Importance of mechanical disaggregation in chemical weathering in a cold alpine environment, San Juan Mountains, Colorado

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ABSTRACT

Weathering of welded tuff near the summit of Snowshoe Mountain (3660 m) in southwestern Colorado was studied by analyzing infiltrating waters in the soil and associated solid phases. Infiltrating waters exhibit anomalously high potassium to silica ratios resulting from dissolution of a potassium-rich glass that occurs as a trace phase in the rock. In laboratory experiments using rock from the field site, initial dissolution generated potassium-rich solutions similar to those observed in the field. The anomalous potassium release decreased over time (about 1 month), after which the dominant cation was calcium, with a much lower potassium to silica ratio.

The anomalous potassium concentrations observed in the infiltrating soil solutions result from weathering of freshly exposed rock surfaces. Continual mechanical disaggregation of the rock due to segregation freezing exposes fresh glass to weathering and thus maintains the source of potassium for the infiltrating water. The ongoing process of creation of fresh surfaces by physical processes is an important influence on the composition of infiltrating waters in the vadose zone.

INTRODUCTION

Chemical weathering is a primary source of solutes in surface and ground water and is also an important source of mineral nutrients in soils for plants and microorganisms. Processes and kinetics of chemical weathering are of interest to the geochemical community because of efforts to understand and model soil development (Sposito, 1985), buffering of watershed acidification (Mast and Drever, 1987), and global chemical cycles (Berner et al., 1983). Accompanying the effort to

quantify chemical fluxes from weathering has been a debate over how to use results of dissolution experiments in modeling of natural processes (Sverdrup and Warfvinge, 1995). At the center of the debate is the observation that experimentally determined rock- and mineral-dissolution rates are often several orders of magnitude faster than rates calculated on the basis of field data.

Discrepancies in laboratory- and field-determined weathering rates have been attributed to various factors including experimental mineral preparation (Holdren and Berner, 1979), differ-

ences in mineral wetting (Swoboda-Colberg and Drever, 1992), and variations in solution compositions (Burch et al., 1993). Minerals prepared for experiments by grinding and sieving exhibit two distinct stages of dissolution-driven solute flux. The first is the initial, rapid release of solutes to solution, which is associated with freshly created, high-energy surfaces, followed by a much slower approach to steady-state dissolution (Holdren and Berner, 1979). In experimental systems, the rapid "pre–steady-state" dissolution is nearly impossible to quantitatively reproduce (Eggleston
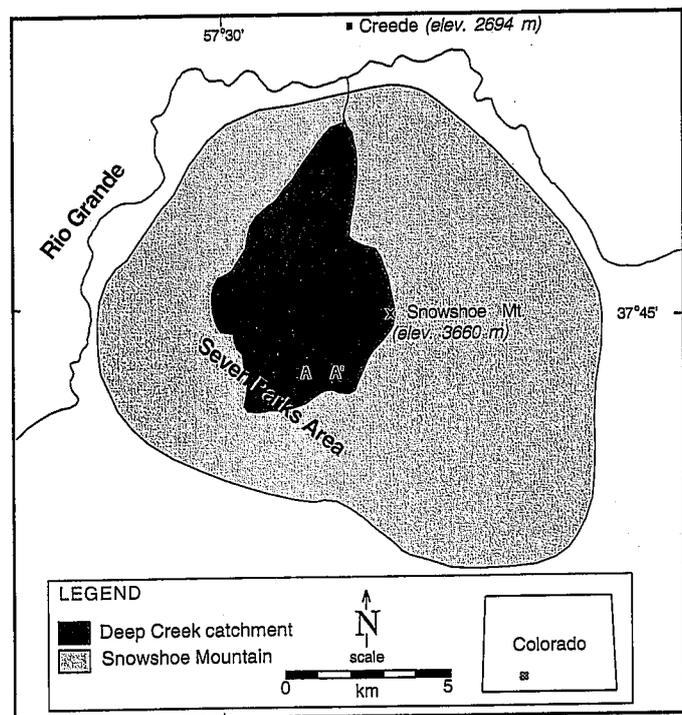

Figure 1. Location map of the Seven Parks study area. Darker shaded area is the Deep Creek drainage on Snowshoe Mountain (after Claassen et al., 1986). The Seven Parks area is at the head of Deep Creek. The cross-section trace at A–A′ includes sampling sites and is shown in Figure 2.

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et al., 1989) and is often ignored and treated as irrelevant to natural systems (Blum and Stillings, 1995), in spite of the fact that the majority of solutes are released during the earliest days of a short-term (weeks or months in duration) experiment. This approach to treatment of the data is due to the widely held opinion that rocks and minerals in natural systems are always "aged" or modified by relaxation of high-energy surface sites (Eggleston et al., 1989), by preferential diffusion of cations to solution (Mogk and Locke, 1988), or by alteration to secondary minerals (Hochella and Banfield, 1995).

In persistently cold environments, chemical weathering mechanisms such as hydrolysis and ion exchange operate at relatively low rates (Ugolini, 1986), especially on aged rock and mineral surfaces. Conversely, mechanical weathering mechanisms in high-relief, alpine environments play an important role in exposing fresh, highly reactive, rock and mineral surfaces to chemical weathering (Stallard, 1995), perhaps providing a natural context for the pre–steady-state dissolution kinetics observed in the laboratory.

In this paper, we explore the nature of solute release in a cold, ephemeral chemical weathering environment, where fresh rock and mineral surfaces are continually produced, in an attempt to address the observation that highly mobile cations having a low charge/size ratio—such as K^+ and Ca^{2+}—are anomalously concentrated in solutions derived from chemical weathering in
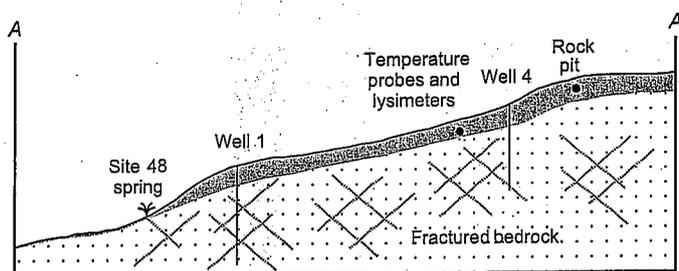

Figure 2. Schematic cross section of water-sampling sites at Seven Parks (not drawn to scale). Infiltrating waters were collected with soil lysimeters and the rock pit sampler (see Fig. 3). Soil temperature was also monitored at the soil lysimeter site. Deeper ground-water samples were collected from the fractured bedrock from well 4, well 1, and the spring at site 48.

alpine watersheds (Drever and Hurcomb, 1986; Mast et al., 1990; Stauffer, 1990; Edmond, 1993; Axtmann and Stallard, 1995).

