

Assessing the use of $^{13}\text{C}\{^1\text{H}\}$ CPMAS NMR for comparisons of boreal watershed soil and dissolved organic matter compositions

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Understanding high latitude ecosystems and their links to global carbon cycling depends greatly on our study of the composition of both dissolved and soil organic matter (DOM and SOM, respectively) and their interactions. DOM plays a major role in aquatic carbon and nutrient cycling, but may also reveal changes in landscape biogeochemistry. Headwater streams are intimately connected to and strongly influenced by the terrestrial environment such that stream DOM likely provides important chemical clues relevant to change in the watershed.

^{13}C cross polarization magic angle spinning nuclear magnetic resonance spectroscopy ($^{13}\text{C}\{^1\text{H}\}$ CPMAS NMR, hereafter referred to as CP) has been used extensively in the study of both DOM and SOM. It allows assignment of types of carbon in relative proportions, which informs our understanding of the chemical composition, source, and diagenetic state. It is well known that CP introduces a matrix effect caused by the dependence of signal strength of different carbon groups on the hydrogen environment surrounding it, resulting in types of carbon being over- or underrepresented in terms of relative proportion. ^{13}C single pulse NMR (^{13}C SPMAS NMR, hereafter referred to as SP) can be performed to determine the actual proportions of carbon types. Samples from a boreal forest headwater stream were run using both CP and SP to determine if an average correction factor (CF) could be applied by carbon type across a larger suite of DOM samples taken from a large boreal watershed in western Newfoundland. Five carbon types (aliphatic, carbohydrate, aromatic, carboxylic, and carbonyl) were assessed across all samples. Amplification or under representation of carbon types via CP was consistent in both stream DOM samples, and CFs were calculated for each carbon type. CFs were tested and consistently predicted results within 5%, on average (ranging from 0.59% to 7.7%), of carbon type percentages obtained via SP. The greatest effect observed was the underrepresentation of aromatic carbon, while both carbohydrate and aliphatic carbon were the most amplified.

This same methodological comparison was applied to litter and organic and mineral horizon soils (from the same watershed), as well as DOM derived from these soil horizons (leachates) to determine if these corrections would be consistent across sample types. While some similar CP effects were observed across both soil and leachate samples, the magnitude of these differences was less than that observed in stream DOM samples, and varied between soil and leachate samples. The larger CFs required for stream DOM samples, perhaps due to the lower carbon abundance relative to other matrix components, are particularly important as we consider how the chemical composition of stream DOM relates to the landscape. Obtaining and applying CFs for a specific study area to enable comparisons of the chemical composition of DOM in both soil and aquatic environments should facilitate our understanding of terrestrial-aquatic biogeochemical linkages, allowing a more accurate comparison across sample types.

A model for copper isotopic fractionation during weathering and transport

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A consensus appears to be forming that the fractionation of Cu isotopes in natural systems is underpinned by redox reactions (chiefly changes from Cu(I) to Cu(II) and vice-versa). The heavier Cu isotope, ^{65}Cu , is preferentially incorporated in the oxidized Cu species relative to ^{63}Cu . This has been speculated for coexisting minerals, coexisting fluid/mineral systems, and for biological systems, including microorganisms, plants, and mammals. Although additional reactions such as adsorption, organic complexation, and diffusion add complexity, Cu isotopes may prove to be a powerful tool for understanding current and historical redox processes in nature. The problem, however, is that we don't yet have a full understanding of how this redox-related fractionation process is reflected in different environments and over different scales.

Using experimental and field data collected from new and previous Cu isotope investigations, we present a conceptual model for the fractionation of Cu isotopes during the aqueous and oxidative weathering of Cu(I) sulfide minerals. The model suggests that the Cu isotopic signature of the fluid phase (relative to the mineral) is controlled by the relative rates of oxidation and leaching/transport.

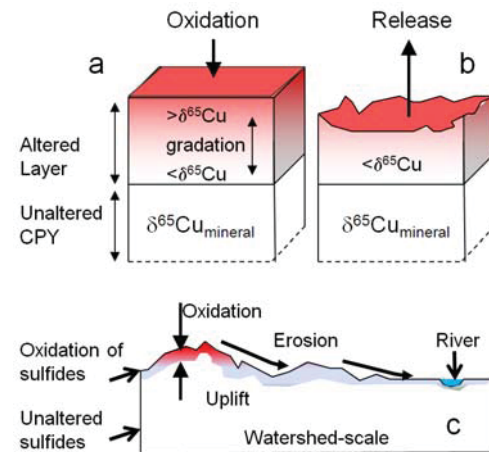


Figure 1: Conceptual model for Cu isotopic fractionation during chalcopyrite (CPY) oxidation, including (a) oxidation of Cu(I) to Cu(II) at the mineral surface followed by (b) the release of Cu into solution. Panel (c) is a cartoon watershed-scale version of this process.

We further examine how this model might be adapted from the molecular scale to watershed and continental scales, highlighting key knowledge gaps. Specifically, we address how Cu isotope controls might change from aqueous systems at low pH that are rich in dissolved Cu to higher pH systems where dissolved Cu is scarce and largely complexed by organic ligands.