Understanding Biomarker Records of Terrestrial Paleoecolgy

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The terrestrial biosphere is fundamental to the global climate system, influencing albedo, circulation, the water cycle, carbon sequestration and weathering. Paleobotanical records offer detailed insights to plant communities and their changes in response to climate perturbations. Leaf fossils do not lend themselves to high-resolution and continuous records through time, and although continous pollen records can be well preserved, they do not offer physiological insights such as those gained from leaf margins or stomata densities, for example. Plant biomarkers reflect plant phylogeny and functionality, and are well preserved in ancient soils and sediments. Both distributions and isotopic signatures of plant lipids are increasingly used in terrestrial paleoclimate studies.

Recent work on both modern and ancient plant biomarkers offers new ways to understand molecular records of terrestrial paleoecology. Lipid biomarker abundance and distribution patterns within modern plants are influenced both by plant phylogeneic affiliation as well as by functional properties, most notably leaf lifespan. Biomarker carbon-isotope signatures reflect both plant type and environmental factors such as seasonality, water availability, light exposure, and canopy closure. In modern leaves, these factors influence *n*-alkane $\delta^{13}C$ values, chain length distributions of homologs and total abundances in leaf tissue. Such data provide frameworks for interpreting plant-wax carbon-isotope signatures in terms of biome type and ecosystem structure, and provide constraints that aid interpretations of lipid δD signatures.

Understanding how growth environment and phylogenetic relationships influence waxes in modern plants engenders new proxies for past communities. Yet, to be useful to paleoclimate applications, biomarker and isotopic proxies based on modern plants must consider the role of litter flux that can both integrate and filter plant signatures in sedimentary archives. We extend observational data from modern flora with a statistical resampling (bootstrap) analysis to evaluate how variability in plant signatures are integrated by soil and sediment geochemical records.

We will present insights from lipid, leaf, biome and catchment-scale studies that inform our understanding of molecular record of the terrestrial biosphere. These insghts will be illustrated using examples from our studies of Cenozoic terrestrial paleoecology.

Chromium isotopes as proxy for surface oxygenation – results from a ~1.9 Ga paleosol developed on oceanic crust (Schreiber Beach, Ontario, Candada)

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The chromium isotope proxy is based on isotopic fractionation believed to accompany the oxidative weathering of Cr(III) minerals in soils. At equilibrium, oxidized Cr (Cr(VI) is predicted to be enriched in heavy isotopes, and consequently, one would expect this heavy and mobile Cr to be liberated to solution leaving an isotopically light soil behind.

In order to explore Cr isotope fractionation during soil formation, we investigated a ~ 1.9 Ga subaerial weathering profile at Schreiber Beach, Ontario, Canada. The section developed on Neoarchean (~2.8 Ga) pillow basalts and is unconformably overlain by the Paleoproterozoic (~1.88 Ga) Gunflint Chert and basal conglomerates. There are gradual textural, mineralogical and geochemical changes from unweathered basalts to strongly weathered hematite-bearing basalts with stratigraphic height.

The $\delta^{53}Cr$ value of unweathered basalts (-0.16 +/- 0.05 ‰) is within the range of mantle inventory values [1], whereas weathered brown to green basalts (soils), exhibiting up to 30% lower Cr concentrations compared to unaltered pillow cores, are isotopically lighter ($\delta^{53}Cr$ = -0.35 +/- 0.11 ‰). Red, hematite-rich (lateritic) basalts and hyaloclastites underlying the brown to green basaltic soils, instead are isotopically heavier ($\delta^{53}Cr$ = +0.05 +/- 0.15 ‰). These results speak for a process whereby ferrous Fe and likewise, Cr(VI), was leached from Fe-bearing minerals in upper soil horizons (mostly now eroded), and transported by oxygenated ground waters to lower portions of the profile where it precipitated as iron oxyhydroxides (later transformed to hematite during greenschist metamorphism after the deposition of the Gunflint Cherts) together with back-reduced isotopically heavy Cr(III) originally mobilized as Cr(VI) during surface weathering. An oxidative atmosphere at ~1.9 Ga, as implied by the results from the Schreiber profile, is furthermore supported by positively fractioned Cr isotopes ($\delta^{53}Cr$ = +0.2 +/- 0.05 ‰) recorded in the iron-rich Gunflint Cherts directly above the palaeo-weathered horizons at Schreiber Bay. These values are interpreted to reflect a positively fractionated shallow seawater chromium composition at ~1.88 Ga, a finding which is in accordance with the results of [2].

The potential of the Cr isotope system in ancient paleosols to untangle the presence of oxidative weathering processes makes this system a viable and important tracer for the reconstruction of surface oxygenation in Earth's history.

[1] Schoenberg et al. (2008) *Chemical Geology* **249**, 294-.306
[2] Frei et al. (2009) *Nature* **461**, 250-253.