] quantified changes in model parameters over several orders of stream reach length and found that there was a negative correlation between A_S/A

and discharge, but no clear correlation between α and discharge.

4.5.2 HE Model Results

[32] The HE model results are presented in Figures 6 and 7, and for each date show very close results for the rate of exchange of weathering products into the stream. Given the varied flow conditions, differences in storage zone areas (A_S), and different initial conditions, λ_S ranges between 4.76×10^{-7} to 1.27×10^{-6} s^{-1} for Si, and from 6.84×10^{-8} s^{-1} to 2.52×10^{-7} s^{-1} for K (Table 5). During the parameterization step, it was found that λ_S was more sensitive to the value of A_S than to the value of α. Thus the overall results of the HE method are sensitive to the A_S value used. The Si weathering rate coefficients are all within an order of magnitude. The difference in the rate coefficients for the two different elements is interpreted to be the result of the differing availability of these elements within the source materials. The hyporheic weathering fluxes from the HE model decreased nonlinearly downstream as the difference between $\hat{C}_S$ and C_S decreased downstream. This result was expected, and is a result of the $\hat{C}_S$ values used here, which were lower than theoretical chemical saturation. Geometric weathering rate results for Si and K also decrease nonlinearly downstream. The results are presented in Figure 8 and summarized in Table 6. As expected, BET weathering rates are 2−3 orders of magnitude lower than geometric weathering rates, as the BET sediment surface area measurements are 2 orders of magnitude higher than the geometric surface area calculations. Geometric weathering rates are found to range from 6.4×10^{-13} to 4.5×10^{-12} mol m^{-2} s^{-1} for Si and 4.3×10^{-13} to 1.9×10^{-12} for K (Table 6).

5. Discussion

5.1. Comparison of Silicate Weathering Rates and Calculation Methods

[33] The LWF calculations of dissolved Si transport from von Guerard Stream supports the findings of *Lyons et al.*

Table 4. Analysis of Sources of Major Ions in von Guerard Stream Based on Increase of Stream Concentration for Each Major Ion

Major Ion	Downstream Concentration Increase, μM	Marine Aerosol[a]	Thenardite (Na$_2$SO$_4$)	Calcite (CaCO$_3$)	Silicate Minerals
12 December 1990					
Cl	35.82	100%	0%	0%	0%
SO$_4$	4.37	42%	58%	0%	0%
Na	68.03	45%	7%	0%	47%
Ca	142.17	0.5%	0%	99.5%	0%
K	ND	-	-	-	-
Si	17.23	0%	0%	0%	100%
16 January 1992					
Cl	33.35	100%	0%	0%	0%
SO$_4$	3.48	50%	50%	0%	0%
Na	48.32	59%	7%	0%	33%
Ca	326.45	0.2%	0%	99.8%	0%
K	30.07	2%	0%	0%	98%
Si	35.11	0%	0%	0%	100%

[a] Marine aerosol ion composition is assumed to be the same as average seas water composition of each ion (1 Cl : 0.05 SO$_4$: 0.86 Na : 0.02 Ca : 0.02 K, as reported by *Morel and Hering* [1993, p. 291]).

Table 5. Parameter Values Used in the Hydrologic Exchange (HE) Modeling Method

| Parameter	12 December 1990	9 January 1992	16 January 1992
A (m^2)	0.25	0.125	0.25
As (m^2)	0.88	0.44	0.88
α (s^{-1})	2.36×10^{-3}	2.36×10^{-3}	2.36×10^{-3}
D (m^2 s^{-1})	0.5	0.5	0.5
Q (L s^{-1})	11.83	1.42	7.59
$C_{0,\ Si}$ (μM)	145.5	143.0	128.7
$C_{0,\ K}$ (μM)	N/A	40.9	33.7
λ_S (s^{-1}) for Si	8.40×10^{-7}	4.76×10^{-7}	1.27×10^{-6}
λ_S (s^{-1}) for K	N/A	6.84×10^{-8}	2.52×10^{-7}
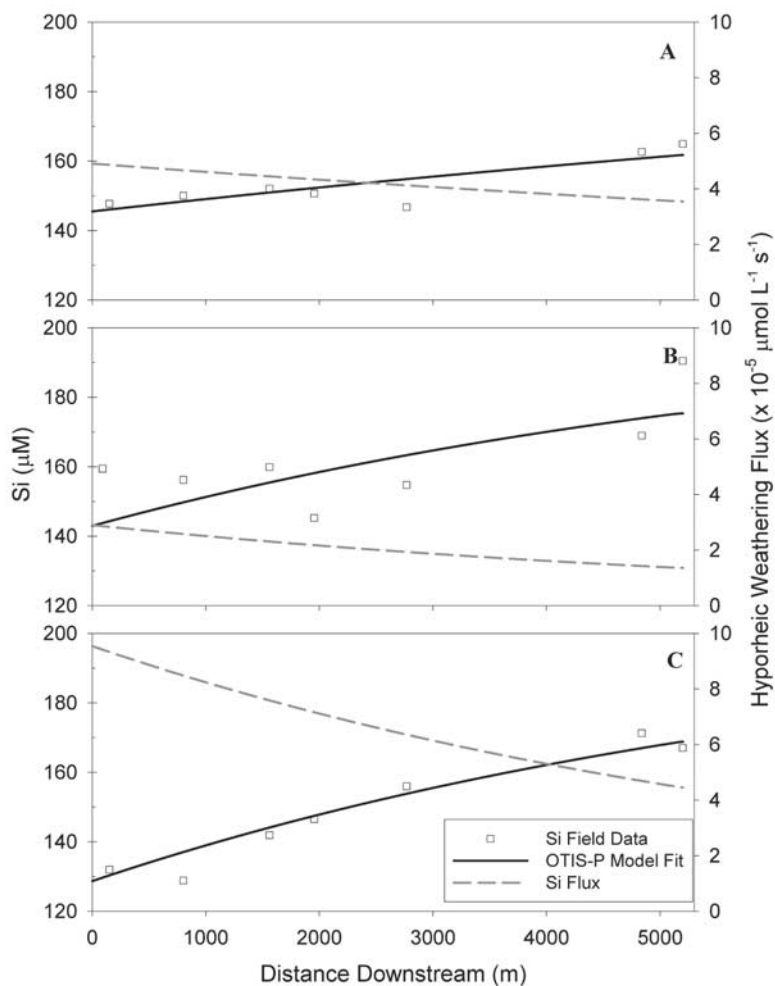
Figure 6. Si model fit and computed weathering flux [$\lambda(\hat{C}_S - C_S)$] from HE modeling for von Guerard Stream on (a) 12 December 1990, (b) 9 January 1992, and (c) 16 January 1992.

