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Cyclophosphates, a new class of native phosphorus compounds, and some insights into prebiotic phosphorylation on early Earth

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ABSTRACT

Cyclophosphates are a class of energy-rich compounds whose hydrolytic decomposition (ring opening) liberates energy that is sufficient for initiation of biomimetic phosphorylation reactions. Because of that, cyclophosphates might be considered as a likely source of reactive prebiotic phosphorus on early Earth. A major obstacle toward adoption of this hypothesis is that cyclophosphates have so far not been encountered in nature. We herein report on the discovery of these minerals in the terrestrial environment, at the Dead Sea basin in Israel. Cyclophosphates represent the most condensed phosphate species known in nature. A pathway for cyclophosphate geosynthesis is herein proposed, involving simple pyrolytic oxidation of terrestrial phosphides. Discovery of natural cyclophosphates opens new opportunities for modeling prebiotic phosphorylation reactions that resulted in the emergence of primordial life on our planet.

INTRODUCTION

Phosphorus belongs to a narrow group of elements that likely determined the emergence of life on the early Earth (Gulick, 1955; Griffith et al., 1977; Pasek, 2020). In living organisms, phosphorus occurs as inorganic orthophosphates, in general as hydroxylapatite [$Ca_5(PO_4)_3(OH)$], as long-chain polyphosphates, and in the form of organophosphorus moieties, with domination of phosphate esters (Qian, 2007; Pasek, 2020). The latter are mandatory building blocks of DNA, RNA, phospholipids, and energy transmitters such as adenosine triphosphate (ATP). The formation of the phosphoester bond, C–O–P (phosphorylation), is an energy-consuming reaction that is realized in the biological kingdom via enzymatic catalysis (Qian, 2007; Pasek, 2020). However, looking back into the expectedly inorganic and hence enzyme-free evolution of primitive Earth, the question arises on which phosphorus compounds could be involved in prebiotic phosphorylation and thus in the emergence of primordial life (Pasek et al., 2017; Horsman and Zechel, 2017; Kitadai and Maruyama, 2018). A plausible hypothesis invokes aqueous oxidation or amidation of natural phosphides—the minerals bearing phosphorus in an oxidation state lower than zero (Gulick, 1955; Bryant and Kee, 2006; Britvin et al., 2015; Gibard et al., 2019). Yet another class of potent phosphorylation agents is cyclophosphates (polymetaphosphates)—high-energy compounds whose hydrolytic ring opening releases energy sufficient for the onset of biomimetic phosphorylation reactions (Yamanaka et al., 1988; Gibard et al., 2018). Unfortunately, cyclophosphates, although widely used in synthetic chemistry and industry (Bezold et al., 2020), have never been encountered in nature. In the course of ongoing research on natural phosphide assemblages at the Dead Sea basin (Britvin et al., 2015, 2021), we have discovered natural cyclophosphate minerals for the first time. We herein provide a brief characterization of their occurrence, explain their origin, and discuss the possible involvement of cyclophosphates in prebiotic phosphorylation reactions that could have occurred on primordial Earth.

THE MOTTLED ZONE (HATRURIM FORMATION)

We discovered cyclophosphates in mineral assemblages confined to a rock complex known as the Hatrurim Formation or the "Mottled Zone" (Gross, 1977; Burg et al., 1999). The outcrops of this enigmatic geological suite spread over a vast area of the Middle East in Israel, Palestinian Authority, and Jordan (Fig. 1A). The name "Mottled Zone" originates from the unusual appearance of its rocks, colored in a variety of red, brown, green, yellow, and black shades (Gross, 1977). The rocks are composed of severely calcined or even melted sedimentary strata that underwent surface-subsurface natural annealing at temperatures approaching 1400 °C—the geological process known as pyrometamorphism or combustion metamorphism. The source of incoming heat required for the onset and maintenance of pyrometamorphic processes remains debatable. Early hypotheses invoked spontaneous combustion of bituminous matter (Gross, 1977; Burg et al., 1999), whereas the latest hypothesis explains high temperatures by firing of natural methane (Novikov et al., 2013). Determinations of the geological age of the pyrometamorphic suite in the Hatrurim Formation give values between 16 and 2.5 Ma (e.g., Sokol et al., 2019). The two largest Mottled Zone fields are exposed in Jordan (the Daba-Siwaqa complex) and Israel (the Hatrurim Basin) (Fig. 1A). The Hatrurim Basin covers an area of ~50 km^2 near the Dead Sea, between the town of Arad and Mount Sedom (Fig. 1B). The Mottled Zone and, in particular,

