1 Long-Term Flow-Through Column Experiments and Their
2 Relevance to Natural Granitoid Weathering Rates

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Abstract

Four pairs of fresh and partly-weathered granitoids, obtained from well-characterized watersheds—Merced River, CA, USA; Panola, GA, USA; Loch Vale, CO, USA, and Rio Icacos, Puerto Rico—were reacted in columns under ambient laboratory conditions for 13.8 yrs, the longest running experimental weathering study to date. Low total column mass losses (<1 wt. %), correlated with the absence of pitting or surface roughening of primary silicate grains. BET surface area (S_{BET}) increased, primarily due to Fe-oxyhydroxide precipitation. Surface areas returned to within factors of 2 to 3 of their original values after dithionite extraction. Miscible displacement experiments indicated homogeneous plug flow with negligible immobile water, commonly cited for column experiments. Fresh granitoid effluent solute concentrations initially declined rapidly, followed by much slower decreases over the next decade. Weathered granitoid effluent concentrations increased modestly over the same time period, indicating losses of natural Fe-oxide and/or clay coatings and the increased exposure of primary mineral surfaces. Corresponding (fresh and weathered) elemental effluent concentrations trended toward convergence during the last decade of reaction. NETPATH/PHREEQC code simulations indicated non-stoichiometric dissolution involving Ca release from disseminated calcite and excess K release from interlayer biotite. Effluent $^{87}\text{Sr}/^{85}\text{Sr}$ ratios reflected a progressive weathering sequence beginning and ending with $^{87}\text{Sr}/^{85}\text{Sr}$ values of plagioclase with an additional calcite input and a radiogenic biotite excursion proportional to the granitoid ages.

Effluents became thermodynamically saturated with goethite and gibbsite, slightly under-saturated with kaolinite and strongly under-saturated with plagioclase, consistent with kinetically-limited weathering in which solutes such as Na varied with column flow rates. Effluent Na concentrations showed no clear trend with time during the last decade of reaction (fresh granitoids) or increased slowly with time (weathered granitoids). Analysis of cumulative Na release indicated that plagioclase dissolution achieved steady state in 3 of the 4 fresh granitoids during the last decade of reaction. Surface-area normalized plagioclase dissolution rates exhibited a narrow range (0.95 to 1.26×10^{-13} moles $\text{m}^{-2} \text{s}^{-1}$), in spite of significant stoichiometric differences ($\text{An}_{0.21}$ to $\text{An}_{0.50}$). Rates were an order of magnitude slower than previously reported in shorter duration experiments but generally 2 to 3 orders of magnitude faster than corresponding natural analogs. CrunchFlow simulations indicated that more than a

hundredfold decrease in column flow rates would be required to produce near-saturation reaction affinities that would start to slow plagioclase weathering to real-world levels. Extending simulations to approximate long term weathering in naturally weathered profiles required additional decreases in the intrinsic plagioclase dissolution and kaolinite precipitation rates and relatively large decreases in the fluid flow rate, implying that exposure to reactive mineral surfaces is significantly limited in the natural environment compared to column experiments.

1. INTRODUCTION

Granitoid rocks are ubiquitous in the earth's crust, comprising about 60% of the continental land mass. Granitoid weathering is complex and inherently heterogeneous with different minerals weathering at different rates, causing their relative abundances in the solid and solute products to change with time. Granitoid weathering occurs along grain boundaries, resulting in physical degradation, sap rock, and grus formation (Piotr and Thomasb, 2002). Rates of physical disaggregation may be more than an order of magnitude faster than rates of chemical weathering (Dixon et al., 2001; Yokoyama and Matsukura, 2006). Large rate increases due to physical decomposition have also been observed experimentally under low pH conditions (Ryu et al. 2011).

Both the chemical and physical weathering of granitoids may be initially dominated by soluble and highly reactive accessory minerals such as calcite and epidote (Mast et al., 1990; 1999a; Price et al., 2002; White et al., 2005a) or by oxidation of minerals containing reduced Fe (Taylor et al., 2000; Buss et al., 2008). The relative weathering rates of granitoid minerals vary due to changing environmental conditions such as pH and temperature. Due to lower activation energies, for example, granitoid weathering under low temperature environments is dominated by biotite relative to feldspar (Anderson et al., 1997; White et al., 1999a). Finally, weathering contributions are related to differences in mineral solubilities. For example, plagioclase and K-feldspar dissolution rates are comparable in experimental solutions far from thermodynamic saturation (Blum, 1994; Brantley, 2004). However, under natural near-saturated conditions, feldspar weathering in granites becomes highly selective due to the lower solubility of K-feldspar relative to plagioclase (Fritz, 1988; Maher et al., 2009; White et al., 2001).

71 Despite their importance, far fewer experimental studies have addressed the weathering
72 complexities of granitoid rocks compared to their individual mineral components. Table 1
73 summarizes field and laboratory-based approaches. Long-term experiments, lasting up to a
74 decade, measured mass losses from crushed or slabbed granitoids buried in soils or exposed to
75 groundwater or rain. Shorter-term laboratory weathering of crushed granitoids in batch, flow-
76 through or column reactors measured release rates of major solutes, trace metals, REEs and
77 isotopes. Many of these experiments were conducted at lower pH or lower rock/water ratios than
78 occur during natural weathering.

79 The time span commonly associated with natural weathering is one parameter that cannot
80 be experimentally reproduced (White and Brantley, 2003). While certainly not overcoming this
81 obstacle, the present study, involving pairs of crushed fresh and weathered granitoids, extends
82 the time span beyond any yet achieved for laboratory weathering. Previous papers described
83 initial phases of this experiment and focused on imposed temperature variations, effects of trace
84 amounts of disseminated calcite, and the distribution of Sr isotopes on column effluents (Bullen
85 et al., 1999; White et al., 1999a; White et al., 1999b). The present paper presents final results,
86 focusing on the last decade of the experiment.

87 88 2. METHODS 89

90 The pairs of fresh and weathered granitoid rocks were obtained from four research
91 watersheds: the Merced River in Yosemite National Park, California, USA; the Loch Vale
92 watershed in Rocky Mountain National Park, Colorado, USA; the Panola Mountain Research
93 Watershed near Atlanta, Georgia, USA; and the Rio Icacos watershed in the Luquillo Mountains
94 of Puerto Rico (Table 2). References describing these watersheds are contained in White et al.
95 (1999a; 1999b). Fresh samples were collected from outcrops (or drill core, for Panola) and
96 weathered samples from surface exposures exhibiting various degrees of Fe-staining and
97 physical disaggregation. As in previous reports, we refer to granitoid rocks by their watershed
98 association rather than their geologic names (Table 2). Although all the granitoids were subjected
99 to experimental weathering, we refer to the granitoid pairs as fresh (crushed whole rock
100 granitoids) and weathered (crushed granitoids exposed to some degree of prior natural
101 weathering).

Appendix I contains rock compositions and elemental losses and gains of weathered relative to fresh granitoids as reported as tau values, where a tau value of -1 represents complete loss of an element, and 0 no change (Brimhall and Dietrich, 1987). Elemental losses associated with weatherable primary silicates vary from ~ 0 to > 0.75 . Mineral abundances and compositions for the fresh granitoids are reported in Appendix II. White et al. (1999a) described the experimental column setup in detail. Briefly, granitoids were crushed and the 0.25 to 0.85-mm fraction retained after removal of adhering fines. Samples (750 g total) were loaded into 2.4 cm ID x 100 cm glass columns. (For details on experimental setup see also Figs. S1 and S2.) DI water was introduced through fritted supports at column bases from an elevated polyethylene reservoir through which a 5% CO_2 –95% air mixture was continually bubbled. To minimize gas trapping, fluid flow was directed upward from the column base and effluents collected at the column top (this geometry is the reverse to that of natural soil weathering). Effluents passed through $0.45\ \mu\text{m}$ acetate filters and then through 0.5 mm capillary tubes whose internal diameters were further restricted by drawing out over a Bunsen burner. Flow rates were calibrated to 10 ± 0.5 ml/hr. Although, not sterilized, no obvious biological activity was observed in the columns during the experiments. When the columns were dismantled, SEM analyses of sediment nearest the inlet indicated sparse biological activity (biofilms) mostly at biotite edge sites (Fig. S3).

Ambient temperatures ($22 \pm 2\ ^\circ\text{C}$) were maintained except for periods of imposed temperature excursions of 5 to $37\ ^\circ\text{C}$ (White et al., 1999b). Collection bottles were replaced on a weekly basis, weighed and filtered for chemical analyses. Solute cations and Si were determined by inductively coupled plasma-mass spectroscopy (ICP-MS) and alkalinity by an auto-titrator. Limited anion analyses were performed by ion chromatography. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined by thermal ionization using a Finnegan-MAT 261 mass spectrometer (Bullen et al., 1999). In situ pore-water pH values were estimated at the end of the experiments by rapid successive collection of volume increments from the columns. Exchangeable base cations and $^{87}\text{Sr}/^{86}\text{Sr}$ were determined by passing $0.1\ \text{M}$ NH_4 -acetate solutions through the columns. Total exchange capacity (CEC) measured by subsequent Mg exchange.

Post-experiment miscible displacement experiments characterized the flow regime including saturated hydraulic conductivities and hydrodynamic dispersion coefficients following methods in Klute and Dirksen (1986) and van Grinsven and Reimdsijk (1992). Briefly, water

was pushed through each column at a nominal flow rate of 10 mL h⁻¹ using paired chromatographic pumps. A variable-reluctance pressure transducer connected to a data logger recorded the pressure drop associated with flow. The outlet solution passed through a conductivity cell to determine electrolytic activity of the effluent. After steady conditions were established with DI water, the inlet solution was switched to 0.05 molar MgCl₂. Breakthrough curves were analyzed using standard regression techniques incorporated into CFITIM (van Grinsven and Reimdsijk, 1992).

Statistical characterizations were performed using the ORIGIN PRO 8 graphing program. Mineral saturations and contributions to solute effluents were determined using PHREEQC/NETPATH model (Plummer et al., 1994; Parkhurst and Appelo, 1999). Comparisons of parameters impacting experimental and natural weathering were made for the Merced granitoids using the CrunchFlow reactive transport model (Steefel and Yabusaki, 1996). The initial CrunchFlow model parameterizations were based on prior CrunchFlow simulations of the Santa Cruz, CA chrosequence soils by Maher et al. (2009) and Lawrence et al. (2014) and on FLOWTRAN simulations by Moore et al. (2012). The Santa Cruz and Merced weathering regimes are similar, except that the Merced soils contain a slightly different starting mineral composition, have lower recharge rates, and have weathered for a longer period of time.

