

## The weathering forefront for permafrost carbon: priorities for critical zone research

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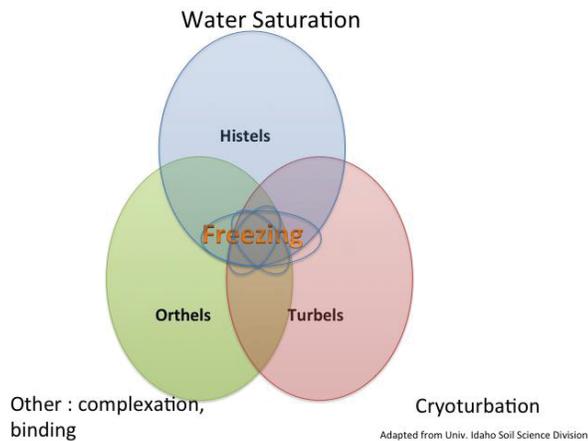
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Little is known about mineral weathering in permafrost soils. Yet as permafrost thaws, mineral stabilization of carbon may become exceedingly important owing to the large stores of permafrost carbon that will thaw over the next century. In areas where permafrost is not present, carbon is often stabilized by organo-mineral binding and complexation driven by mineral weathering. Hydrology and biogeochemistry are key to pathways and transit times of carbon fluxes to the atmosphere. Above the permafrost (the active layer), water and ice contents influence thermal conductance and rates of thawing; decomposition of organic matter increases dramatically upon thaw; organic matter structure is linked to soil moisture and vegetation characteristics. In deeper soils with permafrost, the amounts and forms of carbon have been characterized according to processes of C stabilization (Figure 1), but carbon forms have not been related mechanistically to water, mineral surfaces, and biogeochemistry in a way that addresses processes at meaningful scales.

### Carbon Stabilization by Permafrost



**Figure 1.** Processes of carbon stabilization by the three suborders of permafrost soils called Gelisols.

Thus the processing and microenvironments of permafrost carbon at the micro and macroscale will be key to understanding how and where permafrost carbon may be stabilized or destabilized upon thaw.

## New insights from FOAM: iron and trace metal cycling in highly sulfidic pore waters beneath an oxic water column

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A 50-cm sediment core was collected from the FOAM site (Friends of Anoxic Mud) with pore waters being extracted immediately on-site. FOAM is a well-described, nearshore study site in Long Island Sound characterized by high TOC and pore water sulfide concentrations of a few mM overlain by an oxic water column. Going well beyond any past work at FOAM, and to complement our Fe analyses, we analyzed a suite of trace metals including Mo, Cr, V, and U. Our data for Fe-speciation show high ratios of pyrite ( $Fe_{py}$ ) to highly reactive Fe ( $Fe_{HR}$ ;  $Fe_{py}/Fe_{HR} > .99$ ), intermediate  $Fe_{total}/Al$  ( $\approx .5$ ) and low  $Fe_{HR}/Fe_{total}$  ( $< .3$ ), consistent with near-complete pyritization of the highly reactive Fe delivered with the detrital mineral flux. Importantly, these conditions do not yield high  $Fe_{HR}/Fe_{total}$  and  $Fe_{total}/Al$  ratios and degrees of pyritization, our standard fingerprints of anoxia/euxinia, despite protracted exposure to high dissolved sulfide concentrations. Data from the FOAM site, in combination with past work in the Black Sea, show the necessity for additional inputs of reactive Fe to generate high  $Fe_{HR}/Fe_{total}$ ,  $Fe_{py}/Fe_{HR}$ ,  $Fe_{total}/Al$ , and degrees of pyritization, likely via an Fe-shuttle in association with syngenetic pyrite formation under euxinic conditions. Because of the oxic bottom waters, these processes are not significant at FOAM, confirming past work by Canfield et al. [1, 2]. Then, as now, FOAM provides a mechanistic keystone in our understanding of the Fe paleoredox proxies. Trace metal concentrations in FOAM sediments show only intermediate enrichment, despite very high  $[H_2S]$  in the shallow pore waters. The muted trace metal enrichments at FOAM confirm that water-column euxinia is uniquely responsible for very high concentrations and further validate the utility of the proxies in our search for euxinia in the ancient oceans. In addition, coupled Fe and Mo isotopes from both the FOAM sediments and pore waters have the potential to improve the paleoproxy potential of Fe and trace metal expressions that distinguish between euxinia and sulfide-rich and sulfide-poor diagenetic environments overlain by oxic bottom waters.

[1]Canfield, DE, Raiswell, R, Bottrell, S (1992). *Am. J. Sci.*, **Volume 292**: 659-683

[2]Canfield, DE, Lyons, TW, and Raiswell, R (1996). *Am. J. Sci.*, **Volume 296**: 818-834.