MATERIALS AND METHODS

Field Area

The focus of this study is the Seven Parks area at the head of the Deep Creek watershed on Snowshoe Mountain in the San Juan Mountains of southwest Colorado (Fig. 1). The study area is on the top of an eroded augite-biotite quartz latite welded tuff dome of a caldera complex, which was crystallized at ca. 26.5 Ma (Steven and Lipman, 1976). This area was chosen for study because of its simple recharge pattern, hydrologic isolation, absence of anthropogenic impact, and uniform lithology (Claassen et al., 1983). Seven Parks is in a subalpine environment at an elevation of ~3500 m, with moderate to gentle slopes. The main plant association is Engelmann spruce (*Picea engelmanni*) and grouse whortleberry (*Vaccinium scoparium*). Soil depth in our area of interest ranges from 0.0 to 1.0 m. The soil is classified as a Dystrict Cryochrept, formed in colluvium derived from the tuff bedrock (USDA [U.S. Department of Agriculture] Forest Service, 1996). The Dystrict Cryochrept is an Inceptisol, characterized by weak pedogenic development and close resemblance to its parent material (Buol et al., 1973). The surface layer is covered

TABLE 1. CATION AND SILICA DATA FOR SAMPLING SITES IN THE SEVEN PARKS AREA

	Date	Location	Ca^{2+} (μM)	Mg^{2+} (μM)	Na^+ (μM)	K^+ (μM)	SiO_2 (μM)
Soil Waters							
	6/21/88	Rock pit	64.0	17.0	20.0	11.4	95.7
	10/6/88	Rock pit	143.0	45.5	80.0	105.2	150.3
	6/8/89	Rock pit	40.0	11.5	16.0	14.9	82.5
	10/6/89	Rock pit	119.5	41.0	32.0	36.2	124.5
	6/26/90	Rock pit	59.0	17.5	21.0	13.2	92.1
	10/6/90	Rock pit	63.0	19.5	28.0	73.0	113.0
Wells							
	9/24/83	Well 4	349.3	74.1	147.9	20.5	386.6
	8/9/84	Well 4	192.1	65.8	261.0	28.1	374.0
	5/14/85	Well 4	169.7	57.6	139.2	23.0	338.9
	7/25/85	Well 4	182.1	65.8	156.6	15.3	354.3
	8/28/85	Well 4	174.7	69.9	147.9	20.5	362.8
	10/3/85	Well 4	179.6	61.7	187.0	30.7	368.4
	10/6/83	Well 1	499.0	90.5	174.0	15.3	445.4
	8/9/84	Well 1	202.1	61.7	165.3	23.1	334.7
	5/15/85	Well 1	187.1	57.6	113.1	15.3	299.7
	6/18/85	Well 1	274.5	74.1	143.5	15.3	375.4
	7/25/85	Well 1	274.5	82.3	143.5	14.1	382.4
	10/3/85	Well 1	229.5	65.8	134.8	17.9	359.9
Spring							
	10/1/81	Site 48	266.0*	69.0	123.0	11.2	372.6
	6/16/83	Site 48	374.3	86.4	126.1	13.3	341.7
	9/7/83	Site 48	324.4	78.2	126.1	12.5	351.5
	10/6/83	Site 48	274.5	74.1	130.5	12.0	344.5
	11/1/83	Site 48	374.3	78.2	134.8	14.0*	362.8
	11/16/83	Site 48	548.9	82.3	143.5	17.9	371.2
	12/12/83	Site 48	274.5	69.9	126.1	11.5	351.5

Note: From unpublished data of Doug Halm, U.S. Geological Survey.
*These numbers were estimated based on charge balance considerations.
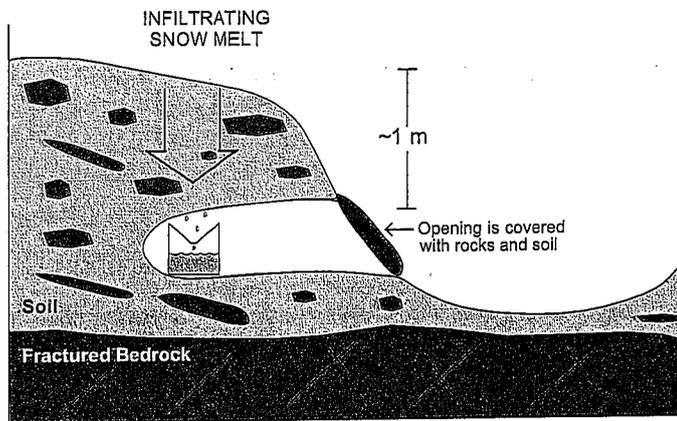
Figure 3. Schematic cross section of the rock-pit, zero-tension, vadose sampling site. Water infiltrates about 1 m of undisturbed soil and is collected in a 15-cm-diameter plastic container with a screen trap to catch falling debris larger than 0.5 mm diameter. The tunnel containing the collector is covered with rocks and soil to minimize evaporation. Horizontal scale is same as vertical scale.

TABLE 2. FREEZE-THAW HISTORY FOR SOIL AT THE SEVEN PARKS AREA, SNOWSHOE MOUNTAIN, FOR THE 1983–1985 SEASONS

Year	Depth (cm)	Thaw date	Freeze date	Thaw duration (days)
1983	6	6/16	9/29	105
	27	6/19	10/13	116
	67	7/5	10/21	108
1984	6	5/28	9/23	118
	27	6/13	9/25	104
	67	7/4	9/28	86
1985	6	6/11	9/17	98
	27	6/15	9/19	96
	67	7/2	9/23	83

Note: Unpublished data from Doug Halm, U.S. Geological Survey.

with a mat of coniferous leaf litter a few centimeters thick. The surface layer is a dark grayish brown gravelly silt loam about 15 cm thick. The upper subsoil (15–33 cm) is a dark yellowish brown, very gravelly loam. The lower subsoil and substratum (>30 cm) are extremely gravelly sandy loams (USDA Forest Service, 1996). The mean annual air temperature is 1.3 °C, and mean annual precipitation is about 53 cm, much of which is in the form of snowfall (Bates and Henry, 1928). Snow accumulation usually begins in November, after soils are frozen, and is typically shallow enough (1 to 2 m) that soils remain frozen until late in the spring.

Field Sampling and Analysis

Regolith temperatures were monitored with mercury-filled Bourdon tube thermometers and a mechanical chart recorder at the lysimeter site shown in Figure 2. Samples from a soil profile were sieved, and smaller fractions were subjected to hydrometer analysis to determine particle-size distribution. Petrography was done on thin sec-

tions of blue-epoxy–impregnated rock fragments from the soil as well as surface rocks and core samples. Scanning electron microscope (SEM) imaging was performed on a JEOL 35CF SEM equipped with an energy-dispersive X-ray spectrometer (EDS), and X-ray diffraction analyses were performed on a Scintag XDS 2000 diffractometer. Soil samples from a profile near the soil lysimeters and bulk-rock samples from the same area were analyzed for major element chemistry at Coors Analytical Laboratory, Golden, Colorado, by X-ray fluorescence spectroscopy. Specific surface areas were determined by nitrogen adsorption (Brunauer et al., 1938) for the same soil-profile samples at Coors. Interstitial glass in tuff material was identified and analyzed by transmission electron microscope (TEM) at the University of New Mexico, Department of Earth and Planetary Sciences, by Yongxiang Guo. Waters (Table 1) were collected by H. C. Claassen and D. R. Halm of the U.S. Geological Survey from sampling sites shown in Figure 2 from 1981 to 1989. Vadose water samples were collected from two zero-tension soil lysimeters and from a zero-tension collector known as the "rock pit" site (Fig. 3), which intercepts water flowing naturally through a 1-m-thick soil profile typical of the area. Rock pit water samples were collected twice a year: after the spring snowmelt event (June) and before the long winter freeze (October). Phreatic waters, for comparison, were collected from wells and a nearby perennial spring (Fig. 2). Field sampling and preservation techniques were discussed in detail by Claassen et al. (1986). Potassium concentrations were determined by atomic absorption spectroscopy. Other cations were analyzed by inductively coupled plasma emission spectrophotometry (ICP), and anions were analyzed by ion chromatography (both at the U.S. Geological Survey in Arvada, Colorado). Silica analyses were performed at the University of Wyoming by the molybdate blue colorimetric method (American Public Health Association, 1992).

