Phosphorous paths to phosphate minerals

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Sedimentary phosphorite (> 6 % P) formation within aqueous environments is curious, as environmental inorganic phosphate (Pi) concentrations are often too low (~1 mM Pi [1]) to exceed the supersaturation for nucleation. However, Pi concentrations exceeding 300 mM Pi have been measured within anoxic, benthic, bacterial mats [2], suggesting a biological mechanism for concentrating environmental Pi.

A 1937 review of geological phosphorite formation mechanisms identified inorganic precipitation, residual skeletons, benthic bacteria, and plankton activity [3]. An inorganic mechanism of Pi generation in anoxic environments was attributed to Fe(III) reduction and subsequent dissolution of ferric hydroxide and its adsorbed Pi species [4]. Skeletal biological apatite represents Pi concentration by biological action. Benthic bacteria accumulate Pi in oxic conditions and generate apatite in anoxic conditions [5]. Concentrated P stores in diatoms are a Pi source for benthic apatite [6] that may explain phosphorite colocated with siliceous deposits [7]. Diatoms and benthic bacteria that generate phosphorite minerals both store accumulated Pi as phosphate polymers.

Biological generation of inorganic, polymeric phosphates (polyPs) is a pathway for the storage of high concentrations of bioavailable P without the threat of exceeding the supersaturation that triggers mineral nucleation within the organism. PolyP stores are an energy source for some benthic bacteria to metabolize in anoxic conditions. Pi cleaved from polyP during this process is transported out of the organism, resulting in apatite precipitation. PolyP stores transported to the benthos within dead diatoms are a P-source for apatite mineral formation, as the Gibbs energy for polyP hydrolysis is negative, although the kinetics are slow. Skeletal apatite biomineralization may also involve a polyP intermediate, suggesting a common biochemical pathway for concentrating P, and either controlling or inducing phosphorite mineral formation in an otherwise low supersaturation environment.

[1] Conkright *et al*. (2000) *Deep Sea Res Part 1 Oceanogr Res Pap* **47**, 159-75 [2] Schulz *et al*. (2005) *Science* **307**, 416-418 [3] Kazakov (1937) *USSR Trans Sci Inst Fert Insectofung* **142**, 93-113 [4] Mortimer (1942) *J Ecol* **30**, 147-201 [5] Goldhammer *et al*. (2010) *Nat Geosci* **3**,557-561 [6] Diaz et al. (2008) *Science* **320**, 652-655 [7] Cayeux *C R Hebd Seances Acad Sci* **203**, 1198-1200