

Silicon isotopes as a tool to capture biogeochemical connectivity in permafrost soils: implications on Fe-organic carbon interactions

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Silicon isotope fractionation upon amorphous silica precipitation is sensitive to freeze-thaw cycles in arctic soils that are composed of carbon-rich permafrost (i.e. ground that remains frozen for at least two consecutive years) covered by an active layer (i.e. layer that thaws in summer and freezes in winter). The active layer is thickening with warming and winter air temperature conditions can locally not be sufficient to freeze it back entirely. This leaves residual unfrozen soil portions in winter, which can remain unconnected (isolated), or create new lateral subsurface water flow paths (connected). These flow-path changes increase the soil biogeochemical connectivity by contributing to the lateral transfer of nutrients such as dissolved organic carbon (DOC) and iron (Fe). Identifying these flow-path changes is essential given the key role of Fe for soil OC stabilization, and hence permafrost C emissions. We posit that isolated and connected systems can be identified using silicon isotopes ($\delta^{30}\text{Si}$): in isolated systems, freezing induces amorphous silica precipitation which preferentially incorporates the light Si isotopes, and the presence of colloidal amorphous silica in soil pore waters (spw; $<0.2\mu\text{m}$) decreases $\delta^{30}\text{Si}_{\text{spw}}$; whereas in connected systems, amorphous silica precipitation is not induced. To test our hypothesis, we collected a temporal series of soil pore water from September to November 2021 on a natural gradient of permafrost degradation palsa-bog-fen in Stordalen (Sweden) to measure their $\delta^{30}\text{Si}$ and Fe and DOC concentrations. Results show that upon freezing: (i) $\delta^{30}\text{Si}_{\text{spw}}$ remains stable in palsa ($\sim -0.74\text{‰}$), decreases in bog (from 0.067 to -0.29‰) and increases in fen (from -0.25 to 0.29‰); (ii) concentrations in DOC and Fe are stable in palsa, increase in bog (Fe-oxides dissolution in reducing conditions), and are divided by two in fen (Fe-oxides precipitation and lateral transfer to rivers). These data support changes in water flow-paths in the active layer between systems that are frozen (palsa), unfrozen isolated (bog) and unfrozen connected (fen). The $\delta^{30}\text{Si}_{\text{spw}}$ in fen can be explained by Si adsorption onto Fe-oxides, highlighting the presence of