Some Observations on the Stoichiometry of Feldspar Hydrolysis in Granitic Soil

JAMES L. CLAYTON*

ABSTRACT

Weathering rates of orthoclase and plagioclase were computed from mass balances of Na, K, and Ca in three forested watersheds in the Idaho batholith. On the basis of stand conditions, two watersheds were assumed to have no net gains or losses of cations in biomass, and increases in biomass were measured in the third watershed. Balanced feldspar hydrolysis reactions were established based on kaolinite as a weathering product. Free silica (SiO_2) release predicted from reaction stoichiometries ranged from 94 to 99% of measured SiO_2 flux from the watersheds. These results suggest that the entire flux of Na, K, and Ca can be attributed to cation release from primary mineral hydrolysis without invoking net loss of cations from exchange sites in these watersheds. The acid neutralizing capacity (ANC) arising from hydrolysis is approximately 1500 to 1700 mol(c) ha^{-1} yr^{-1}. Annual H^+ input from bulk precipitation currently averages 70 mol ha^{-1} yr^{-1}. Attempts by other researchers to check reaction stoichiometry by SiO_2 have not been particularly successful. Simple mineralogy of parent material and lack of anthropogenic sources of acid deposition may explain why predicted and actual SiO_2 fluxes were similar in this study.

Additional Index Words: **Feldspar weathering rate, Soil acid neutralization capacity, Reaction stoichiometry.**

Weathering rates of primary minerals in soil and regolith are of considerable interest to scientists concerned with the geochemistry of natural systems. Aside from the geochemical perspective of understanding the transport fate of some of the more abundant elements on the earth's surface, there are critical ecological considerations. Weathering plays a prominent role in supply of base nutrients to soils and aquatic ecosystems, and rates of supply are important for determining long-term site quality (Leaf, 1979). In addition, hydrolysis of primary minerals can play an important role in the mitigation of atmospheric deposition of acids. Several mechanisms are responsible for the consumption of strong acid inputs to soils including sulfate adsorption (Cosby et al., 1986), protonation of weak organic acids (James and Riha, 1986), and cation removal ("stripping") from base exchange sites (Reuss and Johnson, 1986). Based on quantity, however, weathering is the single most important sink for protons in the ecosystem (Van Breeman et al., 1983; Schnoor and Stumm, 1985).

Although the potential ANC of hydrolysis reactions in soils is large, the reaction rates are slow relative to cation exchange reactions. In addition, separating these two processes as to rate and capacity for proton consumption has proven difficult outside the laboratory. Much has been published recently on rates of mineral weathering. Two research fronts emerge from the literature: laboratory studies, most commonly studying the kinetics of single mineral dissolution under closely controlled conditions, and large field studies (watershed scale) in which weathering rates are computed by studying geochemical transport within a watershed. Distinct differences occur in the observed rates of mineral dissolution between these methods of study. Generally, the laboratory rates are one to three orders of magnitude more rapid than field weathering rates. This is often explained on the basis of cleaner mineral surfaces (Paces, 1983) or a larger ratio of leachate volume to mineral specific surface in laboratory studies. Laboratory studies are unable to emulate the hydrologic pathways in soils that are important determinants of weathering rates. Thus, laboratory studies are considered poor predictors of "field weathering conditions," and estimated rates of weathering derived from them are unrealistically high. These problems will continue until our understanding of flow paths and water residence times in field soils allow for better extrapolation of laboratory results.

Watershed mass-balance studies provide the most reliable estimates of field weathering rates (Clayton, 1979; Velbel, 1985). However, they are not without their problems. Reuss and Johnson (1986) suggest that estimates of soil weathering are often based on questionable assumptions; for example: net cation export equals weathering rate, which assumes that exchangeable bases remain constant. Other frequently encountered problems include inadequate verification of a closed hydrologic system and ignorance of other time-dependent changes in base uptake or release (biomass dynamics). Cleaves et al. (1970) presented a technique to verify if the system is hydrologically tight, and several watershed studies of weathering have included biomass as a source or sink for bases. Detecting a change in the size of the pool of exchangeable bases is difficult over the time frame of a typical watershed study (10 or 20 yr at most) because annual fluxes are rarely more than 1 or 2% of the total pool size, and fluxes are never wholly attributable to cation exchange reactions.

