Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.37239

Linking groundwater residence times to stream chemistry and solute export in a montane Critical Zone

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Fluid-rock interactions taking place within the natural reactor at the Earth's surface, the Critical Zone (CZ), regulate Earth's surface conditions, solute generation, and chemical weathering fluxes. Yet the extent to which subsurface fluid residence times govern watershed scale hydrochemical export remains incompletely constrained. This challenge is particularly relevant in snowmelt-dominated montane catchments, where hydrologic partitioning between shallow and deep flowpaths evolves seasonally and is expected to shift under a warming climate. Resolving how groundwater residence times regulate stream chemistry is therefore essential in predicting the response of montane CZs to ongoing hydrologic change. Towards this goal, we present results from a comprehensive, multi-tracer investigation of Sagehen Creek Basin, a small (27 km^2) montane catchment in the Central Sierra Nevada of Northern California, USA.

Over two water years, we collected > 200 spring, stream, and snow samples spanning snowmelt through baseflow conditions at a bi-weekly to daily frequency. This dataset integrates groundwater age tracers (CFCs, SF_6), stable silicon isotopes ($\delta^{30}Si$), and a suite of major and minor solutes, providing novel high-resolution characterization of groundwater-surface water connectivity and chemical evolution across the catchment. Groundwater model ages derived from CFCs and SF_6 range from 31 to 69 years and show observed systematic shift towards older ages from snowmelt to baseflow conditions. Spring $\delta^{30}Si$ exhibit a strong correlation with groundwater ages over decadal timescales where the oldest springs have the lowest $\delta^{30}Si$ (+0.16 ± 0.08 ‰) and the youngest, the most elevated $\delta^{30}Si$ (+1.45 ± 0.07 ‰). These results are consistent with progressive incongruent silicate weathering along subsurface flowpaths, with $\delta^{30}Si$ reflecting secondary mineral reaction progress.

Stream chemistry is found to closely reflect these groundwater signatures. Stream $\delta^{30}Si$ variability mirrors that of the groundwater with low values (+0.75 ± 0.04 ‰) during late season baseflow conditions to high values (+1.47 ± 0.03 ‰) after peak snowmelt. Convergence of stream $\delta^{30}Si$ toward groundwater endmembers during baseflow indicates increasing contributions from older, chemically evolved groundwaters. These observations indicate that groundwater residence times play an important role in shaping watershed-scale chemical evolution and stream solute export in montane CZ settings.