Two sets of CrunchFlow simulations were performed: (1) short-term column-scale simulations and (2) long-term field-scale simulations. Short-term simulations of Merced granitoid weathering in the experimental columns were discretized with 10 nodes, evenly distributed over a 100 cm column length scale. For both sets of CrunchFlow simulations, fixed model parameters included boundary conditions, primary species composition, protolith mineral volumes, and volume-dependent BET surface areas (Table 6). Only dissolution of primary plagioclase and K-feldspar and precipitation of kaolinite were considered. The parameter values differed somewhat between short- and long-term simulations on account of differences in starting materials and weathering conditions. The short-term model simulations were run for the equivalent of 15 yrs with daily time-steps and a suite of model simulations were run spanning hypothetical Darcy flow rates ranging from 0.003 to 160 m yr⁻¹, the upper bound representing flow rate of the column experiments. Fixed model parameters for the short-term simulations were from laboratory measurements of column material and the effluent produced during the

weathering study (as reported below). The mineral dissolution rates used in the short-term simulations (baseline values in Table 7) came from previous CrunchFlow simulations of water rock interactions at the Santa Cruz Marine Terraces (Maher et al., 2009; Lawrence et al., 2014). Long-term simulations were discretized with 20 nodes evenly spaced over a 5 m soil column. Simulations were run for the equivalent of 3000 kyr with yearly time-steps, however, for conciseness only results from Riverbank soil (250 kyr) are reported here. The parameters for the long-term simulations were taken from measurements made by White et al., 1996; 2005 and compiled by Moore et al., 2012, who used a comparable reactive transport model, FLOWTRAN, to simulate field weathering of the Merced parent material. For the long-term simulations, we varied weathering rate constants (plagioclase) and fluid-flow until modeled data best matched observations (Table 7). We compared two different mineral weathering rate law formulations: (1) transition state theory (TST) describing a linear rate decrease describing a single elementary reaction or (2), a nonlinear parallel rate law (PRL) describing separate reactions dominating fast far-from equilibrium (FFE) and slow close-to-equilibrium (CTE) reactions. Maher et al (2009) and Lawrence et al. (2014) provide a more detailed description of these CrunchFlow subroutines.

3. RESULTS

The number of columns studied, the long duration of the experiments and the number of parameters characterized produced a very large data set which cannot be succinctly characterized in a single paper; however, all effluent data are provided in the supplemental tables. Here we characterize the results using the Merced granitoid columns as examples. Other granitoid data are discussed where significantly different or where enhancement of a point or conclusion is required. The summary of properties of the fresh Merced granitoid column are listed in Table 3 along with that of the Riverbank soil, which comprise end-members of the extensively studied Merced chronosequence (see references in Table 3). The following sections of the paper describe the main parameters of interest.

3.1 Mineralogical Changes

Less than one percent of granitoid masses were lost during the 14 years of reaction, based on total effluent fluxes and solid state compositions. Likewise, post-run SEM observations failed

to detect any significant increases in surface pitting or roughening of the fresh mineral surfaces that are commonly associated with natural weathering (e.g., the Merced soil, Table 3; White et al., 1996). Varied amounts of red Fe-oxyhydroxide stains formed on mineral grains near the inlet ports, most prominently in the Fe-rich Merced and Rio Icacos columns (Fig. 1b, Fig. S4 and S5). In addition, cemented clusters of grains occurred throughout all columns (Figs. 1a, and Figs. S4 and S5) suggesting localized Fe release from Fe-silicates or most likely trace amounts of pyrite common in granitoids (e.g., the Rio Icacos Granite; Seiders, 1971). Effluent sulfate concentrations decreased to below detection levels during the first year of the experiment implying that pyrite dissolution reaction was fast and did not significantly impact long-term column reactions (White et al. 1999). Fe-oxyhydroxide formation was previously reported in column studies of other granitoids (Afifi et al., 1985).

While no additional secondary phases were positively identified within the columns, white precipitates formed on the surfaces of the solute collection bottles. Nitric acid dissolution recovered mostly Al with subordinate amounts of Si, implying the formation of an Al-hydroxide, i.e., possibly amorphous, or a short range order gibbsite and/or a kaolinite phase. CO₂ degassing in sample bottles produced higher pH conditions than in the columns; making the case that *in-situ* formation of secondary phases in the columns is geochemically unfavored. Similar white precipitates collected in previous silicate column studies were described as poorly crystalline–amorphous Al-hydroxides (Afifi et al., 1985).

3.2 Mineral Surface Areas

Initial BET surface areas (S_{BET}) of the fresh granitoids ranged between 0.077 and 0.103 m²g⁻¹ (Table 4 and Fig. 1c). These values are similar to the crushed El Capitan granite from the Merced drainage (Hausrath et al., 2009) and to averages of plagioclase and K-feldspar separates from granitoid soils in the Loch Vale watershed (Clow and Drever, 1996). The naturally-weathered granitoids exhibit both higher values and a larger range in S_{BET} than for the fresh granitoids (Table 4). Weathered Panola and Rio Icacos S_{BET} are significantly higher than for the Loch Vale and Merced granitoids, reflecting more intensive weathering of these older landforms.

S_{BET} profiles at the end of reaction were always higher than their starting values (Fig. 1c and d). Elevated values occurred adjacent to fluid inlets (< 10 cm in Fig. 1c) corresponding to

secondary Fe-oxyhydroxide formation. The Rio Icacos granitoid had the highest hornblende concentration (0.46 wt%) and highest inlet surface area ($1.22 \text{ m}^2 \text{ g}^{-1}$). The Loch Vale Granite had the lowest values ($0.21 \text{ m}^2 \text{ g}^{-1}$ and $> 0.1\%$, respectively). A subset of reacted fresh granitoids, subjected to Fe extraction by dithionite (DCB), produced S_{BET} column trends mimicking the untreated samples but at significantly lower values (Fig. 1d). Small differences in the initial and treated values (factors of 2 to 5) may be related to slight surface roughening, incomplete Fe-hydroxide removal, or opening of biotite interlayers as a result of DCB extraction (Lowell, 1967).

3.3 Fluid Flow

Average flow rates for the fresh and weathered Merced granitoids were only slightly slower than the initial calibrated rates of 8.5 to 9.0 ml hr^{-1} shown by the horizontal lines in Fig. 2a. However, both significantly faster ($\text{max} \approx 16 \text{ ml hr}^{-1}$) and slower short-term rates ($\text{min} \approx 4 \text{ ml hr}^{-1}$) occasionally occurred due to breakage and/or clogging of the capillary tips. Although not initially planned, such variations provided useful in documenting the effect of flow on weathering rates. A less desirable effect would be if flow rates exhibited consistent increases or decreases over the entire course of the experiments, potentially impacting long-term steady state conditions. Cumulative volumes of flow through the fresh granitoids were similar, and linear with time ($r^2 > 0.99$) implying that short-term changes in flow rates were random and produced no long-term extraneous signal (Fig. 2b).

In addition to the macroscopic flow rate, pore-level flow geometry is also important in controlling residence times of fluids in contact with mineral surfaces. If the flow field is highly heterogeneous, as represented by dual-porosity (mobile-immobile) pore-water models, the corresponding weathering rates will also be variable. A review of a large number of solute transport experiments by Haggerty et. al. (2004) indicated that immobile water usually played a key role in transport, even in sands. However, apparatus artifacts are often to blame (James and Rubin, 1972). In the present study, miscible displacement experiments uniformly indicated very narrow distributions of residence times within the columns (e.g., Fig. 2c). The movement of water through the pore space was well approximated by piston flow, with minimal, nearly symmetric tailing. Peclet numbers, representing the ratio of advective to diffusive transport ($P = Lu/D$), were much greater than one ($143 < P < 4500$), providing strong evidence of negligible

impacts of solute exclusion, local non-equilibrium, and immobile water. L , u , and D , are pore-scale characteristic length, local flow velocity, and solute diffusion coefficient, respectively. Dimensionless P values were calculated by CFITM directly from dimensionless breakthrough curves. Retardation factors, R , reflecting adsorption of Mg^{+} on exchange sites, were also relatively small, ranging from 1.0 to 1.6, where R equals the number of pore-volumes eluted at 50% breakthrough. Note that P values do not indicate the degree to which reactive conditions are transport-limited. Indeed, due to interphase mass transport inherent in profile development, weathering rates in natural settings depend primarily on fluid residence times (i.e., flow velocity; Maher, 2010).

3.4.1 Column Solutes

Column effluent compositions during initial phases of the column experiments were previously described (White et al., 1999a; 1999b and White and Brantley, 2003). Data collected at longer times (4.0 to 13.8 yrs) are the focus of the present paper and are summarized in Table 5 (see supplemental tables for the complete data sets). Silica and alkalinity (HCO_3) dominated all column effluents, with concentrations (hence release rates) for fresh and weathered granitoids largely converging by the end of reaction. Initial solute concentrations were significantly lower in effluents from the weathered versus fresh granitoids, presumably reflecting their less-reactive surfaces. Perturbations during 1.5 and 2.5 yrs (Fig. 3) reflected experimentally-induced temperature changes (6 to 34°C) described by White et al. (1999b). Insets in Figure 3 show dilute effluents sampled during the last decade of reaction (Table 5 and supplemental tables). Data scatter reflects changes in experimental conditions, principally flow rate and analytical protocols related to instrument upgrades over time.

Solute concentrations in effluent from the fresh Merced granitoid generally exhibited small but statistically significant decreases over the last decade of the experiments (linear regression fits, Fig. 3). Potassium, Mg, Ca, Si, and alkalinity concentrations declined by a factor of about 2. The decline in Na, assumed to be solely dependent on plagioclase dissolution, is small compared to scatter, and statistically insignificant over long times. The other fresh granitoid columns showed similar trends with no or small statistical declines in Na. In contrast, weathered granitoid solutes, including Na, generally exhibited small increases with time (Fig. 3; also see White and Brantley, 2003).

3.4.2 Column pH

Column input pH (average = 4.65) corresponded to DI water saturated with 5% CO₂ (Fig. 4a) and is comparable to many shallow soils with elevated CO₂ from plant respiration (e.g., White et al., 2005b). In contrast, column discharge pH (average = 5.41), measured from sample collection bottles, is representative of dilute solutions equilibrated with atmospheric CO₂ (Likens and Bormann, 1974). The estimated column in-situ pH values, measured by rapid plug-flow displacement from columns immediately at the end of the experiments, bracketed the input and sample bottle pH values (4.96 to 5.15). The slightly higher average pH values in the fresh granitoids, compared to their weathered counterparts, correlated with more concentrated effluents and faster reaction rates. The fresh Rio Icacos granite exhibited the highest pH, consistent with more reactive calcic labradorite. Except for this granitoid, there is essentially no pH increase along the flow path of any the columns as would be expected if progressive silicate hydrolysis was occurring.

3.4.3 Exchangeable Cations

Cation exchange capacities (CEC) for the fresh and weathered granitoids, measured after reaction, were small compared to natural granitic soils (0.14 to 0.33 meq kg⁻¹ for the columns, versus >10 meq kg⁻¹ for their natural counterparts; White et al., 2005b, (supplemental table L). CECs determined on field samples from the naturally weathered Panola and Merced profile varied between 10 and 180 meq kg⁻¹ s, corresponding to significant clay and Fe-oxyhydroxide precipitation (White et al, 2001; 2005c). In the fresh granitoid columns total exchangeable Ca is the dominant column cation (Fig. 4b-e). Exchangeable Ca is less than 0.1% of the cumulative solute Ca released from the course of fresh Merced experiment. Exchangeable Ca is significantly greater for fresh Puerto Rico granitoid due to the high labradorite content, but is still equivalent to only 6% of the total solute Ca released. These low exchange capacities imply that the major solute cations are not well buffered with respect to changing external effects such as pore water flow (Fig. 2a). This condition is opposite of that for many natural soils in which high CECs serve as effective buffers to changes in solute compositions.

