

CHEMICAL REDUCTION OF PHOSPHATE ON THE PRIMITIVE EARTH

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Abstract. If phosphorus played a role in the origin of life, some means of concentrating micro-molar levels of phosphate (derived from the calcium phosphate mineral apatite), must first have been available. Here we show that simulated (mini)lightning discharges in model prebiotic atmospheres, including only minimally reducing ones, reduce orthophosphates, including apatite, to produce substantial yields of phosphite. Electrical discharges associated with volcanic eruptions could have provided a particularly suitable environment for this process. Production of relatively soluble and reactive phosphite salts could have supplied a pathway by which the first phosphorus atoms were incorporated into (pre)biological systems.

1. Introduction

The relative insolubility of apatite is a recognized problem in the origin of life. In a perceptive review of the role of phosphate in the origin of life, Gulick (1955) proposed that reduction of phosphate might have led to the formation of water-soluble salts of hypophosphorous (H_3PO_2) and phosphorous (H_3PO_3) acids (hypophosphites and phosphites) on the primitive Earth, and that the first organisms utilized such 'low-oxygen compounds' for their metabolisms. This proposal has not been widely accepted, since the reduction of orthophosphate is a highly endergonic process (Miller and Urey, 1959). In a later review of the likely prebiotic sources of phosphorus, it was postulated that the reduction of phosphate to elemental phosphorus, phosphine and phosphorous acid might have occurred as a result of core formation in the early Earth (Schwartz, 1972). The unique conditions at the time of core formation, considered together with the known process of high temperature reduction of phosphate by carbonaceous material, was suggested as a possible mechanism for the reduction. Because of the possibility that the high temperatures generated in lightning discharges might, under reducing conditions, similarly be capable of reducing phosphate, we decided to carry out a test of the hypothesis using simple apparatus.

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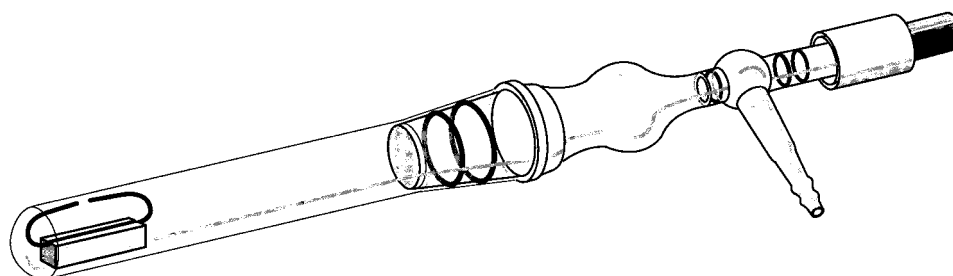


Figure 1. Experimental assembly. After applying samples to quartz caps (not shown) covering the ends of the open tungsten loop and filling the system with gas, the entire assembly was placed into a 1 kW commercial (domestic) microwave oven. A spark discharge between the ends of the loop occurred several seconds after applying a microwave field.

2. Materials and Methods

Sodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, p.a.) was from Merck. Fluorapatite (Mexico) and montmorillonite #26 were purchased from Ward's. Dowex AG 50W-X8 was from Bio-Rad. Methane (99.9995%) and nitrogen (99.999%) were from Air Liquide. Water was double-distilled.

Our experimental arrangement consisted of a 10 cm length of tungsten wire (1 mm diameter) which was bent into the form of an open loop (Figure 1). Samples were applied as solutions (in the case of Na_2HPO_4) or as pastes (mixtures of fluorapatite with montmorillonite) to the ends of the loop. Fluoroapatite and montmorillonite samples were ground separately and mixtures were prepared by grinding with addition of a small amount of water. In order to rule out any possibility that metallic tungsten could play a role in the reduction, we covered the ends of the loop with capillary sleeves constructed of quartz and sealed at one end. The phosphate-containing samples were applied to the quartz and did not come into contact with metal. After application, samples were dried under vacuum over NaOH and weighed by difference (1–3 mg). The loop was placed on a quartz stand and transferred into a quartz tube. Water (1 mL) was introduced into the vessel, frozen by immersion of the tube into liquid N_2 , and the system was degassed under vacuum (three freeze-thaw cycles with back-filling with N_2). After introducing the required gas mixture, the reaction assembly was placed into a 1 kW commercial (domestic) microwave oven, and the microwave source switched on. After several seconds, a bright discharge was observed. The discharge was ended by switching off the power after approximately two seconds (range, 1.6 to 2.1 s). We made no attempt to study the influence of the length of the discharge time on the yield.