[1997a]. With three seasons' worth of data presented here, it is obvious that the Si LWF calculations are greatly dependent on annual streamflow (Figure 5). Dissolved Si concentrations do not vary much from year to year, and watershed areas remain constant. This result is similar to that of *Riebe et al.* [2001], who found chemical weathering to be a relatively constant proportion of total denudation rates in varying Sierra Nevada watersheds. The strong dependence on annual streamflow suggests that the chemical weathering rate in the hyporheic zone must also depend on streamflow. Under any flow regime, hyporheic exchange occurs in the very porous alluvium of these streambeds. The LWF method is very useful in comparing and contrasting either fluxes from various basins, or fluxes from different flow seasons (Figure 5).

[34] Both the CRC and HE models depend greatly on the amount of substrate available in the hyporheic zone, as represented by the simulated size of the hyporheic zone and exchange rate (α). Although entire wetted zone cross sectional areas can be large in Dry Valley streams [*Conovitz*, 2000], data from ^{18}O and D transport modeling [*Gooseff et al.*, 2002] indicate that stream water is not rapidly exchanging with the entire wetted zone. The extent of the hyporheic

zone that exchanges stream water on the timescale of mean advective stream transport is difficult to quantify without stream tracer data. The values used here are reasonable for this stream, thus we propose that our results reasonably characterize hyporheic weathering.

[35] The results of the CRC modeling by linear interpolation are similar (Table 4) to the ranges calculated by HE modeling (Table 6 and Figure 8). In the CRC model, by definition dC/dx is constant down the length of the stream, and therefore yields a constant weathering rate. In contrast, in the HE modeling results, the dC/dx was not constant along the entire stream reach, because dC/dx in equation (8) is nonlinear and concentrations in the hyporheic zone (C_S) and in the stream are changing downstream. The only constant concentration in these simulations is $\hat{C}_S$. The farthest downstream Si concentrations (sites 1 and 2) approach the value of $\hat{C}_S$ that was found in the distant, less strongly connected portion of the hyporheic zone in Green Creek. Lower concentration gradients between stream and storage zone at this section of the stream result in lower exchange fluxes. Hyporheic exchange is still rapidly moving stream water through the hyporheic zone, but the stream water is more solute enriched, so a decreased weathering
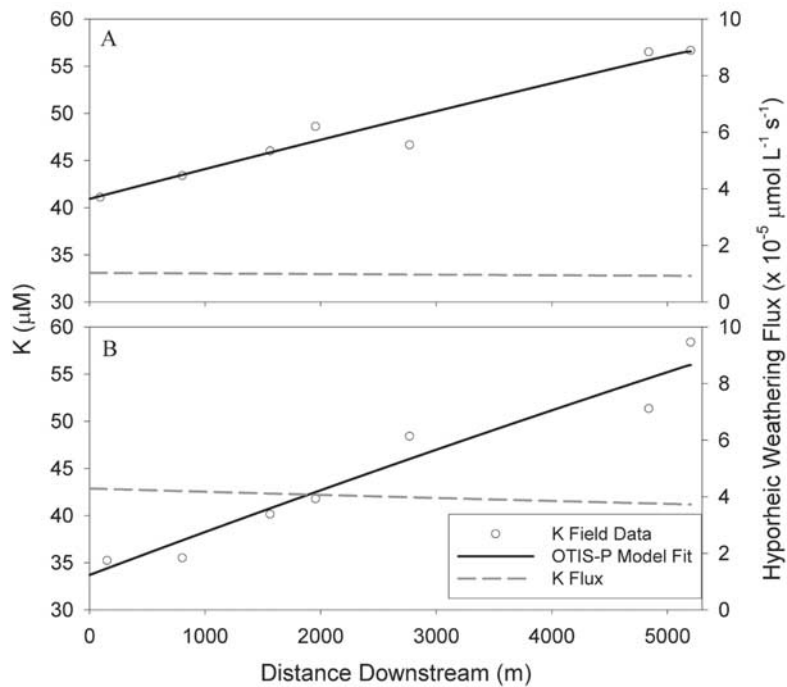
Figure 7. K model fit and computed weathering flux $[\lambda(\hat{C}_S - C_S)]$ from HE modeling for von Guerard Stream on (a) 9 January 1992 and (b) 16 January 1992.
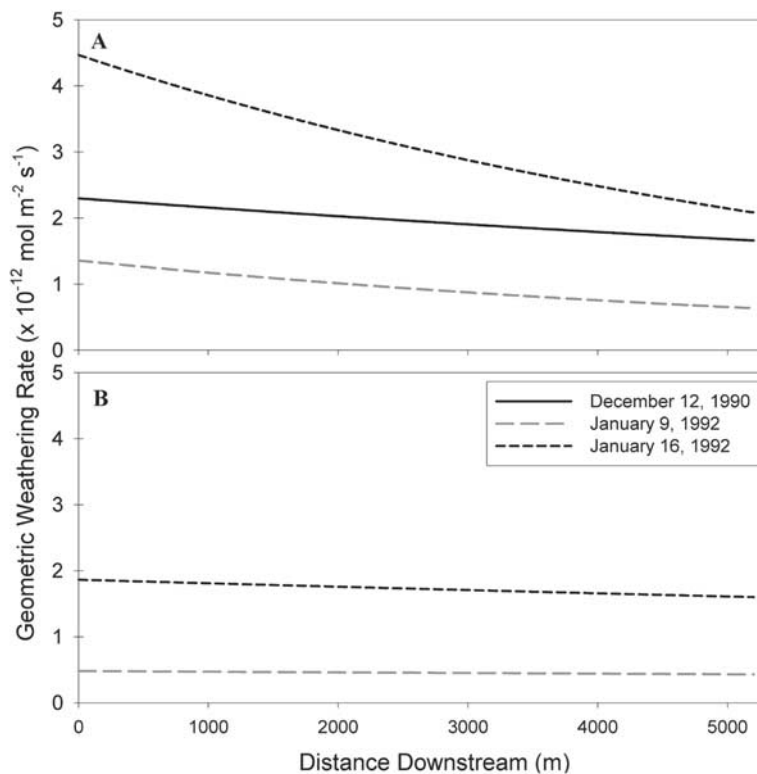
Figure 8. The von Guerard Stream geometric weathering rates of (a) Si and (b) K using the HE modeling method.

