Towards reconstructing climate and ecosystem for paleoVertisols using bulk geochemistry

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Whole-rock molecular oxides, especially the Chemical Index of Alteration Minus Potassium (CIA-K) have been popularly used in the paleosol community for reconstructing climate, especially mean annual precipitation (MAP) [1, 2]. Initial approaches were universal, aggregating soil geochemical data from widely disparate soil types (e.g., soil orders, soil textural classes, soil ages, etc.). Because CIA-K ($Al_2O_3/(Al_2O_3+CaO+Na_2O)*100$) is fundamentally an index of clay formation and base loss related to feldspar weathering, it is inappropriate for one soil order that is especially well-represented in the rock record as paleosols, namely, the Vertisols, which are high clay-content soils (typically smectite mineralogy) that have a high shrink-swell potential, and commonly form from alluvium that has been "pre-weathered". Recent advances in developing MAP proxies specific for paleo-Vertisols, such as the new CALMAG index ($Al_2O_3/(Al_2O_3+CaO+MgO)*100$), have not only improved MAP estimates [3, 4], but have lead to understanding potential use of bulk geochemistry and modern soil characterization data to develop pedotransfer functions for reconstructions of colloidal soil properties such as pH, CEC, Base Saturation, etc. [5]. Carrying this a step further are ecosystem reconstructions of paleosols that evaluate soil conditions influencing net primary productivity using geochemical proxies [6]. Noteworthy is reconstruction of organic C and N in paleo-Vertisols using pedotransfer functions developed using ppm Pb in modern Vertisols [7]. The limits of application of bulk geochemistry to paleosols are as yet unknown, but it is clear that our approach for analyzing separate soil types has merit. We are currently developing a soil database that contains over 1500 US pedon and 6000 soil horizon records that can be queried using different soil wet-chemical and geochemical (whole-soil) parameters to predict specific conditions. Our initial attempts with circa 40 US Vertisol pedons to develop several new proxies specific to paleoVertisols provide more uniform MAP estimates than using CIA-K, as demonstrated by specific examples from Mississippian, Triassic, and K/T boundary paleosols. [1] Sheldon, Retallack & Tanaka (2002), *Journal of Geology* 110, 687-696. [2] Driese et al. (2005*) Journal of Sedimentary Research* 75, 339-349. [3] Nordt & Driese (2010), *Geology* 38, 407-410. [4] Adams, Kraus & Wing (2011) *Palaeo^3* 309, 358-366. [5] Nordt & Driese (2010), *American Journal of Science* 310, 37-64. [6] Nordt, Dworkin & Ashley (2011) *GSA Bulletin* 123, 1745-1762. [7] Nordt et al. (2012) *Geochimica et Cosmochimica Acta* (accepted).

Wind-driven diurnal variability in freshwater surface microlayer biogeochemistry

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Introduction

Understanding the compositional dynamics of the surface microlayer (SML) at the air-water interface of surface waters is critical because of its role in regulating the exchange of matter between the atmosphere and hydrosphere [1,2]. Temporal variability in SML biogeochemistry is poorly understood, particularly with respect to changing physico-chemical conditions. The objective of this study was to examine the geochemical and microbial composition of the SML and underlying water column (0.5 m depth) in two contrasting freshwater environments (Sunnyside Beach, Lake Ontario, a littoral hard water environment heavily impacted by anthropogenic inputs; Coldspring Lake, a pelagic environment in a small (<1 km^2) and relatively pristine soft water lake) over a diurnal timeframe during the summers of 2010 and 2011.

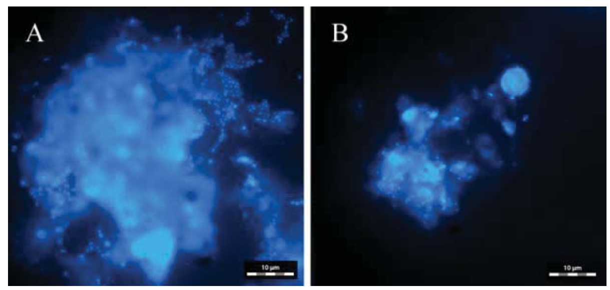

Figure 1: Fragmentation of SML microbial aggregates with increasing wind speed (from A to B, DAPI stained).

Results and Conclusion

Diurnal variability in SML biogeochemistry was closely linked to wind speed in both environments. The visual fragmentation of microbial aggregates (Fig. 1), a reduction in prokaryotic cell numbers, and an increase in dissolved organic carbon accompanied the diurnal transition from relatively quiescent to windy conditions. These changes were not observed at 0.5 m. In both environments, SML enrichment in total particulate matter and particulate iron was negatively correlated with wind speed. Particulate iron decreased in the SML and increased at 0.5m from morning to afternoon with increasing wind speed.

Collectively, these results suggest that particulate matter, including organic carbon and iron, is enriched in the SML under quiescent conditions and undergoes fragmentation over the course of a day in concert with increased wind speed. Further, wind-driven diurnal changes in SML biogeochemistry appear to be (a) conserved between contrasting freshwater environments, and (b) distinct from changes occurring at a depth of 0.5m, highlighting the unique characteristics of the SML.

[1] Cunliffe *et al.* (2011) *FEMS Microbiol. Rev.* **35**, 233-246.
[2] Hardy (1982) *Prog. Oceanogr.* **11**, 307-328.