

Chemical weathering in glacial and proglacial environments

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Physical weathering in glaciated environments initially produces debris which is fine-grained (predominantly silt-sized) and coated in microparticles. Geochemically reactive phases, such as carbonates and sulphides, are liberated from the interior of silicate mineral masses and so become more readily available for chemical weathering. Chemical weathering in glacial environments is microbially mediated, since ingress of atmospheric gases to glacier beds and water-laden proglacial sediments is often limited. Instead, the protons required to push chemical weathering beyond simple hydrolysis reactions are generated from the oxidation of sulphides and organic matter. This is the case beneath smaller glaciers, and appears to be the case beneath ice sheets, from waters sampled either directly or indirectly to date. A fundamental difference between the chemical weathering regimes beneath larger and smaller ice masses is the residence time of water beneath the larger ice masses. It is more likely that low oxygen and anoxic conditions are found beneath ice sheets than beneath smaller glaciers. Hence, it is likely that Fe-rich, anoxic waters will be found beneath sectors of the Antarctic and Greenland Ice Sheets. Such waters have the potential to act as fertilisers of Fe-poor circumpolar seas. Chemical weathering is not limited to the aquatic zones that underlie the ice sheets. Movement of ice over bedrock produces localised pressure melting, and the regelation waters produce micro-chemical weathering environments that allow oxidation of sulphides by oxygen, and the formation of nano-particulate iron oxyhydroxides. The refreezing of these waters back onto the glacier sole traps basal debris, which, following ice berg calving at the ice sheet margin, transport potentially labile Fe further afield into the surrounding sea. Glacial debris is also a source of labile P to aquatic ecosystems. Finally, a spectrum of surface and basal processes result in glacial runoff often containing labile DOC and DON. Hence, glaciers and ice sheets are currently being thought of as biogeochemical reactors that convert relatively bedrock into a cocktail of relatively labile, potentially bioavailable, nutrients.

The chemical weathering of proglacial sediments too has potential to effect global nutrient and geochemical cycles. Recent work of potential impacts on the global P cycle is reviewed.

Technetium Reduction and Permanent Sequestration by Formation of Low-Solubility Sulfide Mineral Phases

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Under anoxic conditions, soluble $^{99}\text{TcO}_4^-$ can be reduced to less soluble $\text{TcO}_2 \cdot n\text{H}_2\text{O}$, but the oxide is highly susceptible to reoxidation. One way to minimize the mobility of the Tc^{VII} oxyanion pertechnetate (TcO_4^-) is to effect reduction under sulfidogenic conditions (generated abiotically by Fe^0 or biotically) to form TcS_x , which is significantly slower to oxidize than $\text{Tc}^{\text{IV}}\text{O}_2$. Here we investigate a novel strategy for remediation of Tc-contaminated groundwater whereby sequestration as Tc sulfide is favored by sulfidic conditions stimulated by nano zero-valent iron (nZVI). Fundamental aspects of this hypothesis have been investigated using batch and column experiments under abiotic and biotic conditions.

In the abiotic batch experiments, nZVI was pre-exposed to increasing concentrations of sulfide in simulated Hanford groundwater for 24 h to mimic the onset of aquifer biotic sulfate reduction. Solid-phase characterizations of the sulfidated nZVI confirmed the formation of nanocrystalline FeS phases, but higher S/Fe ratios (> 0.112) did not result in the formation of significantly more FeS. The kinetics of Tc sequestration by these materials showed faster Tc removal rates with increasing S/Fe between $S/\text{Fe} = 0-0.056$, but decreasing Tc removal rates with $S/\text{Fe} > 0.224$. The more favorable Tc removal kinetics at low S/Fe could be due to a higher affinity of TcO_4^- for FeS than iron oxides, and electron microscopy confirmed that the majority of the Tc was associated with FeS phases. X-ray absorption spectroscopy revealed that as S/Fe increased, the pathway for Tc(IV) formation shifted from $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ to TcS_2 . The most substantial change of Tc speciation occurred at low S/Fe, coinciding with the rapid increase in Tc removal rate. This agreement further confirms the importance of FeS in Tc sequestration. The inhibition of Tc removal at high S/Fe appears to have been caused by excess HS^- , which, however, is expected to be mitigated under natural conditions due to the abundance of iron oxides that can scavenge sulfide. The reoxidation kinetics of Tc sequestered under sulfidic conditions was significantly slower than that under non-sulfidic conditions, confirming that Tc(IV) sulfide is more resistant to oxidation than Tc(IV) oxide.