6. M. R. Tansey and T. D. Brock, *Proc. Nat. Acad. Sci. U.S.A.* **69**, 2426 (1972).
7. T. D. Brock, *Science* **158**, 1012 (1967).
8. A new photosynthetic bacterium of filamentous morphology and capable of gliding motility has been found to be widespread in alkaline hot springs [B. K. Pierson and R. W. Castenholz, *Nature* **233**, 25 (1971)]. This organism does not produce O_2 during photosynthesis, and would probably not appear in enrichment cultures. The presence of organisms with the morphology of this photosynthetic bacterium would be observed by microscopy. Although detailed studies on its distribution have not been done, filamentous organisms resembling gliding bacteria are rare in samples from acid habitats, and I have the distinct impression that they are not even found at moderately acid *p*H values where blue-green algae are present.
9. Although the exact taxonomic position of *Cyanidium caldarium* is not certain, it seems most closely related to the red algae (Rhodophyta). W. N. Doemel and T. D. Brock, *Arch. Mikrobiol.* **72**, 326 (1970); *J. Gen. Microbiol.* **67**, 17 (1971).
10. T. D. Brock and M. L. Brock, *J. Phycol.* **6**, 371 (1970).
11. M. B. Allen, *Arch. Mikrobiol.* **17**, 34 (1952).
12. R. Y. Stanier, R. Kunisawa, M. Mandel, G. Cohen-Bazire, *Bacteriol. Rev.* **35**, 171 (1971).
13. G. E. Fogg, *ibid.* **20**, 148 (1956).
14. J. W. G. Lund, in *Physiology and Biochemistry of Algae*, R. A. Lewin, Ed. (Academic Press, New York, 1962), p. 759; in *Soil Biology*, A. Burges and F. Raw, Eds. (Academic Press, London, 1967), p. 129.
15. G. W. Prescott, *Bull. Cranbrook Inst. Sci. No. 31* (1951).
16. F. Gessner, *Hydrobotanik* (VEB Deutscher Verlag der Wissenschaften, Berlin, 1959), vol. 2.
17. K. Rosa and O. Lhotsky, *Oikos* **22**, 21 (1971).
18. K. Negoro, *Sci. Rep. Tokyo Bunrika Daigaku Sect. B* **6**, 232 (1944).
19. M. Ueno, *Verh. Int. Ver. Theor. Angew. Limnol.* **13**, 217 (1958).
20. H. D. Bennett, *Castania* **34**, 306 (1969).
21. L. G. M. Baas-Becking, I. R. Kaplan, D. Moore, *J Geol.* **68**, 243 (1960).
22. I. R. Kaplan, *N.Z. J. Sci. Technol. Sect. B* **37**, 639 (1956).
23. T. D. Brock and M. L. Brock, *N.Z. J. Mar. Freshwater Res.* **5**, 233 (1971).
24. L. Margulis, *Origin of Eukaryotic Cells* (Yale Univ. Press, New Haven, Conn., 1970).
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Struvite and Prebiotic Phosphorylation

Abstract. *Struvite, $MgNH_4PO_4 \cdot 6H_2O$, rather than apatite or amorphous calcium phosphate is precipitated when phosphate is added to seawater containing more than 0.01M NH_4^+ ions. Struvite may have precipitated from evaporating seawater on the primitive earth, and may have been important for prebiotic phosphorylation.*

The concentration of dissolved inorganic phosphate in the oceans, at present, is in the range from 10^{-5} to $10^{-6}M$ (*1, 2*). It is believed that the concentration is maintained at this low value by the insolubility of minerals of the apatite group, particularly hydroxylapatite, $Ca_5(OH)(PO_4)_3$. Hydroxylapatite is a relatively inert material and cannot easily be used as a source of phosphate for the synthesis of organic phosphates of prebiological interest. A number of authors have suggested, therefore, that the insolubility and low reactivity of the most abundant phosphate mineral constitute major difficulties for theories of prebiotic synthesis (*1, 3*).

There are already a number of reports in the literature which suggest that the problem may not be as severe as it seems at first. Miller and Parris have shown that pyrophosphate is formed on the surface of apatite as a result of the action of cyanate ion (*4*). Perhaps pyrophosphate could be used as a phosphorylating agent rather than the apatite itself. We have shown that, in the presence of urea and ammonium chloride, at temperatures in the range from 85° to 100°C, hydroxylapatite will phosphorylate nucleosides and nucleotides, although slowly (*5, 6*).

There are a number of reasons for doubting that hydroxylapatite was, in fact, the only phosphate mineral at the site where life began. It is possible that the crucial site for the origin of life was an inland lake, for example, in which case the state of phosphate in the oceans would have been irrelevant. Even if life began in tide pools, it is unlikely that apatite was the major phosphate mineral available. It has been shown that hydroxylapatite is precipitated from aqueous solution only if the Ca^{2+} concentration exceeds the Mg^{2+} concentration by a factor of 5; otherwise, a much more soluble amorphous calcium phosphate is obtained (*2*). In fact, the ratio of Ca^{2+} to Mg^{2+} in present-day seawater is in the range 0.2 to 0.3 (*7*). This makes it seem unlikely that the concentration of Ca^{2+} was ever greatly in excess of that of Mg^{2+} in the prebiotic ocean, and likely, therefore, that an amorphous phosphate rather than hydroxylapatite was precipitated in evaporating tide pools.

