## $\delta^{30}Si - Q$ relationships in headwater catchments reveal site-specific solute dynamics

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As part of a cross-CZO (Critical Zone Observatory) international project (SAVI: Science Across Virtual Institutes) involving collaboration between French, Canadian, and American Critical Zone networks, this study presents measured silicon stable isotope ratios ( $\delta^{30}$ Si) of over 150 stream water samples of seven storm events (i.e., transient periods of high discharge (Q) variability) from six headwater catchments spanning different climates and lithology. Relationships of  $\delta^{30}$ Si vs. Q display large variability in  $\delta^{30}Si$  within and across sites (-0.22 ‰ to +2.27 ‰), on the order of what is observed globally in large rivers. Notably, the distinct  $\delta^{30}Si$  signatures observed between sites are preserved regardless of the application of normalization metrics such as bedrock and atmospheric corrections or area-normalized discharge. Thus, inter-site variability is principally driven by differences in location and Critical Zone architecture where hydrological plumbing and sitespecific secondary weathering processes (i.e., clay formation and biological cycling) exert clear influence on observed dissolved silicon fluxes. Isotope mass balance approaches were used to identify net secondary weathering controls from site to site, showing that storm events are capable of reflecting a wide range of weathering regimes. The results of this unprecedented, largescale dataset demonstrate the advantages of high frequency geochemical datasets in analyzing water quality and solute dynamics in the Critical Zone.