# CLAYS AS PROTOTYPICAL ENZYMES FOR THE PREBIOLOGICAL FORMATION OF PHOSPHATE ESTERS

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Bernal (1951) suggested that clays may have served to concentrate and orient small molecules for prebiological reactions and then protect these intercalated products from destructive reactions. This concept was extended by Cairns-Smith (1982) in his postulate that life processes were originally effected by clays and that contemporary organic compounds took over the "clay life" at a later evolutionary stage. There are no experimental reports of clay catalysis in prebiological systems that approach the chemical complexity proposed by Bernal and Cairns-Smith. In this report is outlined a system where a clay mineral behaves as a prototypical enzyme which binds substrate molecules, activates a condensing agent which causes the substrate to be converted to a product and, because the product binds less strongly than the substrate to the clay, releases it from the clay surface. This is the first example, to our knowledge, where a clay mineral exhibits these enzyme-like properties in the context of a prebiological reaction.

The catalytic role of montmorillonite clays in the formation of the phosphodiester link was demonstrated using the DISN-mediated conversion of 3'-AMP to 2',3'-cAMP (Ferris et al., 1984). The highest yield of product was obtained using homoionic $Na^+$-montmorillonite. Catalysis by the montmorillonite was demonstrated by the observation that no 2',3'-cAMP was detected in a solution-phase reaction performed under identical conditions in which the clay was omitted but a concentration of $Na^+$ was added equivalent to that associated with $Na^+$-montmorillonite.

DISN undergoes rapid hydrolysis, and so in unlikely to have served as a prebiotic nucleotide condensing agent unless it was generated in the presence of a nucleotide. We have found that the montmorillonite clay will oxidatively convert DAMN, a masked form of the condensing agent DISN, to the active condensing agent (Ferris et al., 1982). The 5.8% $Fe^{+3}$ present in the aluminosilicate clay lattice (Ferris et al., 1982) oxidizes DAMN to DISN, which in turn effects the conversion of the 3'-AMP bound to the clay to 2',3'-cAMP. The relative yields of 2',3'-cAMP were approximately the same order as observed with DISN with the exception of the higher yield observed using $Fe^{3+}$-montmorillonite.

These findings provide direct experimental support for the postulate that clays may have served as prototypical enzymes on the primitive Earth. In addition, a plausible prebiotic molecule generated from HCN via DAMN, was used as the condensing agent (Ferris and Hagan, 1982). Finally, binding studies established that the reaction product 2',3'-cAMP is not bound as strongly to $Na^+$-montmorillonite as is 3'-AMP, and so the 2',3'-cAMP will be displaced by 3'-AMP as it is formed.

Applications to the template directed reactions of 5'-AMP on montmorillonite will be discussed.

Bernal, J. D.: 1951, The Physical Basis of Life", Routledge and Keegan Paul, London.

Cairns-Smith, A. G.: 1982, "Genetic Takeover and the Mineral Origins of Life", Cambridge University Press.

Ferris, J. P., Edelson, E. H., Mount, N. M. and Sullivan, A. E.: 1979, J. Mol. Evol. 13, 317.

Ferris, J. P. and Hagan, W. J., Jr.: 1984, Tetrahedron 40, 1093.

Ferris, J. P., Hagan, W. J., Jr., Alwis, K. W., and McCrea, J.: 1982, J. Mol. Evol. 18, 304.

Ferris, J. P., Yanagawa, H., Dudgeon, P. A., Hagan, W. J., Jr., and Mallare, T. E.: 1984, Origins of Life 15, 29.

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