Hydrogen ions generally dominated over other base cations on the exchange sites (Fig 4b-e), which buffered solute column pH values. Increasing pH indicative of silicate hydrolysis was observed only in the Rio Icacos columns, where exchange sites were dominated by Ca rather

than H^+ (Fig 4e). Base saturation, defined as the percentage of CEC occupied by cations other than H^+ and total Al (Driscoll et al., 1985), was low (2 to 23%). Base saturation in the columns of this study is comparable to soils impacted by acid precipitation, a condition commonly occurring in watersheds underlain by granitoid rocks. The acidity of column input solution (pH = 4.6 at 5% CO_2) is slightly higher than acid precipitation, which has an average pH value of 4.0. The high exchangeable H^+/Al ratio is also atypical of natural acid-impacted environments. Low base saturation reflects the rapid column flow rates and attendant low base cation weathering status rather than a strong acid input.

3.4 Effluent thermodynamic saturation

Mineral saturation indices (SI) are defined as the log ratio of aqueous activities, IAP, divided by the mineral solubility constants, K_s ($SI = \log IAP/K_s$). Calculations were performed using the PHREEQC code (version 2), using K_s values cited in the user's manual (Parkhurst and Appelo, 1999). Values of $SI < 0$ thermodynamic under-saturation and values > 0 denote supersaturation. The fresh granitoid effluents are initially saturated or supersaturated with respect to goethite (Fig. 5a). Rio Icacos effluents remain relatively high in Fe concentration. Solute Fe generally falls below detection limits for the other granitoids (Table 5). However, based on randomly distributed Fe-oxyhydroxide cemented clusters which occurred in all fresh granitoid columns (SEM/EDAX data Fig.1a and b; Figs. S4 and S5), secondary goethite was supersaturated locally, where pyrite dissolution occurred.

Both gibbsite and kaolinite are supersaturated in the initial effluents, principally due to high solute Al concentrations (Figs. 5b and 5c). Over longer time frames, effluents become closely equilibrated with gibbsite and slightly under saturated with kaolinite. As previously mentioned, neither phase was positively identified in reacted column material by SEM/EDAX, presumably due to poor crystallinity. The white precipitate formed in the collection bottles and composed of mainly Al with lesser Si indicate a possible mixed gibbsite-kaolinite phase, formed at a higher pH than existed in the columns (Fig. 4a).

Except for some early samples, effluents were significantly undersaturated with respect to primary aluminosilicates—as indicated by sequentially more negative SI values for biotite, K-feldspar, and plagioclase (Fig 5d –f). Plagioclase solubility was calculated as albite. The

saturation state for ferrous-Fe containing biotite is dependent on undefined column redox conditions, thus end-member phlogopite mica (no Fe) was used to estimate biotite solubility.

3.5 Relationship Between Flow Rate and Solute Concentrations

Mineral weathering is transport-limited under thermodynamically saturated conditions ($SI \geq 0$), i.e. weathering occurs only when saturated fluids are displaced with incoming unsaturated fluids that can themselves become saturated. Under such chemostatic behavior effluent concentrations do not vary with flow rate (Maher, 2011). In contrast, under strongly under-saturated conditions, assuming sufficient inputs of reactants, e.g. H^+ , reaction rates remain constant and increasing or decreasing flow rates will decrease or increase effluent concentrations.

These two contrasting conditions are shown by the horizontal and upward concave lines in Fig. 6 which are fitted to pass through the average flow rates and Na effluent concentrations from the fresh Merced, Panola, and Loch Vale columns. Clearly effluents are not invariant but fall along the curves predicted for fixed reaction rates controlled by flow. Data variability primarily corresponds to flow rate and solute concentration variations, as shown in Figs. 2a and 3. This relationship indicates that Na is produced primarily from kinetically-controlled weathering of plagioclase which is the silicate furthest from thermodynamic saturation (Fig. 5f).

3.6 Mineral Contributions to Column Effluents.

Effluent compositions reflect granitoid mineral abundances and stoichiometry as well as relative reaction rates. A mass balance approach was first employed by Garrels and Mackenzie (1967) to explain stream compositions in granitoid watersheds of Sierra Nevada (USA) and was later modeled using inverse NETPATH model (Plummer et al., 1994). Chemical mass-balance modeling was subsequently used to characterize natural weathering in a number of granitoid watersheds, including Loch Vale (Mast et al., 1990), Rio Icacos (White et al., 1998), and Panola (Bowser and Jones, 2002). In the present NETPATH calculations, the number of elements was set either equal to or one less than the numbers of mineral phases present (mineral abundances and compositions are found in Appendix II.). Primary silicate minerals were allowed only to dissolve and the secondary minerals only to precipitate, as implied by their calculated saturation states (Fig. 5).

Unique NETPATH outputs for Loch Vale and Panola granitoids were generated by applying six elemental constraints (Na-K-Mg-Ca-Al-Fe) to six mineral phases, i.e., plagioclase, K-feldspar, biotite and calcite and secondary kaolinite and goethite. Hornblende concentrations in these granitoids were low and not entered into the calculations. Effluents were initially dominated by calcite dissolution (positive values at < 1 yrs in outer plots in Fig. 7 a and b). Over time, more dilute effluents reflected inputs from plagioclase and sub-equal contributions from K-feldspar (interior plots in Fig. 7 a and b). Aluminum and Si generated during dissolution were incorporated into kaolinite, the precipitation of which gradually declines concurrently with feldspar dissolution (negative losses in Fig 7a and b). Compared to feldspars, biotite dissolution declined over time but remained the primary source of Fe incorporated into secondary goethite.

The modeled Rio Icacos weathering granitoid contains plagioclase, biotite, hornblende and disseminated calcite but essentially no K-feldspar (Fig.7c). Stoichiometric biotite dissolution caused NETPATH to fail due to disproportionally high effluent K relative to Na and Mg. Fresh biotite undergoes fast non-stoichiometric oxidation of structural Fe and subsequent release of interlayer K (White and Yee, 1985; Amonette et al., 1988; Taylor et al., 2000), likely explaining the observed excess K in effluent. Using interlayer biotite K as separate phase required seven constraints (Na-K-Mg-Ca-Al-Fe-Si) and resulted in a successful NETPATH convergence. After initially large calcite inputs, effluent from the Rio Icacos granitoid becomes dominated by constant inputs of interlayer K and sub-equal amounts of plagioclase (Fig. 7c).

The modeled Merced granitoid involved the largest number of phases, including plagioclase, K-feldspar, biotite, hornblende, biotite-interlayer-K, calcite, kaolinite and goethite (Fig. 7d). As with the Rio Icacos granitoid, interlayer-biotite-K was required to reproduce high effluent K. A maximum of seven constraints representing major elements measured in the effluents (Na-K-Mg-Ca-Al-Fe-Si) resulted in two possible mineral assemblages differentiated by hornblende/no biotite and biotite/no hornblende. Both phases contained approximately equal proportions Mg and Fe and, as such, their contributions were not uniquely defined. A recent Mg isotope study indicated that biotite initially reacted faster than hornblende (Ryu et al., 2011). Mineral solute contributions shown in Fig 7d (inset) include overlapping biotite and hornblende results. Over time, the interlayer biotite K loss remained constant, with biotite representing the dominant reactive phase (as with the Rio Icacos quartz diorite, Fig 7c). Loss of interlayer biotite

K was accompanied by gradual decreases in plagioclase and K-feldspar dissolution and kaolinite precipitation.

3.7 Mineral Contributions and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

$^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca ratios have been used to gain insights into relative rates of mineral weathering in granitoid column experiments (Erel et al., 2004; Ganor et al., 2005). While potentially serving as an additional constraint in NETPATH (Plummer et al., 1994), calculations using $^{87}\text{Sr}/^{86}\text{Sr}$ compositions listed Appendix II and Table 5 failed to converge, due to strongly incongruent release of $^{87}\text{Sr}/^{86}\text{Sr}$ (Brantley et al., 1998; Taylor et al., 2000).

When plotted together, changes in fresh granitoid $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca effluent ratios follow a counter clock-wise triangular pathway established for shorter-term data (White et al., 1999; White and Brantley, 2003) (Fig. 8a-c). For Merced and Panola, the longer-term solute data presented here (Table 5, and Supplemental Tables) completes the patterns in which the final $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca ratios approximate the initial ratios. The initial solute ratios corresponded most closely to plagioclase, presumably representing rapid dissolution of highly reactive surfaces produced by sample preparation that were quickly exhausted. Over the next days to weeks, Ca/Sr ratios generally paralleled mixing lines with calcite, confirming the initial importance of this phase in the NETPATH results (Fig. 7).

After several months of reaction, effluent $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca/Sr ratios trended toward higher $^{87}\text{Sr}/^{86}\text{Sr}$, values which are proportional to the age of the granitoids and radiogenic Sr content of the biotite (note that the biotite Ca/Sr ratios were not determined). Finally, over the next several years, effluent $^{87}\text{Sr}/^{86}\text{Sr}$ declined back toward ratios reflecting long-term plagioclase dissolution. This occurred for the Merced granitoid in spite of the NETPATH results indicating interlayer K continuing to be the dominant solute source in the column (Fig. 7d). This discrepancy implies that ^{87}Sr produced from the decay of ^{87}Rb substituting for K in the biotite interlayer is preferentially released early in the experiments. This effect is also dependent on the magnitude of the biotite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The final Loch Vale effluent $^{87}\text{Sr}/^{86}\text{Sr}$ ratios remained significantly more radiogenic than plagioclase (Fig 8c) reflecting continued inputs of small amounts of very radiogenic biotite Sr (note that excess interlayer K was not a required phase; Fig. 7a).

The initial Ca/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the weathered granitoid effluent were similar to their fresh counterparts, reflecting rapid plagioclase dissolution (Fig 8 d-f). However these effluents lacked subsequent Ca/Sr increases, indicating calcite loss during previous natural weathering. Rather, effluents moved directly upward to more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This effect was minor for the weathered Merced granitoid (Fig 8d). However, the maximum $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the older weathered Panola Granite and Loch Vale granitoids approached those of their unweathered counterparts (Fig. 8e and f). While acetate exchangeable $^{87}\text{Sr}/^{86}\text{Sr}$ from the Merced granitoid was found to be in equilibrium with the final column effluent, exchangeable Sr from the older Panola and Loch Vale granitoids remained much higher, providing an ongoing radiogenic source to the effluents. Solute Ca/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were comparable to plagioclase in the corresponding watersheds (Fig 8d-f) implying that both the reactive calcite and radiogenic biotite components have been removed during natural weathering at this larger scale.

4. DISCUSSION

A major gap in our understanding of chemical weathering centers on the large apparent differences between experimental and natural silicate weathering rates. A relevant point of departure in this discussion is a plot of experimental and natural plagioclase weathering rates as functions of reaction duration (Fig. 9; after White and Brantley, 2003). Plagioclase is emphasized because it commonly dominates weathering in granitoid rocks and its weathering rate generally is estimated from Na concentrations in solids and solutes. Figure 9 includes time-dependent plagioclase rates for fresh and weathered granitoids from this study and updated literature rates for previous experimental and field studies (Bandstra et al., 2013; White and Buss, 2014). Values are plotted on a log scale to accommodate the large ranges in the rates and times, which in turn corresponded either to the duration of experimental reaction or to the approximate age of the natural weathering environment.

