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Lithium isotopes in groundwater and its apparent age in connected aquifers

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Groundwater chemical and isotopic composition result from water-rock reactions controlled by complex factors, including the aquifer hydrogeological structure. Identifying groundwater compositional sources becomes challenging when it can be a mix of different aquifer systems. Here we use lithium concentrations and isotopes measured for open-hole (n=32) and for discrete (n=3) groundwater sampled from deep tubular wells (~200 m) of three partially intermixed aquifers (granite-gneissic aquifer, diabase aquifer, and sandstone aquifer) to relate their Li isotope signatures with groundwater evolution.

The overall measured lithium concentrations, [Li] in groundwater samples collected over three years ranged between 7.6 to 16.7 µg/L (Med= 10.0 µg/L) and correlated with [Si] ($0.36 < r < 0.61$), indicating silicate weathering as a common source. For normalized concentrations ([Li]/[Na] vs. [Si]/[Na]), samples cluster almost perfectly by well. Measured δ^7Li values in groundwater ranged from +2.5‰ to +16.4‰ (Med= 9.6‰). Still considering all samples, [Li] and δ^7Li are not correlated ($r = 0.05$); however, for some wells, trends among those variables become visible and nicely pop up for the few discrete samples, with ($r = -0.78$) between [Li] and δ^7Li.

Considering water-solid interaction, Li isotope composition in groundwater should reproduce the respective rock isotope signature at the first stages of mineral dissolution. However, Li isotopes fractionate with time because secondary phases sorb the lighter ^{6}Li preferentially over, the heavier ^{7}Li through ion exchange, shifting the water δ^7Li to higher values. For the few samples (n=7) with groundwater apparent age (radiocarbon age, GAA) that ranged from *Modern* to 4264 years, a correlation with the respective δ^7Li values ($r=0.60$) confirms that groundwater with longer residence times has a more enriched isotopic signature in ^{7}Li. Despite such evidence, other compositional data indicate that the complex local hydrogeology still requires further characterization to understand how the water fluxes among the aquifers influence the wells' groundwater composition.