Tracing the Precambrian co-evolution of atmospheric oxygen with the nitrogen and sulfur biogeochemical cycles

Common descriptions of modern biogeochemical cycles generally do not address their evolution or the crucial role of the microbial diversity. For instance the modern nitrogen cycle involves an interplay of neutral, reduced, and oxidized nitrogenous species such as molecular nitrogen (N\textsubscript{2}), ammonium (NH\textsubscript{4}\textsuperscript{+}), and nitrate (NO\textsubscript{3}\textsuperscript{−}). The nitrogen isotopic composition of modern seawater nitrate and sedimentary organic matter indicates that denitrifying bacteria and archaea (anaerobic reducers of NO\textsubscript{3}− to N\textsubscript{2}) play a dominant role in modulating the \textsuperscript{15}N/\textsuperscript{14}N ratio. However, mass-independently fractionated sulfur isotopes of sulfide and sulfate phases indicate, among other lines of evidence, that the Archean atmosphere had very low concentrations of oxygen (Farquhar et al., 2000) and therefore that NO\textsubscript{3}− may not have been stable nor abundant in the Archean. This may indicate that the Archean nitrogen cycle was different and that it may not have included major denitrification. In fact, Archean sedimentary organic matter (kerogen) is often depleted in the heavier nitrogen isotope (\textsuperscript{15}N), which may indicate that the Archean nitrogen cycle may have been dominated by nitrogen-fixing and/or ammonium-assimilating microorganisms (Beaumont and Robert, 1999). When dominant, these two metabolisms are known to result in biomass depleted in \textsuperscript{15}N and this isotopic signature is opposite to denitrification. This hypothesis is consistent with phylogenetic analyses indicating that ammonium assimilation is probably a very ancient metabolism (Kumada et al., 1993) and that likewise, nitrogen fixation may have originated before the last common ancestor. 

I perform Fourier Transform InfraRed microspectroscopic (\textmu FTIR) analyses to estimate the concentration of NH\textsubscript{4}\textsuperscript{+} in metapelitic phyllosilicates from the early Archean and the Proterozoic. When more than about 200ppm of NH\textsubscript{4}\textsuperscript{+} is present in biotite for instance, the results imply that the nitrogen originated from the biodegradation of organic matter. The isotopic composition of this ammonium is then measured by laser mass spectroscopy and our results up to now are consistent with the hypothesis that the Archean nitrogen cycle was dominated by biological nitrogen fixation and/or ammonium assimilation. Our results also indicate that the nitrogen isotopic shift observed in Paleoproterozoic kerogens (Beaumont and Robert, 1999) exists in the NH\textsubscript{4}\textsuperscript{+} of metapelitic phyllosilicates. The early Proterozoic age of the nitrogen isotopic shift is consistent with the age of the Great Oxygenation Event. Multiple sulfur isotopic ratios measured by Secondary Ion Mass Spectroscopy (SIMS) can be used to trace the rapidity of the oxygenation of Earth’s atmosphere. Archean sulfides, like pyrite, and sulfates, like barite, show mass-independent fractionation effects presumably caused by photochemical reactions in an atmosphere with very low oxygen levels (Farquhar et al., 2000). This deviance from terrestrial mass fractionation sulfur isotopic composition disappears in the early Proterozoic and I also search to evaluate how this relates to the evolution of the nitrogen cycle.