4.1 Calculation of Column Plagioclase Weathering Rates

Plagioclase rates for the fresh and weathered granitoids in Figure 9 are calculated from individual sampling events by the relationship

$$R_r = M_{Na} / t \beta S_A \quad (1)$$

where R_r (moles $\text{m}^{-2} \text{s}^{-1}$) is an empirical rate; more accurately described as a mass flux. It does not correspond directly to an intrinsic plagioclase rate constant as will be subsequently described. M_{Na} , is the mass of Na dissolved in effluent and collected in individual sample bottles over a given sampling interval t (s), β is the stoichiometric coefficient relating the moles of solute Na per mole of plagioclase (moles mole^{-1}), and S_A ($\text{m}^2 \text{g}^{-1}$) is the maximum DCB- extracted BET surface area measured at the termination of the experiments (Table 4).

Two-to-five orders of magnitude differences exist between experimental and field weathered plagioclase rates reported from the literature and plotted in Fig. 9 (see data compilation in White and Buss, 2014). Relatively large differences in time frames also exist between individually determined experimental rates and natural weathering environments. In spite of the large uncertainties associated with this diverse dataset, a general relationship of decreasing weathering rates with increasing time is evident (White and Brantley, 2003), described by the empirical regression (diagonal dashed line in Fig 9)

$$R_r = 3.47 \times 10^{-13} t^{-0.56} \quad (2)$$

$$r^2 = 0.68$$

This power law predicts a 10-fold decrease in the weathering rate of a silicate mineral after 50 yr, a 100-fold decrease after 2000 yrs, and a 1000-fold decrease after 10,000 kyr etc. A comparable power law was previously proposed by Taylor and Blum (1995) to describe the decrease in weathering fluxes from a suite of weathering environments with increasing time. The chemical or physical basis of this apparent continual decrease in reaction rates with time remains controversial. Experimental time spans, even for the present study, do not come close to simulating the long-term aspect of these proposed relationships.

A time-dependent weathering function (Eqn. 2) runs counter to conclusions of many relatively short experimental studies that suggest silicate reaction rates reach steady state. For example, Hausrath et al. (2009) reported that plagioclase weathering in granite column experiments became constant after 40-45 weeks of reaction with unbuffered DI water, a conclusion not supported by present study. Short-term plagioclase dissolution rates, R_r , in both fresh and weathered granitoids, generally fell within the previously reported range (Fig 9). In the

present study, which exceeded the time spans of previous experimental studies, the fresh granitoid plagioclase weathering rate continued to decline, albeit at progressively slower rates than predicted by the power law (Eqn. 2). After 13.8 yrs. of reaction, the average plagioclase rates were approximately an order of magnitude less than the average of the shorter term literature rates (1.2×10^{-13} versus 1.5×10^{-12} moles $\text{m}^{-2} \text{s}^{-1}$).

The question arises as to whether or not extending experimental reaction times, as done in the present study, actually produces closer estimates of state steady-state reactions. If not, the remaining inconsistencies with natural weathering rates could simply be explained by not running experiments long enough, as suggested by the power function (Eqn. 2 and Fig. 9). While log scales (Fig 9) are useful in comparing large ranges in rates and time, they emphasize large changes in reaction rates during the initial stages of the column experiments. Cumulative solute Na is as linear function of time (Fig 10), demphasizing this effect and reducing the data scatter attributable to short-term sampling effects such as changing flow rates (Figs. 2a).

Initial cumulative solute Na increases are different for the four granitoids. In particular, the Rio Icacos quartz diorite exhibited relatively large increases (Fig. 10a). However, cumulative outputs became very similar for all the fresh granitoids during the last ten years of reaction, as characterized by linear regression fits (straight lines in Fig. 10), with slopes ranging from 1.22 to 1.32 mmoles/yr. This similarity occurred in spite of significant differences in plagioclase compositions (An_{21} for Loch Vale to An_{50} for Rio Icacos granitoids). Plutonic plagioclase is commonly composed of extremely fine intergrown lamellae of albitic and anorthitic compositions. Thus, the more soluble Ca component may become shielded and dependent on the reaction and removal by the less soluble Na phase (White et al. 2008; Maher et al. 2009).

Fits of cumulative solutes with time produced linear regression coefficients $r^2 > 0.94$ for the time period 4.0 to 13.8 years. The distribution of residuals (insets in Fig 10) shows the extent to which cumulative increases deviated from a linear steady state. Random residuals (i.e., for the Merced, Loch Vale, and Rio Icacos granitoids) cluster around zero and lack consistent trends with time. Such distributions are expected for solutes that are primarily dependent on flow rates, which themselves similarly distributed with time (Fig. 2a).

In contrast, the Panola Granite exhibited a consistent convex pattern (Fig. 10b, inset), indicating that variations in the residual distributions were not random and that weathering slowly continued to decline. This trend was previously observed in the shorter-time Panola data

(White and Brantley, 2003). Except for Panola, steady state weathering appears to have been achieved over the time spans of the experiment. Note however, that these times occupy a very small portion of the entire log time scale shown for the combined experimental-natural rates plotted in Fig. 10.

4.2 Surface Areas and Reactivities

Weathering trends with time, whether under experimental or natural conditions, are commonly ascribed to physico-chemical changes in silicate surfaces, either as physical surface areas that are expected to increase due to pitting and etching, or surface reactivity, e.g. the density of reactive sites per unit of surface area, which are expected to diminish with time (Brantley et al. 1999).

The initial Na decrease in the fresh granitoid effluents (1 to 2 orders of magnitude; Fig. 3) evidently reflects rapid declines in surface reactivity induced in part by sample preparation, i.e., grinding. The opposing solute increase associated with short-term increases in physical surface area (less than factors of 2 in the first 1.6 years of reaction, Table 4) was negated by these declining reactivities. The lower initial Na releases from the weathered granitoid counterparts (Fig. 3) reflect lower surface reactivities, presumably due to previous exposure in the natural environment.

The roles of physical surface areas and surface reactivities in controlling solute Na release becomes less obvious over longer time frames (>4 yrs, Fig. 3). Except for Panola, Na effluents from the fresh granitoids remained essentially constant (Fig.10). Limited BET surface area data (Table 4) suggest that physical surface areas continued to increase, less than doubling over the last decade of reaction. Surface area increases alone should correlate with increases in solute Na, an effect not observed for the fresh granitoids. Near constant release rates (Fig.10) suggests that small increases in physical surface areas were countered by corresponding decreases in surface reactivity over the same time period.

In contrast to the fresh granitoids, solute outputs, including Na, from the weathered granitoids exhibited small increases during the final decade of reaction (Fig. 3). Two previous studies observed solute increases with time under much more acidic conditions. Ganor et al., (2005) reacted hydrothermally-altered granite containing Fe-oxide-coatings at pH 1. A

correlation between the mass of Fe dissolved and a factor-of-six increase in Na release with time was attributed to accelerated plagioclase weathering caused by increasing exposure of reactive surfaces as coatings dissolved. The weathered granitoids in our study also contained Fe-oxide and clay coatings (based on visual and SEM observations). However, under the four-order-of-magnitude higher pH conditions of the current study, these coatings appear to be more stable. Goethite is supersaturated in output solutes (Fig. 5a) and Fe-containing coatings precipitated near the column inputs of the fresh granitoids. These observations, coupled with low effluent Fe, suggests that removal of Fe-oxide coatings may not effectively increase silicate surface reactivity within a decadal time frame.

Ryu et al. (2011) measured solute increases over time while reacting fresh Precambrian Boulder Creek Granite (similar to the Loch Vale Granite) at pH 1. The solute trends were attributed to a “sugar lump effect” (Norri et al, 2009) in which solute rates initially increased as large mineral grains disaggregated into progressively increasing numbers of smaller particles, thereby increasing total surface areas. No measurements of final surface areas were reported, but a mass-balance model was consistent with a significant (29%) plagioclase loss (Ryu et al., 2011). While this model may also be applicable to highly porous friable plagioclases present in intensely weathered soils (White et al. 1996), grain disaggregation in the naturally-weathered granitoids of this study was not observed at column disassembly. The grain size fraction used in the experiments generally consisted of single silicate phases that exhibited sound structural integrity, with only minor pitting and etching. The low mass losses (<1%) produced during the present experiment were insufficient to initiate disaggregation.

Surface roughening by itself would be sufficient to produce small surface area increases and therefore increases in weathered column solutes if surface area change dominated over any concurrent decreases in surface reactivity (Fig. 3). In effect this would be the opposite of what occurred in the initial phase of the experiments during which time solute concentrations decreased with time (Fig. 5). Unfortunately, BET surface area data for the weathered granitoids were ambiguous due to the presence of high-surface-area hydroxides and clays which were difficult to completely remove by dithionite extraction. As indicated by the converging solute trends (Fig. 3 inserts), lengthening the time of the experiment would have led to comparable solute concentrations suggesting the combined effects of surface area and reactivities would

become equal for the pairs of fresh and weathered granitoids. However, as indicated in Fig. 9, weathering rates of both the fresh and weathered granitoids remained 1 to 3 orders of magnitude higher than natural field rates. This discrepancy is investigated in further detail in the following section.

4.3 Direct Comparisons of Experimental and Natural Weathering Rates

A unique feature of the present study is that the column plagioclase rates can be compared to natural rates previously reported for weathering environments from which the granitoids were obtained (Fig. 9). A detailed discussion of general approaches used to quantify field weathering rates is presented elsewhere (Brantley and White, 2009; White and Buss, 2014).

4.3.1 Loch Vale

The Loch Vale field-based plagioclase rates (0.9 to 3.2×10^{-13} moles $\text{m}^2 \text{s}^{-1}$) were calculated from solute mass losses (Eqn. 1) in an upland alpine catchment comprised of a pocket veneer of thin soil resting on Precambrian granite (Drever and Clow, 1995). The site was artificially irrigated during two consecutive summers, maintaining soils in a continuously wet condition. Weathering rates during the field experiments were comparable to corresponding column rates reported by Drever and Clow (1995) and observed in the present study (Fig. 10a) but are one to two orders of magnitude faster than those reported for other Pleistocene-glaciated watersheds subjected to natural precipitation (Fig. 9a). This discrepancy suggests that magnitude and timing of accelerated artificial recharge had a significant impact; essentially producing weathering rates in a field setting that were comparable to a laboratory rate determined in the present study.

4.3.2 Panola

Plagioclase content increases linearly downward from saprock to fresh bedrock over a six-meter weathering profile within the semi-tropical Panola watershed (White et al., 2001; White et al., 2002). Based on ^{36}Cl , the isovolumetric weathering profile is advancing at rate of 7 m per million years (Bierman et al, 1995), establishing the duration of weathering (Figure 9b). Very low initial bedrock permeability, coupled with relatively high recharge, requires that most pore water move downslope along the saprolite-granite interface.

Loss of highly soluble disseminated calcite serves as a silicate weathering precursor, increasing bedrock permeability sufficiently that transport-limited plagioclase weathering occurs. In contrast, less soluble K-feldspar continues to reflect parent-material abundances, being weathered only at the more-permeable, saprolite-saprock interface. A plagioclase rate of 2×10^{-16} moles $\text{m}^2 \text{s}^{-1}$ resulted from fitting a spreadsheet model to the bedrock plagioclase weathering profile (White et al., 2001). This rate is comparable to that for other older weathering environments (data points along the time line in Fig. 9b) and is about three orders of magnitude slower than the Panola plagioclase column rates of this study (Fig 10b), which reacted far from thermodynamic saturation (Fig. 5f).