One approach to distinguish between cation exchange and primary mineral hydrolysis is a comparison with the stoichiometry of the assumed weathering reaction. For watershed geochemical studies, the stoichiometry is rationalized from annual fluxes of mobile compounds. The proposed weathering reaction is stated as a net reaction, with no accounting for the formation or fate of intermediate weathering products, although the stoichiometry will not balance if intermediate compounds are either stable or transported. For example, consider the reaction:

$$\text{M-feldspar} + n\,H^+ + H_2O \rightarrow$$

$$n/2 \text{ kaolinite} + M^{n+} + (2n. . .0)\,H_4SiO_4, \quad [1]$$

which is a typical assumed hydrolysis reaction. In watershed studies, the rate of feldspar dissolution is computed

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from the measured, dissolved stream flux of cation M^+ corrected for precipitation inputs and biomass uptake or release. An independent check on the stoichiometry of the reaction can be made by comparing free SiO_2 predicted to be released from the feldspar with measured stream flux of SiO_2 plus SiO_2 required to form clay in the balanced reaction. If SiO_2 is partly immobilized, if the proposed clay mineral is incorrect, or if the source of the cation M^+ is not from feldspar weathering, then the stoichiometry will not balance. There is little reason to go through this exercise without strong evidence for a known mineral weathering product (clay) or if the soil is known to immobilize SiO_2 through some other mechanism. Efforts to independently check the stoichiometry of weathering reactions developed from watershed studies have not been particularly successful. Drever (1985), Drever and Hurcomb (1986), and Velbel (1985) suggest that uncertainties in mass balances arise from an inability to correctly characterize weathering reactants and products. If the inaccuracies lead to attributing time-variant cation fluxes from the exchange pool to weathering, then this suggests that estimates of base release for nutrient supply and soil ANC from weathering are too large.

MATERIALS AND METHODS

Study Area

The Silver Creek study area is in the southwestern Idaho batholith, 44°25'N 115°45'W. Precipitation and streamflow have been monitored in six watersheds since the mid-1960s and stream and precipitation chemistry since 1972. Three watersheds ranging from 1.09 to 1.86 km² were selected for this study. All three are considered hydrologically tight based on a 4-yr chloride budget (Clayton, 1986), and two (SC-1 and SC-2) are dominated by mature forest stands that suggest that annual biomass increment may be ignored. The third watershed (SC-5) has a multicanopied stand, and annual biomass increment is estimated at 5 Mg/ha (Clayton and Kennedy, 1985). Data on annual increment of nutrients, calculated from biomass increment and chemical concentration in plant tissue, are also available. Principal overstory species are ponderosa pine (*Pinus ponderosa* Laws.) and Douglas-fir [*Pseudotsuga menziesii* (Mirbel) Franco]. Bedrock in the area is a uniform, light-colored quartz monzonite, typical of a large portion of the main inner facies of the batholith (Ross, 1963). This rock contains approximately equal amounts of quartz, orthoclase, and An_{19} plagioclase, with minor amounts of biotite. Other accessory minerals are notably absent from this pluton.

Soils in the Idaho batholith are coarse-textured and lack cohesion. Four families of soils make up a mosaic on the watersheds and are distributed primarily on the basis of slope and aspect. On southerly slopes, sandy-skeletal, mixed Typic Xerorthents predominate. On other aspects are found sandy-skeletal mixed Typic Cryorthents, sandy-skeletal mixed Typic Cryumbrepts, and mixed Alfic Cryopsamments. All soils have one or two A horizons, typically with a thickness ranging from 100 to 250 mm, overlying C horizons. Surface and subsoil horizons are gravelly, loamy coarse sand or gravelly coarse sandy loam textures. It is generally <1 m to the lithic contact.

The area has a Mediterranean climate with dry summers and cool, moist winters. Average daily temperature is 4 °C, with an average daily minimum of −2 °C and average daily maximum of 12 °C. Annual precipitation averages approximately 1000 mm, with about 65% falling as snow in the winter (November–April). Peak runoff coincides with the spring snowmelt, and annual water yield has averaged 35 to 40% of precipitation (Clayton and Megahan, 1986).

