Arsenic and phosphorus dynamics in Early Proterozoic oceans

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Arsenate and phosphate are chemically very similar and therefore tend to substitute each other in biological and non-biological molecules. However, the various chemical forms of arsenic are toxic to cells while phosphate is an essential nutrient. It is therefore important to understand the relationship between arsenic and phosphorus cycling in the discussion of phosphate bioavailability in modern and past marine ecosystems, especially those affected by hydrothermal activity. The Early Proterozoic is an important period when Earth experienced its first permanent rise in atmospheric oxygen, leading to a change in the availability and behaviour of redox sensitive elements. Particularly, increased atmospheric oxygenation likely increased the concentration of arsenate in the shallow oxygenated surface oceans. Here, we have carried out a large number of batch experiments under Early Proterozoic open marine conditions of elevated Si and Fe(II), demonstrating that arsenic may have been crucial in the regulation of dissolved phosphate content in the shallow waters through interactions with an Fe(III)(oxyhydr)oxide shuttle operating at the chemocline. We propose that competitive coprecipitation and adsorption of phosphate in the presence of arsenic species are two distinct processes, with adsorption being negligible. Strong competitive coprecipitation of phosphate by fresh Fe(III)(oxyhydr)oxides in and above the chemocline at the expense of arsenate, may have led to arsenate-rich Early Proterozoic surficial waters. Mass balance calculations coupled to regeneration of phosphate in the anoxic Fe(II)-rich bottom waters of the open ocean suggest long-term severe phosphate famine in the ocean surface waters compared to depth. Our results have implications for primary productivity and the trajectory of atmospheric oxygenation through the Proterozoic.