4.3.3 Rio Icacos

In the tropical Rio Icacos watershed in Puerto Rico, isovolumetric plagioclase weathering occurs beneath a thick saprolite regolith (White et al., 1998). Unlike Panola, plagioclase losses here are confined to near the bedrock surface within a series of thin concentric “onion-skin” rindlets bounded within thicker fracture blocks (Fletcher et al., 2006; Buss et al., 2005; 2008). Interstitial porosity is first created from weathering of altered calcic cores of plagioclase and apatite inclusions. Porosity is then expanded by strain and fracture propagation produced through oxidation and expansion of biotite (Buss et al., 2008). This reaction also releases K and radiogenic Sr from biotite (Petite-Ridge et al, 2009), as demonstrated by NETPATH simulations (Fig. 7c). In a very rapid steady-state denudation in a tropical climate, the Rio Icacos weathering front propagates through a meter of rindlets in about 10^4 yrs, based on ^{10}Be estimates of Brown et al. (1995).

An average plagioclase weathering rate of 3×10^{-15} moles $\text{m}^{-2} \text{s}^{-1}$ was first calculated from solid state Na losses across sets of rindlets (Turner et al., 2003). This rate is an order of magnitude slower than for bedrock weathering at Panola but falls along the time line in Figure 9c. In contrast, a significantly faster rate (1.1×10^{-13} moles $\text{m}^2 \text{s}^{-1}$), equivalent to the Rio Icacos column experiment (Fig. 10c), was subsequently determined using a simplified geometric fit to rindlets’ mineral abundances at a different watershed location (Buss et al. 2008). While plagioclase was completely depleted in the rindlet interiors of this study, only partially depleted plagioclase was observed in the Turner et al. (2003) study. These differences are attributed to the

highly heterogeneous nature of fracture flow and corresponding large differences in the extent of thermodynamic saturation.

4.3.4 Merced Soils

The Merced column experiments most closely approximate weathering resulting from vertical percolation of pore water through the sandy sediments of the Merced soil chronosequence. Physical, hydrologic and mineralogic characteristics of the fresh Merced granitoid are compared to the relatively unweathered deep horizon (5.5 m) of 250 ka Riverbank soil in Table 3. Similarities include plagioclase concentrations, soil porosities and laboratory-measured saturated hydraulic conductivities and mineral surface areas.

The sandy sediments of the Merced soil chronosequence were derived primarily from granitoids in the Merced River and Toulumne River drainages in the Sierra Nevada Mountains of central California, including the granodiorite of Arch Rock from Yosemite (Table 2). These soils are up to ten meters thick and range in age from 10 kyr to 3000 kyr. Total mass losses calculated for specific soil horizons and coupled to BET surface area measurements suggest declining plagioclase rates with increasing soil age (from 8.1 to 0.5×10^{-16} moles $\text{m}^{-2} \text{s}^{-1}$; White et al., 1996). These rates are orders of magnitude slower than for the fresh Merced column (1.2×10^{-13} moles $\text{m}^{-2} \text{s}^{-1}$) but fall along the time-dependent weathering line in Fig. 9d. Natural weathering rates (3 to 7×10^{-16} moles $\text{m}^{-2} \text{s}^{-1}$) were calculated in a subsequent study based on solute Na fluxes, recharge inputs, evapotranspiration, and pore water residence times (White et al., 2005b). Comparable rates imply that present day weathering rates were stable over very long times at Merced.

4.4 Effects of Pore Water Velocity

Aside from time, the biggest difference between column and natural soil weathering is rate and composition of pore water flow (Table 3). The column pore waters were fluid-saturated as imposed by a upward flow direction while the Riverbank soil is generally unsaturated due to low recharge and gravitational drainage (White et al., 2005b). Corresponding pore water residence times are about ten days in the Merced column versus more than a year in a comparable meter of soil.

We used the CrunchFlow reactive transport model to investigate the role of fluid flow rates in bridging the large differences in experimental and natural weathering rates of the Merced granitoid (Fig. 9d). As described in the methods section, parameters for our CrunchFlow simulations were modified from parameters used for a similar chronosequence weathering environment near Santa Cruz, CA (Maher et al., 2009; Lawrence et al., 2014) and those based on the FLOWTRAN Merced soil weathering simulations (Moore et al., 2012).

We simulated the influence of variable fluid (Darcy) velocities, ranging from the experimental flow ($q_{\text{exp}} = 160 \text{ m yr}^{-1}$) to the much slower rates representative of natural field conditions ($q_{\text{field}} = 0.6 \text{ m yr}^{-1}$; Table 3) on plagioclase saturation and reaction rate (Fig. 11a and b). The flow rates at field conditions were estimated by the net difference between average rainfall and evapotranspiration based on Cl mass balance (White et al., 2005b). Flow effects were investigated using both the transition state theory (TST) rate law, employing only a far-from-equilibrium rate constant (FFE), and the parallel rate law (PRL), employing both a FFE and a close-to-equilibrium rate (CTE) (Maher et al., 2009; Lawrence et al., 2014). In both cases, the FFE rate was set equal to the experimental plagioclase rate for the fresh Merced column, while the CTE rate constant for plagioclase dissolution was taken from Maher et al. (2009).

Although measured only in column discharge, porewater solutes cumulatively increased with increasing reaction and fluid residence times within the columns in a manner similar to that observed for pore waters measured at various depths in the Merced soils. For comparison, saturation-versus-flow and rate-versus-flow relations for column nodes near the inlet and outlet (0.05 and 0.95 m) are shown in Fig. 11a and b. Assuming that a steady state reaction rate is achieved after 4 years (Fig 10d), the relationships shown in Fig. 11 will remain constant with time. This condition is only applicable to CrunchFlow simulations over relatively short time spans (like those of the column experiments) during which negligible changes in reactive mineral masses and surface areas occur.

Simulations starting with the experimental column flow velocity ($q_{\text{exp}} = 160 \text{ m yr}^{-1}$), produced highly unsaturated conditions under both the TST and PRL scenarios (Fig. 11a). As expected, effluent concentrations for the model node corresponding to the column inlet was thermodynamically less saturated than at the distal node. In this case, the plagioclase saturation index ($\text{SI} \approx 10^{-12}$) was consistent with the SI values previously calculated from effluent outputs

(Fig. 5f). Both the TST and PRL simulations reproduced the experimental plagioclase rate (Fig. 11b) indicating weathering was kinetically-limited and not dependent on transport distance or time, a conclusion previously shown by the effluent concentration-flow rate relationships (Fig. 6).

The SI values increased as the modeled flows were progressively decreased (Fig. 11a). However, reaction affinities remained sufficiently negative such that the TST and PRL simulations continued to return the same far-from-equilibrium rate constant (Fig. 11b). Only after flow rates were reduced below ~1% of q_{exp} were close-to-saturation conditions approached (Fig. 11a). While not significantly impacting rates near the column inlet, decreased flow resulted in the onset of transport limiting reaction at the distal node (Fig. 11b). The linearity of the TST formulation resulted in a rapid approach to saturation with further flow decreases, leading to a precipitous drop in the reaction rate.

At a flow rate of 0.1% of q_{exp} (0.12 m yr^{-1}), CrunchFlow results predicted a distal reaction rate comparable to that calculated from the solute fluxes under Merced field conditions ($3 \text{ to } 7 \times 10^{-16} \text{ mol m}^{-2} \text{ s}^{-1}$ at 0.06 m yr^{-1}). At even slower flow rates, the porewaters became fully saturated and plagioclase dissolution approached zero. The corresponding PRL simulation produced a more dampened approach to saturation due to the previously described plateauing interaction between the CTE and FFE rate constants (Burch et al., 1993; Hellmann and Tisserand, 2006). Even for flow rates significantly less than Merced field values, plagioclase thermodynamic saturation is never completely achieved. As discussed by Maher et al. (2009) and Moore et al. (2013), near-equilibrium conditions also reflect competing kinetics of kaolinite precipitation, which were included in CrunchFlow but not investigated in detail.

Simulations which decreased column flow rates to within the range of deep percolation rates measured in the Merced soils were capable of approximating natural weathering rates (Fig. 11b). Most natural plagioclase rates are significantly slower than laboratory rates suggesting the predominance of transported-limited weathering. However, large differences in natural profiles occur. Major discrepancies in the plagioclase rates of Turner et al. (2008) and Buss et al. (2013) at Rio Icacos may be related to the highly heterogeneous fracture flow and differences in transport and kinetic limitations (Fig. 9c). These conditions are contrasted to the more homogeneous, albeit slow, matrix flow occurring in the Panola regolith. This latter condition

produced very old and deeply weathered profiles, with highly depth dependent zones of weathered primary minerals (Fig 9b). Using CrunchFlow simulations, Maher (2011) concluded that differences in solute discharge fluctuations in small watersheds are also related to differences in fluid flow and transport (chemostatic) or kinetic controls. The rapid weathering rate in the Loch Vale catchment study (Clow and Drever, 1996) may be related to artificial irrigation, which favored the shift to kinetic-controlled weathering comparable to experimental conditions (Fig. 9a).

4.5 Long-term Weathering Simulations

Despite some success projecting experimental column data to natural soil flow rates for approximating corresponding natural reaction rates over short time intervals, the extrapolation to much longer time intervals for natural weathering was less successful. As an example of long-term weathering, the 250 kyr Merced Riverbank soil (Table 3) is described in terms of fraction of residual plagioclase remaining relative to initial concentrations (Fig. 11c). The Riverbank soil plagioclase values were adjusted for total mass losses in addition to physical compaction and dilation using quartz as a conservative component (see White et al., 1996 and Moore et al., 2012, for detailed discussion of mineral distributions at Merced).

As a baseline simulation, we parameterized CrunchFlow using the estimated natural pore water flow rate (White et al., 2002), a FFE rate constant equivalent to the experimental reaction rate from this study (Fig. 10d), and other CrunchFlow parameters listed in Table 6. The baseline predicted residual soil plagioclase distributions were significantly depleted relative to observations. Over-estimation of long-term weathering for the Santa Cruz and Merced soils using baseline simulations was previously noted (White et al., 2008, Maher et al., 2009 and Moore et al., 2012). A much closer fit to the observed Merced soil plagioclase distribution using the PRL model was obtained (Fig. 11c) using the fitted parameters in Table 7. This required decreasing the FFE plagioclase dissolution rate (initially equivalent to the experimental rate; Table 7) by a factor of ten, with corresponding smaller decreases in the CTE and kaolinite rates as initially established by Maher et al. (2009). These adjustments are comparable to a previous simulation of the Riverbank soil using the reactive transport code FLOWTRAN (Moore et al., 2012), which required decreasing the reactive surface area parameters by a factor of fifty (note the relationship between reaction rate and surface area in Eqn. 1).