Table 6. Si and K Weathering Rates Calculated From Hydrologic Exchange (HE) Modeling Method

Rate Ranges	12 December 1990		9 January 1992		16 January 1992	
	Si	K	Si	K	Si	K
Average dC/dx (mol L^{-1} m^{-1})	3.12×10^{-9}	N/A	6.30×10^{-9}	3.03×10^{-9}	7.75×10^{-9}	4.29×10^{-9}
Γ (mol m^{-2} s^{-1}), BET, low	5.1×10^{-15}	N/A	2.0×10^{-15}	1.3×10^{-15}	6.4×10^{-15}	4.9×10^{-15}
Γ (mol m^{-2} s^{-1}), BET, high	7.1×10^{-15}	N/A	4.2×10^{-15}	1.5×10^{-15}	1.4×10^{-14}	5.8×10^{-15}
Γ (mol m^{-2} s^{-1}), geometric, low	1.7×10^{-12}	N/A	6.4×10^{-13}	4.3×10^{-13}	2.1×10^{-12}	1.6×10^{-12}
Γ (mol m^{-2} s^{-1}), geometric, high	2.3×10^{-12}	N/A	1.4×10^{-12}	4.8×10^{-13}	4.5×10^{-12}	1.9×10^{-12}

flux results. While the value of $\hat{C}_S$ is lower than an expected chemical equilibrium concentration of dissolved Si, the observations from a location in Green Creek that was not rapidly exchanging with the stream suggest that this is a reasonable assumption for an observed Si field equilibrium value.

[36] Calculations presented here also inherently depend on measured sediment grain surface area. BET surface areas were about three orders of magnitude higher than geometric calculated surface areas as is typical, resulting in geometric surface area normalized weathering rates calculated to be about 3 orders of magnitude faster than those computed with BET surface areas. *White et al.* [1996] conclude that BET surface areas represent a more realistic surface area value during the weathering process. We interpret the BET surface area as an upper limit that represents the ideal mineral sediment surface area that could be weathering. Hyporheic zone flow paths are generally heterogeneous. Thus BET surface areas presented here may overestimate actively weathering sediment surface area, and may underestimate the true chemical weathering rate. By comparison, geometric surface areas are probably an underestimate of available weathering surface area, but are more reliably computed in various weathering studies, based on sediment size distribution, or atomic force microscopy (AFM) estimates. *White and Peterson* [1990] suggest that the actual reactive area may well be less than either the computed geometric or BET sediment surface areas, leading to the conclusion that computed field weathering rates may be underestimates of actual weathering rates. The geometric and BET surface area measurements presented here bracket the geometric measurements made by *Maurice et al.* [2002] who used AFM to assess the volume of a fresh mica chip dissolved by chemical weathering after 39 days of deployment in the hyporheic zone of Green Creek.

[37] For all weathering simulations, the CRC weathering rates are within the range of the computed HE weathering rates. For example, for 12 December 1990, the geometric Si weathering rate from the CRC modeling is 2.1×10^{-12} mol Si m^{-2} s^{-1}, which is within the range determined from the HE modeling (1.7×10^{-12} mol Si m^{-2} s^{-1} 2.3×10^{-12} mol Si m^{-2} s^{-1}). Also as expected, the CRC weathering rate is generally closer to the upper end of the HE value range, lending confidence to our approach. For the two dates on which there is both Si and K data (9 and 16 January 1992), the CRC and HE modeling results show that the K weathering rates are slower than the Si weathering rates. This suggests that the minerals weathering have more available Si than K. Further, the range of HE weathering rates for K is smaller than the range of Si weathering rates, because K concentration increases are generally smaller than for Si and the $\hat{C}_S$ value for K is lower than the $\hat{C}_S$ value for Si.

[38] The lowest weathering rates from both the CRC and HE models were computed for the low flow date. Under low flow, the volume of water in the stream is 650 m^3 (assuming A, the cross sectional area of the stream, is 0.5 m^2), which is 25 less than the volume of water in the hyporheic zone, roughly 2288 m^3 (assuming A_S, the cross sectional area of the hyporheic storage zone, is 0.88 m^2). Thus under low flow, the solute concentrations in the stream are likely to approach those in the hyporheic zone, and the stream water will strongly reflect the hyporheic zone solution chemistry. If the stream water is less dilute, and more like hyporheic water, it is unlikely that chemical weathering rates would be high. The highest Si weathering rates for the CRC and HE model runs were found for the intermediate flow conditions, because the hyporheic zone parameters used for that date were the same as those for the high flow date.

[39] Working in northern polar regimes, *Huh et al.* [1998a, 1998b] and *Darmody et al.* [2000] have also found high weathering rates in cold environments, and suggest that physical weathering, such as freeze-thaw cycles or frost action, may contribute to chemical weathering. We do not believe that freeze-thaw effects have a large influence on chemical weathering in the hyporheic zone on short timescales of a day or less, but may have a seasonal effect. Freeze-thaw cycles may be important on a daily timescale at the edges of the wetted sediment zone, which would not influence the rapidly exchanging portion of the hyporheic zone. However on an annual timescale, the freezing and thawing of the hyporheic zone could provide fresh sediment surfaces for hyporheic weathering. Typical weathering scenarios are either transport limited, in which high localized weathering rates may occur, but limited transport of the weathering products hinders replacement of chemically saturated water, or weathering limited, in which dilute water is constantly moving through the porous media in intimate contact with mineral surfaces. High solute loads to streams are generally not found in transport limited systems. Dry Valley streams appear to be weathering limited as hyporheic exchange provides rapid transport of solutes into the stream.