Dissolution Experiment

A tuff-dissolution experiment was conducted in order to observe time-dependent changes in solute release by chemical weathering of an ar-

TABLE 3. PARTICLE SIZE DISTRIBUTION AT DIFFERENT DEPTH INTERVALS IN A SEVEN PARKS SOIL PROFILE

Depth (cm)	<2 μm (%)	2–50 μm (%)	50–100 μm (%)	100–250 μm (%)	>250 μm (%)
0–18	16	40	10	15	19
18–34	14	38	9	16	23
34–51	16	38	8	16	22
51–66	15	34	11	17	23
66–86	10	30	12	19	29

Note: Analyses were performed by Colorado School of Mines Research Institute, 1980.

tificially disaggregated sample. (Details of rock preparation, reactor design, and solution analyses are in Hoch et al. [1996]). A flow-through reactor was employed for this experiment; its volume was 100 mL. The reactor allowed deionized water to flow through an unweathered, ultrasonically cleaned, crushed tuff sample from Seven Parks (150–495 μm size fraction) at 25 °C ± 4 °C and a flow rate of 4 mL/h. Fluxes for individual solutes were calculated on the basis of chemistry of daily samples so that relative releases could be tracked over the 47-day duration of the experiment.

The experiment was conducted at 25 °C for consistency with other ongoing studies of mineral-dissolution rates. Reddy and Werner (1987) conducted dissolution experiments on Snowshoe Mountain Tuff at both 5 and 25 °C. Their 5 °C experiments, which were better analogues for field temperatures at Snowshoe Mountain, yielded rates that were 2 to 3 times slower than the rates determined at 25 °C.

RESULTS

Hydrology

The annual hydrologic cycle in the colluvial soil is dependent on ambient temperature, which controls freezing and thawing. Soil probes continuously monitored soil temperatures at the Seven Parks lysimeters (Fig. 2) at depths of 6, 27, and 67 cm. Soil freeze and thaw records for 1983 to 1985 (Table 2) show that soil waters are frozen for 8 or 9 months per year, at least down to the soil-bedrock interface. This time frame is in close agreement to similar data of Bates and Henry (1928) for the years 1911 to 1926. During the period when the soil was frozen, temperatures remained at about –4 °C. The duration between thawing and freezing represents a maximum time for wetting of soil minerals. Well-level records of ground water near the soil-temperature probes suggested that actual time of water infiltration was between 40 and 60 days in the early summer. There was late-summer precipitation, but these events were short lived and probably did not uniformly saturate the soil, unlike the slower, more volumetrically significant, annual snowmelt events.

Particle-Size Distribution

A profile of Seven Parks soil collected from near the soil lysimeter site was analyzed to determine particle-size distribution at various depths (Table 3). The 2–50 μm (silt) size fraction represents the most abundant grain size in all profile intervals and is the size of microphenocrysts in the tuff matrix. The other dominant size fraction
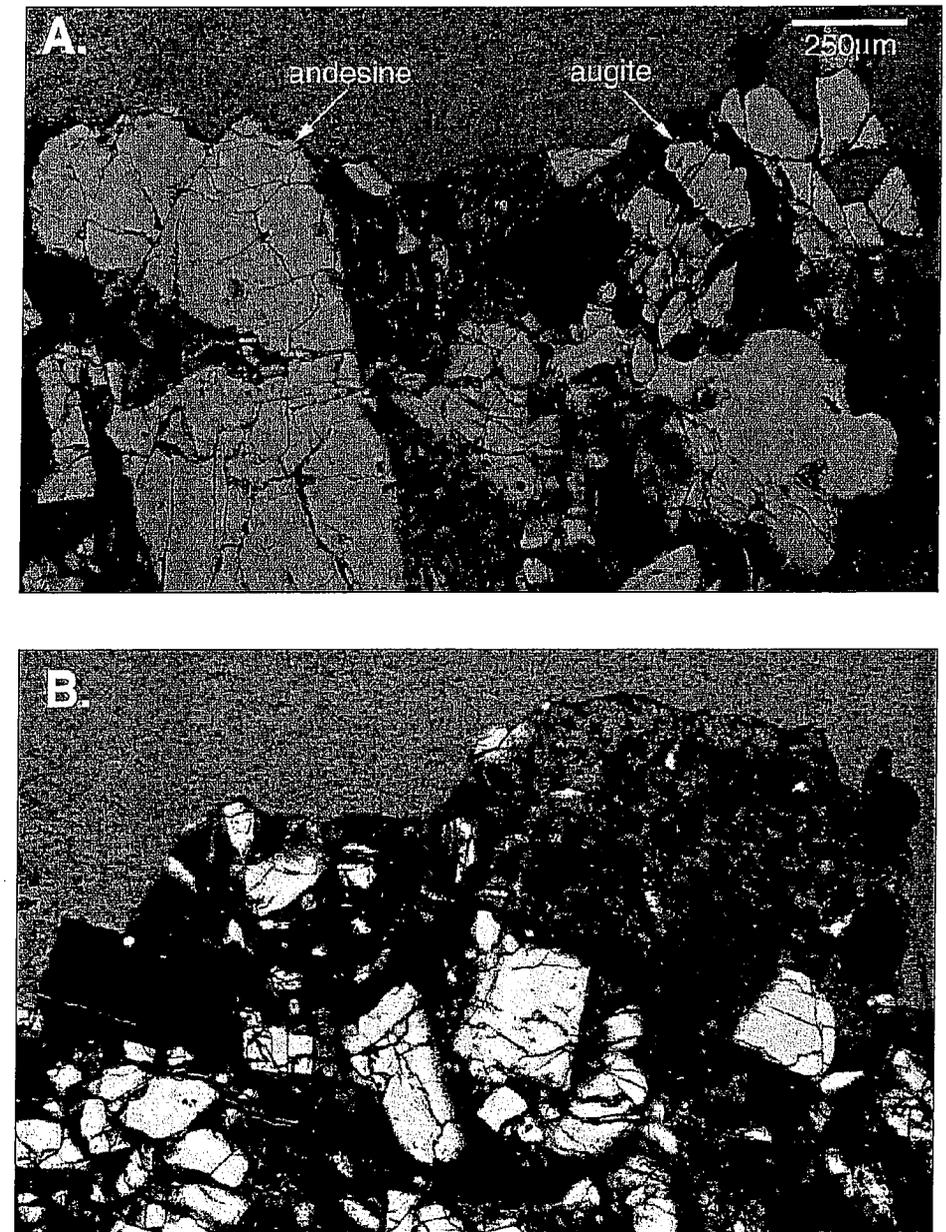

Figure 4. Photomicrographs of rock fragments from soil. (A) Andesine feldspar exposed at the surface and augite near the surface of a rock fragment from the soil exhibit little evidence of chemical weathering (plane-polarized light). (B) Fractures, impregnated with blue epoxy, extensively permeate a rock fragment from the soil, crosscutting both matrix material and phenocrysts. Secondary clay minerals are not observed in these near-surface openings (scale is the same as in A).

(>250 μm) is composed of disaggregated phenocrysts and remaining lithic fragments. The deepest soil sample has the least-abundant fine fraction and the most-abundant coarse fraction in the profile, suggesting less rock disaggregation closer to the bedrock.

