Phosphate Metabolism in a Heterogeneous Iron-Sulfur World.

A.J. PRATT[1]

[1] Department of Chemistry, University of Canterbury, NZ; andy.pratt@canterbury.ac.nz

Introduction

Iron-sulfur rich hydrothermal vent systems mediate a wide variety of processes that are required for the origin of metabolism and hence life on earth [1]: they provide a continuous input of redox energy; and catalyse a range of transformations that mimic extant FeS-dependent processes of anaerobic metabolism including carbon [2] and nitrogen [3] fixation reactions. How might phosphate be integrated as a further key element in a metabolism originating in such hydrothermal environments?

Iron(II) catalysis of biomimetic polyphosphate formation

We have shown [4] that co-precipitating activated phosphate metabolites and inorganic phosphate with iron(II) at near neutral pH in water leads to efficient formation of pyrophosphate. Acetyl phosphate and phosphoenol-pyruvate both act as activated phosphoryl donors, in yields of up to 25% and 14% respectively. The catalysis of pyrophosphate formation is tolerant of sulfide ions. These reactions mimic the extant biosynthesis of ATP from acetyl phosphate or phosphoenolpyruvate. These minerals also retard the hydrolysis of pyrophosphate. Hence heterogeneous iron(II) mineral catalysis can lead to the accumulation of polyphosphate in hydrothermal environments. The ability of iron to catalyse this reaction is in marked contrast to other metal ions, which typically are poor catalysts for this reaction in an aqueous environment.

Implications for the origins of polyphosphate metabolism

The capacity of iron (II) minerals to: concentrate phosphates; mediate phosphoryl transfer; and foster the accumulation of polyphosphates carries major implications for the origins of phosphate metabolism. This chemistry complements the range of biomimetic processes catalysed by iron-rich metal sulfide systems. It allows the interconversion of activated carbon metabolites, arising from FeS-mediated carbon fixation, with polyphosphates. This paper will discuss these implications and the possible role of polyphosphates in the bioenergetics of a heterogeneous iron-sulfur-based life in hydrothermal vent systems.

References

[1] Martin W. and Russell M.J. (2003) *Phil. Trans. R. Soc. B* **358**, 59-83.

[2] Huber C. and Wächtershäuser G. (1997) *Science* **276**, 245-247.

[3] Dörr M. *et al*. (2003) *Angew. Chem. Int. Edn. Engl.* **42**, 1540-1543.

[4] de Zwart I.I., Meade S.J. and Pratt A.J. (2004) *GCA* **68**, 4093-4098.