Ge/Si as a tracer for Si in paired catchments of the Luquillo CZO

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Catchment lithology is a significant factor influencing the generation and transport of solutes in the critical zone. In the Luquillo Mountains of Puerto Rico, the Quebrada Guaba and Bisley catchments are studied to understand how lithology affects concentration-discharge (C-Q) relationships. Ge/Si ratios in pore water and stream samples are used to identify sources of Si to streams in the Bisley 1 watershed.

Quebrada Guaba is underlain by quartz diorite and is characterized by strong Si dilution behavior (power law slope = -0.47)[1]. During baseflow, Ge/Si = 0.27-0.47 μmol mol^{-1} due to weathering of plagioclase and precipitation of Ge enriched kaolinite in the bedrock-saprolite interface[2]. During storms, hydrologic pathways shift to shallower flow paths with lower Si concentrations and higher Ge/Si (1.0-4.0 μmol mol^{-1})[3]. The shift to saprolite-dominated flow paths carrying dilute Si end-members drives the Si-Q pattern in this catchment.

The volcaniclastic sub-catchment of Bisley 1 has a more chemostatic Si-Q relationship (power law slope of = -0.30)[1]. In this study, lysemeters at the Bisley sites of B1S1, B1S2 and B1R show higher Si pore water concentrations than the LG sites at Quebrada Guaba. Ge/Si ratios for Bisley are lower than Guaba except for 200-300 cm depth were ratios increase to 2.87 μmol mol^{-1} (B1S1). Dissolved Si concentrations increase markedly from 200 cm to the surface at B1S1 and B1S2. Ge/Si shows the opposite trend with ratios decreasing from 2.87 to 0.86 μmol mol^{-1}. This pattern of increased pore water Si and low Ge/Si may be due to phytolith dissolution also observed in Quebrada Guaba[2,4]. Bisleys greater Si depletion near the surface may result in more sensitivity to phytolith inputs. Stream samples from Bisley 1 will be analyzed for major cations and Ge/Si to understand how pore water or other shallow surface reservoirs influence Si-Q patterns in this catchment.

[1] Wymore et al. (2017) *Water Resources Research* **53**, 6279-6295. [2] Lugolobi et al. (2010) *Geochimica et Cosmochimica Acta* **74**, 1294-1308. [3] Kurtz et al. (2011) *Water Resources Research* **47**. [4] Ziegler et al. (2005) *Geology* **33**, 817-820.