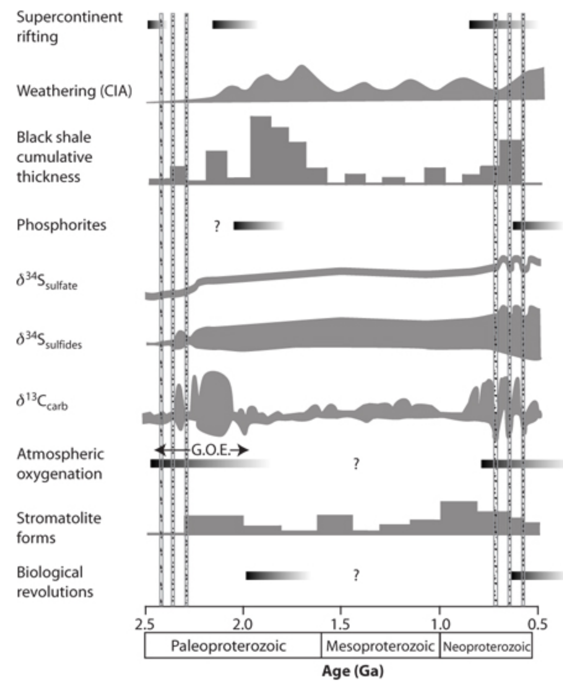
GLOBAL BIOGEOCHEMICAL CHANGES AT BOTH ENDS OF THE PROTEROZOIC: INSIGHTS FROM PHOSPHORITES. D. Papineau, Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch rd NW, Washington DC 20015, dpapineau@ciw.edu

The distribution of major phosphate deposits in the Precambrian sedimentary rock record is restricted to periods that witnessed global biogeochemical changes, but the cause of this distribution is unclear. The oldest known phosphogenic event occurred around 2.0 Ga and was followed, after more than 1.3 billion years, by an even larger phosphogenic event in the Neoproterozoic-Cambrian. Phosphorites (phosphate-rich sedimentary rocks that contain more than 15% P_2O_5) preserve a unique record of seawater chemistry, biological activity, and oceanographic changes during these periods of global change. In an attempt to emphasize the potentially crucial significance of phosphorites in the evolution of Proterozoic biogeochemical cycles, I will discuss a new model for their spatial and temporal modes of occurrence along with possible connections to global changes at both ends of the Proterozoic. Central to the new model is that periods of atmospheric oxygenation at both ends of the Proterozoic may have been caused by globally elevated rates of primary productivity stimulated locally by high fluxes of phosphorus delivery to seawater as a result of increased chemical weathering of continental crust over geologic time scales. This connection is becoming increasingly apparent with new geological and geochemical data from independent proxies as illustrated in the figure below.

A surge in tectonic activity appears to have occurred during the assembly of large continental landmasses in the Neoarchean (possibly one or more supercontinents) and when these began to break up in the earliest Paleoproterozoic. Rifting of these ancient large pieces of continental crust led to the creation of new passive margins and sedimentary basins in the Paleoproterozoic. These marine extensional basins are often sites where glacially-derived diamictites are preserved. Increased chemical weathering rates during rifting are expected to perturbed the carbon-silicate cycle by decreasing atmospheric CO_2 levels. At least three major glaciations occurred during the Paleoproterozoic.

The consequences of higher tectonic activity combined with glaciations in the Paleoproterozoic likely caused increased chemical weathering rates. Over geologic timescales (i.e. tens of millions to a few hundreds of millions of years), increased delivery to seawater of sulfate and phosphate by rivers (the dominant source of these compounds) are likely to have induced changes in biogeochemical cycles by favoring microbial sulfate reduction (as seen with larger ranges of $\delta^{34}S_{sulfide}$ values) and primary productivity. The latter may be evidenced by worldwide carbon isotope excur-



sions in carbonates, increased stromatolite forms and abundances, and the occurrence of major phosphate deposits after the glaciations. Combined with the demise of mass independently fractionated sulfur isotopes during the Paleoproterozoic glaciations, these geological and geochemical signatures have been related to the Great Oxidation Event. The ensuing biological revolution, during the latest Paleoproterozoic, is preserved as millimeter- to centimeter-size fossils from Michigan, China, India, Canada, and Russia that may represent morphological evidence of multicellular oxygen-respiring eukaryotic organisms.

A similar geodynamic context also unravelled during the Neoproterozoic with the break-up of the supercontinent Rodinia. This was also followed by several major glaciations (including snowball Earth events), increased weathering rates, and isotope excursions in sulfides, sulfates, and carbonates. Furthermore, the well-known biological revolutions of the Ediacaran and Cambrian occurred at the time of the most significant phosphogenic event in Earth's history and may thus have been the result of high rates of primary productivity and atmospheric oxygenation caused by increased nutrient delivery by rivers over geologic time scales. This new model of increased riverine phosphorus delivery leads to the conclusion that phosphorus was a key ingredient for the step-wise rise of atmospheric oxygen and for the evolution of life on Earth.