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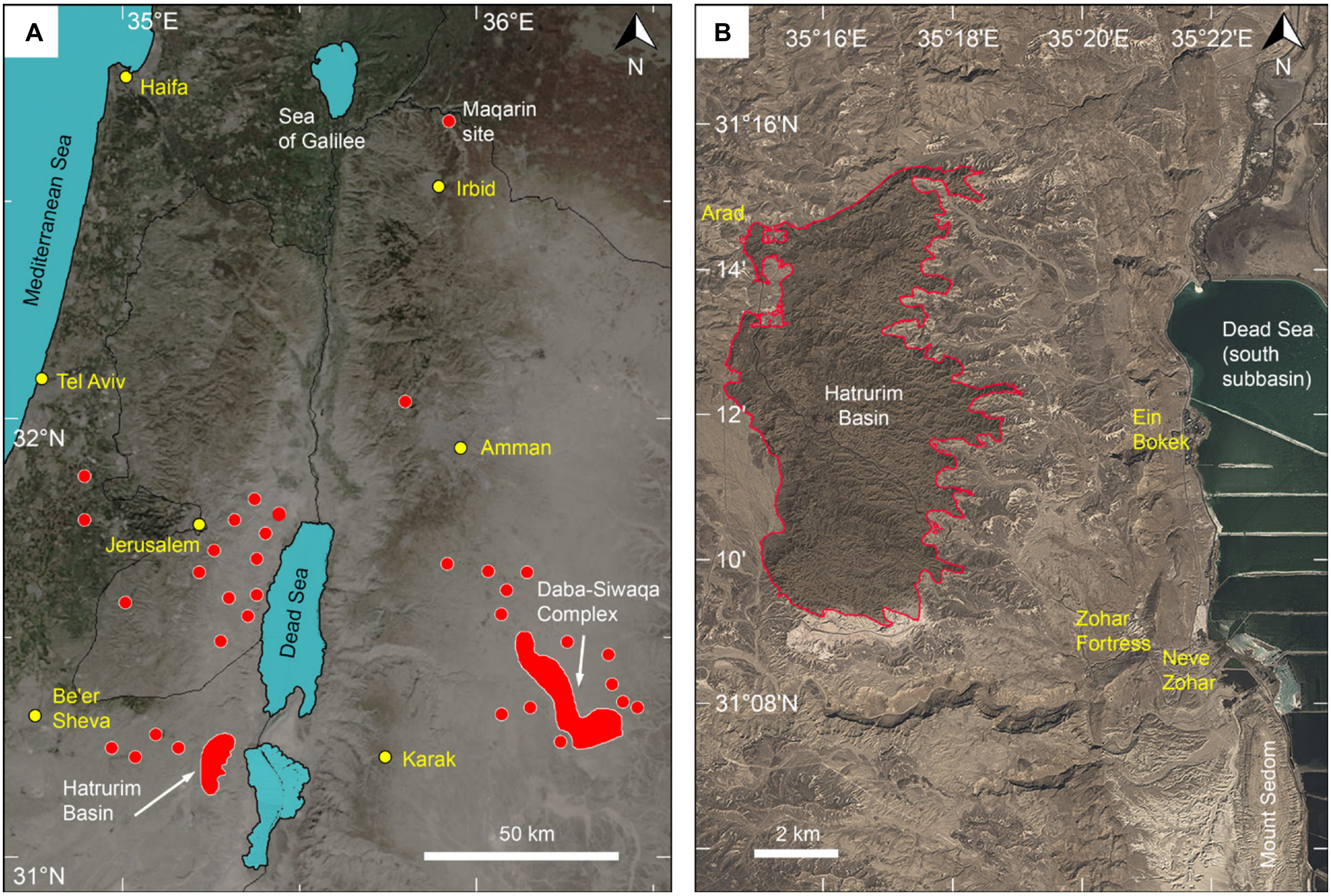