[40] It is also unlikely that the downstream solute increases are due to evaporation of stream water, even in such a dry environment. *Gooseff et al.* [2002] computed an open water evaporation rate to be 7.1×10^{-5} L m^{-2} s^{-1} from an evaporation pan experiment. Given that the active stream width is 2 m and the stream is 5200 m long, an evaporation loss of 1 L s^{-1} would correspond to an evaporation rate of 9.61×10^{-5} L m^{-2} s^{-1} over the entire open water surface area. We assume that evaporation of 1 L s^{-1} of over 5200 m does not substantially affect the weathering results, thus considering evaporation would change the weathering rates by much less than an order of magni-

Table 7. A Comparison of Mineral Surface Area Normalized Weathering Rates From Previous Studies

Location	Study	Surface Area	Weathering Rate, 10^{-12} mol Si m^{-2} s^{-1}
	Laboratory Rates		
Coweeta, USA Oligoclase	*Velbel* [1985]	BET	3 – 20
Coweeta, USA Garnet	*Velbel* [1985]	BET	10
Coweeta, USA Biotite	*Velbel* [1985]	BET	200
Loch Vale, USA Oligoclase	*Clow* [1992]	BET	0.09[a] 0.32[b]
Loch Vale, USA Biotite	*Clow* [1992]	BET	0.002[a] 0.012[b]
Loch Vale, USA Microcline	*Clow* [1992]	BET	0.006[a] 0.020[b]
Bear Brook, Maine, USA Bulk	*Swoboda-Colberg and Drever* [1993]	geometric	33.8[c] 25.0[d]
	Field Rates		
Coweeta, USA Oligoclase	*Velbel* [1985]	geometric	0.89
Coweeta, USA Garnet	*Velbel* [1985]	geometric	3.8
Coweeta, USA Biotite	*Velbel* [1985]	geometric	0.12
Loch Vale, USA Oligoclase	*Clow* [1992]	BET	0.22[e] 0.22[f]
Loch Vale, USA Biotite	*Clow* [1992]	BET	0.06[e] 0.03[f]
Bear Brook, Maine, USA Bulk	*Swoboda-Colberg and Drever* [1993]	geometric	0.202[c] 0.078[d]
Green Creek, Dry Valleys Mica	*Maurice et al.* [2002]	geometric	0.083

[a] Under low-flow conditions, 34 L d^{-1}.
[b] Under high-flow conditions, 154 L d^{-1}; see *Clow* [1992] for details.
[c] At pH of 4.
[d] At pH of 4.5; see *Swoboda-Colberg and Drever* [1993] for details.
[e] Column experiment with treated soil.
[f] Crushed granite; see *Clow* [1992] for details.

tude. The reported weathering rates include the in-hyporheic weathering process as well as evaporation effects on solute concentration.

5.2. Implication for Other Systems

[41] The HE and CRC model chemical weathering rates compare well with chemical weathering rates found in other studies (Table 7). The geometric HE Si weathering rates are generally higher than or on par with all geometric weathering rates reported in Table 7, except for the Bear Brook laboratory rates [*Swoboda-Colberg and Drever*, 1993], which represent bulk weathering rates of multiple minerals. The data presented in Table 7 is mostly mineral-specific. The weathering rates of the Dry Valley hyporheic zone sediment presented here are representative of multiple minerals weathering, although the sediment mineralogy and saturation state analyses suggest that Dry Valley hyporheic weathering is dominated by pyroxines and amphiboles. Due to uncertainties in hyporheic water chemistry (namely the absence of Al, bicarbonate, and Fe concentrations), these analyses are not conclusive. Thus comparison between these results and those from other sites is a qualitative exercise.

[42] The volume of the hyporheic zone and the rate of exchange with surface water are shown to be important controls on the downstream changes in stream chemistry. Because of the dilute glacial meltwater and absence of liquid water in the surrounding landscape, hyporheic zone weathering is a dominant control on stream Si and K concentrations in the Dry Valleys. Additionally, the cold temperatures and absence of organic phases in Dry Valley streams do not appear to suppress the bulk weathering rate of silicate minerals compared to laboratory weathering experiments or field denudation studies in warmer regions.

[43] Hyporheic zone weathering is likely to contribute solutes to temperate streams to some extent. Weathering rates can be substantial in any fully saturated environment with rapid exchange of water through a porous medium, and a suitable weathering substrate. In most temperate systems, it is likely that evidence of such processes is masked by other influences on water chemistry, such as varying lateral inflow chemistries, and inputs from hillslope chemical weathering processes. It is also likely that hyporheic sediments have been extensively weathered in the past and are not likely to weather rapidly anymore. The HE modeling method presented here could be useful in assessing chemical weathering contribution to stream solute loads from hyporheic zone processes. In particular, the HE model allows for the discritization of chemical reaction ($\lambda_S(\hat{C}_S - C_S)$) and hyporheic exchange ($\alpha(C_S - C)$) controls on stream water chemistry. For the present experiment, model runs were steady state, and therefore these two fluxes were equal in magnitude. But, for a dynamic simulation, it is possible to discern the dominant flux.

[44] It has long been proposed that cold temperatures suppress the weathering rates in surficial systems, because this relationship would be expected based upon the decrease in solubility products with temperature. The high apparent activation energies for silicate dissolution in both experimental and natural weathering systems ($\sim$60 kJ mol^{-1}) suggest a temperature effect on the kinetics of silicate weathering. Although during the short flow season, the hyporheic sediments experience warmer and wetter conditions than the Dry Valleys climate suggests, our results do not follow this expectation, as rates are high enough to produce high fluxes of weathered solute to the lakes over short flow seasons. In addition, the cold temperatures also suppress microbial activity and thus lower both the rate of carbon dioxide and organic acid production, the primary sources of acidity generated in soils and groundwater. This concept of lower weathering rates at high latitudes has recently been challenged by studies of large river systems in the Arctic [*Huh et al.*, 1998a, 1998b; *Huh and Edmond*, 1999], which show higher than expected concentrations of

major ions in rivers from these cold drainages. These results suggest that the hypothesis that catchments in warmer, wetter climates experience higher weathering rates [*White and Blum*, 1995] can be augmented by considering hydrologic controls on weathering. We propose that the difference in the Dry Valleys, which has a cold and dry climate, is due to (1) the continual saturation of the weathering minerals during the flow season, as opposed to intermittent saturation in other watershed hillslopes around the world, (2) the hydrologic control of rapid exchange of dilute water, and (3) the differences in substrate that is being chemically weathered.