Sampling, Laboratory Procedures, and Data Analysis

Precipitation chemistry was sampled at four locations in the Silver Creek area in bulk collectors (May through October) or by monthly collections of clean snow when available during winter months. Samples were returned to the laboratory, filtered through 0.45 μm membrane filters, and refrigerated until analysis. Stream water was collected at biweekly intervals from June through October and monthly from November through March. During spring snowmelt, stream samples were collected more frequently to adequately sample the rising and receding limbs of the melt-generated hydrograph. Stream samples were filtered and subsamples acidified with HOAc and refrigerated.

Water samples were analyzed for a variety of elements and compounds. Sodium and K^+ were determined by flame emission spectroscopy, Ca^{2+} and Mg^{2+} by atomic absorption spectroscopy. Silica was determined colorimetrically following formation of the silicomolybdate complex and reduction to the heteropoly form with sulfite (Greenberg et al., 1980).

Stream discharge was monitored continuously through Parshall flumes using Stevens model A-35 recorders.[1] A network of 12 recording rain gauges and six snow gauges measured precipitation. An isohyetal map based on 17 yr of precipitation data was used to calculate annual precipitation (Clayton and Megahan, 1986).

Watershed SC-5 was sampled to provide annual biomass increment, and the increment data were linked with tree chemistry data (Clayton and Kennedy, 1980) to provide net annual uptake of Na, K, and Ca (Clayton and Kennedy, 1985).

Annual fluxes of Na, K, Ca, and SiO_2 from streams were calculated using equations that correlate a log transform of instantaneous concentration with a log transform of instantaneous stream discharge. These correlations explain 55 to 82% of the variance in Na concentration, 58 to 67% of the variance in K, 65 to 73% of the variance in Ca, and 87 to 93% of the variance in dissolved SiO_2. Using these regression equations, daily fluxes were generated from mean daily flow, and these were summed over a year to compute annual fluxes in kg ha^{-1} yr^{-1}. Annual fluxes were corrected for the statistical bias that arises from back transforming the log-log data (Ferguson, 1986). This technique averages the error of the regression over 365 observations, thus providing a reliable flux estimate for an unbiased regression model.

Fresh and weathered rock samples were analyzed chemically and mineralogically by a variety of techniques. Thin sections were prepared and observations of fresh and altered minerals were made by optical techniques. Selected minerals in thin section and single mineral grains were observed by backscatter imaging on a JEOL T-300 scanning electron microscope (SEM), and standardless semiquantitative analyses were performed with an energy dispersive x-ray analyzer. Bulk rock samples were analyzed chemically by hydrofluoric–perchloric acid digests ($HF–HClO_4$) and x-ray fluorescence (XRF).

RESULTS AND DISCUSSION

Proposed Weathering Reactions

Observations of thin sections and x-ray diffraction (XRD) studies of weathered plagioclase and orthoclase feldspars in saprolites that have weathered sufficiently

[1] The use of trade or firm names in this paper is for reader information and does not imply endorsement by the USDA of any product or service.

to observe a weathering product suggest that kaolinite is the alteration product (Clayton, 1986). Clayton (1974), in a study of clay mineral distribution in soils throughout the Idaho batholith, concluded that kaolinite (and halloysite) predominate in all adequately drained soils not affected by volcanic ash inputs and probably reflect equilibrium conditions with the present soil-forming environment. In addition, kaolinite as the weathering product is consistent with stream chemistry from all three watersheds based on thermodynamic considerations (Clayton, 1986) and on calculation of Tardy's Re index, a method for estimating the ratio of silica to alumina retained in weathering products calculated from dissolved cation and silica concentrations (Tardy, 1971). The SEM observations coupled with spot energy dispersive analysis (EDS) were inconclusive. A variety of alteration products, both crystalline and amorphous, are suggested by both the morphology and Si/Al molar ratios. This is consistent with other research suggesting that feldspars do not alter directly to kaolinite, but rather that kaolinite arises as crystal growth from solution (Eggleton, 1986).

