Exploring the relative influence of fluid and particle residence times on chemical weathering using a coupled geomorphic and geochemical model

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Minerals enter the weathering zone as landscapes erode and weathering fronts propagate downward through the near surface. In many, if not most landscapes, this process involves minerals first being chemically weathered and subsequently being subject to both chemical weathering and mechanical disturbance. The timescale of mineral transformation is on the order of thousands to millions of years [1]; this timescale is similar to the residence time of minerals within the physically disturbed, mobile regolith of eroding landscapes [2]. The chemistry of mobile weathered material on eroding hillslopes will reflect the integrated effects of different weathering environments along the hillslope profile. Thus it is crucial to account for sediment transport if one is to use the solid state chemistry of hillslope materials to infer weathering rates over long (10^3-10^6 yr) timescales [3, 4]. It has been postulated that the rate that minerals weather is partly a function of the time they spend in the weathering zone [5] and this time is closely related to the erosion rate. It has also been suggested that fluid, rather than mineral residence time plays a dominant role in determining the rate of chemical weathering in near-surface materials [6]. To examine the relative importance of mineral vs. fluid residence time or to examine if these two factors co-evolve we have developed a numerical model that traces minerals through the weathering zone, including their transit through a mobile, mixed regolith. The model is designed to assimilate field data so that hypotheses concerning the controls of chemical weathering rates can be tested with solid state chemistry and mineralogy from soil pits or cores. Chemical weathering in the model can be simulated using either the time the mineral has spent in the weathering zone or using a geochemical model that accounts for fluid flow and chemistry. Here we use the model to examine the sensitivity of weathering zone evolution to erosion rate. We also compare model predictions to geochemical data from a transect in Tennessee Valley, California in order to explore if variations in either fluid or mineral residence times can explain the observed geochemical patterns.

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[2] Mudd and Yoo (2010) *Journal of Geophysical Research-Earth Surface* **115**, doi:10.1029/2009JF001591.
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Binding environment of As(V) during microbial reduction of As-bearing biogenic Fe(III) minerals

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Aqueous As in As-contaminated groundwater and soil enters the human food chain (in)directly via drinking water, plants and animals, potentially having a devastating impact on the health of people. Correspondingly, research has put its focus on (bio)geochemical processes leading to the mobilization (release) and immobilization (removal) of As from aquifers and soil. Previous studies by Hohmann *et al.* [1] revealed that Fe(II)-oxidizing bacteria efficiently immobilize the two most common inorganic As species, As(V) and As(III), in aqueous systems by the formation of biogenic Fe(III) oxyhydroxides (ferrihydrite and goethite). Detailed analyses of these biogenic precipitates formed in the presence of dissolved As indicated As is efficiently removed from the aqueous phase via sorption to the mineral surfaces [2].

Environments that contain Fe(III) minerals and organic matter are usually also inhabited by Fe(III)-reducing microorganisms, suggesting that potentially microbial reduction of the biogenic Fe(III) (oxyhydr)oxides occurs. The microbially-mediated dissolution of these biogenic Fe(III) minerals could cause a release of the bound As or result in further immobilization of As due to the formation of secondary Fe(II/III) mineral phases. Additionally, the redox state of As might change during microbial Fe cycling and thus affect the mobility of As, since As(III) is generally more mobile than As(V).

In the study presented here, we followed the reduction of biogenic As-bearing Fe(III) minerals by the Fe(III)-reducer *Shewanella oneidensis* MR-1. Arsenic concentration and oxidation state were monitored in the liquid and solid phases. Mineralogy of the incubated solid phases was determined by X-ray diffraction and electron microscopy, whereas the As redox species and bonding environment in the mineral precipitates were analyzed by X-ray adsorption spectroscopy. We found that As(V) is immobilized during microbial reduction of biogenic As-bearing Fe(III) (oxyhydr)oxides while As(III) is mobilized to a significant extent. The immobilized As(V) is bound either to the remaining goethite or to the newly formed Fe(II) minerals and no mobilization occurred even though As(V) was transformed to As(III).

[1] Hohmann *et al.* (2010) *ES&T* **44**, 94-101. [2] Hohmann et al. (2011) *GCA* **75**, 4699-4712.