Petrography

The bedrock is the Snowshoe Mountain Tuff, a lithologically homogeneous augite-biotite quartz latite welded tuff with about 50% phenocrysts and 50% groundmass (Ratte and
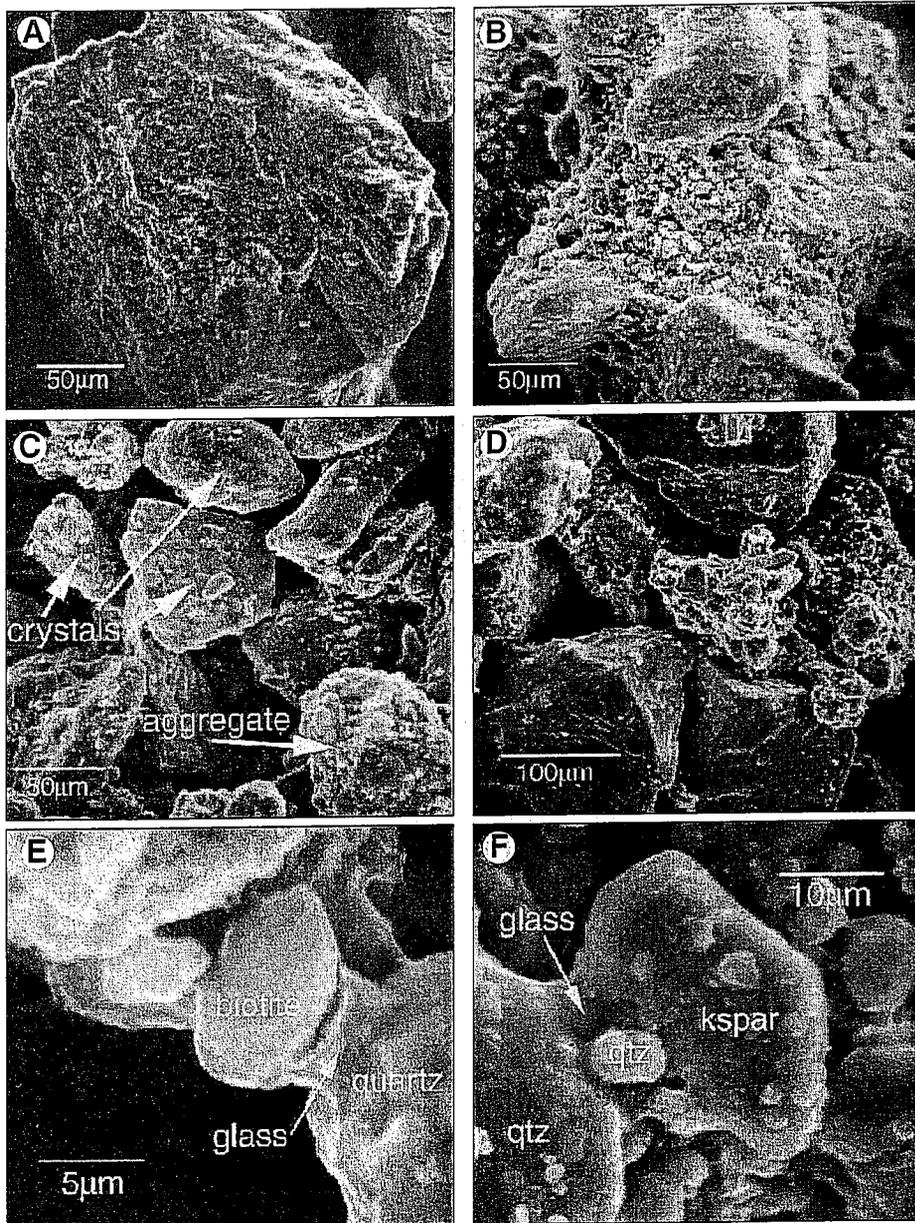
Figure 5. Scanning electron microscope images of samples from the Seven Parks area. (A) Unaltered, crushed, tuff with indistinguishable matrix and phenocrysts. (B) Lithic fragment from the >250 μm fraction of a soil sample collected from near the top of the profile; here microphenocrysts and phenocrysts *are* distinguishable, probably because of preferential dissolution of interstitial glass. (C) Disaggregated mineral phases in the 125–250 μm fraction of the same soil sample showing little evidence of chemical etching. (D) Grains in the 62.5–125 μm fraction composed almost entirely of disaggregated crystals. A remaining rock fragment (center of image), is made up of microlites of quartz and K-feldspar, probably bound together by glass. (E and F) Grains from the <62.5 μm fraction bound together by residual glass.

Steven, 1964), which is mostly devitrified. Phenocryst phases include oligoclase-andesine plagioclase, augite, hornblende, biotite, and magnetite. In the unweathered rock, deuteric processes have oxidized hornblende and biotite almost beyond recognition. The groundmass is composed primarily of K-feldspar (probably sanidine) and quartz, along with trace amounts of interstitial glass (described in this study) and submicroscopic expandable clay as a macropore filling (Reddy and Claassen, 1994).

Rock samples on the land surface are angular and difficult to break because of the silicic groundmass. Weathered surfaces are iron stained and have pits where augite phenocrysts have preferentially weathered away.

Impregnated petrographic thin-section examination of smaller (2-cm-diameter) rock fragments in the soil indicated that the phenocrysts at or near the surface are unaltered (Fig. 4A). Blue epoxy within fractures shows that the fractures permeate phenocrysts and matrix alike (Fig. 4B). Secondary clay minerals are notably absent from the near-surface fractures.

SEM images of freshly crushed tuff and various size fractions of soil material suggest that unaltered tuff (Fig. 5A) has a small volume of interstitial material between the phenocrysts (>0.05 mm) and microphenocrysts (<0.05 mm), effectively filling in the unweathered, broken surface. This interstitial substance is a K^+-rich residual volcanic glass, rather than the somewhat similar K-feldspar, which would not have significant amounts of Fe nor detectable amounts of Ti and P (Deer et al., 1963). The fact that several X-ray spectral analyses of various interstitial fillings yielded similar elemental distributions (Fig. 6) supported the idea that it is indeed a single glass phase. Larger rock fragments in the soil (Fig. 5B) are disaggregating into phenocryst and microphenocryst components, probably because of dissolution of interstitial glass. Smaller size fractions from the soil (Fig. 5, C and D) have cleanly exposed phenocrysts and microphenocrysts. Only with close inspection at higher magnifications is the interstitial glass visible (Fig. 5, E and F).

The rock from which the soil is forming is represented by core sampled from Seven Parks bedrock. At depths greater than 4 m, the tuff fractures contain vein fillings up to 2 mm thick and composed of calcite and aragonite, surrounded by thin layers of expandable clays, identified by X-ray diffraction (Hoch, 1997). One localized occurrence of zeolite was identified in thin section. A qualitative energy-dispersive X-ray spectrum showed that the zeolite is composed of Ca, Al, Si, and O. The origin of the calcite is unresolved and may be related to earlier mineralization associated with in the Creede caldera system (Hoch, 1997; Rye et al., 1988). In the shallower

core sample (<5 m), the calcite is absent, and open fractures as wide as 2 mm allow easy access for infiltrating waters.

Changes in Mineralogy During Pedogenesis

X-ray diffraction patterns were obtained for the silt-size fraction (2–50 μm) and sand-size (100–250 μm) fraction of a soil sample (0–10 cm depth) as well as for the bulk, unweathered rock. The sand-size fraction, which corresponds to the phenocrysts, produced a pattern that is strikingly similar to that of the bulk rock, with plagioclase feldspar as the dominant phase; the only difference is that the weak biotite peak in the fresh rock pattern is absent from the soil pattern. In the silt-size fraction of the soil, K-feldspar and quartz are the dominant phases, corresponding to the microphenocrysts in the rock matrix. The minerals forming the soil material in our study area are nearly identical to those of the parent material, and thus we conclude that atmospheric dust input was minimal (Reheis et al., 1995).