[45] Another challenge in low temperature geochemistry has been explaining the differences in weathering rates for silicate minerals determined in the laboratory compared to weathering rates estimated from watershed scale field studies, which generally are several orders of magnitude lower [e.g., *Swoboda-Colberg and Drever*, 1993]. The differences between lab and field weathering rates have been attributed to temperature differences [*Velbel*, 1990] and discrepancies among hydrologic flow path, temperature, pH, and particle size [*Malmstrom et al.*, 2000]. It is not surprising that actual chemical weathering rates would be modified from rates determined in a controlled laboratory setting because of the complexities of the natural environment in terms of flow paths, mineral coatings, humic substances, microbial processes, and precipitation of secondary minerals. But, it is surprising that all these processes would work to lower the weathering rates to such an extent. The methods and results presented here may also provide a solution to the laboratory versus field weathering rate discrepancy. Rather than compute both, field rates are computed here based on field data and lab analyses of substrate material. This approach quantifies in situ chemical weathering by accounting for the influence of hyporheic exchange.

6. Conclusions

[46] Three different approaches for quantifying watershed solute fluxes, one from the total watershed contribution perspective, and two considering solute production by dissolution of sediment in the hyporheic zone, were presented and compared. The hydrologic modeling approach increases the mechanistic understanding of the chemical weathering processes and the influence of hydrology on chemical weathering rates. The inclusion of hydrologic flow paths in considering available weathering substrate was important in computation of sediment surface area normalized weathering rates. The differences in weathering rates calculated by both methods also suggest the temporal variability of chemical weathering rates in the natural environment. Changes in temperature, pH, flow, flow path, etc. complicate the fundamental concept of weathering processes in watersheds.

[47] The calculated primary silicate weathering rates were comparable to those for temperate watersheds. This study has shown that the dependence of weathering rates on the hydrologic exchange of water between the stream and the hyporheic zone is significant in Dry Valley streams. We believe that hyporheic exchange may also be an important source of dissolved solutes due to chemical weathering in temperate systems. This study represents one extreme, in that there were no hillslope processes occurring to influence stream chemistry, only stream exchange processes. Adapting this approach to temperate watersheds would have to address lateral solute loading as a result of hillslope chemical weathering and solute transport and influences of groundwater interaction.

References

Aiken, G., D. M. McKnight, R. Harnish, and R. Wershaw, Geochemistry of aquatic humic substances in the Lake Fryxell Basin, Antarctica, *Biogeochemistry*, *34*, 157–188, 1996.

Alger, A. S., D. M. McKnight, S. A. Spaulding, C. M. Tate, G. H. Shupe, K. A. Welch, R. Edwards, E. D. Andrews, and H. R. House, Ecological processes in a cold desert ecosystem: The abundance and species of algal mats in glacial meltwater streams in Taylor Valley, Antarctica, *Occasional Pap. 51*, Inst. of Arctic and Alpine Res., Boulder, Colo., 1997.

Anderson, S. P., W. E. Dietrich, R. Torres, D. R. Montgomery, and K. Loague, Concentration-discharge relationships in runoff from a steep, unchanneled catchment, *Water Resour. Res.*, *33*(1), 211–225, 1997a.

Anderson, S. P., J. I. Drever, and N. F. Humphrey, Chemical weathering in glacial environments, *Geology*, *25*, 399–402, 1997b.

Angino, E. E., K. B. Armitage, and J. C. Tash, Chemical stratification in Lake Fryxell, Victorialand, Antarctica, *Science*, *138*, 34–36, 1962.

Bencala, K. E., and R. A. Walters, Simulation of solute transport in a mountain pool-and-riffle stream: A transient storage model, *Water Resour. Res.*, *19*(3), 718–724, 1983.

Benner, S. G., E. W. Smart, and J. N. Moore, Metal behavior during surface-groundwater interaction, Silver Bow Creek, Montana, *Environ. Sci. Technol.*, *27*(7), 1789–1795, 1995.

Berner, R. A., and G. R. Holdren Jr., Mechanism of feldspar weathering, II, Observations of feldspars from soils, *Geochim. Cosmochim. Acta*, *43*, 1173–1186, 1979.

Berner, R. A., and J. Schott, Mechanism of pyroxene and amphibole weathering, II, Observations of soil grains, *Am. J. Sci.*, *282*, 1214–1231, 1982.

Boissier, J. M., P. Marmonier, C. Claret, D. Fontvieille, and P. Blanc, Comparison of solutes, nutrients, and bacteria inputs from two types of groundwater to the Rhone river during an artificial drought, *Hydrobiologia*, *319*, 65–72, 1996.

Bomblies, A., Climate controls on stream flow generation from Antarctic glaciers, McMurdo Dry Valleys, Antarctica, M. S. thesis, Univ. of Colo., Boulder, 1999.

Bomblies, A., D. M. McKnight, and E. D. Andrews, Retrospective simulation of lake-level rise in Lake Bonney based on recent 21-yr record: Indication of recent climate change in the McMurdo Dry Valleys, Antarctica, *J. Paleolimnol.*, *25*(4), 477–492, 2001.

Chinn, T. J., Physical Hydrology of the dry valley lakes, in *Physical and Biogeochemical Processes in Antarctic lakes*, *Antarct. Res. Ser.*, vol. 59, edited by W. J. Green and E. I. Friedman, AGU, Washington, D. C., pp. 1–51, 1993.

Claridge, G. G. C., and I. B. Campbell, The salts in Antarctic soils, their distribution and relationship to soil processes, *Soil Sci.*, *123*, 377–384, 1977.