Table 1. Phosphates precipitated from artificial seawater to which ammonia has been added.

NH_4^+ concentration ($\times 10^{-2}M$)	Nitrogen in solid (%)	X-ray pattern
5	5.45	Struvite
2	5.38	Struvite
1	2.69, 4.23	Struvite
0.5	0.15	Amorphous calcium phosphate
Authentic $MgNH_4PO_4 \cdot 6H_2O$	5.42*	Struvite

* The nitrogen values obtained in the micro-Kjeldahl determinations were consistently low by 5 to 6 percent, both for the struvite precipitated in our experiments and for authentic samples of struvite treated in the same way. Calibrations with ferrous ammonium sulfate gave correct nitrogen values. We attribute this discrepancy to the loss of ammonia during the work-up procedure.

Here we wish to examine a different possibility, namely, that the major phosphorylating mineral was struvite, $MgNH_4PO_4 \cdot 6H_2O$. There are two arguments supporting this point of view. Struvite may be used with particular advantage in certain prebiotic phosphorylation reactions (*6*). When struvite is heated with urea at 65°C, it is converted into magnesium pyrophosphate (yield, 20 percent in only 10 days). When struvite is heated with urea in the presence of nucleotides, nucleoside pyrophosphates such as uridine 5′-diphosphate and the pyrophosphate P_1,P_2-diuridine 5′-pyrophosphate are formed in good yield. The second argument is of quite a different kind. Ammonia may have been abundant in the primitive ocean, and struvite, which is surprisingly insoluble in water, precipitates readily from solutions containing Mg^{2+}, NH_4^+, and PO_4^{3-} ions. In this report we show that, under the conditions prevailing on the primitive earth, struvite may well have been the major phosphate mineral deposited from evaporating tide pools.

Magnesium ammonium phosphate of unspecified purity was purchased from Pfaltz and Bauer. All other inorganic salts were analytical reagent grade. Artifical seawater was prepared from Rila Marine Mix (Rila Products, Teaneck, New Jersey). The final concentrations of Ca^{2+}, Mg^{2+}, and HPO_4^{2-} in the artificial seawater were: Ca^{2+}, $1.13 \times 10^{-2}M$; Mg^{2+}, $4.96 \times 10^{-2}M$; HPO_4^{2-}, $5.75 \times 10^{-6}M$ (*8*).

We prepared a series of solutions of artificial seawater to which we added varying amounts of ammonium chloride. One liter of each of these solutions was maintained at *p*H 8.0 ± 0.1 at room temperature in an automatic titrater, while a solution of sodium orthophosphate was added slowly. The amount of phosphate added was never enough to precipitate more than 20 percent of the NH_4^+, Ca^{2+}, or Mg^{2+} ions. Stirring was always continued for at least 18 hours after the uptake of base had stopped. Carbon dioxide was excluded from the system by means of a tube containing granules of BaO.

The suspension of inorganic phosphates was filtered through a Millipore filter. The solid was washed with 10 ml of distilled water, then with 10 ml of 95 percent ethanol, and then with 100 ml of absolute ethanol. The solid was finally dried in a vacuum over silica gel for several hours. The dried mixture of phosphates was then analyzed for ammonia by a micro-Kjeldahl method (*9*). Finally, x-ray powder photographs of the solids were taken and compared with those of struvite, hydroxylapatite, and the amorphous phosphate that is precipitated when sodium phosphate is added to seawater. The results of the precipitation experiments are shown in Table 1.

According to Bada and Miller, the concentration of NH_4^+ in the primitive oceans when life began is likely to have been in the range from 10^{-3} to $10^{-2}M$ (*10*). Other authors have questioned whether so much ammonia could have been present (*11*). If the interpretation of Bada and Miller is correct, the concentration of NH_4^+ in evaporating tide pools may have been $10^{-2}M$ or even higher. We have shown here that under those circumstances struvite would have precipitated rather than hydroxylapatite or the more soluble amorphous calcium phosphate. We emphasize that the precipitation of struvite does not represent an equilibrium process; hydroxylapatite is much less soluble than struvite but cannot form in the presence of Mg^{2+}.

If ammonia was abundant on the primitive earth, the evaporation of prebiotic lakes or tide pools could have led to the formation of solid films containing struvite, urea, and other organic compounds including, perhaps, nucleosides and nucleotides (*5*). Then phosphorylation would certainly have occurred at the temperatures reached by dark-colored rock surfaces in strong sunlight. [Temperatures up to 90°C have been recorded in deserts (*12*). We do not have corresponding values for tropical shorelines, but we think it likely that the temperature exceeds 65°C in many places.] We believe that this interpretation provides an attractive mechanism for the prebiotic synthesis of nucleotides such as uridine 5′-phosphate and, particularly, of nucleoside diphosphates such as uridine 5′-diphosphate on the primitive earth.