Chemical Characteristics of the Soil

Anthropogenic acidity from atmospheric input is lacking (Claassen et al., 1983), the ground vegetation is relatively sparse, and the bedrock weathers relatively rapidly; thus, we infer that the biomass has only a minor effect on the solute budget (Mast et al., 1990). Therefore, changes in bulk chemistry of the soil are attributed to rock- and mineral-dissolution processes. Averaged bulk chemical analyses of unweathered tuff (solid rock samples with no weathering rind) collected from outcrops in Seven Parks and analyses of samples from a soil profile near the Seven Parks lysimeter site are presented in Table 4. Tuff compositions are similar to those reported by Ratte and Steven (1964). In the soil profile, the concentrations of the highly leachable ions Ca^{2+}, Mg^{2+}, and Na^+ are within the standard deviations of the parent-rock analyses. In contrast, K^+ concentrations in soil samples are all below the range of values listed for parent-rock material.

Comparison of Infiltrating Waters to Well Waters

Infiltrating soil waters have 3 to 4 times lower solute concentrations than phreatic well waters (Table 1), presumably the result of shorter residence time. Another striking difference between soil and well waters is the K^+/SiO_2 ratio (Fig. 7). Vadose soil waters have a K^+/SiO_2 ratio an order of magnitude higher than that of phreatic well waters. This observation is consistent with the noticeable depletion of K^+ in bulk soil samples (Table 4). Precipitation at Seven Parks typically has very low K^+
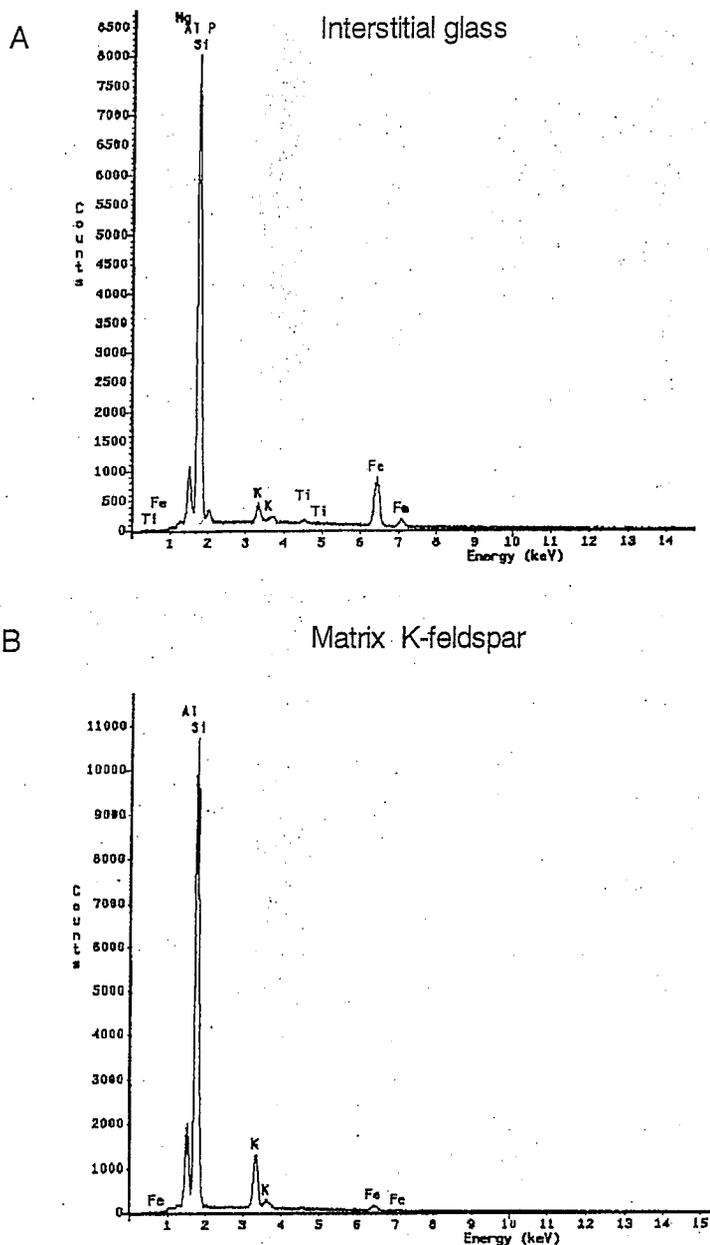
Figure 6. Qualitative X-ray energy spectra for (A) matrix interstitial glass and (B) matrix K-feldspar (sanidine), showing distinct compositional differences. The feldspar is more Al and K rich, whereas the glass contains significant Fe and Ti.

concentrations (~5 μM) and SiO_2 below detection limit (<10 μM) (Claassen et al., 1983).

Experimental Tuff Weathering

Unweathered Snowshoe Mountain Tuff from Seven Parks was reacted in distilled and deionized water in a flow-through reactor for 6 weeks (1000 h) in order to determine the relative release rates of chemical constituents via dissolution. Solution pH, which was unbuffered, was nearly neutral through the duration of the experiment.

The resulting ionic strength of reactor solutions ranged from $10^{-2.9}$ to $10^{-4.5}$ M and bracketed the solution compositions produced by water-rock interactions in the regolith ($10^{-3.3}$ to $10^{-3.9}$ M). These data indicate that the experiment is a chemically reasonable analogue to processes occurring in the field. However, the experimental temperature was 20 to 25 °C higher, and water flow rates are two orders of magnitude faster than in the natural setting.

K^+ behavior (Fig. 8) was characterized by an extremely rapid initial flux, which decreased by

TABLE 4. BULK CHEMICAL ANALYSES OF SOIL AND TUFF
AND SPECIFIC SURFACE AREAS (SSA) OF SOIL AT VARIOUS DEPTHS, SEVEN PARKS

Oxide	Soil						Tuff*
	from 0 to 10 cm	from 10 to 20 cm	from 30 to 40 cm	from 50 to 60 cm	from 70 to 80 cm	from 90 to 100 cm	
SiO_2 (wt%)	63.0	65.2	65.2	65.5	61.4	61.3	61.54 (1.93)
Al_2O_3 (wt%)	15.3	16.5	16.4	16.8	17.9	18.6	15.23 (0.50)
Fe_2O_3 (wt%)	4.2	3.9	4.1	4.5	5.6	4.6	5.46 (0.52)
FeO (wt%)	0.8	0.6	0.5	0.5	0.7	1.2	0.37 (0.33)
MgO (wt%)	1.2	1.0	1.2	1.2	1.4	1.4	1.27 (0.29)
CaO (wt%)	2.3	2.0	2.3	2.2	2.4	2.7	2.92 (1.07)
Na_2O (wt%)	2.2	2.0	2.6	2.3	2.3	2.7	2.70 (0.81)
K_2O (wt%)	2.7	2.4	2.6	2.9	2.5	2.7	3.22 (0.29)
SSA (m^2/g)	13.5	13.6	16.6	17.7	20.3	8.2	

*Average (and standard deviation) of analyses of five unweathered Snowshoe Mountain Tuff samples collected from the same area as the soil samples. Analyzed at the Coors Analytical Laboratory, Golden, Colorado.

two orders of magnitude, to approach a "steady-state" value after about 2 weeks (~350 h) (see White and Brantley [1995] for a discussion of the term "steady state"). Na^+ and Mg^{2+} showed a decrease in flux over the same time period, but not on the same order of magnitude as K^+. Ca^{2+} exhibited an order of magnitude decrease in flux over a longer period of time and probably never reached steady state during the experiment. Interpretation of Ca^{2+} behavior is complicated by the possibility of calcite dissolution operating in the system. Experimental data were presented by Hoch (1997).