Clow, D. W., Weathering rates from field and laboratory experiments on naturally weathered soils, Ph.D. dissertation, Univ. of Wyo., Laramie, 1992.

Clow, G. D., C. P. McKay, G. M. Simmons, and R. A. Wharton Jr., Climatological observations and predicted sublimation rates at Lake Hoare, Antarctica, *J. Clim.*, *1*(7), 715–728, 1988.

Conovitz, P. A., Active layer dynamics and hyporheic zone storage in three streams in the McMurdo Dry Valleys, Antarctica, M. S. thesis, Colo. State Univ., Fort Collins, 2000.

Conovitz, P. A., D. M. McKnight, L. H. MacDonald, A. G. Fountain, and H. R. House, Hydrol.ogical processes influencing streamflow variation in Fryxell Basin, Antarctica, in *Ecosystem Dynamics in a Polar Desert: The McMurdo Dry Valleys, Antarctica*, *Antarct. Res. Ser.*, vol. 73, edited by J. C. Priscu, pp. 93–108, AGU, Washington, D. C., 1998.

Dahlgren, R. A., F. C. Ugolini, and W. H. Casey, Field weathering rates of Mt. St. Helens tephra, *Geochim. Cosmochim. Acta*, *63*(5), 587–598, 1999.

D'Angelo, D. J., J. R. Webster, S. V. Gregory, and J. L. Meyer, Transient storage in Appalachian and Cascade mountain streams as related to hydraulic characteristics, *J. N. Am. Benthol. Soc.*, *12*(3), 223–235, 1993.

Darmody, R. G., C. E. Thorn, R. L. Harder, J. P. L. Schlyter, and J. C. Dixon, Weathering implications of water chemistry in an arctic-alpine environment, northern Sweden, *Geomorphology*, *34*, 89–100, 2000.

de Mora, S. J., R. F. Whitehead, and M. Gregory, Aqueous geochemistry of major constituents in the Alph River and tributaries in Walcott Bay, Victoria Land, Antarctica, *Antarct. Sci.*, *3*, 73–86, 1991.

Denton, G. H., J. G. Bockheim, S. C. Wilson, and M. Stuiver, Late Wisconsin and early Holocene glacial history, inner Ross embayment, Antarctica, *Quat. Res.*, *31*, 151–182, 1989.

Doran, P. T., R. A. Wharton Jr., and W. B. Lyons, Paleolimnology of the McMurdo Dry Valleys, Antarctica, *J. Paleolimnol.*, *10*, 85–114, 1994.

Drever, J. I. and D. W. Clow, Weathering rates in catchments, in *Chemical Weathering Rates of Silicate Minerals*, edited by A. F. White and S. L. Brantley, *Rev. Mineral.*, *31*, 463–483, 1995.

Duff, J. H., and F. J. Triska, Denitrification in sediments from the hyporheic zone adjacent to a small forested stream, *Can J. Fish. Aquat. Sci.*, *47*, 1140–1147, 1990.

Findlay, S., D. Strayer, C. Goumbala, and K. Gould, Metabolism of stream-water dissolved organic carbon in the hyporheic zone, *Limnol. Oceanogr.*, *38*(7), 1493–1499, 1993.

Ford, T. E., and R. J. Naiman, Groundwater-surface water relationships in boreal forest watersheds: Dissolved organic carbon and inorganic nutrient dynamics, *Can. J. Fish. Aquat. Sci.*, *46*, 41–49, 1989.

Fuller, C. C., and J. W. Harvey, Reactive uptake of trace metals in the hyporheic zone of a mining-contaminated stream, Pinal Creek, Arizona, *Environ. Sci. Technol.*, *34*, 1150–1155, 2000.

Gooseff, M. N., D. M. McKnight, R. L. Runkel, and B. H. Vaughn, Determining long time scale hyporheic zone flow paths in Antarctic streams, *Hydrol. Processes*, *48*, in press, 2002.

Green, W. J., and D. E. Canfield, Geochemistry of the Onyx River (Wright Valley, Antarctica) and its role in the chemical evolution of Lake Vanda, *Geochim. Cosmochim. Acta*, *48*, 2457–2467, 1984.

Green, W. J., M. P. Angle, and K. E. Chave, The geochemistry of Antarctic streams and their role in the evolution of four lakes of the McMurdo Dry Valleys, *Geochim. Cosmochim. Acta*, *52*, 1265–1274, 1988.

Green, W. J., T. J. Gardner, T. G. Ferdelman, M. P. Angle, L. C. Varner, and P. Nixon, Geochemical processes in the Lake Fryxell Basin (Victorialand, Antarctica), *Hydrobiologia*, *172*, 129–148, 1989.

Grimm, N. B., Nitrogen dynamics during succession in a desert stream, *Ecology*, *68*(5), 1157–1170, 1987.

Hall, R. D. and R. E. Martin, The etching of hornblende grains in the matrix of alpine tills and periglacial deposits, in *Rates of Chemical Weathering of Rocks and Minerals*, edited by S. M. Colman and D. P. Dethier, pp. 101–128, Academic, San Diego, Calif., 1986.

Harvey, J. W., and C. C. Fuller, Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance, *Water Resour. Res.*, *34*, 623–636, 1998.

Harvey, J. W. and B. J. Wagner, Quantifying Hydrol.ogic interactions between streams and their subsurface hyporheic zones, in *Streams and Ground Waters*, edited by J. B. Jones and P. J. Mulholland, pp. 3–44, Academic, San Diego, Calif., 2000.

Hendricks, S. P., and D. S. White, Physicochemical patterns within a hyporheic zone of a northern Michigan river, with comments on surface water patterns, *Can. J. Fish. Aquat. Sci.*, *48*, 1645–1654, 1991.

Hendricks, S. P., and D. S. White, Seasonal biogeochemical patterns in surface water, subsurface hyporheic, and riparian ground water in a temperate stream ecosystem, *Arch. Hydrobiol.*, *134*(4), 459–490, 1995.

Hendy, C. H., T. R. Healy, E. M. Raymer, J. Shaw, and A. T. Wilson, Late Pleistocene glacial chronology of the Taylor Valley, Antarctica and the global climate, *Quat. Res.*, *11*, 172–184, 1979.