Fresh plagioclase in bedrock, saprolite, and soil horizons was characterized chemically by XRF, analyses of HF digests, and by optical means. Modal anorthite content is An_{16-21} based on these techniques and is similar to other published data for this region of the Idaho batholith (Schmidt, 1964; Larsen and Schmidt, 1958). Both normal (anorthite-enriched core) and oscillatory zoning of plagioclase crystals is common, and preferential weathering of anorthite is observed in thin section. This preferential weathering results in larger amounts of Ca release relative to Na than would be expected from congruent dissolution of an An_{19} plagioclase. Based on the molar Ca and Na in stream chemistry from SC-1 and SC-2, Clayton (1986) suggested that the reactant acts as an An_{45} plagioclase, and a balanced reaction is:

$$222\ Na_{0.55}Ca_{0.45}Al_{1.45}Si_{2.55}O_8 + 322\ H^+ + 649\ H_2O \rightarrow 161\ Al_2Si_2O_5(OH)_4 + 244\ H_4SiO_4 + 122\ Na^+ + 100\ Ca^{2+}. \quad [2]$$

Orthoclase crystals contain little or no Na, and a balanced hydrolysis reaction for orthoclase is:

$$2\ KAlSi_3O_8 + 2\ H^+ + 9\ H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 4\ H_4SiO_4 + 2K^+. \quad [3]$$

Stoichiometric Balances

Based on the measured annual fluxes of Na, Ca, and K, the amounts of albite, anorthite, and orthoclase weathered were calculated from the single mineral formulas. These data are presented for watersheds SC-1 and SC-2 in Tables 1 and 2. The measured SiO_2 fluxes, sum of the base flux and H^+ required in the hydrolysis reactions, are also presented. From the stoichiometry of reactions [2] and [3], the quantity of kaolinite formed can be predicted, as well as the total SiO_2 released and SiO_2 consumed in kaolinite formation. The difference between SiO_2 released during hydrolysis and consumed in forming kaolinite is free SiO_2, potentially available for stream transport. Predicted SiO_2 flux is 98.5% of measured flux in watershed SC-1 and 94.3% in watershed SC-2.

Table 1. Cation and SiO_2 fluxes measured at the mouth of watershed SC-1, H^+ consumed in feldspar hydrolysis, feldspar weathering predicted from cation flux, and predicted SiO_2 flux from weathering reaction stoichiometry.

Process	Mass transferred		
	kg ha^{-1} yr^{-1}	mol ha^{-1} yr^{-1}	mol(c) ha^{-1} yr^{-1}
Na flux†	12.5	544	544
Ca flux†	18.0	450	900
K flux†	1.25	32	32
SiO_2 flux†	69.4	1150	--
Sum M⁺‡	--	--	1480
H^+ consumed§	--	--	1480
Ab weathered¶	142	542	--
An weathered¶	125	448	--
Or weathered¶	9	32	--
Kaol. formed#	190	735	--
SiO_2 release#	157	2606	--
SiO_2 consumed#	89	1471	--
SiO_2 flux††	68.4	1135	--

† Measured at stream mouth; corrected for precipitation input.
‡ Na + Ca + K.
§ Set equivalent to sum M^+.
¶ Calculated from measured net Na, Ca, or K flux.
# From stoichiometry of three monomineralic hydrolysis reactions.
†† SiO_2 released minus SiO_2 consumed.

Table 2. Cation and SiO_2 fluxes measured at the mouth of watershed SC-2, H^+ consumed in feldspar hydrolysis, feldspar weathering predicted from cation flux, and predicted SiO_2 flux from weathering reaction stoichiometry.

Process	Mass transferred		
	kg ha^{-1} yr^{-1}	mol ha^{-1} yr^{-1}	mol(c) ha^{-1} yr^{-1}
Na flux†	13.3	579	579
Ca flux†	18.1	452	904
K flux†	1.71	44	44
SiO_2 flux†	79.6	1321	--
Sum M⁺‡	--	--	1530
H^+ consumed§	--	--	1530
Ab weathered¶	152	580	--
An weathered¶	126	453	--
Or weathered¶	12	44	--
Kaol. formed#	197	765	--
SiO_2 release#	167	2772	--
SiO_2 consumed#	92	1526	--
SiO_2 flux††	75	1246	--

† Measured at stream mouth; corrected for precipitation input.
‡ Na + Ca + K.
§ Set equivalent to sum M^+.
¶ Calculated from measured net Na, Ca, or K flux.
# From stoichiometry of three monomineralic hydrolysis reactions.
†† SiO_2 released minus SiO_2 consumed.