Two sets of experimental dissolution rates were obtained from the dissolution experiment (Table 5). The "initial experimental flux" is pre–steady-state solute release and is an estimate of weathering flux from freshly exposed (crushed) rock surfaces. The "steady-state" flux is that observed at the end of the experiment—a value representing weathering of aged surfaces and typically reported in experimental weathering studies (e.g., Brantley and Chen, 1995). We acknowledge that after 1000 h, true steady-state dissolution reactions at mineral surfaces are probably not achieved; however, for our purposes of illustrating initial rate decreases and relative elemental release rates, this time should be sufficient.

Field Weathering Rates

Field weathering rates were calculated from the chemistry of the infiltrated water samples from the rock pit, collected after snowmelt events in the years 1988 to 1990. The rock-pit site was treated as a flow-through reactor, and fluxes were calculated as in Hoch et al. (1996). Calculations were based on the following assumptions: the flow path is a vertical, 15-cm-diameter (size of collector mouth) cylinder, 1 m in length; the sample volume flows uniformly and continuously through the cylinder; the infiltrating water is in contact with the entire surface area of the soil (Table 4); and evaporation from the collector was negligible during the snowmelt events (Hoch, 1997). The time for the snowmelt sample to infiltrate the cylinder of soil material was estimated at 30 days, on the basis of soil-temperature data, well levels, and sampling dates. A comparison of field fluxes to laboratory dissolution rates is presented in Table 5. The fluxes obtained from the experiments are 3.3 to 4 orders of magnitude greater than those calculated for weathering in the field.

DISCUSSION

Mechanical Disintegration by Freezing

Thin-section analysis showed that rock fragments in the soil are extensively fractured. These rock fractures are important in the overall disintegration of the otherwise hard, impermeable tuff. When a fracture in a silicate solid forms and water is available, the surfaces of the fracture will be rapidly hydrated by capillary action (Parks, 1990). The hydrology of the Seven Parks field site is characterized by an annual snowmelt-recharge event, commencing in late spring when the ground thaws and ending in late September or October when the system refreezes. The Seven Parks soils remain frozen 8–9 months per year (Table 2). Theoretical (Walder and Hallet, 1985) and experimental stud-
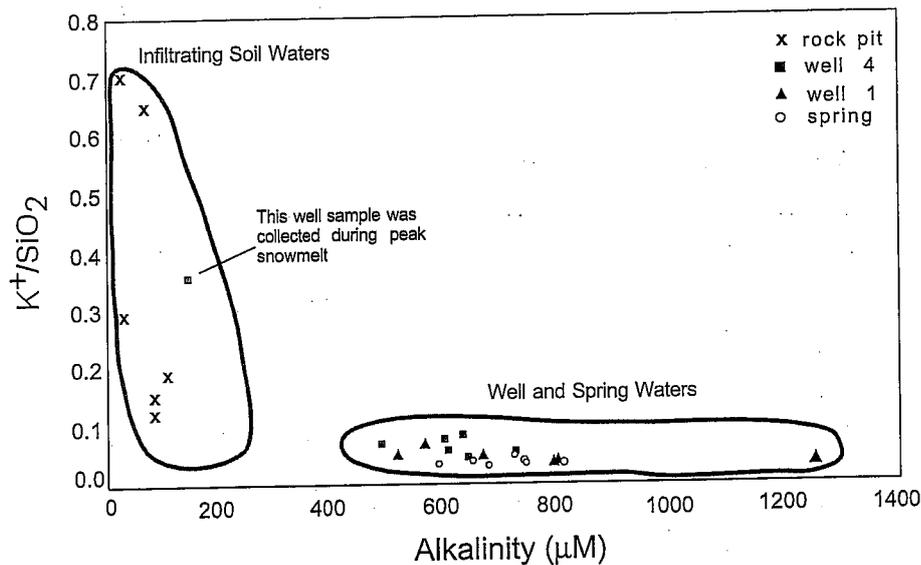

Figure 7. K^+/SiO_2 molar ratios vs. alkalinity for water samples from the rock pit, wells, and the nearby perennial spring. Rock-pit water compositions are due to weathering of disaggregated rock and mineral surfaces, which are continually produced by physical weathering processes. Well-water compositions are due to weathering in fractures that do not freeze and are therefore less prone to physical weathering processes. K^+/SiO_2 ratios are consistently higher, and alkalinity lower, in waters that infiltrate soil.

ies (Hallet et al., 1991) concluded that fracture propagation in rocks occurs by a process known as "segregation freezing" and is optimal in systems residing in sustained subfreezing temperatures, similar to those observed in the study area. In segregation freezing, water moves through a solid in response to a pore-water pressure gradient induced by temperature gradients at temperatures below freezing (Akagawa and Fukuda, 1991). This mechanism of crack production does not require saturation of cracks with water, only sustained subfreezing temperatures and localized hydraulic conductivity. Segregation freezing was demonstrated to be responsible for the rapid and complete disaggregation of the Ohya welded tuff in laboratory experiments (Akagawa and Fukuda, 1991). This mechanism is inferred to be responsible for the mechanical disintegration processes operating in the soil on Snowshoe Mountain.

Surface Area Formation by Rock Disaggregation

Particle-size distribution, electron microscopy, mineral abundances, and bulk chemistry of the soil material suggest that the soil is formed by disaggregation of tuff with little alteration of crystal phases. However, it is difficult to estimate how much geometric surface area is exposed annually by disaggregation of fresh tuff in the soil and at the regolith-bedrock interface. We infer that the disaggregation process has been going on for a long time, but there is no well-defined point in time when bare bedrock began to form soil or when the soil began to be exported by transport processes.

In order to apply what is known about reactivity and kinetics of mineral-water interactions to natural and experimental systems, the amount of mineral surface available for reaction must be known. White and Peterson (1990, p. 462) stated that the *reactive surface area* of a system is the greatest source of error in kinetic models. They defined reactive surface area as "the surface containing chemically reactive sites." We refine that definition to include the surface containing chemically reactive sites that are accessible to infiltrating waters with short residence times.