Hill, A. R., C. F. Labadia, and K. Sanmugadas, Hyporheic zone Hydrology and nitrogen dynamics in relation to the streambed topography of a N-rich stream, *Biogeochemistry*, *42*(3), 285–310, 1998.

Hinkley, T., Alkali and alkaline earth metals: Distribution and loss in a high Sierra Nevada watershed, *Geol. Soc. Am. Bull.*, *85*, 1333–1338, 1974.

Hooper, R. P., and C. A. Shoemaker, A comparison of chemical and isotopic hydrograph separation, *Water Resour. Res.*, *22*, 1444–1454, 1986.

Huh, Y., and J. M. Edmond, The fluvial geochemistry of the rivers of eastern Siberia, III, Tributaries of the Lena and Anabar draining the basement terrain of the Siberian Craton and the Trans-Baikal Highlands, *Geochim. Cosmochim. Acta*, *63*(7–8), 967–987, 1999.

Huh, Y., M. Tsoi, A. Zaitsev, and J. M. Edmond, The fluvial geochemistry of the rivers of Eastern Siberia, I, Tributaries of the Lena River draining the sedimentary platforms of the Siberian Craton, *Geochim. Cosmochim. Acta*, *62*(10), 1657–1676, 1998a.

Huh, Y., G. Panteleyev, D. Babich, A. Zaitsev, and J. M. Edmond, The fluvial geochemistry of the rivers of eastern Siberia, II, Tributaries of the Lena, Omoloy, Yana, Indigirka, Kolyma, and Anadyr draining the collisional/accretionary zone of the Verkhoyansk and Cherskiy ranges, *Geochim. Cosmochim. Acta*, *62*(12), 2053–2075, 1998b.

Kennedy, V. C., Silica variation in stream water with time and discharge, in *Nonequilibrium Systems in Natural Water Chemistry*, *Adv. Chem. Ser.*, vol. 106, edited by J. D. Hem, pp. 94–130, Am. Chem. Soc., Washington, D. C., 1971.

Keynoyer, G. J., and C. J. Bowser, Groundwater chemical evolution in a sandy silicate aquifer in northern Wisconsin, 1, Patterns and rates of change, *Water Resour. Res.*, *28*(2), 579–589, 1992a.

Keynoyer, G. J., and C. J. Bowser, Groundwater chemical evolution in a sandy silicate aquifer in northern Wisconsin, 2, Reaction modeling, *Water Resour. Res.*, *28*(2), 591–600, 1992b.

Keys, J. R., and K. Williams, Origin of crystalline, cold desert salts in the McMurdo region, Antarctica, *Geochim. Cosmochim. Acta*, *45*, 2299–2309, 1981.

Kim, B. K., A. P. Jackman, and F. J. Triska, Modeling transient storage and nitrate uptake kinetics in a flume containing a natural periphyton community, *Water Resour. Res.*, *26*(3), 505–515, 1990.

Kim, B. K., A. P. Jackman, and F. J. Triska, Modeling biotic uptake by periphyton and transient hyporheic storage of nitrate in a natural stream, *Water Resour. Res.*, *28*(10), 2743–2752, 1992.

Legrand, M., and P. Mayewski, Glaciochemistry of polar ice cores: A review, *Rev. Geophys.*, *35*, 219–243, 1997.

Legrand-Marcq, C., and H. Laudelout, Longitudinal dispersion in a forest stream, *J. Hydrol.*, *78*, 317–324, 1985.

Lyons, W. B. and P. A. Mayewski, The geochemical evolution of terrestrial waters in the Antarctic: The role of rock-water interactions, *Physical and Biogeochemical Processes in Antarctic Lakes*, *Antarctic Research Series*, vol. 59, edited by W. J. Green and E. I. Friedman, pp. 135–143, AGU, Washington, D. C., 1993.

Lyons, W. B., and K. A. Welch, Lithium in waters of a polar desert, *Geochim. Cosmochim. Acta*, *61*, 4309–4319, 1997.

Lyons, W. B., K. A. Welch, C. A. Nezat, K. Crick, J. K. Toxey, and J. A. Mastrine, Chemical weathering rates and reactions in the Lake Fryxell Basin, Taylor Valley: Comparison to temperate river basins, in *Ecosystem Processes in Antarctic Ice-Free Landscapes*, edited by W. B. Lyons, C. Howard-Williams, and I. Hawes, pp. 147–154, A. A. Balkema, Brookfield, Vt., 1997a.

Lyons, W. B., R. L. Bartek, P. A. Mayewski, and P. T. Doran, Climate history of the McMurdo Dry Valleys since the Last Glacial Maximum: A Synthesis, in *Ecosystem Processes in Antarctic Ice-Free Landscapes*, edited by W. B. Lyons, C. Howard-Williams, and I. Hawes, pp. 15–22, A. A. Balkema, Brookfield, Vt., 1997b.

Lyons, W. B., K. A. Welch, K. Neumann, J. K. Toxey, R. McArthur, C. Williams, D. M. McKnight, and D. Moorhead, Geochemical linkages among glaciers, streams and lakes within the Taylor Valley, Antarctica, in *Ecosystem Dynamics in a Polar Desert: The McMurdo Dry Valleys Antarctica*, *Antarct. Res. Ser.*, vol. 72, edited by J. C. Priscu, pp. 77–92, AGU, Washington, D. C., 1998.

Malmstrom, M. E., A. Destouni, A. S. Banwart, and B. H.E. Stromberg, Resolving the scale- dependence of mineral weathering rates, *Environ. Sci. Technol.*, *34*, 1375–1378, 2000.

Maurice, P. A., D. M. McKnight, L. Leff, J. E. Fulghum, and M. Gooseff, Direct observations of aluminosilicate weathering in the hyporheic zone of an Antarctic Dry Valley stream, *Geochim. Cosmochim. Acta*, *66*(8), 1335–1347, 2002.

Maybeck, M., Global chemical weathering of surficial rocks estimated from river dissolved loads, *Am. J. Sci.*, *287*, 401–428, 1987.

