Biogeochemical cycling of P: Isotopic insights into the P-redox cycle

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Phosphorus occurs primarily as PO_4 in the +5 oxidation state and is conventionally thought of as having no significant redox chemistry. The recent discovery of several bacteria capable of using phosphite (PO_3, +3 valence) and hypophosphite (PO_2, +1 valence) as a sole source of P via oxidation to PO_4, however, led to the hypothesis that an active "P-redox cycle" exists in natural Earth systems (Metcalf and Wolfe, 1998). Subsequent investigations reveal that ca. 1% of all microorganisms are capable of Pt oxidation. More recently, a sulfate-reducing bacterium, *Desulfotignum phosphitoxidans*, that uses Pt as an electron donor has been isolated from marine sediments (Schink and Friedrich, 2000). Pt and other reduced-P compounds although not abundant, are very widespread as is the ability to metabolize these compounds. It has been put forth that on an oxygen-free early Earth, reduced-P compounds were more abundant and that Pt may have been the first water-soluble, bio-available form of P. It has been recently demonstrated for organic P-org compounds that specific phosphoenzymes have specific isotope effects that are distinguishable in laboratory and natural systems, and that PO_4 derived from P-org compounds inherits O from the Porg source (Blake *et al.*, 2005). In effort to identify and further elucidate sources and reactions of reduced-P compounds, a study of the O-isotope systematics of Pt oxidation was undertaken. The reaction mechanisms and isotopic fractionations accompanying Pt oxidation by 2 different enzymatic pathways have been investigated: (1) non-respiratory PO_3 oxidation by Pt-dehydrogenase (PtxD); and (2) Pt oxidation by *D. phosphitoxidans.* Results from these studies provide new insights into PO_3 oxidation mechanisms and specific isotopic signatures that may be used to elucidate processes in the P-redox cycle operating in modern systems and possibly on early earth.

Boron isotopic composition correlates with ultra-structure in the deep-sea coral *Lophelia pertusa*: Implications for biomineralization processes and paleo-pCO$_2$

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Using the CRPG-CNRS Cameca 1270 ion microprobe facility we have measured B isotopic compositions in different ultra-structural components in the deep-sea scleractinian coral *Lophelia pertusa*. We observe a systematic difference in the B isotopic composition of Early Mineralization Zone (EMZ) and adjacent fibrous aragonite skeleton. In EMZ, the measured $\delta^{11}B$ values are consistently low. Fibrous aragonite is characterized by systematically higher $\delta^{11}B$ values, but also display B isotopic heterogeneity associated with specific growth bands in the calyx wall. The magnitude of the observed B isotopic variations cannot be explained by changes in environmental conditions (such as seawater temperature) and are to be considered the result of biological processes involved in the biomineralization of new skeleton; i.e. ‘vital’ effects. The observed B isotopic variations are directly opposite to the predictions of existing geochemical models for vital effects, which are based on the idea that stable isotopic fractionations (including C and O) in coral skeleton are driven by changes in pH of the fluid from which the skeleton is presumed to precipitate. Our data indicate that pH variations are not responsible for the observed stable isotopic fractionations. Existing geochemical models therefore do not provide an adequate framework within which to understand coral skeletal formation. Furthermore, our observations cast in doubt efforts to reconstruct paleo-pH variations in the oceans on the basis on coral skeletal B isotopic composition.