It is recognized that the bulk tuff has a high specific surface area because of internal porosity features (Reddy et al., 1994); however, petrographic inspection of weathered rock surfaces indicates that permeability within the unfractured rock is low (Hoch et al., 1997). For chemical weathering to occur during the annual snowmelt event, geometric surface area must be created by breaking larger rock fragments into smaller individual rock and mineral constituents, which may be easily accessed by infiltrating waters. For example, if a 20-mm-diameter rock sphere is disaggregated into 50% phenocrysts (0.5-mm-radius
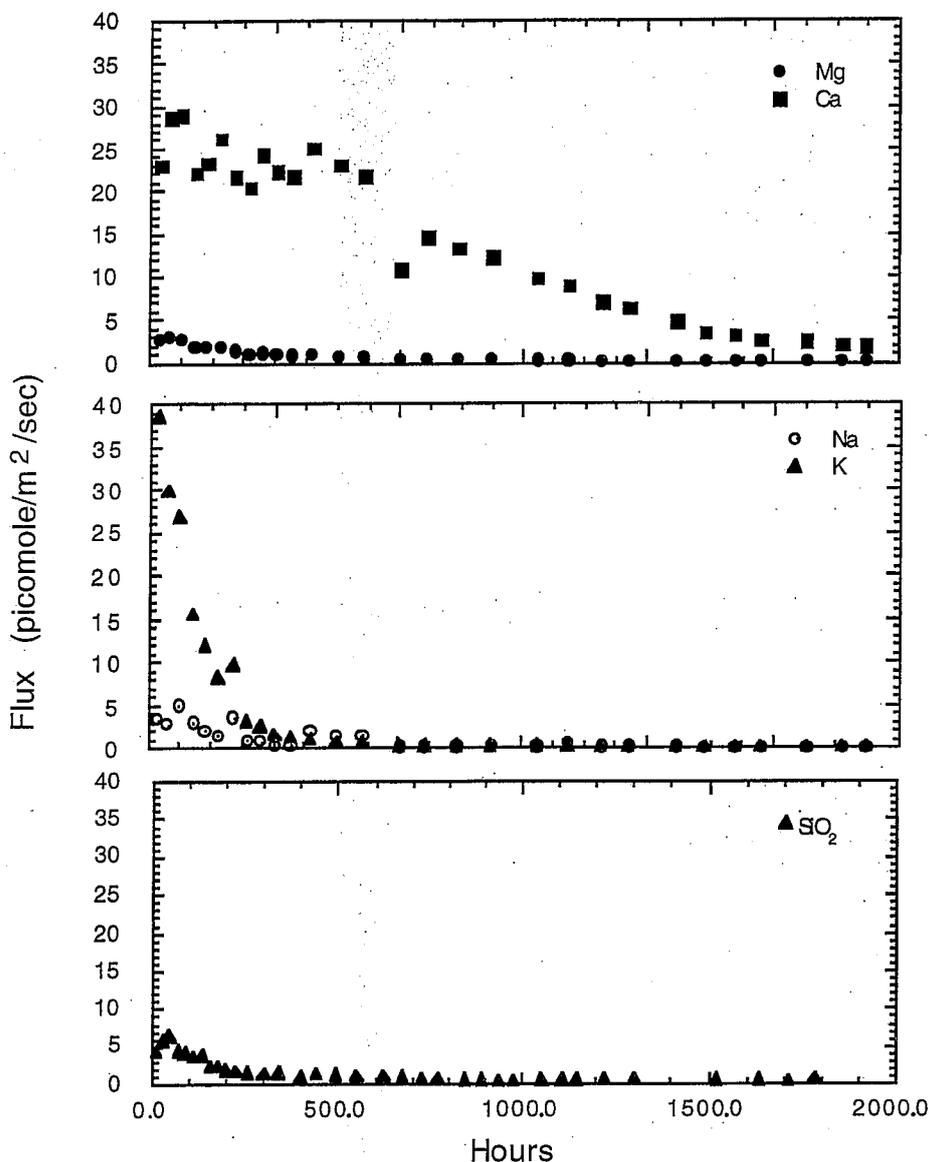
Figure 8. Solute flux vs. time for tuff-dissolution experiment. K^+ exhibits rapid initial release, owing to the rapid exchange of the highly mobile ion with water and/or H^+, through high-energy, freshly created fresh rock and mineral surfaces.

spheres) and 50% microphenocrysts (0.01-mm-radius spheres), the geometric surface area will increase by three orders of magnitude. In the context of the Seven Parks soil, the most important consequence of rock disaggregation is the exposure of the highly reactive, interstitial glass.

The premise of this paper is that mechanical disaggregation exposes fresh rock surfaces that produce high K^+/SiO_2 ratios in infiltrating soil waters when chemically weathered. Given what we have learned about chemical weathering in the field and in the earliest stages of our tuff-dissolution experiment, we can estimate what fraction of the soil's surface area must be cre-

ated annually by rock disaggregation to produce the observed K^+/SiO_2 ratios in the rock-pit water samples (Fig. 7). A series of binary-mixing calculations was performed by using flux values for K^+ and SiO_2 from "aged surfaces" and "fresh surfaces" as end members. All surfaces are assumed to remain in contact with infiltrating water during the annual snowmelt events. Flux values used for the fresh-rock-surface end member (Table 6) were derived from initial experimental fluxes (Table 5) and were corrected for temperature differences on the basis of the results of Reddy and Werner (1987). The SiO_2 flux value used for the aged-surface end mem-
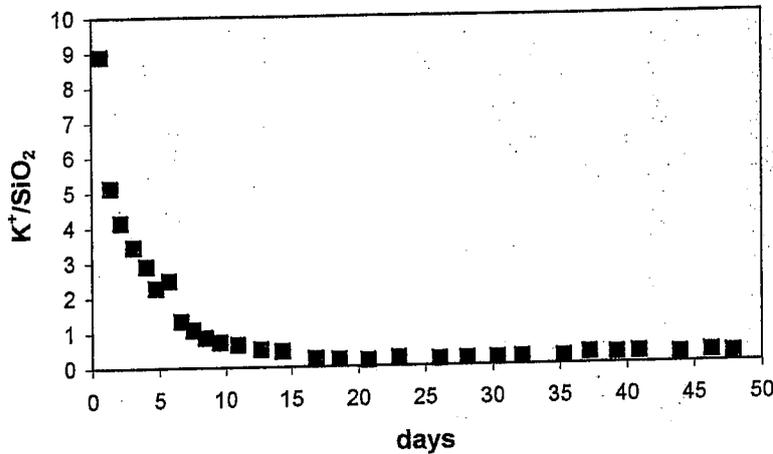
Figure 9. K^+/SiO_2 molar ratios vs. contact time for tuff dissolution experiment. The ratio decreased by a factor of 30 as the rock and mineral surfaces "aged" during the 49-day duration of the experiment.

number of years for the parent rock to completely disaggregate. Although the range of K^+/SiO_2 ratios presented in Figure 7 corresponds to a wide range of time scales for rock disaggregation, we conclude that this exercise illustrates the plausibility of our model for fresh rock surfaces producing a unique chemical signature in this natural system.

Interstitial Glass Dissolution and Other K^+ Sources

In contrast to mineral phases, the residual glass phase in a vitric tuff is the most susceptible to dissolution and most likely to affect infiltrating water chemistry in a freshly disaggregated rock (Claassen and White, 1979). As an analogy, dissolution experiments performed on albite ($NaAlSi_3O_8$) crystals and a Na^+-rich glass equivalent at pH = 4 and 70 °C showed that Na^+ and SiO_2 release from the glass is much faster than from the crystal phase and that Na^+/SiO_2 ratios are much higher for solutions produced by dissolving glass than those produced by dissolving crystals (Zellmer and White, 1986). Thus, the K^+-rich glass in the matrix of the Snowshoe Mountain Tuff should be more susceptible to

ber was that estimated for the 1988 snowmelt event (Table 5). The corresponding aged-surface K^+ flux (Table 5) was estimated to be 0.05 of the SiO_2 flux, on the basis of K^+/SiO_2 ratios from well waters (Fig. 7). Results indicate that very small fractions of fresh surfaces exposed can produce K^+/SiO_2 ratios observed in the infiltrating rock-pit waters (Table 6). If we assume that a given fraction of fresh rock surface is exposed annually, the reciprocal of that number is the

TABLE 5. SOLUTE FLUXES DETERMINED FROM TUFF DISSOLUTION EXPERIMENTS DURING RAPID INITIAL FLUX AND "STEADY-STATE" FLUX, COMPARED TO SOLUTE FLUX CALCULATED FROM ROCK PIT SAMPLES