McKnight, D. M., and K. E. Bencala, Reactive iron transport in an acidic mountain stream in Summit County, Colorado: A Hydrologic perspective, *Geochim. Cosmochim. Acta*, *53*, 2225, 1989.

Ming-hui, R., R. F. Stallard, and J. M. Edmond, Major ion chemistry from some large Chinese rivers, *Nature*, *298*, 550–553, 1982.

Morel, F. M. M. and J. G. Hering, *Principles and Applications of Aquatic Chemistry*, John Wiley, New York, 1993.

Morrice, J. A., H. M. Valett, C. N. Dahm, and M. E. Campana, Alluvial characteristics, groundwater-surface water exchange and Hydrological retention in headwater streams, *Hydrol. Processes*, *11*, 253–267, 1997.

Mulholland, P. J. and D. L. DeAngelis, Surface-subsurface exchange and nutrient spiraling, in *Streams and Ground Waters*, edited by J. B. Jones

and P. J. Mulholland, pp. 149–166, Academic, San Diego, Calif., 2000.

Nesbitt, H. W., G. Markovics, and R. C. Price, Chemical processes affecting alkalis and alkaline earths during continental weathering, *Geochim. Cosmochim. Acta*, 44, 1659–1666, 1980.

Nezat, C. A., W. B. Lyons, and K. A. Welch, Chemical weathering in streams of a polar desert (Taylor Valley, Antarctica), *Geol. Soc. Am. Bull.*, 113(11), 1401–1407, 2001.

Parkhurst, D. L. and C. A. J. Appelo, User's guide to PHREEQC (version 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, *U. S. Geol. Surv. Water Resour. Invest. Rep., 99-4259*, 1999.

Péwé, T. L., Multiple glaciation in the McMurdo Sound Region, Antarctica—A progress report, *J. Geol.*, 68, 498–514, 1960.

Riebe, C. S., J. W. Kirchner, D. E. Granger, and R. C. Finkel, Strong tectonic and weak climatic control of long-term chemical weathering rates, *Geol.*, 29(6), 511–514, 2001.

Runkel, R. L., One-dimensional transport with inflow and storage (OTIS): A solute transport model for streams and rivers, *U. S. Geol. Surv. Water Resour. Invest. Rep., 98-4018*, 1998.

Runkel, R. L., D. M. McKnight, and E. D. Andrews, Analysis of transient storage subject to unsteady flow: Diel flow variation in an Antarctic stream, *J. N. Am. Benthol. Soc.*, 17(2), 143–154, 1998.

Runkel, R. L., B. A. Kimball, D. M. McKnight, and K. E. Bencala, Reactive solute transport in streams: A surface complexation approach for trace metal sorption, *Water Resour. Res.*, 35(12), 3829–3840, 1999.

Smith, T. R., and T. Dunne, Watershed geochemistry: The control of aqueous solutions by soil materials in a small watershed, *Earth Surf. Processes*, 2, 421–425, 1977.

Srodon, J., V. A. Drits, D. K. McCarty, J. C. C. Hsieh, and D. D. Eberl, Quantitative X-ray diffraction analysis of clay-bearing rocks from random preparations, *Clays Clay Mineral.*, 49(6), 514–528, 2001.

Stumm, W. and J. J. Morgan, *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, 2nd ed, Wiley-Interscience, New York, 1981.

Swoboda-Colberg, N. G., and J. I. Drever, Mineral dissolution rates in plot-scale field and laboratory experiments, *Chem. Geol.*, 105, 51–69, 1993.

Treonis, A. M., D. H. Wall, and R. A. Virginia, Invertebrate biodiversity in Antarctic Dry Valley soils and sediments, *Ecosystems*, 2, 482–492, 1999.

Velbel, M. A., Geochemical mass balances and weathering rates in forested watersheds of the Southern Blue Ridge, *Am. J. Sci.*, 285, 904–930, 1985.

Velbel, M. A., Influence of temperature and mineral surface characteristics on feldspar weathering rates in natural and artificial systems: A first approximation, *Water Resour. Res.*, 26(12), 3049–3053, 1990.

Vincent, W. F., and C. Howard-Williams, Antarctic stream ecosystems: Physiological ecology of a blue-green algal epilithon, *Freshwater Biol.*, 16, 219–233, 1986.

Vincent, W. F., and C. Howard-Williams, Microbial communities in southern Victoria Land Streams (Antarctica), II, The effects of low temperature, *Hydrobiologia*, 172, 39–49, 1989.

von Guerard, P., D. M. McKnight, R. A. Harnish, J. W. Gartner, and E. D. Andrews, Streamflow, water-temperature, and specific-conductance data for selected streams draining into Lake Fryxell, Lower Taylor Valley, Victoria Land, Antarctica, 1990–92, *U. S. Geol. Surv. Open File Rep., 94-545*, 1995.

White, A. F., Chemical weathering rates of silicate minerals in soils, in *Chemical Weathering Rates of Silicate Minerals*, edited by A. F. White and S. L. Brantley, *Rev. Mineral.*, 31, 407–461, 1995.

White, A. F., and A. E. Blum, Effects of climate on chemical weathering in watersheds, *Geochim. Cosmochim. Acta*, 59, 1729–1747, 1995.

White, A. F. and M. L. Peterson, Role of reactive-surface-area characterization in geochemical kinetic-models, in *Chemical Modeling of Aqueous Systems, II, ACS Symp. Ser.*, vol. 416, edited by D. C. Melchior and R. L. Bassett, pp. 461–475, Am. Chem. Soc., Washington, D. C., 1990.

White, A. F., A. E. Blum, M. S. Schulz, T. D. Bullen, J. W. Harden, and M. L. Peterson, Chemical weathering rates of a soil chronosequence on granitic alluvium, I, Quantification of mineralogical and surface area changes and calculation of primary silicate reaction rates, *Geochim. Cosmochim. Acta*, 60, 2533–2550, 1996.

Wondzell, S. M., and F. J. Swanson, Seasonal and storm dynamics of the hyporheic zone of a 4th-order mountain stream, II, Nitrogen cycling, *J. N. Am. Benthol. Soc.*, 15(1), 20–34, 1996.

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