At the conclusion of each experiment, the tubes were cooled and the contents were extracted several times with water (total volume 30 mL). Water extracts were filtered and evaporated to dryness under vacuum. Residues were dissolved in 3–4 mL of water, passed through a column (10 × 0.8 cm) of Dowex 50W-X8 (H^+ , 50–100 mesh) to convert sodium salts to free acids and evaporated to dryness.

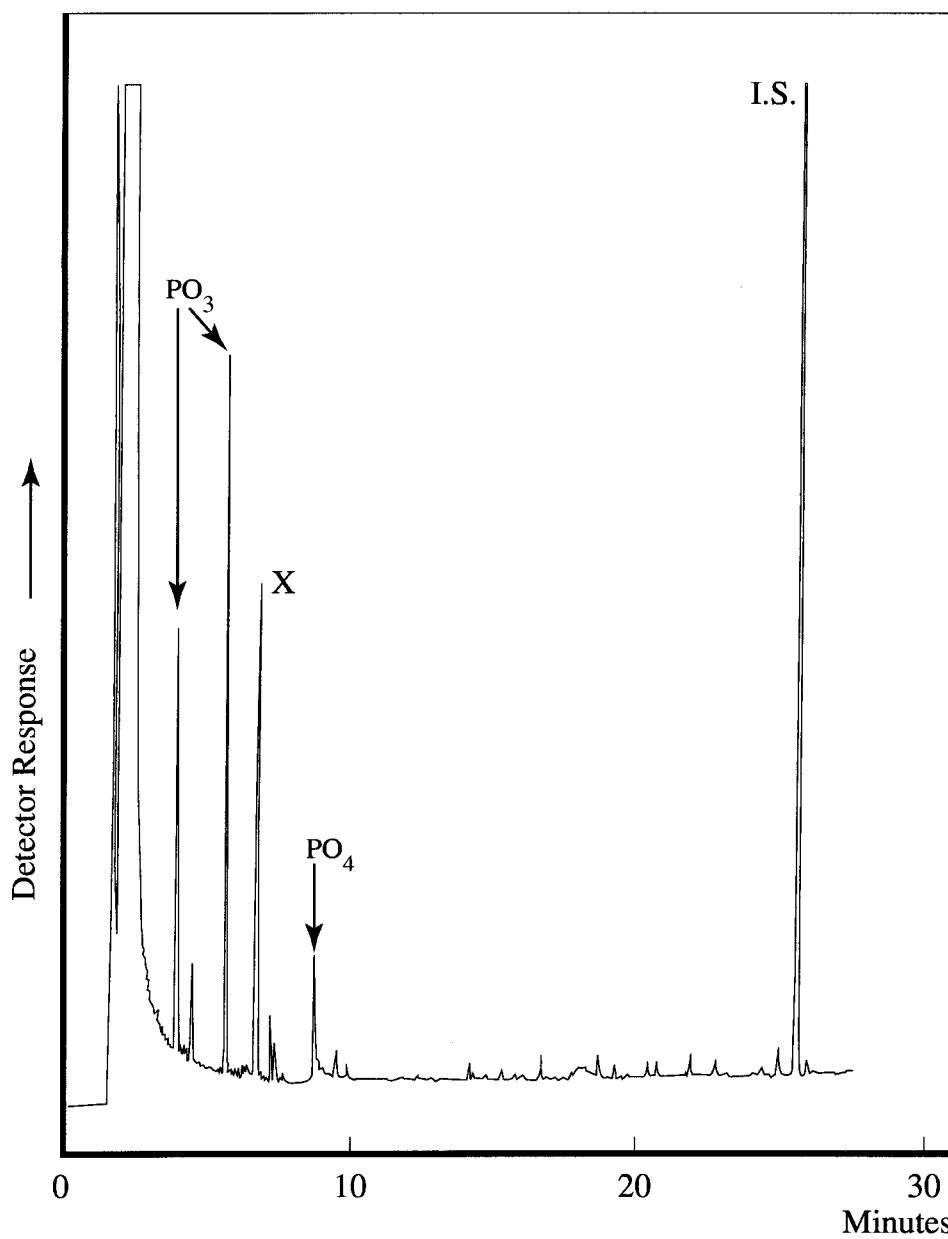


Figure 2. A typical gas chromatographic analysis of products. The peaks are labelled as follows: PO₃, the di(trimethylsilyl) and tri(trimethylsilyl) derivatives of phosphorous acid; PO₄, the tri(trimethylsilyl) derivative of orthophosphoric acid; X is derived from H₂WO₃ (tentatively identified as the di(trimethylsilyl) derivative) and is an artifact of the extraction of the tungsten loop. I.S. is the internal standard (phenanthrene).