Similar data appear in Table 3 for watershed SC-5. Total bases released from weathering are calculated as the sum of stream flux plus net annual uptake in vegetation. The stoichiometry of the plagioclase weathering reaction is essentially the same in this watershed based on Na and Ca flux. Anorthite is again preferentially removed and the base transport suggests dissolution of an An_{46} plagioclase. Total feldspar weathering rate is somewhat higher in this watershed, possibly due to gentler topography and deeper soils that result in a longer residence time for water. Clayton and Megahan (1986) discuss this effect on stream chemistry in SC-5. Total

Table 3. Cation and SiO_2 fluxes measured at the mouth of watershed SC-5, net cation uptake, weathering release of cations (flux + uptake), H^+ consumed in hydrolysis, feldspar weathering predicted from cation release, and predicted SiO_2 flux from weathering reaction stoichiometry.

Process	Mass transferred		
	kg ha^{-1} yr^{-1}	mol ha^{-1} yr^{-1}	mol(c) ha^{-1} yr^{-1}
Na flux†	11.6	505	505
Na uptake‡	1.9	83	83
Na release§	13.5	588	588
Ca flux†	10.0	250	500
Ca uptake‡	10.1	252	500
Ca released§	20.1	500	1000
K flux†	1.9	49	49
K upake‡	2.4	61	61
K released§	4.3	110	110
SiO_2 flux†	82.1	1360	--
Sum M^+¶	--	--	1700
H^+ consumed#	--	--	1700
Ab weathered††	154	587	--
An weathered††	140	504	--
Or weathered††	31	111	--
Kaol. formed‡‡	220	853	--
SiO_2 release‡‡	184	3054	--
SiO_2 consumed‡‡	103	1710	--
SiO_2 flux§§	81	1344	--

† Measured at stream mouth; corrected for precipitation input.
‡ Net annual biomass increment.
§ Weathering release; equal to uptake plus stream flux.
¶ Sum of Na, Ca, and K weathering release.
# Set equivalent to sum M^+.
†† Calculated from net Na, Ca, or K flux plus uptake.
‡‡ From stoichiometry of three monomineralic hydrolysis reactions.
§§ SiO_2 released minus SiO_2 consumed.

albite, anorthite, and orthoclase weathering are calculated from Na, Ca, and K release (stream flux plus net uptake), and kaolinite formation, SiO_2 release, and consumption calculated in the same way as SC-1 and SC-2. Predicted SiO_2 flux is 98.6% of measured flux in SC-5.

DISCUSSION

The fact that SiO_2 fluxes predicted from reaction stoichiometry are approximately equal to measured SiO_2 fluxes for all three watersheds suggests that primary mineral hydrolysis is sufficient to explain annual stream cation flux plus uptake in these watersheds. Further, if cation stripping occurs over the short term, it appears that weathering release of bases over a year is more than sufficient to replace exchangeable bases lost during periods of high vegetation demand or during high leaching that accompanies snowmelt. This conclusion is strengthened by the fact that reaction stoichiometry was balanced both in watersheds with a mature forest canopy and assumed steady-state biomass increment (SC-1 and SC-2), and in a watershed with a multicanopied overstory with measured net growth (SC-5).

The annual ANC arising from primary mineral hydrolysis is approximately 1500 to 1700 mol(c) ha^{-1} yr^{-1} (Tables 1, 2, 3; H^+ consumed). The current annual acid input estimated from pH of bulk precipitation is about 70 mol ha^{-1} yr^{-1}. Van Breeman et al. (1984) suggest that the ratio of external proton inputs (acid deposition) to internal proton production (mainly net cation uptake and oxidation reactions such as nitrification) is a good measure of ecosystem sensitivity to acid. The EIPR values >0.5 generally show Al mobilization and SO_4^{2-} retention in soil, and result in Al export and pH depressions. The EIPR ratio has a value of <0.1 in watershed SC-5 under current conditions (inputs of 70 mol ha^{-1} yr^{-1}; uptake and nitrification estimated at 800 mol ha^{-1} yr^{-1} from Clayton and Kennedy, 1985; the other source of protons is from carbonic acid dissociation). Even if dry deposition doubled the acid input, it appears that weathering rates provide a sufficient sink for protons without removing bases from the exchange phase. If the average pH of precipitation were to decline from 5.2 to 4, inputs of acid would increase to about 1000 mol ha^{-1} yr^{-1} annually for our range of annual precipitation. Then the buffer system in the soil would likely be stressed because of the magnitude of internal proton-producing reactions. One might expect base stripping from the exchange phase under this acid deposition regime and probable ecosystem deterioration, unless mineral hydrolysis reaction rates were sufficiently increased by lower pH.

