

Scaling of Ecological and Critical Zone Processes in the Prairie Pothole Region, USA and Canada

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The Prairie Pothole Region (PPR), occupying 715,000 km² of the north central U.S. and S. central Canada, is a vital ecosystem in North America. It contains >10 million wetlands that are habitat for shore and migratory birds. The wetlands are underlain by glacial till and are internally drained within discrete, km-scale basins. We studied the geochemistry of sediments, wetland water, and groundwater in the 92 hectare Cottonwood Lakes area (CWLA) of North Dakota, USA. The CWLA has upland groundwater recharge wetlands with TDS ~150 mg/kg (Ca-HCO₃ dominant), and a discharge wetland at a local topographic low only 200m distant with TDS>3000 mg/kg (Mg-SO₄ dominant). Groundwater and wetland chemistry is controlled by critical zone oxidation of marine shale-derived pyrite in the upper glacial till (mean $\delta^{34}\text{S}$ of unoxidized till = -19.9‰). A sample of the underlying marine shale has $\delta^{34}\text{S}$ value of -16.5‰. Oxidation produces an upper iron oxide rich brown zone in the till (mean depth 6.1m) supplying mobile and isotopically light SO₄ ($\delta^{34}\text{S}$ from -18.2 to -7.5‰) to the local discharge area. Dissolution of dolomite in the till is the source of Mg. Thus, critical zone oxidation processes dominate wetland water composition, which in turn is a primary control on ecology.

The same combination of upland recharge areas and local discharge areas occurs at a range of scales throughout the PPR. Information from nearly 500 well logs from a 10³ km² area surrounding the study site document oxidation of surface till to an average depth 7.8m. Comparison of CWLA geochemistry with that of literature data from 178 wetlands in this same surrounding area both document the progressive formation of SO₄ with increasing salinity. Thus, geochemical processes identified in the CWLA are likely occurring across a much larger area. Furthermore, based on our analysis of literature data, the same wetland geochemical trends occur in >300 wetlands in southern Canada.

The broad regional impact of critical zone pyrite oxidation on ecology is reflected in two published studies on the S isotope composition of juvenile mallard feathers throughout North America. These feathers are isotopically light ($\delta^{34}\text{S}$ from -5 to -16‰) in the PPR in contrast to other mallard migration corridors ($\delta^{34}\text{S}$ from -2 to +13‰), reflecting the pyrite source for sulfur in PPR breeding ground waters. We conclude that critical zone oxidation of glacial till is a key control on geochemistry and biology in the PPR ecosystem.

Multi-proxy investigation of paleoredox indicators in a permanently euxinic, low sulfate lake

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Many paleoclimate investigations require knowledge of the redox state of the ocean-atmosphere system at the time of sediment deposition. This is an essential question because it has implications for what chemical reactions are favored or suppressed in a given system and, importantly, what kinds of organisms could have lived during the time period studied. Yet, it can be very challenging to conclude with certainty whether or not a system was oxic, and could therefore support animal life. Geochemical signatures of sulfur (S) and iron (Fe) preserved in marine sediments have been utilized as paleoredox indicators because they are redox sensitive elements that are transformed as organic matter is degraded in sediment. Many of these proxies have been developed and calibrated using empirical and experimental studies of the modern, high sulfate (~28mM) ocean. However, sulfate concentration in the ocean has varied widely through Earth history from a low of <200µM to the high modern value of 28mM [1].

In this study we examine Fe speciation, S isotopes, and elemental ratios in a modern low sulfate (~275-330µM) system with permanently euxinic (i.e. anoxic and sulfidic) bottom waters. We investigate both a shallow site with oxic overlying water and a deep site with euxinic overlying water. Given the current paradigm of these paleoredox proxies, the S-Fe geochemistry preserved at these disparate sites would lead to interpretations of redox state that are different than what is observed in the modern system. We hypothesize that this is due to the small size of the sulfate reservoir and differences in sedimentation patterns between the two sites. Because sulfate levels are low and organic carbon availability is high, a relatively large fraction of the sulfate reservoir is quickly consumed during early diagenesis resulting in sediment S-Fe geochemistry that would lead to incorrect interpretations of the redox state of the environment. This investigation and future studies in low-sulfate systems are imperative towards improving our understanding of how the redox state of the ocean-atmosphere system varied during long periods of Earth history when marine sulfate levels were much lower than they are in the modern ocean.

[1] Lowenstein, T.K., Hardie, L.A., Timofeeff, M.N., & Demicco, R.V. (2003) *Geology*, **31**, 857-860.