Figure 1. Mottled Zone (Hatrurim Formation) in the Middle East. (A) General view of the study area. Mottled Zone outcrops are marked with red circles and patches. (B) Hatrurim Basin in Israel, site of our cyclophosphates discovery. Topographic background was adapted from an image freely distributed under the CC-BY 2.0 license (flickr.com/photos/148318224@N03/34460561521/).

the Hatrurim Basin are known for a diversity of unusual minerals originated as a result of combustion metamorphism (Gross, 1977; Galuskina et al., 2017; Sokol et al., 2019). A suite of terrestrial phosphides—the minerals containing this element in a negative oxidation state—was recently discovered in the Hatrurim Basin and in Daba-Siwaqa (Britvin et al., 2015, 2020).

THE CYCLOPHOSPHATES

Cyclophosphates (cyclotetraphosphates) related to a solid solution of tetrametaphosphates $Fe_2P_4O_{12}$–$Ni_2P_4O_{12}$ were discovered in the phosphide-bearing rock samples from the Halamish wadi (Nahal Halamish) in the Hatrurim Basin. Cyclophosphates occur as translucent, yellow-green microcrystalline aggregates disseminated in the silicate-carbonate rock matrix. Figure 2 shows the largest encountered cyclophosphate aggregate, 0.15 mm in the maximum dimension. The minerals form intimate intergrowths with other, yet unnamed, natural orthophosphates and pyrophosphates (Fig. 2). It is noteworthy that in all rock fields where we detected cyclophosphates, they are confined to the grains of zuktamrurite, $(Fe,Ni)P_2$ (Fig. S1 in the Supplemental Material[1]) (Britvin et al., 2019). The identity of the discovered minerals was proven *in situ* by a combination of three complementary analytical techniques. We determined the chemical composition using an electron microprobe analysis. The different cyclophosphate grains vary in composition from Ni-dominant to Fe-dominant (Table S1 in the Supplemental Material) and, in fact, represent two different minerals, $(Ni,Fe)_2P_4O_{12}$ and $(Fe,Ni)_2P_4O_{12}$, respectively. The structural identity of cyclophosphates was confirmed by electron backscatter diffraction (EBSD) (Fig. S2), which unambiguously showed that the minerals are isostructural with synthetic $Fe_2P_4O_{12}$ and $Ni_2P_4O_{12}$ (Nord, 1983; Genkina et al., 1985). It is noteworthy that the structural type of $Ni_2P_4O_{12}$ (Nord, 1983) is unique in both lattice metrics and unit-cell contents, having no analogs among inorganic compounds. The Raman frequencies in the spectra of natural cyclophosphates (Fig. 3) are consistent with the data previously reported for synthetic $Fe_2P_4O_{12}$ and $Ni_2P_4O_{12}$ (Viswanathan et al., 1985). The absence of Raman bands in the O-H stretching region evidences the lack of hydroxyl groups, in accordance with the crystal structure of the mineral.

