

Effects of climate on chemical weathering in watersheds underlain by granitoid rocks

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Introduction

Chemical weathering is strongly affected by climate, principally by precipitation, runoff and temperature. Recently, intensive interest in global climate change has renewed efforts to quantitatively understand feedback mechanisms between climate and chemical weathering rates, which are primarily responsible for buffering atmospheric CO₂ over geologic time, and moderating fluctuations in global temperature. Most natural studies used to calibrate the feedback between weathering and climate have focused on large scale river systems. Surprisingly few attempts have been made to discern the interconnection between climate and chemical weathering in smaller scale watersheds and catchments (0.1–10 km²). Although geographically more limited, such watersheds have better defined hydrogeochemistry, solute budgets and more uniform lithology and climate. This study tabulates and interprets available solute concentrations and fluxes for a worldwide distribution of watersheds.

Methodology

Comparison of weathering rates based on climatic differences requires physical and hydrologic similarities in the watersheds in addition to a degree of uniformity in measurement and computational approaches. In this synthesis, only watersheds underlain predominantly by plutonic granitoid rock types or high grade metamorphic gneisses are considered. Climatic impacts on chemical weathering ultimately reflect fundamental differences in thermodynamic and kinetic interactions between minerals and solute phases. However most watershed weathering studies have utilized simpler approaches, using either solute concentrations or fluxes as surrogates for weathering intensity. Cation and silica concentrations (μM) in streams are typically reported as mean annual values weighted by volume of runoff. The weathering flux

$$Q_{i,w} = Q_{i,d} - Q_{i,b} - \left[\frac{C_i}{C_{Cl}} \right]_{sea} (Q_{Cl,d} - Q_{Cl,i,p}) \quad (1)$$

$Q_{i,w}$ for a specific solute (Eqn.1) is calculated as the

difference between discharge $Q_{i,d}$ and bulk precipitation $Q_{i,b}$ minus a correction for excess dryfall based on the product of elemental ratios C_i/C_C in seawater times the difference between Cl discharge $Q_{Cl,d}$ and input $Q_{Cl,i,p}$. The above computations do not account for net biological or ion exchange fluxes.

Results

Sixty watersheds meeting the preceding criteria encompass significant differences in mean annual precipitation (620 to 4500 mm/yr), runoff (90 to 3700 mm/yr) and air temperature (–2 to 22°C). In watersheds with similar temperatures (i.e. alpine/temperate or tropical), absolute evapotranspiration ET (mm) is similar, and largely independent of the amount of precipitation and runoff. However, the proportion of precipitation lost through ET(%) increases significantly as precipitation decreases. This produces a strong trend of increasing solute concentration with decreasing precipitation (and increasing %ET). Thus, comparisons of solute concentrations are an ineffective tool for distinguishing climatic effects on watershed weathering rates. In contrast, solute fluxes are not susceptible to ET effects. Climatic variability in Mg, Ca, and K weathering fluxes are apparently obscured by differences in watershed lithology, nutrient cycling, and soil cation exchange. Correlations of SiO₂ and Na fluxes as independent linear functions of precipitation and exponential functions of temperature produce statistically meaningful results but also display consistent anomalies, particularly for watersheds with both wet and warm climates.

The above inconsistencies suggest that weathering fluxes can best be defined in terms of coupled climatic variables (Eqn. 2). The pre-exponential term on the right-hand side of the equation assumes a

$$Q = (a_0 + b_0 * P) \exp \left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (2)$$

linear correlation between precipitation P and flux where a_0 is the intercept and b_0 is the slope. The Arrhenius term describes the variation in fluxes as a function of the difference between T and a

