

Size-associated distribution of ferrous and ferric iron in two Algonquin Park lakes

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Iron is integral to global biogeochemical cycling, and is increasingly studied in marine systems based on both speciation as well as size distribution. However, to date, the size-associated distribution of iron species in freshwater lakes has not been investigated. The physico-chemical properties of a lake, as well as interaction with suspended particles, bed sediments, and floc, affect the stability and bioavailability of iron compounds. Iron compounds and trace metals may be present within several operationally defined size fractions, each representing a pool that can differ in bioavailability, sorption reactivity, and mobility. In addition to trace metal concentrations, iron species and abundances are likely to change with depth as well as along creek-lake transects, indicating finer depth scale assessment will provide a more accurate picture of iron-metal dynamics in freshwater systems. Here, the objective is to gain a more thorough understanding of iron distribution within (1) a stratified, anoxic water column as well as (2) along a wetland-lake transect, (Algonquin Park, ON), by determining the relative proportion of iron species in four operationally defined size fractions: particulate (>0.45 μm), large colloidal (0.45>0.2 μm), small colloidal (0.2>0.02 μm), and dissolved (< 0.02 μm). Samples from ten depths within the Coldspring Lake water column (July 20-21, 2011) and twelve sites along the Costello Creek - Lake Opeongo transect (August 25-28, 2011) were sequentially filtered into four size fractions, and preserved for trace metal analysis by ICP-MS, and $\text{Fe}^{2+}/\text{Fe}^{3+}$ quantification by the Ferrozine method. Results assessing $\text{Fe}^{2+}/\text{Fe}^{3+}$ speciation and abundances, with linkages to trace metal concentrations, in each of these systems will be presented.

OXIDATIVE WEATHERING ON THE EARLY EARTH

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Recently accumulating evidence suggests that the biological production of oxygen in Earth's surface oceans preceded the initial accumulation of large amounts of oxygen in the atmosphere by 100 million years or more. However, the potential effects of oxygen production on surface ocean chemistry have remained little explored, and questions persist regarding both the potential role of oxidants other than molecular oxygen and the locus of oxidation of crustal material (i.e., subaerial and/or submarine settings). Here, we revisit the notion of transient and/or spatially restricted 'oxygen oases' in the Archean surface ocean by employing a simple steady-state box model of the surface ocean in a coastal upwelling system, and explore the plausibility that such a system could support the widespread oxidation of reduced crustal minerals. We find that although it is possible to establish strong air-sea gas exchange disequilibrium with respect to O_2 , there is an apparent timescale mismatch between the kinetics of oxidative dissolution and the rate at which reduced minerals delivered physically to shallow marine sediments will be buried below the zone of oxidant penetration. In addition, the circum-neutral pH of marine environments places stringent constraints on the efficacy of Fe^{3+} as an oxidant for crustal sulfides, rendering the most important sulfide oxidant in modern weathering systems ineffective. Estimated dissolution timescales compare more favorably with typical timescales of soil development, despite the much lower dissolved oxygen concentrations inferred for a subaerial environment at gas exchange equilibrium with atmospheric $p\text{O}_2$. We suggest that, although the production and accumulation of dissolved O_2 in the Archean surface ocean is probable under certain conditions and should be explored as a biogeochemical agent, it is unlikely that extensive oxidative weathering of chalcophile elements such as Mo, Re, and S occurred within the marine realm.