

Serpentinization and reduction of phosphate to phosphite in the environment

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Phosphorus is generally presumed to present in the environment as phosphate (bearing PO_4^{3-} tetrahedra) in which P bears a +5 oxidation state. As a result, in many ecosystems P is presumed to be precipitated as or adsorbed to solids due to the tight bond between phosphate and divalent and trivalent metal cations such as Ca^{2+} , Fe^{2+} , Fe^{3+} and Al^{3+} . We investigated two environments known for a highly reducing character to determine if lower redox states of P may exist in those environments, as P as phosphite (HPO_3^{2-} , P^{3+}) and hypophosphite (H_2PO_2^- , P^{1+}) are more soluble in the presence of divalent cations. Extracts of serpentinites from southwestern Oregon (USA) and from seamounts in the west Pacific both bear phosphorus as phosphite. This phosphite likely formed as olivine and pyroxene reacted with water, coupling the oxidation of Fe^{2+} to Fe^{3+} to the reduction of P^{5+} to P^{3+} [1]. Though the solid phase material that contained this phosphite could not be identified, we investigated a fulgurite from New Port Richey (Florida, USA) that bore large metallic spherules of iron silicide. Between these iron silicides a new material with formula CaHPO_3 was identified based on comparison to the diffraction patterns of the synthetic material [2]. Therefore, the solid phase carrier of phosphite in serpentinite rocks may be CaHPO_3 or something similar. These studies both highlight a potential for P redox in the environment, which is consistent with a widespread utilization of phosphite by microbes, and suggests P redox may have influenced the development of life on the earth.

[1] Pasek, M.A., et al. Serpentinization as a route to liberating phosphorus on habitable worlds. *Geochim. Cosmochim. Acta* 336 (2022): 332-340.

[2] Bindi, L., Feng, T., and Pasek, M.A. Routes to reduction of phosphate by high-energy events. *Comm. Earth. Envi.* (2023) accepted.