TABLE I
Formation of phosphite by reduction of orthophosphate in CH₄ + N₂ mixtures^a

Phosphate source	Matrix ^b (wt % phosphate)	CH ₄ (% in N ₂)	Phosphite produced ($\mu\text{mol}/\text{mg sample} \times 10^2$)	Yield (%)
Na ₂ HPO ₄	–	10	30.0±9	11
Na ₂ HPO ₄	–	1	11.0±3	4
Na ₂ HPO ₄	–	0	0.3±0.4	0.1
Hydroxyapatite	Mont. (20)	10	7.0±1	6
Fluorapatite	Mont. (20)	10	9.0±0.7	7
Fluorapatite	Mont. (20)	1	4.0±2	4
Fluorapatite	Mont. (20)	0	0.6±0.6	0.5
–	Mont.	10	<0.1	–

^a The yield of phosphite is based on the amount of phosphate deposited on the loop. For hydroxyapatite and fluorapatite the theoretical formula weights have been used. Yields are averages of three to seven determinations and \pm indicates the average deviation of the mean.

^b Mixtures were prepared with montmorillonite #26, containing the indicated wt % of the phosphate mineral shown.

Analysis by gas chromatography-mass spectrometry (GC-MS) was as described previously (De Graaf *et al.*, 1995). In a few cases we also checked for the presence of hypophosphite by qualitative thin-layer chromatography (Grassine and Ossicine, 1962).

3. Results

The experimental conditions and results are summarized in Table I. In 10% CH₄ in N₂ (v/v) an average yield of 11% phosphite was obtained using Na₂HPO₄ as the source of phosphorus. In several of these experiments we could also detect small yields (up to about 0.5%) of methylphosphonic acid by gas-chromatography (data not shown) as well as traces of hypophosphite. The yield of phosphite decreased to 4% in 1% methane, and to 0.1% in pure N₂.

In order to extend these results to a geochemically more plausible model, we then examined the reduction of fluorapatite – the most important accessory phosphate mineral in igneous rocks (Koritnig, 1978) – by preparing mixtures of fluorapatite (20%) with the clay mineral montmorillonite. In these experiments, a yield of 7% phosphite was obtained in the presence of 10% methane. As with the experiments with Na₂HPO₄, the yield of phosphite decreased, but was still substantial, as CH₄ was decreased from 10% to 1% in N₂. These results suggest that gas mixtures which are only marginally reducing may be effective for this process.

4. Discussion

We suggest the following mechanism of reduction of phosphate. The electrical discharge produces a hot plasma containing atomic and molecular radicals which originate from the gases present, as well as by volatilization of the target solid phase. We have not been able to measure the spark temperature in our simulations exactly, but estimate that the temperature of the sample may have approached 3000 K. By rapid cooling of the plasma, recombination products such as phosphite are kinetically trapped. Although we have thus far only been able to systematically examine materials containing relatively high proportions of phosphate, we are encouraged to think that apatite present in most common igneous minerals, which typically contain 0.2% P_2O_5 (equivalent to about 0.5% fluorapatite) but can exceed this value (Koritnig, 1978), might be similarly reduced.

We do not believe that the direct effect of lightning upon minerals has been considered previously in the prebiotic context. Although lightning is often thought to have been a potent source of chemical activation on the primitive Earth, it is generally the atmospheric effects of lightning or corona discharge processes which have been modelled (Miller, 1953). Several authors have called attention to the possible prebiotic importance of lightning associated with volcanic activity and the presence of reduced gases (Podkletnov and Markhinin, 1981; Lavrentiev *et al.*, 1984; Hill, 1992; Basiuk and Navarro-Gonzalez, 1996; Navarro-Gonzalez *et al.*, 1996, 1998). Although the potential significance of the presence of volcanic ash in proximity to lightning has therefore been considered, and even modelled (Lavrentiev *et al.*, 1984; Navarro-Gonzalez *et al.*, 1998), the role envisioned has been that of adsorption and catalysis of reactions among the initial products of gas-phase reactions. We now suggest that the direct interaction of volcanic lightning with ash particles in a volcanic eruption cloud, in which locally higher concentrations of reduced gases are combined with the presence of highly dispersed phosphate-containing minerals, represents a possible source of soluble phosphorus-containing compounds on the primitive Earth. The mineral andesite, which is a reasonable average composition for volcanic ash in such clouds, contains 0.3% P_2O_5 (Macdonald, 1972).