It is likely that some of the K^+ attributed to orthoclase hydrolysis may originate from weathering of biotite, a common accessory in Silver Creek rock. In humid environments, biotite commonly weathers to other 10 or 14 Å phyllosilicates (Afifi et al., 1985) or less commonly directly to kaolinite (Harris et al., 1985). Clayton et al. (1979) found highly birefringent sericitic alteration of biotite in thin section, and clay-sized mica (10 Å peaks) is common in XRD analysis of Idaho batholith soils (Clayton, 1974). This weathering includes release of some Mg^{2+} and K^+ by hydrolysis, and Fe(II) by oxidation. Proton consumption during hydrolysis of orthoclase or biotite is the same for equivalent K^+ release, but it is not clear how the stoichiometry could be resolved because much of the K is immobilized in interlayer sites in the weathering product. Based on Mg^{2+} weathering in SC-5 (Clayton and Kennedy, 1985) and if all K were transported, up to half the K^+ attributed to orthoclase weathering could originate from biotite. For this worst-case error, the SiO_2 flux would change by $<5\%$.

Drever and Hurcomb (1986), studying weathering rates in an alpine basin underlain by igneous and metamorphic rocks in the Cascade Mountains of Washington, found Ca transport in drainage water exceeded expected values based on Na and SiO_2 transport. They concluded that the source of Ca was from calcite in veins and on joint surfaces, and that plagioclase weathering was negligible. The absence of calcite or other carbonate alteration products in rock in the Silver Creek watersheds possibly sustains sufficient H^+ activity in leaching water to assure feldspar hydrolysis. They suggested that feldspar weathering is commonly not a source of solutes in alpine basins underlain by granitic rock. Forested catchments typically have larger cation denudation rates than alpine basins because of biotic and climatic infuences (Saunders and Young, 1983), and this may explain the differences in plagioclase weathering between the alpine Cascades and Silver Creek.

Unlike many other areas, the stoichiometry of feldspar hydrolysis in the southwestern Idaho batholith appears to balance based on SiO_2 flux. There are several possible

reasons for this. The geographic area is relatively unaffected by anthropogenic sources of acid deposition, and mature forest cover is present on the watersheds. These factors suggest long-term stability with regard to hydrochemical and biological effects on weathering. Steep slopes are common on the watersheds (30–35 °), and result in high-erosional denudation rates, rejuvenating soil parent material and providing an abundance of fresh primary minerals in the solum. Presence of fresh minerals is also enhanced by granular disintegration of the quartz monzonite rock. This steady supply of reactants also lends stability to the weathering reaction. Bedrock in the area is uniform lithologically and simple mineralogically, and kaolinite is relatively compositionally pure compared to other secondary aluminosilicates. This rather simple monomineralic product differs from other watershed studies where multiple or poorly defined clay minerals and gibbsite are present. The presence of multiple Al-bearing products with different Al/Si ratios prohibits a unique definition of Si-release stoichiometry.

One could speculate that zoning of fractured plagioclase grains might enhance the disproportionately high An hydrolysis observed in these watersheds by assuring that domains of relatively An-rich feldspar surfaces are in contact with soil water. Without zoning, Ab and An molecules would be distributed randomly and uniformly in proportion to their abundance in the bulk plagioclase mineral. Preferential depletion of An along the small fractures that allow water entry would result in these fractures being bordered exclusively by more resistant Ab molecules. Weathering rate might then be time dependent, approaching the slower Ab hydrolysis rate.

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