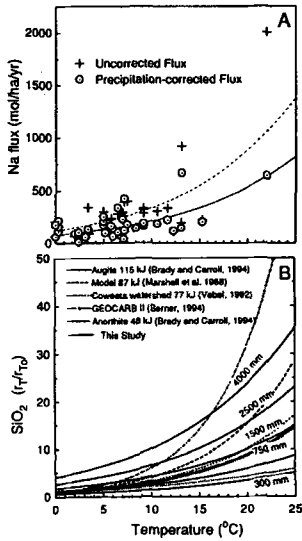


Fig. 1. (A) Uncorrected and precipitation-corrected (Eqn. 2) Na weathering fluxes versus mean annual air temperature. (B) Comparison of SiO₂ weathering rate as a function of T (r_T) relative to rate at 0°C (r_0) at constant precipitation (solid lines). Also shown are other temperature-dependent weathering rates cited in the literature.

reference temperature T_0 (5°C). The expression is solved numerically for a_0 , b_0 and E_a which minimize the residual between the predicted and measured fluxes as functions of temperature and precipitation. The resulting fit to the SiO₂ fluxes produces a respective slope and intercept of $a_0 = 127$ and $b_0 = 0.339$, and an activation energy of 58.8 kJ. Na fluxes produce values of $a_0 = 34.4$ and $b_0 = 0.096$ and an activation energy of 62.3 kJ.

A useful way to evaluate the coupled effects of temperature and precipitation on watershed weathering is to correct the measured solute fluxes to standard temperature and precipitation conditions. An example of Na fluxes normalized to a standard precipitation (1000 mm) shows the exponential impact of temperature on weathering (Fig. A). The principal effect of the precipitation correction is to bring the uncorrected weathering rates for Na in the warmer watersheds with high rain fall in line with the more temperate watershed data. The effect of using a standard precipitation value different from 1000 mm has a small effect on the curvature of the lines in Fig A, but does not influence the calculated activation energies.

The above analysis of watershed fluxes has important implications for weathering reactions. The strong correlation between solute concentrations and ET implies that weathering fluxes must

originate in shallow soil regimes accessible to plant and atmospheric interaction. Both the reaction stoichiometry, based on Na/SiO₂ flux ratio of 4:1, and calculated activation energies are compatible with weathering rates dominated by feldspar dissolution. The strong reinforcement effects between precipitation and temperature imply that such dissolution in the soil zone must be strongly dependent on soil moisture content that affects reactive surface areas, reaction affinities, secondary mineral formation, and solute transport. No correlation was found between chemical weathering rates and average hillslope steepness nor the extent of recent glaciation. This implies that in watersheds with at least minimal topography, physical erosion rates and the age of soil development are of secondary importance when compared with precipitation and temperature in controlling chemical weathering rates. Weathering fluxes in these small watersheds are very similar to those for large scale world rivers. This is surprising when considering that watersheds represent upland headwaters of large rivers, and are commonly typified as having anomalously high rates of both physical and chemical weathering.

Ratios of weathering rates for silica (r/r_0) based on coupled climate variability (Eqn. 2) (precipitation = 300 to 4000 mm) bracket temperature dependencies (Fig. B) predicted from experimental activation energies proposed by Brady (1994) for common Ca and Mg silicate minerals (anorthite, 48 kJ; and augite, 115 kJ). Past calibrations for weathering feedback have relied principally on the solute chemistry of large rivers (Meybeck, 1979) and have considered only the effects of temperature on SiO₂ concentrations. The failure to consider precipitation and/or ET effects on Si concentrations may explain the high apparent activation energy (87 kJ) obtained by Marshall *et al.* (1988). Velbel (1993) obtained a lower activation for Na fluxes (77 kJ) representing feldspar hydrolysis in the Coweeta watershed. Recently Berner (1994) in the GEOCARB II model considered the coupled effects of temperature and runoff on weathering fluxes based on the experimental activation energies of Brady (1994) and river runoff/concentration data. Fig. B shows that weathering rates produced by GEOCARB II and the present coupled approach (Eqn. 2) produce comparable rates for moderate precipitation environments (1000–1500 mm) but that the GEOCARB II weathering would estimate lower watershed weathering rates in tropical environments.