While extrapolating column flow rates to field estimated flow approximated natural weathering rates over short timescales (Fig. 11b), a further decrease in field flows (from 0.060 to 0.0054 m yr⁻¹; Table 7) was required to simulate the long-term weathering profile (Fig. 11c). The simulated flow (0.0054 m yr⁻¹) rate was also slower than estimated flow rate of 0.016 m yr⁻¹ used in the best fit FLOWTRAN simulation for the Riverbank soil (Moore et al. 2012). This order-of-magnitude decrease was a significantly different from pore-water net-flow field estimates (White et al., 2005b) based on the difference between average rainfall and evapotranspiration based on Cl balances. Although climate information inclusive of the age span of the Merced soils (240 kyr) does not exist, shorter-term evidence covering the last 20 kyr do not suggest past drier conditions that would be reflected in lower recharge (Street et al., 2012).

The discrepancy more likely relates to the physical nature of pore water flow and the method by which it is estimated. Column tracer tests documented near-ideal break-through curves indicating homogenous flow (Fig. 2c). However, heterogeneous pore water flow is ubiquitous in soils as evidenced by bromide tracer tests indicating uptake of pore waters into dead end pore spaces in the Merced soils (Green et al., 2005). In contrast, soil pits documented progressive development of vertical conduits in argillic horizons, which transmit pore water relatively rapidly (White et al., 2005b). This more active flow is preferentially measured in pore water samples along with lower Cl concentrations, reflecting less total evapotranspiration.

In addition, the rate of pore water flow is strongly dependent on the extent of fluid saturation. Semi-arid conditions at Merced are reflected in average field saturation of about 70% for the Riverbank soil (White et al., 2005b). However, this value varies widely, particularly at relatively shallow depths due to the strong seasonality in rainfall (White et al. 2005b). An experimental Riverbank soil study by Stonestrom et al. (1998) indicated that small decreases in moisture produced exponential decreases in unsaturated hydrologic conductivities, implying that pore waters were essentially immobile except during seasonal wetting. Fluid stagnation under dry conditions is expected to increase thermodynamic saturation and decrease reaction rates, as suggested by column experiments. Evans and Banwart (2006) found a factor of four decrease in mineral dissolution rates in unsaturated columns compared to saturated conditions. The role of secondary surface effects is also suggested by Ganor et al. (2005), who documented decreased reaction rates after drying of plagioclase surfaces for extended times. The combined results of

CrunchFlow in this study and the FLOWTRAN simulations of Moore et al. (2012) emphasize the inhibitory role of external factors controlling weathering rates under field conditions. In both cases, the intrinsic rate constants derived from laboratory studies result in over-prediction of plagioclase dissolution compared to field observations. This is compensated by reducing the reactive surface area of the weathering minerals and/or by reducing the long-term flow velocity.

CONCLUSIONS

Natural granitoid weathering is complex and inherently heterogeneous, with different minerals weathering at different rates. This problem is accentuated in experimental studies due to rapid reactions of more soluble trace components, normally exhausted during the early stages of natural weathering. Uncertainties also exist as to whether major mineral phases achieve steady state reaction rates during short experimental reaction times due to gradual changes in surface reactivity. Additionally, differences in fluid flow dynamics and rates and of experimental and natural systems can profoundly affect mineral surface availability and the extent to which minerals approach thermodynamic saturation. These issues are addressed in this study using pairs of fresh and partially naturally weathered granitoids reacted in flow-through columns under ambient conditions. This study is unique in terms of the decadal scale of the experiments and in the direct comparison to previously determined natural weathering rates for the same granitoids.

Miscible displacement experiments at the end of the study revealed nearly uniform piston-like flow with little tailing, implying very narrow distributions of pore-water residence times. These conditions are contrasted to previous column studies which invoked dual permeability and stagnant pore spaces to explain apparently slower dissolution rates in columns compared to well-stirred batch dissolution experiments.

Total mineral mass losses from both fresh and weathered granitoids, based on total solute discharge, were less than one percent of total mass over nearly 14 years of reaction. This is consistent with a general lack of surface dissolution features and only small BET surface area increases after dithionite (DCB) extraction. Pre-DCB treated surface areas were significantly higher due to the precipitation of secondary Fe-oxyhydroxides, the only secondary phase positively identified as forming in the columns.

Initial higher effluent concentrations from the fresh versus weathered granitoids, are attributed to rapid reaction of fresh surfaces and unstable trace minerals. Over decadal time frames, solute trends converged, with fresh granitoid solute rates decreasing linearly with time and weathered granitoid release rates increasing slightly, associated with measured dissolution of naturally formed protective surface coatings. These relatively small changes (less than a factor of 2) indicated that minerals producing these solutes had not achieved but are approaching steady state reaction rates after nearly 14 years. The results contrast with previous studies, which made the case for steady-state conditions after much shorter reaction times.

Decreases in solute release rates from fresh granitoids partly reflected decreasing trace minerals and possibly heterogeneous reactivities, as supported by NETPATH mass-balance calculations. Calcium and Sr release were dominated by early dissolution of disseminated calcite, which diminished with time leading to eventual dominant control by plagioclase. High initial solute K from interlayer biotite represented a reaction that continued to dominate in some fresh granitoids, while others reflected proportionally greater inputs from K-feldspar. Sequential reactions, as verified by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, were of the order: surface-perturbed plagioclase $\rightarrow$ trace calcite dissolution $\rightarrow$ biotite oxidation $\rightarrow$ bulk plagioclase dissolution. While possibly present in some very young natural weathering environments, the complete sequence was not observed for any of the weathered granitoids used in this study.

Only Na release truly approached steady-state by the end of the experiment, reflecting the fact that plagioclase was the sole source of Na. Interestingly, Na release was very similar for all the granitoids in spite of significantly differing stoichiometries (An_{21} to An_{50}). This result supports micro-texture shielding of the more reactive calcic component.

Plagioclase reaction rates were about an order of magnitude slower than reported for shorter-term experiments. This implies that assumptions of steady-state conditions in previous column studies failed to account for the very gradual declines in surface reactivity that occur over longer time frames. The duration of this study is still very short compared to natural weathering. Extending reaction times by additional orders of magnitude, although experimentally implausible, could potentially produce further downward rate adjustments and further bridge the differences between experimental and natural reaction rates.

841 In addition to reaction time, fluid flow rates represent the largest difference between
842 experimental and natural weathering for the granitoids used in this study. Much faster column
843 flow produced highly unsaturated thermodynamic conditions for plagioclase and other major
844 primary silicates. This resulted in kinetic controlled dissolution during which small increases or
845 decreases in flow produced reciprocal changes in effluent concentrations. This is contrasted to
846 transport-limited chemostatic weathering observed in most natural environments, where
847 thermodynamically saturated fluids are slowly displaced by incoming unsaturated fluids which
848 themselves become saturated. Under these conditions, effluent concentrations do not vary with
849 fluid flow rate.

850 The significant difference between fast mineral weathering rates under kinetically
851 controlled experimental conditions and transport-limited natural weathering was examined using
852 a reactive transport model in which measured experimental flow rates were progressively
853 decreased to those reproducing natural flow. Baseline simulations over relatively short
854 experimental time scales reproduced the progressive thermodynamic saturation and declining
855 reaction rates observed in the natural environment. However, extending these simulations to the
856 duration of natural weathering still resulted in significant discrepancies between predicted and
857 observed solid-state weathering profiles. Approximating the observed mineral profiles required
858 moderate decreases in intrinsic reaction rates for primary plagioclase and K-feldspar and for
859 kaolinite precipitation. The attendant need for large decreases in fluid flow rates suggests that,
860 unlike the column experiments, fluid flow and exposure to reactive mineral surfaces is
861 significantly limited in natural environments.

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Figure Captions

Figure 1. Relationship between secondary Fe precipitation and BET surface areas. (a) Stereo microscope image of secondary Fe-hydroxides, likely from dissolution of pyrite cementing secondary silicates from the fresh Merced column. Aggregate is ~2 mm in diameter. (b) Secondary Fe-hydroxides coating feldspar grain in the reacted fresh Merced column 5 cm from inlet of the column. (c) BET surface areas of reacted fresh granitoids measured along column length (labeled as Depth) after reaction for 13.8 years. (d) Surface areas of reacted samples after Fe extraction by DCB. Also included are bulk surface areas of unreacted starting material.

Figure 2. Column pore water flow characteristics. (a) Fresh and weathered Merced granitoid flow rates based on effluent volumes collected over approximately one week intervals. Averages are indicated by horizontal lines (b) Cumulative volumes collected over the course of the fresh granitoid experiments. (c) Example of measured and fitted breakthrough curves with MgCl_2 solution displacing water in fresh Merced granitoid. K_{sat} (red line) is the saturated hydraulic conductivity during the displacement and C and C_{in} are the effluent and influent concentrations, respectively.

Figure 3. Effluent concentrations as functions of time for fresh (solid red circles) and weathered (open black circles) Merced granitoids. Outer plots contain complete data sets. Large solute variability's measured between 1.7 and 2.5 years reflect experimentally imposed temperature variations of between 5 and 34°C (White et al., 1999b). Inserts show concentrations measured between 5 and 13.8 years of reaction time (data in Table 5; supplemental tables). Trends are linear regressions to data.

Figure 4. (a) Column pore-water pH measured by rapid step-wise pore water displacement at the conclusion of the fresh (F) and weathered (W) granitoid experiments. Also shown are pHs of input solutions (5% CO₂ in DI water) and average pHs measured in collection bottles. (b-e) Relative proportions of major NH₄-acetate exchangeable cations measured at the conclusion of the fresh granitoid experiments.

Figure 5. Extent of effluent thermodynamic saturation with respect to (a-c) secondary and (d-f) primary minerals using the PHREEQC speciation code based on effluent compositions. Solid horizontal lines denote fully saturated conditions.

Figure 6. Relationship between flow rate and effluent Na concentrations for fresh granitoids. Predicted trends assuming transport-limited reactions (horizontal lines) and kinetically-limited reactions (convex lines). The lines intercept at average flow and concentration for times greater than four years. While not shown, a similar relationship exists for the Rio Icacos data.

Figure 7. Predicted mineral contributions (mmoles) to column effluents over time. Positive values indicate additions from dissolution and negative values subtractions resulting from precipitation. Inserts are expanded scales for times ranging from 2 to 13 years. Elemental constrains are described in text. Mineral compositions are from White et al. (1999a).

Figure 8. Ca/Sr and ⁸⁷Sr/⁸⁶Sr ratios of effluents produced from fresh (a-c) and weathered (d-e) granitoids compared with corresponding calcite, plagioclase, and biotite ratios. Circles correspond to solute samples (labels are reaction times in years). Dashed lines are solute

mixing lines based on plagioclase and calcite inputs. Calcite contents (ppm) are also indicated. Arrows indicate $^{87}\text{Sr}/^{86}\text{Sr}$ value of biotite (off scale). Sr was not measurable (below detection) in biotites so the position of the biotite arrows on the Ca/Sr axes are arbitrary. Effluents from the Tertiary Rio Icacos quartz diorite produced very small variations in Sr isotopic ratios and are not shown. Mineral data are from Bullen et al., (1999) and White et al. (2005a). Estimates for average watershed ratios are included on the weathered granitoid plots. Data from Blum et al. 1994; Bullen et al. 1996; Bullen et al., 1999; Clow et al. 1997; and Pett-Ridge et al. 2009.

