The Chemical End Member of the Coupled Physical and Chemical Weathering System

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In natural systems both physical and chemical weathering processes are occurring and erosion is constantly removing chemically weathered material making it difficult to decouple physical and chemical contributions. In order to understand these coupled systems it will be necessary to examine end-member systems where primary processes that control chemical and physical weathering can be considered separately. We use 3 cm weathering rinds developed on basalt clasts within 125 ka fluvial terraces along the Pacific coast of Costa Rica as a proxy for saprolite development in the absence of physical weathering. This highly controlled system enables us to examine the weathering interface in detail. The weathering interface is comprised of thin reaction fronts where element concentrations vary from parent rock to rind concentrations. Electron microprobe data indicate a 2 mm thick reaction front of mobile elements (i.e., Ca and Na) at the interface and ~ 4 mm thick reaction fronts of less mobile elements (i.e., Si). These reaction fronts are 3 orders of magnitude narrower than those recognized at the bedrock-saprolite interface in landscape-scale studies. Iso-volumetric weathering of the labradorite and augite has produced a rind of gibbsite and iron oxide. This transition is accompanied by a pronounced change in porosity from $< 1% in the core to 50% in the rind. Petrographic and SEM images reveal labradorite dissolution coreward of the rind/core interface producing secondary porosity and increased permeability into the core. Reactive transport modeling allows simulation of rind development using appropriate values of diffusion, mineral surface area, and reaction rate. A controlling feature appears to be porosity of the basalt clast which controls both diffusion of reactants and products into and away from the weathering front. Initial reaction-diffusion simulations were based on the assumption of constant porosity so as to understand important controls on the thickness of the reaction front and the rate at which it advances. Results indicate that the initial rate of rind advancement is a mix of interface- and transport-control. However, once a dissolution front is established, the long-term rate of rind advancement becomes transport-limited and shows parabolic time dependence characteristic of diffusion processes. Field data, however, indicate that rind advance rates are constant through time, suggesting that transport within the rind is more complicated than simple diffusion. One possibility is that the increase in rind porosity allows for flow through the rind, thus causing the fixed concentration boundary condition to migrate coreward along with the weathering front. Such a mechanism could result in a linear rather than parabolic rind advancement rate with time. Diffusion rates and mineral surface area were varied to match initial rind advance rates to approximately $2x10^{-4}$ mm/year calculated from field data. The effective diffusion coefficients for dissolved aqueous species ranged from $0.51x10^{-5}$ cm^2/sec to $8.57x10^{-5}$ cm^2/sec for Fe^{3+} and H^+, respectively. Initial rind advance rate ($2.1x10^{-4}$ mm/yr) and reaction front thickness (2 mm) were closest to observed values when formation factor, labradorite surface area, and augite surface area values

were 6.7E-5, 1500 m^2/m^3, and 500 m^2/m^3, respectively. Further modeling is ongoing to investigate how porosity changes affect transport within the weathering rind and rind advance rate. These modeling efforts will help clarify how physical changes at the reaction front are coupled to chemical processes.