

Effects of elevation, lithology, climate, and erosion on hillslope rock fragment distribution and abundance in diverse settings

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Hillslope rock fragment production influences critical zone processes including weathering styles, ecosystem functions and landscape evolution. However, little is known about how hillslope boundary conditions such as erosion rate, climate, and lithology, affect the production of bedload-sized rock fragments (> 2mm) on soil-mantled hillslopes. To uncover patterns in the mass fraction and size distribution of rock fragments we analyzed data from: 1) soil survey archives from hillslope settings with active sediment production in Hawaiian basalts, and mixed lithologies in the northern Sierra Nevada and eastern Cascade Mountains, and 2) three climatically diverse settings in California (one sandstone and two granitic terrains) with variable erosion rates at each field site. We find positive correlations between erosion rates, rock fragment abundance and median grain size. Preliminary data suggests that biotite concentrations may control grain size distributions in granitic terrains. Rock fragment abundance is greatest at higher elevations in the Sierra Nevada and Cascade sites and at lower elevations in the Hawaii sites, possibly due to differing influence of precipitation and temperature in windward and leeward settings. We observe surface-rich rock distributions in the drier colder climatic settings, with the percent rock fragments above a median depth increasing as precipitation decreases. In the sandstone, bedrock is less durable than soil column clasts, suggesting a winnowing during the bedrock to soil conversion process.

YREE sorption on HFO in 0.5 M NaCl

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The sorption behavior of cerium (Ce) on marine particles is distinct from that of other members of the yttrium and rare earth element (YREE) series, due to its unique redox chemistry. Assuming limited YREE mobility during early diagenesis, sedimentary 'Ce anomaly' records have been interpreted in terms of episodic shifts of bottom water oxygenation in the paleo-ocean. However, the Ce anomaly may be decoupled from the redox potential of ambient seawater by catalytic Ce oxidation on the particle surface. Sedimentary Ce anomalies could thus be partly 'preformed' and influenced by variations in particle composition. We are investigating YREE sorption in 0.5 M NaCl on mixtures of three main components of marine particles: Fe and Mn oxides, and organic matter. Here we report on new results for one pure endmember, hydrous ferric oxide (HFO).

Batch experiments were conducted over a range of pH (4-8) at 25.0±0.1°C while continuously bubbling with ultra-high purity nitrogen to prevent YREE complexation with carbonate. After at least 6 hours of equilibration at each pH, solution samples were filtered to 0.22 µm and dissolved YREE concentrations analyzed by ICP-MS to determine the solid/solution distribution coefficient, K. At low ionic strength, YREEs interact with either one or two neutral hydroxyl groups on the HFO surface to release an average of 1.5 protons per YREE ion sorbed [1]. In 0.5 M NaCl, HFO surface protonation is diminished, causing the formation of negative hydroxyl groups onto which YREE ions can sorb without releasing a proton. The slope of the log K vs. pH curve is consequently lowered to less than 1. Our data are fit well with an extension of the non-electrostatic model of Quinn *et al.* [1], yielding conditional stability constants for several YREE surface complexes, as well as for the second HFO protonation constant.

No Ce anomaly was observed in our YREE sorption experiments, at any pH. Our data are thus in agreement with a majority of studies showing that Ce is not oxidized on the HFO surface, notwithstanding occasional claims to the contrary. It appears that sedimentary Ce anomalies can, in principle, provide an unbiased, instantaneous record of bottom water redox conditions, at least where Fe oxides (and organic matter) are the dominant mode of YREE transfer from seawater solution to the particulate phase. Whether that record is meaningfully preserved upon early diagenesis remains an open question.

[1] Quinn, Byrne & Schijf (2006) *Marine Chemistry* **99**, 128-150.