Climate impacts on (in)congruent silicate weathering constrained by Ge/Si ratios

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The extent of secondary mineral formation during incongruent weathering acts as a critical buffer for dissolved silica. Ge acts as pseudo-isotopic tracer for Si and is sensitive to the degree of incongruency. Two CZO sites, the Southern Sierra CZO (SSCZO California) and the Hakai CZO (Calvert Islands, British Columbia) are developed on granodioritic bedrock but under different climates (Mediterranean vs. perhumid). The Providence Creek catchments at SSCZO include a thick regolith; groundwater is an important source of stream flow. At Hakai, soils (podzols, histosols) are thin and organic carbon-rich, and streams have very high DOC[1].

Providence Creek catchments have 300-600 μM Si and show slight dilution effects during peak discharge (mixed snowmelt-rain). Groundwater is the dominant source of DSi. Ge/Si ratios are < 0.12 pmol/μmol. Mass balance calculations indicate nearly complete sequestration of Ge (and Al) by kaolinite formation, as is ca. 40% of Si of released by feldspar weathering. We hypothesize that long groundwater transit times permit near-equlibration of fluid with kaolinite. In contrast, Hakai stream DSi varies from 36 - 52 μM and Ge/Si is near 1.6 pmol/μmol. At Hakai stream water values are $\approx$ feldspar Ge/Si, and are consistent with essentially congruent weathering. Model calculations indicate that a combination of short transit times, high dilution and organic complexation of Al by high DOC create undersaturated conditions for kaolinite, preventing secondary mineral precipitation. 90-100% of Si released by weathering is exported. Reaction yields for Si can be strongly climate dependent, but can be masked by dilution effects without an effective reaction tracer such as Ge/Si.

[1] A. Oliver *et al.*, A global hotspot for dissolved organic carbon in hypermaritime watersheds of coastal British Columbia. *Biogeosciences* **14**, 3743-3762 (2017).