Development of a new proxy for past terrestrial nitrogen cycles from chlorophyll degradation products in soil

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Nitrogen (N) is the nutrient which most commonly limits terrestrial primary production, and has an important regulatory role on the structure and functioning of ecosystems. Reconstructing past terrestrial N cycles would inform our understanding of the behavior of this nutrient in response to future changes in climate, atmospheric CO_2 levels, and plant community composition. Natural abundance stable isotopes of plant leaf N ($\delta^{15}N_f$) are useful integrators of N cycle processes in modern terrestrial systems; few tools have been available, however, for reconstructing past plant $\delta^{15}N_f$. We find that the nitrogenous plant compound, pheophytin *a* (pheo *a*), a degradation product of the chlorophyll molecule long used as a paleo-proxy in subaqueous sediments, is present at depth in soils. A trend of increasing total organic matter age with depth suggests that depth-for-time relationships may be appropriate. We here explore nitrogen isotope offsets across the leaf-litter-soil continuum, to evaluate whether plant $\delta^{15}N_f$ may be quantitatively retained in pheo *a* $\delta^{15}N$. We here report plant pheo *a* $\delta^{15}N$ ($\delta^{15}N_{phe\text{-}leaf}$) and bulk leaf $\delta^{15}N_f$ of six species across a rainfall gradient in the Kohala Mountains of Hawaii, and find that $\delta^{15}N_{phe\text{-}leaf}$ tracks $\delta^{15}N_f$ over a wide range of environmental conditions (210mm – 2500mm annual precipitation and 23°C – 17°C mean annual temperature). Comparison of bulk soil and pheo *a*-specific $\delta^{15}N$ in soil depth profiles across the same rainfall gradient reveals that the soil pheo $\delta^{15}N$ ($\delta^{15}N_{phe\text{-}soil}$) record is different from the bulk soil $\delta^{15}N$ ($\delta^{15}N_s$) record. $\delta^{15}N_{phe\text{-}soil}$ does not follow $\delta^{15}N_s$, nor does it track $\delta^{15}N_{phe\text{-}leaf}$ of modern plants at the same sites, therefore there is potential for $\delta^{15}N_{phe\text{-}soil}$ to provide a window into past plant $\delta^{15}N_f$.