CYCLOPHOSPHATES AND PREBIOTIC PHOSPHORYLATION

The main building block of cyclotetraphosphate structure is a ring, $(P_4O_{12})^{4-}$, composed of four orthophosphate tetrahedra, corner linked via shared oxygen atoms (Fig. 4). The bridging P–O–P bonds, also known as "phosphoanhydride bonds" (Müller et al., 2019), are substantially longer (>1.6 Å), and hence considerably weaker, than the terminal P = O bonds of isolated $(PO_4)^{3-}$ groups of ordinary orthophosphates (Nord, 1983; Genkina et al., 1985). Because of their relative weakness, phosphoanhydride bonds are prone to hydrolytic breakdown (Watanabe et al., 1975). The latter reaction, occurring with highly strained tri- or tetracyclic rings of cyclophosphates, is accompanied by

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[1] Supplemental Material. Topographic coordinates of collected samples, details of analytical procedures, and characterization of minerals. Please visit https://doi.org/10.1130/GEOL.S.13182980 to access the supplemental material, and contact editing@geosociety.org with any questions.

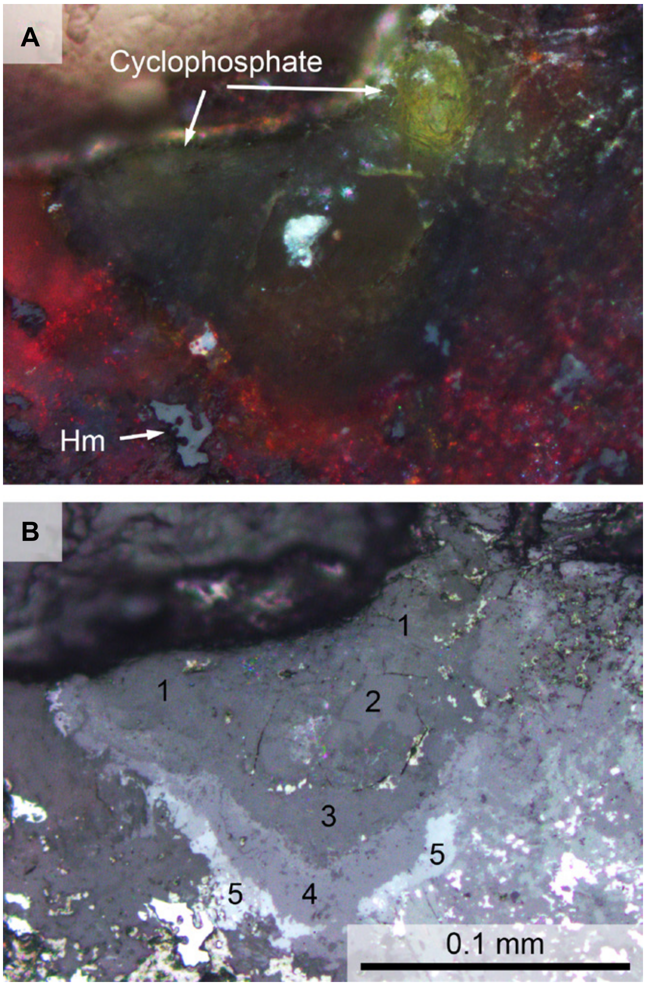

Figure 2. Cyclophosphate in metamorphic rock of the Hatrurim Basin, Israel. (A) Yellow-green aggregate of $(\mathrm{Ni,Fe})_2\mathrm{P}_4\mathrm{O}_{12}$ surrounded by a complex phosphate assemblage (red-colored area), together with hematite, $\mathrm{Fe}_2\mathrm{O}_3$ (Hm) (polished section, photomicrograph in scattered light). (B) Same area in polarized reflected light under crossed polars (electron backscatter image of the same area is provided in Figure S1 [see footnote 1]).Phosphate phases numbering: 1—$(\mathrm{Ni,Fe})\mathrm{P}_4\mathrm{O}_{12}$; 2—$(\mathrm{Ca,Ni})_3(\mathrm{PO}_4)_2$; 3—$\mathrm{K(Fe,V)P}_2\mathrm{O}_7$; 4—$\mathrm{NaCa(Fe,Ni)}_3(\mathrm{PO}_4)_3$; 5—$\mathrm{FeNi(PO}_4)\mathrm{O}$.

ring opening to form linear polyphosphates, with the liberation of chemical energy up to 40 kJ mol^{-1} (Meyerhof et al., 1953; Pasek, 2020).

