# Controls on silicate weathering rates in soils

A. Blum      U.S. Geological Survey, Boulder, CO 80303, USA

M. Schulz      U.S. Geological Survey, Menlo Park, CA 94025, USA
A. White

## The issue of surface area

By far the largest uncertainty in comparing experimental and field weathering rates is surface area (i.e. White *et al.*, 1996). Geometric surface areas are clearly an underestimate, since even fresh experimental materials have surface roughnesses of 3–20. Measuring the BET surface areas of cleaned mineral separates from the soils, even with some ambiguity in the physical interpretation, is a more consistent approach. Natural materials typically have surface roughnesses of 200–2000, which effectively lowers the weathering rates calculated using geometric surface areas by several orders of magnitude, and places all the previously reported weathering rates in soils clearly below experimental rates.

## Hints from watershed studies

Elemental fluxes from watersheds are used to calculate weathering rates per land surface area (i.e. mol ha$^{-1}$ yr$^{-1}$). This 'weathering rate' is integrated over the entire flow path, and does not consider differences in soil thickness, mineral abundance and grain size, mineral surface roughness (often correlated with soil age), and with the length of the flow path. Nevertheless, weathering rates from granitic watersheds fall within a factor of ~10 of each other, and show positive trends with precipitation and temperature (White and Blum, 1995; Berner *et al.*, this volume). Thus, not only are watershed weathering rates slower than laboratory rates, they are systematically slower, suggesting the retarding processes are similar in most watersheds, and may even moderate the magnitude of variation between distinctly different soil systems.

## Why the difference?

Explanations for differences between natural and laboratory weathering focus on three differences, 1) solids, 2) solution compositions, and 3) physical differences between the hydrologic conditions.

## Solids

Many minerals display extensive etch pitting, suggesting defects are important loci for dissolution. It is often suggested that experimental rates may be dominated by dissolution from the highest energy sites, which are quickly depleted on a geologic time scale, and might not be reflected in natural weathering rates. This observation suggests that soil age could have a large influence on weathering rates. Evidence for the importance of imperfections is mixed. Dissolution experiments using 'pre-weathered' soil minerals do not yield vastly slower dissolution rates (Drever and Clow, 1995), and experiments using deformed materials with high dislocation densities do not drastically increase dissolution rates. Compilations of watershed weathering rates, such as White and Blum (1995), do not show large differences between younger and older soils. Field evidence from a chronosequence of soils (White *et al.*, 1996) do suggest that the weathering rates of hornblende, oligioclase and K-feldspar decrease modestly by factors of 45, 16 and 4.5, respectively, over soil ages ranging from 10 to 3000 Ka. However, the BET surface areas increase at nearly the same rate as the reaction rates decrease. Perhaps fortuitously, the loss of more reactive mineral at etch pits is nearly compensated by increases in the surface area of the residual, less reactive material. The result is no net change in the reaction rate per mineral mass. This compensating effect may explain the apparent lack of dependence of soil age on elemental fluxes per land surface area in watershed compilations.

## The solutions

Experimental solution chemistries are much simpler than natural systems, and the potential for catalysis/retardation in soils are numerous. Experimental studies of the alkali feldspars suggest increasing saturation state and/or Al inhibition may be more important than theoretically predicted, with up to a 10 fold decrease in reaction rate at <50% of the

saturation state. Aluminosilicate dissolution rates are both highly pH dependent, and consume protons, leading to the possibility of proton limitation of dissolution rates. Proton mass balances in bulk soil solutions indicate pH is not a major factor, but proton limitation could apply to isolated pores. The relative importance of poisoning and/or armoring the surface by other constituents is unknown, but arguments for inhibition by Fe and/or organic coatings are plausible, but largely unsubstantiated. Dissolved organic acids do not appear to be a critical factor beyond their effect on pH, having a modest accelerating effect on feldspar dissolution rates.

## Hydrology

Most soils are unsaturated environments whereas dissolution experiments are conducted in a well mixed saturated environment. This has two potentially important consequences. First, not all soil material may be exposed to water at all times, with significant wetting and drying cycles. However, the similarity between elemental fluxes from watersheds with different soil moisture regimes suggests this is not a dominant (orders of magnitude) effect.

Secondly, flow in the unsaturated environment is much more heterogeneous than saturated flow. Whereas the saturated permeability ($K_{sat}$) of soils is highly variable, the unsaturated permeability ($K_{unsat}$) is both spatially variable and a strong function of the moisture content, with $K_{unsat}$ varying by orders of magnitude in the normal range of soil moisture. This makes it kinetically difficult to flush water through the lower permeability regions during high flow events. Higher permeability zones will tend to wet first, further increasing their effective permeability and reinforcing preferred flow paths. Consequently, there may be extensive regions of the soil where the flow is exclusively inward by capillary tension, with the only outflows by evaporation and plant transpiration, both processes which concentrate solutes. It is the combination of immobile pore water, and the retarding effects of accumulated solutes, which appear to be the greatest contributor to slower weathering rates in natural systems.

## Field examples of agreement between natural and experimental rates

The importance of saturated versus unsaturated flow is supported by measured weathering rates along the Von Guerard stream in the Taylor Valley, Antarctica. The stream is analogous to a saturated flow column reactor. Dilute surface flow from a dry bottom glacier flows ~5.2 km to Lake Fryxell, interacting along the channel with saturated gravels in the hyporheic zone, defined by the thawed permafrost. The gravels are sub-equal quantities of i) granites, ii) intermediate intrusive and metamorphic rocks, and iii) diabase and basalt. Silica fluxes, calculated from changes in solution chemistry along the stream, were used to quantify weathering. Silica concentrations increase linearly downstream from 128 to 167 µM ($R^2$ = 0.94). Using the hyporheic zone volume and stream flow yields a weathering rate of $10^{-15.3}$ mol Si cm$^{-2}$ sec$^{-1}$ using BET surface area and $10^{-12.8}$ using geometric surface area. These weathering rates are greater than watershed studies, and similar to experimental dissolution rates for hornblende and augite. The rapid dissolution rates suggest that the saturated aqueous environment, with constant flow through the matrix, is more reactive than the restricted flushing of porosity in unsaturated soils. The strong contribution of weathering in the hyporheic zone may have two other implications; i) the interaction of streams with bed material may be a stronger influence on the stream compositions than expected, and ii) chemical weathering of bed load in fluvial systems may be more important in on the fining of sediments downstream than previously appreciated.

Another study by Schulz and White (1998) examined quartz weathering in an 8 m saprolite profile in Puerto Rico. Below the biologically active zone, soil solution Si concentrations increase systematically with depth from 90 to 220 µm/l. They used inverse mass balance modelling to calculate the contribution of quartz dissolution to Si in solution. Using the quartz BET surface areas and soil solution resonance times, they calculated a quartz dissolution rate of $10^{-12.8}$ to $10^{-13.5}$ mol m$^{-2}$ s$^{-1}$. This is similar to experimental rates, even though Si concentrations in the soil solutions approach quartz saturation. This appears inconsistent with the ideas that; i) unsaturated hydrology is a major control on weathering rates, and ii) the concentrated immobile solutions retard the dissolution rates. Two of simplest explanations of this discrepancy are; i) this soil has high porosity (50%), high rainfall (4200 mm/yr) and a high and nearly constant moisture content, all of which might reduce the heterogeneity of flow, and ii) the processes retarding aluminosilicates dissolution are not acting on quartz in this profile. Quartz dissolution rates have a low pH dependence and do not consume protons. Thus, if proton depletion in isolated pores is the process retarding aluminosilicate weathering rates, it would not be expected to effect quartz dissolution rates.