Solute	Initial experimental flux (mol · m⁻² · s⁻¹)	Steady-state experimental flux (mol · m⁻² · s⁻¹)	Field flux from rock pit, 6/88 (mol · m⁻² · s⁻¹)	Field flux from rock pit, 6/89 (mol · m⁻² · s⁻¹)	Field flux from rock pit, 6/90 (mol · m⁻² · s⁻¹)
Ca^{2+}	2.5×10^{-11}	$*1.8 \times 10^{-12}$	1.75×10^{-16}	8.42×10^{-17}	9.38×10^{-17}
Mg^{2+}	2.5×10^{-12}	1.0×10^{-13}	4.65×10^{-17}	2.42×10^{-17}	2.78×10^{-17}
Na^+	3.0×10^{-12}	1.0×10^{-13}	5.47×10^{-17}	3.37×10^{-17}	3.34×10^{-17}
K^+	3.8×10^{-11}	1.5×10^{-13}	3.12×10^{-17}	3.14×10^{-17}	2.10×10^{-17}
SiO_2	5.0×10^{-12}	5.0×10^{-13}	2.62×10^{-16}	1.74×10^{-16}	1.46×10^{-16}
Sample volume (L)			3.13	2.41	2.50

Note: A specific surface area of 10 m²/g was assumed for the soil.
*Ca^{2+} flux was still significantly decreasing after 40 days reaction time.

TABLE 6. BINARY-MIXING CALCULATION ILLUSTRATING HOW ANNUAL DISAGGREGATION OF ROCK IN SOILS CAN PRODUCE HIGHER K^+/SiO_2 RATIOS OBSERVED IN INFILTRATING WATERS COLLECTED FROM THE ROCK PIT SITE

	SiO_2 flux (mol · m⁻² · s⁻¹)	K^+ flux (mol · m⁻² · s⁻¹)	K^+ flux/SiO_2 flux
Solute end-member 1 (produced from fresh rock surfaces)	1.0×10^{-12}	7.6×10^{-12}	7.6
Solute end-member 2 (produced from aged rock surfaces)	2.6×10^{-16}	1.3×10^{-17}	0.05

% new rock surface (area/yr)	Years required to disaggregate rock*	K^+ flux/SiO_2 flux
0.0001%	1 000 000	0.08
0.0002%	500 000	0.11
0.0005%	200 000	0.19
0.0010%	100 000	0.33
0.0013%	75 000	0.42
0.0017%	60 000	0.51
0.0020%	50 000	0.59
0.0025%	40 000	0.71
0.0033%	30 000	0.90
0.0100%	10 000	2.14

*Years were calculated by taking the reciprocal of the fraction of new rock surface area/yr.

rapid chemical dissolution leading to enhanced K^+ release than its chemically similar sanidine $(KAlSi_3O_8)$ counterpart.

Freshly exposed sanidine in the matrix is probably also a solute contributor, because of its abundance (25% of the rock) and its high K_2O concentration (16 wt%). Sanidine is a high-temperature polymorph of K-feldspar and dissolves more rapidly than orthoclase, the low-temperature equivalent (Schweda, 1990). Biotite, which contains 6 to 9 wt% K_2O (Deer et al., 1963), is not likely to be an important source of K^+ because it occurs only as a phenocryst (larger crystals have smaller specific surface areas), it is strongly oxidized, and it only occupies 4 vol% of the rock.

The effect of dissolution of glass-containing surfaces on natural, infiltrating solutions would be to increase the K^+/SiO_2 ratios to higher levels than would be expected on the basis of the mineral abundances in the tuff. Experimental results indicated that freshly created surfaces, rather than aged surfaces of tuff in the regolith, can enhance dissolved K^+ with respect to SiO_2 because the initial rapid release of K^+ to solution slows by two orders of magnitude within a few weeks of reaction in water (Fig. 9). Laboratory tuff dissolution confirms that a biological source of K^+ is not required to explain high K^+ concentrations in infiltrating waters, as suggested by Claassen et al. (1983).

Discrepancies between Laboratory and Field Rates

Solute fluxes determined in laboratory and field differed by 3 to 4 orders of magnitude (Table 5), a common observation in coupled laboratory- and field-weathering studies, as discussed by Schnoor (1990) and Drever et al. (1994). Drever et al. (1994) concluded that the discrepancy between laboratory and field rates in water-saturated or near-saturated environments can be explained under low-flow conditions by accumulations of solutes that inhibit dissolution (particularly dissolved Al) and/or approach the chemical saturation of individual mineral phases. Under higher flow conditions, they proposed that preferential water flow through higher-permeability channels hydraulically isolates much of the soil. In the example presented in this study, however, the fact that water chemistry (ionic strength, pH) is similar in the laboratory and field rules out saturation or inhibition effects. The annual snowmelt event is relatively slow, and the soil appears to be uniformly saturated; nevertheless, hydrologic reasons for the discrepancy, which may result in a two-orders-of-magnitude rate discrepancy (Schnoor, 1990), cannot be ruled out. Temperature difference certainly produces slower reactions in the field (Velbel, 1990), but not enough to account for a difference of three orders of magnitude.

It is not the purpose of this paper to determine exactly why there is such a large discrepancy between field and laboratory weathering rates; however, the major theme of the paper, natural mechanical disaggregation, may be part of the explanation. If we once again look at ratios of K^+/SiO_2 for field waters (Fig. 7) and compare these to ratios observed early (1 day) and later (40 days) in the experiment (Fig. 9), we can see a drastic decrease from the early experiment to the later experiment. This trend is thought to be related to "aging" of the tuff, by a combination of preferential dissolution of interstitial glass and the preferential diffusion of K^+ out of sanidine in the matrix. The early parts of experiments have higher K^+/SiO_2 ratios, presumably because crushing exposed abundant fresh surfaces of mineral and glass phases. The infiltrating soil waters are exposed to rock surfaces ranging in age from months to thousands of years, producing solutions with K^+/SiO_2 ratios influenced in part by recent mechanical weathering. Phreatic waters from the wells have K^+/SiO_2 ratios that are lower yet, because freezing-driven disaggregation mechanisms are not dominant and thus exposed surfaces are likely already aged by preferential dissolution of the most reactive phases or by formation of secondary minerals.

SUMMARY AND CONCLUSIONS

Chemical weathering of the Snowshoe Mountain Tuff at this cold, high-elevation site is strongly affected by physical disintegration of the tuff. Infiltrating solutions in the vadose zone show anomalously high ratios of K^+/Na^+ and K^+/SiO_2. We interpret the anomalous compositions as being due to rapid weathering of a reactive glass phase present in trace amounts in the tuff. Phreatic waters at the site do not show this anomalous K^+ concentration because, in our interpretation, the K^+-rich glass phase has been depleted and the dominant source of solutes is the weathering of pyroxene and feldspar. These conclusions are supported by laboratory experiments on dissolution of fresh Snowshoe Mountain Tuff in distilled water in flow-through reactors. During the first 3 weeks of reaction, solutions resembled the vadose water from the field site, particularly the high K^+/SiO_2 and K^+/Na^+ ratios. Over longer times, the anomalous K^+ source disappeared, and the waters in the laboratory experiments resembled the phreatic water in the field.

Chemical weathering at this site does not simply reflect the steady-state dissolution of existing mineral surfaces, but is strongly influenced by transitory effects associated with the initial weathering of fresh surfaces. Surfaces are created on an annual basis as a consequence of low temperatures. We do not know the extent to which

similar processes affect the chemistry of weathering of other rock types in cold environments.

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