Figure 9. Plagioclase dissolution rates calculated over time for fresh and weathered granitoids (this study) compared to experimental and natural rates reported in the literature (data summarized from (White and Brantley, 2003; Bandstra et al., 2008 and White and Buss, 2014). Significant excursions at times between 1.2 and 1.5 yrs correspond to induced temperature changes (White et al., 1999b). Rectangular boxes enclose longer term data (4.0 to 13.8 yrs; Table 5 and Fig. 10). Dashed line corresponds to linear fits to all literature data as described in White and Brantley (2003). Starred data are literature rates reported for field-sites associated granitoids used in the present study.

Figure 10 Cumulative solute Na outputs from fresh granitoids calculated from effluent Na concentration and column discharge volume. Solid lines correspond to linear regression fits to data between 4 and 13.8 years with residuals shown in the lower right inserts. The horizontal zero line corresponds to a perfect fit to the linear regression.

Figure 11. CrunchFlow simulations showing (a) increasing plagioclase thermodynamic saturation and (b) decreasing reaction rates with declining flow rates. Data derived using both transition state theory (TST) and parallel rate law (PRL) subroutines as applied to example computational nodes at the inlet and outlet of the column (0.05 and 0.95 m). (c) comparison of measured fractional plagioclase losses (fraction of residual plagioclase remaining relative to initial concentrations) with depth over Merced Riverbank soil (data points) with simulations using baseline (thin blue line) and best-fit assumptions (thick black line) employing the parameters listed in Table 6.

Table 1. Summary of experimental granite weathering studies.

Material	Experiment type	Duration	pH	Primary measurements	Reference
Old Rag granite, VA, USA	Columns, flow 3-12 ml/hr	365 days	2–5	Major solutes/clay formation	Afifa et al., 1985
Biotite granite, Chile	Flow-thru reaction cells	4200 hrs	1	U isotopes	Andersen et al., 2009
Elat granite, Israel	Batch hand-shaken bottles	168 hrs	0.3–2	Fe isotopes	Chapman et al., 2009
El-Capitan granite, CA, USA	Disks in soils, Sweden	5-10 yrs	2–8	Bulk weight loss	Dixon et al., 2001; Thorn et al., 2002
Abukuma granodiorite, Japan	Flow-thru reaction cells	4200 hrs	1	Pb/Sr isotopes	Erel et al. 2004
Granite, GA, USA	Flow-thru reaction cells	4200 hrs	1	Solutes, surface coating and saturation	Ganor et al., 2005
Elat granite, Israel	Batch hand-shaken bottles	2600 hrs	1	REE, Pb isotopes	Harlavan et al., 2002
Toulomne granite,CA USA	Columns, flow 1.7-2.6 ml/hr	45 weeks	6	Major solutes, REE, role of citrate	Hausrath et al., 2009
Toulomne granite,CA USA	Lab, mechanical shaking	4 weeks	6	Solutes, effects of organics	Neaman et al., 2006
Boulder Ck. granodiorite CO, USA	Rectangular blocks	26 days	nd	Effects of salt solutions	Rivas et al., 2003
Elat granite, Israel	Column, flow 3.1 ml/hr	5794 hrs	1	Major solutes, Ca and Mg isotopes	Ryu et al., 2011
Granitoids	Slabs	2 yrs	3.7	Rain on solutes, effects on mass losess	Sweevers et al., 1995
Granitoids, global distribution	Batch, hand shaken bottles	75 days	6.5–8.5	Major solutes, effects of trace calcite	White et al., 2005a
Granitoids (this study)	Columns, flow 6-10 ml/hr	14000 hrs	5–6	Major solutes, effects of trace calcite	White et al., 1999a
Granitoids (this study)	Columns, flow 6-10 ml/hr	20000 hrs	5–6	Major solutes, effects of temperature	White et al., 1999b
Leinster granite, Ireland	Sawed tablets, field and lab	1-10 yrs	6–7	Bulk weight loss	Yokoyama & Matsukura, 2006

Table 2. Description of granitoid rocks used in experimental study.

Location	Rock	Dominant Mineralogy	Age	Source	Reference
Upper Merced River, Yosemite, National Park, CA, USA	Granodiorite of Arch Rock	Quartz, oligoclase, microcline, biotite, hornblende	Cretaceous	Road cut and weathered exfoliated surface	Calkins et al., 1985
Loch Valle, Rocky Mtn. National Park, CO, USA	Silver Plume granite	Quartz, oligoclase, microcline, biotite,	Precambrian	Fresh and weathered surface exposures	Cole, 1977
Panola Mtn. Research Watershed, GA, USA	Panola granite (granodiorite)	Quartz, oligoclase, microcline, biotite muscovite	Mississippian-Pennsylvanian	Drill core, fresh and weathered fractures	Higgins et al., 1988
Rio Icacos watershed, Luquillo Mtns., PR	Rio Blanco quartz diorite	Quartz, andesine, biotite, hornblende, microcline	Tertiary	Road cut and weathered core stone	Seiders, 1971

Table 3. Comparison of major physical properties, hydrology and compositions of the fresh Merced granitoid column experiment and the 250 ka Riverbank soil at a depth of 5.5 m. Soil data from Harden (1987), White et al. (1996, 2002), and Stonestrom et al., 1998).

Parameter	Column	Soil
Total weathering depth (m)	0.90	5.5
Soil state weathering duration (yrs)	13.8	2.5×10^4
Porosity (%)	40	38
Rate of fluid input (m yr^{-1})	160	0.060
Average pore water residence time (yrs)	0.056	20.0
Clay (wt %)	0	12.3
Plagioclase (wt%)	36	33
Plagioclase surface area ($\text{m}^2 \text{g}^{-1}$)	0.18	0.31
Fluid saturation (%)	100	40–80
Saturated hydraulic conductivity (m s^{-1})	3.7×10^{-6}	3.5×10^{-6}
Unsaturated hydraulic conductivity	na ^a	$9.4 \times 10^{-8} - 8.9 \times 10^{-10}$
Solute Na at maximum depth (μmolar)	1.6	100

^a not applicable

Table 4 BET-measured surface areas (S_{BET} ; $\text{m}^2 \text{g}^{-1}$) of bulk granitoid samples at the start (5/14/96), intermediate and end times of experiments. Data in parenthesis are surface areas after DCB extraction for Fe. S_{BET} data are plotted in Fig. 1c and d.

	Starting material 1/28/1998	Inlet 1.6 yrs	Inlet 6.2 yrs	Inlet 13.8 yrs	Outlet 13.8 yrs
Merced (F)	0.077 (0.119)	0.181	nd ^a	5.39 (0.704)	0.313 (0.174)
Rio Icacos (F)	0.103 (0.228)	0.242	nd	6.74 (1.26)	0.614 (0.463)
Loch Vale (F)	0.084 (0.105)	0.155	nd	0.442 (0.290)	0.506 (0.213)
Panola (F)	0.088 (0.104)	0.244	0.298	1.15 (0.316)	0.619 (0.280)
Merced (W)	0.79	0.34	nd	1.97	1.71
Rio Icacos (W)	2.91	2.37	nd	6.63	4.09
Loch Vale (W)	0.15	0.21	nd	0.63	0.68
Panola (W)	4.12	2.35	5.33	5.62	5.88

^a not determined

Table 5. Effluent parameters and compositions of selective effluent samples collected during the last four years of granitoid reaction (shorter term data previously reported in White et al., 1999a and 1999b).

