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Precipitation of Phosphates in a Primeval Sea

Handschuh and Orgel (*1*) have reported experiments in which struvite ($MgNH_4PO_4 \cdot 6H_2O$) was produced by the addition of ammonia to simulated (artificial) modern seawater. On this basis they surmise "that struvite may have precipitated from evaporating seawater on the primitive earth, and may have been important for prebiotic phosphorylation."

Although their speculation is interesting, it contains several unmentioned assumptions that do not seem to have attracted their attention. What precipitates from modern seawater, presumably under biochemical influences (*2*), is not hydroxyapatite but a carbonate apatite (*2, 3*). Under these circumstances it becomes difficult to understand why "Carbon dioxide was excluded from the system by means of a tube containing granules of BaO." Both present-day seawater and the phosphatic solid which forms in contact with it contain CO_2, and one wonders why Handschuh and Orgel should assume that primeval seawater did not.

The chemistry of seawater appears to be extremely complex, and the francolite (carbonate fluorapatite) which usually forms—in addition to carbonate minerals and others—cannot be predicted from a simple knowledge of the ionic activities. This is true because the types and extents of complexing are not known but probably are related to organic components of seawater that behave as positive or negative catalysts (*2*).

Although the concentration of Cl^- in seawater exceeds that of F^- by a factor of more than 10,000, it has been estimated that F^- is being removed from seawater about a hundred times faster than Cl^-, principally as phosphates and carbonates of calcium (*4*), and, while phosphorites may contain a few percent fluorine, their chlorine contents usually are almost negligible (*5*). Although it has been estimated that the concentration of F^- in vitro would have to be 100 to 1000 times greater in order for the precipitation of fluorapatite to occur (*6*), the marine brachiopod genus *Lingula* apparently does not know this and forms its shell of francolite (the fluorine content of the ash is 2.44 percent) (*7*).

Shifting consideration from seawater to physiological solutions of vertebrates can lead to some interesting analogies; with the exception of their fluorine contents, these solutions have several similarities. Whereas Handschuh and Orgel (*1*) were concerned with the greater insolubility of apatite and felt compelled to consider struvite as an alternative, there appears to be no problem connected with the resorption of deciduous teeth among mammals, and this raises a question of the extremely complex organic-inorganic relationships.

Finally, even the most ancient phosphatic sediments (phosphorites) generally contain less than 1 percent MgO, so speculations concerning relict struvite receive no support from this direction. Indeed, as Handschuh and Orgel (*1*) admit in the last sentence of their report, struvite is uncommon even as a biomineral (*8*), and it is difficult to believe that primeval seawater would behave in any such manner as their in vitro experiment implies even after the exclusion of CO_2, which was found by McConnell *et al.* (*9*) to be one of the most important factors in the precipitation of dahllite (carbonate hydroxyapatite).

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In our report we suggested that struvite would have precipitated during the evaporation of tide pools if ammonia was present in seawater at a concentration in excess of $10^{-2}M$. We did not question that apatite would also have been present in the oceans, but, since Mg^{2+} inhibits the direct precipitation of apatite, we believed that prebiotic apatites would have formed by *slow* replacement, for example, from calcium carbonate (*1*). Since the direct formation of apatites nowadays is believed to be a biological process, this process throws no light on the dynamics of prebiotic phosphate precipitation.

We did not consider the possibility that, in the presence of carbonate, carbonate apatite would precipitate in place of struvite. We took it for granted that, during evaporation, calcium carbonate would have deposited first. In view of the acknowledged complexity of such systems, we believe that it is now up to McConnell to show by experiment that this reasonable assumption (*2*) was incorrect.

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2. The same assumption seems to have been implicit in earlier studies. See, for example, (*1*), in which Mg^{2+} was shown to inhibit the precipitation of apatite, apparently in the presence of CO_2.

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