These considerations lead to one further speculation. All living cells are rich in K^+ and poor in Na^+, although Na^+ is much more abundant than K^+ in the inorganic environment. We would like to suggest the possibility that the K^+ in contemporary organisms replaces NH_4^+ that was present in the Precambrian organisms. The isomorphism of many NH_4^+ and K^+ salts is well recognized, and it is a striking fact that NH_4^+ can replace K^+ in protein synthesis, although NH_4^+ is toxic to most contemporary cells. If this hypothesis is correct, then the possibility that struvite was important for the origins of life becomes particularly attractive. Struvite would have provided the major intracellular inorganic ions, other than chloride, for primitive cells. The fact that substantial amounts of K^+ can replace NH_4^+ isomorphously in struvite (*13*) allows us to understand how a continuous transition from a biological system rich in NH_4^+ to one containing K^+ could have taken place when the atmosphere became oxidizing and ammonia began to disappear from the surface of the earth. Nowadays struvite occurs only in association with organic matter, for example, in bat caves and canned fish (*14*).

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References and Notes

1. A. Gulick, *Amer. Sci.* **43**, 479 (1955); *Ann. N.Y. Acad. Sci.* **69**, 309 (1957).
2. C. S. Martens and R. C. Harriss, *Geochim. Cosmochim. Acta* **34**, 621 (1970), and references therein.
3. S. L. Miller and H. C. Urey, *Science* **130**, 245 (1959).
4. S. L. Miller and M. Parris, *Nature* **204**, 1248 (1964).
5. R. Lohrmann and L. E. Orgel, *Science* **171**, 490 (1971).
6. G. J. Handschuh, unpublished data.
7. R. A. Horne, in *Advances in Hydroscience*, V. T. Chow, Ed. (Academic Press, New York, 1970), vol. 6, p. 116.
8. The concentrations in seawater are: Ca^{2+}, $1.0 \times 10^{-2}M$; Mg^{2+}, $5.6 \times 10^{-2}M$; HPO_4^{2-}, variable in the range from 10^{-5} to $10^{-6}M$.
9. C. J. van Nieuwenburg and J. W. L. van Ligten, *Quantitative Chemical Micro-Analysis* (Elsevier, Amsterdam, 1963), pp. 158–162.
10. J. L. Bada and S. L. Miller, *Science* **159**, 423 (1968).
11. P. H. Abelson, *Proc. Nat. Acad. Sci. U.S.A.* **55**, 1365 (1966); J. P. Ferris and D. E. Nicodem, *Nature* **238**, 268 (1972).
12. See some statements of D. Halvorsen, National Weather Service, cited in the San Diego, *Union*, 15 July 1972, p. B1; J. H. Chang, *Ground Temperature I* (Blue Hill Meteorological Observatory, Harvard University, Cambridge, Mass., 1958).
13. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, J. I. Hoffman, *Applied Inorganic Analysis* (Wiley, New York, ed. 2, 1953), p. 637.
14. J. R. Van Wazer, *Phosphorus and Its Compounds* (Interscience, New York, 1958), vol. 1, p. 852.
15. This work was supported by NASA grant NGR 05-067.

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Sexual Differentiation of Pituitary Function: Apparent Difference between Primates and Rodents

Abstract. *Surges in luteinizing hormone secretion resembling those which occur spontaneously during the menstrual cycle were induced by acute elevations in circulating estrogen concentrations in both male and female rhesus monkeys gonadectomized in adulthood. These experiments demonstrate that in primates, in contrast to rodents, exposure of the hypothalamohypophyseal unit to androgens throughout fetal and postnatal development does not prevent the differentiation of the control system that governs cyclic gonadotropin secretion.*

The control of gonadal function in all mammals is mediated by the secretion of follicle-stimulating hormone (FSH) and luteinizing hormone (LH) by the anterior lobe of the pituitary gland. In a number of species, including man, the secretion of these hormones in males is relatively constant (tonic), whereas secretion of these gonadotropins in females is cyclic, characterized by periodic discharges (surges) that eventuate in ovulation (*1*).

In the rat, gonadotropin secretion by the pituitary is governed by two hypothalamic control systems, one regulating tonic secretion, the other governing cyclic release of the preovulatory gonadotropin surge (*2, 3*). Both systems are normally operative in the female, but the cyclic system appears to be nonfunctional in the male (*1, 2*). This sexual difference in the rat is attributable to an irreversible organizing action of testicular androgens during a critical period of neural differentiation (*1, 2*).

In the adult female rat, a daily signal, coupled to the diurnal light-dark cycle, is transmitted to the control system for cyclic gonadotropin secretion but is relayed only when concentrations of circulating estrogens are elevated (*3, 4*). Thus, estrogen administration to ovariectomized rats will result in LH surges at the appropriate time of day (*5, 6*). This response to estrogen cannot be elicited in male rats castrated in adulthood or in females exposed to androgen during the neonatal period, but can be evoked in male rats cas-