Time	Flow	Volume	Alk	Na	Mg	Al	Si	K	Ca	Mn	Fe	Rib	Sr	Time	Flow	Volume	Alk	Na	Mg	Al	Si	K	Ca	Mn	Fe	Rib	Sr
Years	ml/hr.	L						μmolar						Years	ml/hr.	L						μmolar					
Approx. detection limits			2.0	0.04	0.04	0.07407	0.68966	0.05	0.13	0.00073	0.04	0.0001	0.00011	Approx. detection limits			2.0	0.04	0.04	0.07407	0.68966	0.05	0.13	0.00073	0.04	0.0001	0.00011
Fresh Merced Granodiorite														Weathered Merced Granodiorite													
4.26	4.9	340	21.5	2.78	1.37	0.12	19.03	4.81	3.10	0.064	<0.01	0.0120	0.0110	4.25	5.9	332	4.0	0.22	0.10	0.84	4.35	0.62	0.23	0.012	<0.01	0.0008	0.0016
5.26	8.0	384	23.0	1.95	1.86	0.25	10.26	5.99	3.91	0.094	<0.01	0.0146	0.0175	5.25	9.9	382	4.4	0.21	0.07	2.46	2.70	0.51	0.14	0.011	<0.01	0.0011	0.0011
6.12	11.7	473	16.7	1.52	0.76	0.56	8.71	6.00	1.96	0.050	0.065	0.0133	0.0082	6.10	8.9	450	7.0	0.49	0.12	2.36	5.42	0.94	0.33	0.015	<0.01	0.0013	0.0017
6.35	11.7	496	17.4	1.89	0.76	0.36	10.11	5.67	1.92	0.046	0.073	0.0137	0.0086	6.33	9.0	469	7.1	0.59	0.14	1.72	6.31	1.15	0.42	0.016	0.024	0.0015	0.0020
7.13	7.2	553	8.0	1.41	0.45	0.34	7.55	5.42	1.22	0.031	<0.01	0.0118	0.0065	7.44	8.0	547	6.8	0.68	0.11	1.17	4.11	0.81	0.45	0.013	<0.01	0.0012	0.0019
8.16	10.4	622	11.7	1.38	0.40	0.36	7.05	4.74	1.16	0.029	0.033	0.0107	0.0068	8.48	6.2	610	6.1	0.83	0.14	0.98	6.65	0.89	0.36	0.016	<0.01	0.0013	0.0025
9.28	10.9	724	13.7	1.57	0.52	0.48	7.67	4.42	1.23	0.040	0.041	0.0100	0.0079	9.26	9.8	667	4.1	0.68	0.08	0.91	4.11	0.92	0.19	0.014	0.055	0.0014	0.0020
10.35	10.1	818	9.2	1.43	0.69	0.31	8.26	3.60	1.39	0.049	<0.01	0.0084	0.0072	10.34	10.8	746	7.7	0.58	0.12	1.09	3.91	0.77	0.37	0.012	<0.01	0.0013	0.0015
11.24	9.7	898	10.5	1.73	0.50	0.66	6.85	4.39	1.59	0.021	0.155	0.0074	0.0066	11.23	10.7	814	10.3	0.90	0.12	1.19	3.18	1.18	0.40	0.015	<0.01	0.0015	0.0025
12.16	11.3	972	7.4	1.35	0.38	1.11	6.05	4.28	0.93	0.029	0.333	0.0101	0.0064	12.14	9.5	881	10.7	0.71	0.09	1.67	3.45	1.11	0.35	0.012	<0.01	0.0018	0.0018
12.87	8.8	1030	10.9	1.22	0.51	0.53	5.99	4.05	1.27	0.035	0.143	0.0097	0.0066	12.90	9.3	918	6.8	0.61	0.14	0.79	3.67	0.83	0.21	0.011	<0.01	0.0016	0.0019
13.86	9.2	1099	9.8	1.65	0.41	0.71	4.88	4.32	1.80	0.030	<0.01	0.0106	0.0071	13.85	8.5	1011	7.2	0.60	0.12	1.42	4.09	1.23	0.26	0.020	0.014	0.0020	0.0020
Fresh Rio Icaos Quartz Diorite														Weathered Rio Icaos Quartz Diorite													
4.26	6.5	324	35.0	2.33	0.47	0.17	18.67	6.16	5.35	0.042	0.220	0.0098	0.0086	4.14	12.0	423	13.5	1.30	0.30	0.33	11.01	3.63	2.48	0.028	0.232	0.0062	0.0080
5.26	7.7	383	22.0	2.03	0.42	0.20	12.49	5.83	5.67	0.045	0.340	0.0092	0.0101	5.19	13.9	521	16.8	1.15	0.31	0.90	9.02	3.94	2.44	0.030	0.351	0.0069	0.0085
6.11	10.9	467	21.0	1.53	0.33	0.26	11.26	5.53	3.41	0.030	0.310	0.0073	0.0063	6.28	11.4	648	21.9	1.80	0.35	0.48	15.72	4.37	3.39	0.032	0.428	0.0068	0.0102
6.34	10.1	489	16.8	1.66	0.32	0.08	13.47	5.50	3.54	0.029	0.206	0.0077	0.0069	6.54	12.1	669	17.8	1.83	0.31	0.32	14.83	4.11	3.22	0.028	0.340	0.0064	0.0096
7.13	9.2	555	10.0	1.48	0.26	0.14	12.12	4.84	3.20	0.023	0.113	0.0063	0.0059	7.13	6.6	714	13.1	2.11	0.38	0.07	17.53	3.74	4.65	0.035	0.096	0.0056	0.0122
8.16	7.2	626	15.4	1.68	0.25	0.17	13.36	4.22	3.93	0.023	0.127	0.0058	0.0071	8.17	11.8	815	16.7	2.24	0.34	0.24	17.77	4.66	4.12	0.035	0.367	0.0068	0.0124
9.28	10.4	717	12.2	1.80	0.24	0.10	13.72	4.52	4.00	0.026	0.123	0.0061	0.0081	9.32	16.9	932	11.6	1.99	0.30	0.34	15.59	4.39	3.42	0.026	0.492	0.0062	0.0107
10.35	5.1	806	13.3	1.36	0.34	0.04	16.63	3.68	3.60	0.031	0.180	0.0052	0.0065	10.03	4.9	982	16.2	2.00	0.44	0.04	17.57	2.48	5.34	0.039	0.210	0.0042	0.0116
11.24	12.0	877	13.5	2.01	0.28	0.30	11.12	4.89	5.03	0.300	0.069	0.0027	0.0071	11.28	7.8	1078	24.3	2.36	0.32	0.11	16.48	3.59	4.83	0.037	0.196	0.0054	0.0143
12.16	10.6	949	15.5	1.66	0.21	0.30	9.11	4.33	3.52	0.023	0.264	0.0059	0.0064	11.94	11.1	1126	13.8	2.27	0.22	0.24	15.15	3.42	3.29	0.028	0.269	0.0052	0.0116
12.91	8.2	1011	16.7	1.46	0.31	0.12	12.14	4.51	3.59	0.029	0.211	0.0064	0.0072	12.59	9.7	1186	16.5	2.22	0.34	0.11	14.79	3.39	4.41	0.032	0.310	0.0056	0.0116
13.89	8.0	1091	15.1	1.78	0.21	0.38	8.19	4.17	5.29	0.022	0.200	0.0058	0.0063	13.51	0.3	1254	14.0	2.57	0.37	0.26	13.99	3.91	6.41	0.038	0.573	0.0050	0.0139
Fresh Loch Vale Granite														Weathered Loch Vale Granite													
4.26	8.4	388	6.0	1.46	0.09	0.46	6.58	0.58	1.05	0.006	<0.01	0.0074	0.0011	4.24	7.0	306	6.0	1.40	0.07	0.64	7.29	0.39	0.28	0.003	<0.01	0.0010	0.0008
5.26	13.9	474	9.2	0.92	0.10	0.74	3.78	0.37	0.79	0.006	<0.01	0.0056	0.0011	5.24	13.0	388	5.6	0.91	0.04	1.63	4.51	0.28	0.16	0.002	<0.01	0.0019	0.0008
5.52	8.8	497	6.0	1.22	0.06	1.04	5.08	0.51	0.83	0.006	0.027	0.0066	0.0012	6.10	13.3	487	6.0	1.06	0.08	1.67	5.36	0.38	0.33	0.002	<0.01	0.0018	0.0007
6.34	9.1	563	5.9	1.76	0.12	0.78	7.72	0.83	0.76	0.005	<0.01	0.0063	0.0013	6.33	13.0	514	7.0	1.38	0.09	1.43	8.17	0.76	0.40	0.003	0.040	0.0024	0.0009
7.13	8.8	624	0.0	1.58	0.08	0.67	6.82	0.66	0.54	0.003	<0.01	0.0049	0.0011	7.12	8.9	578	5.9	1.62	0.08	0.99	6.60	0.68	0.35	0.002	<0.01	0.0024	0.0009
8.15	9.2	702	8.2	1.45	0.08	0.69	6.96	0.54	0.50	0.002	<0.01	0.0044	0.0011	8.10	10.1	656	1.9	1.33	0.08	1.03	5.61	0.53	0.35	0.001	0.041	0.0023	0.0008
9.28	8.9	792	5.3	1.65	0.06	0.74	6.18	0.57	0.46	0.003	<0.01	0.0045	0.0012	9.26	9.8	759	3.1	1.51	0.07	0.97	6.05	0.54	0.25	0.003	<0.01	0.0023	0.0009
10.35	8.0	904	3.6	1.36	0.08	0.51	6.70	0.45	0.49	0.002	<0.01	0.0031	0.0006	10.34	8.9	846	6.8	1.31	0.09	0.77	6.61	0.41	0.23	0.002	<0.01	0.0020	0.0005
11.24	9.4	977	5.0	1.13	0.06	1.18	4.72	0.93	0.56	0.003	<0.01	0.0030	0.0009	11.23	9.7	915	7.3	1.18	0.08	1.48	5.52	0.94	0.55	0.002	<0.01	0.0020	0.0007
12.15	10.3	1054	2.7	1.20	0.07	1.47	4.24	0.60	0.40	0.002	<0.01	0.0036	0.0010	12.14	10.5	986	6.9	1.14	0.06	1.89	4.54	0.49	0.40	0.002	<0.01	0.0024	0.0008
12.27	8.2	1063	9.6	1.70	0.05	1.25	5.20	0.47	0.55	0.003	<0.01	0.0032	0.0010	12.89	9.5	1053	6.7	1.07	0.10	1.35	4.86	0.48	0.30	0.002	<0.01	0.0026	0.0008
13.83	4.4	1198	6.1	1.17	0.09	1.03	4.78	0.55	0.35	0.002	<0.01	0.0032	0.0010	13.88	11.6	1106	5.8	1.26	0.10	1.95	3.20	0.66	1.50	0.001	<0.01	0.0024	0.0010
Fresh Panola Granodiorite														Weathered Panola Granodiorite													
4.26	9.8	390	21.0	1.36	0.31	1.14	11.16	0.72	2.94	0.053	0.130	0.0047	0.0074	4.25	7.7	345	4.0	0.30	0.07	0.90	6.09	0.49	0.23	0.032	<0.01	0.0012	0.0010
5.26	9.7	477	17.4	1.56	0.24	1.05	8.93	1.00	2.19	0.046	0.126	0.0058	0.0082	5.25	11.7	417	2.3	0.12	0.05	2.04	3.01	0.50	0.07	0.019	<0.01	0.0031	0.0014
6.11	9.4	533	17.4	1.86	0.28	1.05	11.13	1.30	2.26	0.041	0.122	0.0048	0.0082	6.10	11.7	504	6.0	0.33	0.10	2.10	5.00	0.94	0.30	0.018	<0.01	0.0034	0.0011
6.34	13.6	554	16.5	1.51	0.23	0.92	7.96	1.27	1.78	0.031	0.144	0.0050	0.0067	6.33	12.2	529											

Table 6. Selective parameters used in CrunchFlow simulations of short- and long- term plagioclase weathering of the Merced granitoid and Merced Riverbank soil, respectively. Model parameters for the long-term simulations are taken from Moore et al., 2012, whereas parameters for short-term simulations are from laboratory measurements reported in the present study.

CrunchFlow parameters	Long-term	Short-term	Secondary species
<i>Boundary/initital conditions</i>			Al(OH)^{2+}
Temp °C	22	22	AlO_2^-
$\text{CO}_2(\text{g})$ bars	0.05	0.05	AlOH^{2+}
pH	5.79	4.67	CaCl^+
Solid Density (g m^{-3})	2.6	2.6	$\text{CaCl}_2(\text{aq})$
Porosity ($\text{m}^3 \text{m}^{-3}$)	0.34	0.42	$\text{CaCO}_3(\text{aq})$
			CaHCO^{3+}
<i>Primary species concentration (mol kg^{-1})</i>			CaOH^+
Na^+	1.98E-04	1.00E-09	CO_3^{2-}
Al^{3+}	2.08E-07	1.00E-09	$\text{H}_2\text{SiO}_4^{2-}$
Mg^{2+}	7.64E-05	1.00E-09	$\text{HAlO}_2(\text{aq})$
Ca^{2+}	1.06E-04	1.00E-09	$\text{HCl}(\text{aq})$
K^+	7.03E-05	1.00E-09	HCO_3^-
Sr^{2+}	1.00E-09	1.00E-09	HSiO_3^-
Fe^{2+}	1.00E-09	1.00E-09	$\text{KCl}(\text{aq})$
Fe^{3+}	1.00E-09	1.00E-09	MgCl^+
$\text{SiO}_2(\text{aq})$	1.12E-06	1.00E-09	$\text{MgCO}_3(\text{aq})$
$\text{O}_2(\text{aq})$	1.00E-02	1.00E-02	MgHCO_3^+
Cl^-	2.72E-04	1.00E-09	$\text{NaAlO}_2(\text{aq})$
SO_4^{2-}	9.88E-05	1.00E-09	$\text{NaCl}(\text{aq})$
			NaCO_3^-
<i>Initial mineral abundance ($\text{m}^3 \text{m}^{-3}$) and surface area ($\text{m}^2 \text{g}^{-1}$)</i>			$\text{NaHCO}_3(\text{aq})$
Plagioclase	0.250 (0.18)	0.21 (0.18)	$\text{NaHSiO}_3(\text{aq})$
K-Feldspar	0.087 (0.18)	0.09 (0.18)	$\text{NaOH}(\text{aq})$
Kaolinite	0.035 (12.0)	Trace (12.0)	OH^-
Quartz	0.243 (0.18)	0.21 (0.18)	$\text{SrCO}_3(\text{aq})$

Table 7. Baseline from experimental results are compared with best fit parameter values need to produce a closer model fit to long-term development of the Merced Riverbank soil plagioclase profile.

Variable parameters	Units	Baseline	Best fit
Plagioclase log k (FFE)	moles m ² s ⁻¹	-13.1	-14.1
Plagioclase log k (CTE)	moles m ² s ⁻¹	-14.9	-15.1
Kaolinite log k	moles m ² s ⁻¹	-19.9	-20.6
Flow rate	m yr ⁻¹	0.06	0.0054

Figure 1 White et al.

Figure

Figure 2

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Time (years)

Figure

Fig 11. White et al.