We find the production of several percent of phosphite under the relatively crude conditions of our experiments to be surprisingly high. An eruption cloud could have provided much more favourable circumstances for reduction. An idea of the amount of ash which might be exposed to lightning in an eruption can be given by the eruption of Sakurajima, for which the mass loading of the plume was calculated to be $5 \times 10^{-3} \text{ kg m}^{-3}$, and by the Mount St. Helens eruption, for which the initial eruption cloud was calculated to have supported a total of $8.5 \times 10^{-3} \text{ kg m}^{-3}$ of fine particles (Gilbert and Lane, 1994). Let us suppose that 10 m^3 of such a cloud, containing up to 100 g of dust, were heated by each flash of lightning, so as to approximate the conditions in our experiments. We calculate, similarly to Hill (1992) that, on the primitive Earth, the rate of production of phosphite rained out of the cloud into a typical 'catchment area' could have been $1.3 \times 10^{-9} \text{ mol cm}^{-2} \text{ yr}^{-1}$

(Based on of 3.15×10^5 lightning flashes per year in a typical volcanic eruption, a phosphite yield per flash of 0.1, and an average catchment area of 10^{11} cm^2). This rate is about two orders of magnitude less than Hill's estimate of the production rate of HCN in prebiotic volcanic areas ($3.5 \times 10^{-7} \text{ mol cm}^{-2} \text{ yr}^{-1}$), but is still more than two orders of magnitude greater than the global rate estimated by this author. Considering the fact that HCN is thought to have been the single most important precursor compound in chemical evolution, this does not seem to be a highly unfavourable ratio. In addition, phosphite could have been concentrated by evaporation in a catchment pool, a process which could not have been of significance with HCN because of its volatility. It should be noted that Hill's calculations were based on a 'reducing model' of primitive volcanic gases. In calculations and simulations in which 'neutral' models (or gas mixtures containing substantially more O than C) have been studied, NO rather than HCN is the major product (Chameides and Walker, 1981; Navarro-Gonzalez *et al.*, 1998). Our experiments have produced several percent yields of phosphite with gas mixtures containing as little as 1% CH_4 in N_2 . In addition, preliminary results indicate that CO may be substituted for CH_4 with little effect on the yields. These observations suggest that primitive volcanoes, which may have produced higher concentrations of reduced gases than contemporary ones (Kasting, 1993), may have been important sources of phosphite on the primitive Earth.

Volcanic areas are, of course, quite commonly mentioned in scenarios for the origin of life, since rapid evaporation and the resulting increased concentration would be favourable for chemical evolution (Schwartz and Henderson-Sellers, 1983). The present work adds a new perspective to such considerations.* In previous work, we have shown that ultraviolet irradiation of solutions of phosphite in the presence of simple organic compounds leads to the synthesis of phosphonic acids (De Graaf *et al.*, 1995, 1997), the only group of phosphorus-containing organic compounds to have been detected in meteorites (Cooper *et al.*, 1992). The photochemical reaction pathway for the synthesis of phosphonic acids from phosphite solutions can now be regarded as a potentially sustained source of phosphorus-containing compounds for chemical evolution. In addition, since calcium phosphite is approximately $1000\times$ more soluble in water than calcium phosphate,† the probabilities of reaction with other prebiotic molecules are correspondingly greater. Thus, phosphite may also have reacted thermally with nucleosides to form nucleoside phosphites, a pathway to nucleotides which we are currently investigating.

* An additional source of phosphorus which should be mentioned in this context is direct volatilization of P_4O_{10} . Yamagata *et al.* (1991) demonstrated volatilization of phosphate at 1200°C and found concentrations of several micromoles per liter of condensed phosphate in a fumarole at Mount Usu, Japan.

† The solubility of CaHPO_3 has apparently not been determined exactly. In preliminary measurements, we find that the solubility is greater than 0.001 M, which was the concentration of phosphite employed by De Graaf *et al.* (1995, 1997).

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