As a consequence, cyclophosphates have been shown to trigger catalyst-free phosphorylation reactions under very mild conditions typical of the biochemical environment (e.g., Mitsutomo et al., 1981; Yamanaka et al., 1988; Gibard et al., 2018). Because of that, cyclophosphates (cyclotriphoshates and cyclotetraphosphates) are considered prime candidates for a role as phosphorylation agents involved in the emergence of primordial biota on early Earth (Horsman and Zechel, 2017; Pasek et al., 2017; Pasek, 2020). Unfortunately, all hypotheses relying upon cyclophosphate-based phosphorylation have met an unavoidable obstacle: until now, cyclophosphates have been neither encountered in nature (Yamagata et al., 1991) nor detected among the products of experimental aquatic treatment of natural phosphides (Bryant and Kee, 2006; Pasek, 2020). A hypothetical mechanism for their formation in nature, starting from (also hypothetically occurring) phosphoric anhydride, $\mathrm{P}_2\mathrm{O}_5$ ($\equiv \mathrm{P}_4\mathrm{O}_{10}$), has been invoked (Griffith et al., 1977; Yamagata et al., 1982), and all subsequent works have relied upon this hypothesis (e.g., Mitsutomo et al., 1981; Yamanaka et al., 1988; Gibard et al., 2018).

The discovery of cyclophosphates at the Dead Sea basin can invoke a reliable pathway for their native origin. As noted here, terrestrial cyclophosphates always associate with the natural iron diphosphide zuktamrurite, $(\mathrm{Fe,Ni})\mathrm{P}_2$ (Britvin et al., 2019). The relationships between zuktamrurite and cyclophosphates (Fig. S1) allow us to suggest that cyclophosphates were formed as products of phosphide oxidation. The pyrometamorphic, and thus high-temperature, origin of cyclophosphates implies that the process has proceeded through pyrolitic oxidation of phosphide under conditions mimicking, for example, the industrial dephosphorization of ferrophosphorus (Sarkulov et al., 1991). The overall reaction can be expressed as:

$$2(\mathrm{Fe,Ni})\mathrm{P}_2 + 6\mathrm{O}_2 \rightarrow (\mathrm{Fe,Ni})_2\mathrm{P}_4\mathrm{O}_{12}. \tag{1}$$

However, taking into account the very low O_2 concentrations in the modeled Archean atmosphere (e.g., Kasting, 1993; Hao et al., 2019), the process could also involve oxidation with more-abundant carbon dioxide:

$$2(\mathrm{Fe,Ni})\mathrm{P}_2 + 12\mathrm{CO}_2 \rightarrow (\mathrm{Fe,Ni})_2\mathrm{P}_4\mathrm{O}_{12} + 12\mathrm{CO}. \tag{2}$$

There are no experimental data on the oxidation of phosphides with CO_2, but the results of a similarly proceeding desulfurization of sulfide-bearing ores show that carbon dioxide readily oxidizes, for example, pyrite (FeS_2) to iron sulfates at 800–900 °C (e.g., Zhunev and Yur'ev, 2009).

Both oxidation pathways are readily explainable in the framework of pyrometamorphic processes, contrary to invoking the occurrence of hypothetical $\mathrm{P}_2\mathrm{O}_5$. The main processes were likely complicated by secondary reactions, including partial

