

Geochemical Proxies Linked to Astronomical Climate Forcing in Dynamic Sedimentary Environments: Western Canada Sedimentary Basin.

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Abstract

Generally, coal-deposits and associated organic-rich horizons in continental successions in North-America have been interpreted to represent swamp deposits, which accumulated on the floodplain as a consequence of autocyclic or tectonic processes. However, spectral-based analyses of geochemical proxies have shown precession-eccentricity controlled stacking patterns in the Tongue River Member of the Fort Union Formation in the US. Similarly, Upper Cretaceous alternations of sand-silt-organic-rich horizons likely represent precession-controlled cycles in the Horseshoe Canyon Formation in the Western Canada Sedimentary Basin. To support the lithological proxy-data, mainly represented by the color, geochemical data has been generated for each single layer that include some of the soluble, moderately soluble and insoluble elements, and compared them with seawater and upper crustal partition abundances. All different lithologies show the same characteristics: increased abundances of Mg, Ba, Cr, Zn and lower abundances of Ca relative to the very homogeneous Coal 13 or Nevis Coal. Although the chemical index of alteration (CAI) is the most widely accepted weathering index applied to siliciclastic sedimentary rocks and it has been successfully applied to evaluate various climatic conditions in the Precambrian, in the Horseshoe Canyon Formation the CAI does not yield any clear paleoclimatic information, most probably due to mobilisation of Na⁺, K⁺ and Ca²⁺ during diagenesis or the presence of apatite. In addition a combination of grain-size effects and the possible incorporation of older weathered material may have affected the CAI-values for the deposits. For some of the elemental ratios, the redox sensitive (Cr/V)-proxy, and the Mg#, the data show trends that mirror those observed in the color proxy when normalized to the reference layer coal. Furthermore, when applying wavelet analysis to the records, periodicities appear to be more evident. This, in combination with new paleomagnetic, Ar-Ar and U-Pb (CA-TIMS) data, will enable us to link our records to the Maastrichtian, including the C29R and the K-Pg boundary. This research is funded by the European Community's Seventh Framework Program (FP7/2007-2013) under grant agreement no. 215458.

Micro- to macro-scale investigations of manganese in soil-plant systems

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Industrial processes have emitted large quantities of metals into the atmosphere which have been subsequently redistributed across the Earth's surface. As a result, we can observe enrichment of many metals in air, water, soil, and biota. Vegetation can impact the residence time of these metals in soils and their rate of transfer from soils to river systems. In particular, biotic uptake into vegetation can slow leaching and outflux of manganese contaminants from soils. Mn that is taken up by vegetation can be stored in standing biomass or returned to the soil through litterfall. In order to better predict Mn mobility in the environment, it is necessary to characterize the abundance and chemical forms of Mn-compounds in mineral soil, soil organic matter, and vegetation. Here, we combine spectroscopic techniques with molecular modeling and mass balance models to develop better ecosystem-scale understanding of Mn transport through vegetation and soils.

Spectroscopic techniques (XRF and XANES) reveal the chemical transformations of Mn that occur during its movement through the plant-soil system. Mn(II) is complexed to organic matter in roots, branches, and foliar tissue. Mn is concentrated in the foliage, where Mn(II)-organic complexes dominate, but where we have also observed a distinct chemical form of Mn localized in Mn-rich black spots. Foliar Mn is oxidized and immobilized as mixed-valence Mn-oxides in the soil during decomposition of litterfall.

To complement the spectroscopic data, molecular modeling is being used to calculate ligand-dependent shifts in the Mn K-edge energy and provides insight into the Mn oxidation state and coordination environment. Furthermore, bulk chemistry data is combined with the spectroscopic data to create mass balance models and estimate Mn fluxes between reservoirs in the soil-plant system. While bulk chemistry itself alone yields important information about Mn dynamics, techniques such as μ XRF and μ XANES can deliver further insight into the spatial distribution, oxidation state, and chemical form of Mn in soils and vegetation. As demonstrated here, integration of microscale techniques with ecosystem analysis can prove valuable to understanding ecosystem metal dynamics.