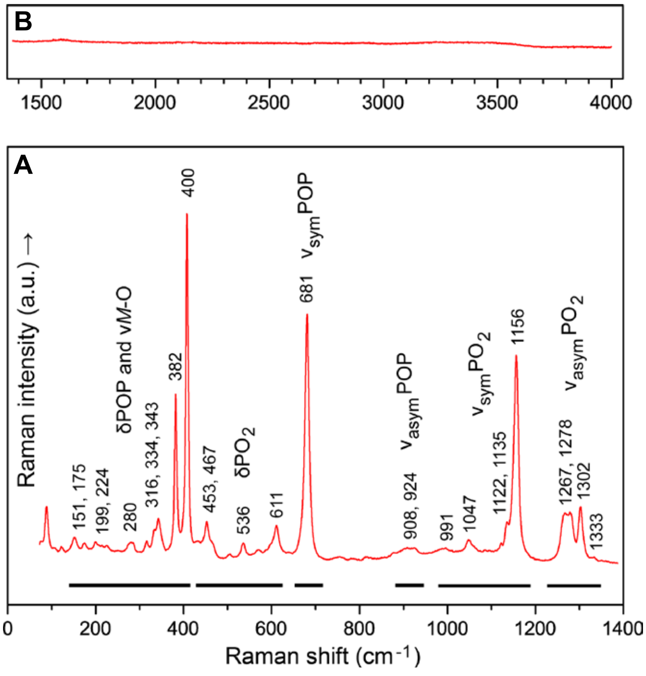

Figure 3. Raman spectrum of natural $(\mathrm{Ni,Fe})_2\mathrm{P}_4\mathrm{O}_{12}$. (A) Fingerprint region. Band assignments are according to data reported for synthetic $\mathrm{Ni}_2\mathrm{P}_4\mathrm{O}_{12}$ (Viswanathan et al., 1985). (B) Flat curve of Raman spectrum in the region 1400–4000 cm–^{1} shows the absence of molecular water and hydroxyl groups in the mineral composition. Intensity scale in A and B is the same. a.u.—arbitrary units; ν—stretching vibrations; δ—bending vibrations; sym—symmetric; asym—asymmetric.

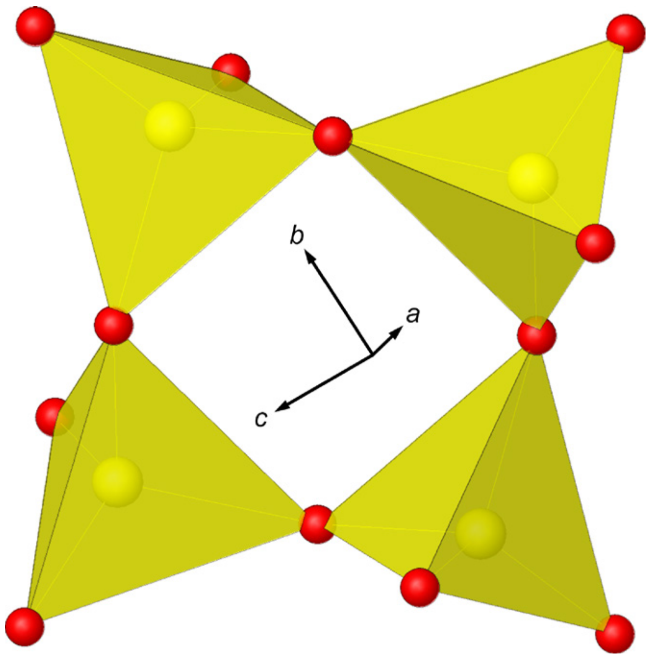

Figure 4. Cyclotetraphosphate ring in the crystal structure of $Ni_2P_4O_{12}$ (phosphorus atoms in yellow, oxygen atoms in red). Four orthophosphate tetrahedra are condensed via phosphoanhydride P–O–P bridges to form the P_4O_{12} ring. Drawn based on structural data reported by Nord (1983).

ferrous-ferric oxidation with formation of Fe^{3+}-bearing phosphates, whereas oxidation-resistant Ni^{2+} accumulated in cyclophosphates and Ni-containing orthophosphates (Fig. 2). Vanadium in the reported assemblages may have come from some unrecognized precursor because vanadium-bearing minerals are known in the Mottled Zone (e.g., Galuskina et al., 2017). Besides zuktamrurite, other recently discovered Fe-Ni phosphides (Britvin et al., 2015) might serve as a phosphorus source via similar oxidation pathways.

The origination of natural cyclophosphates via oxidative pyrolysis of phosphides might open new insights into the possible pathways of prebiotic phosphorylation. To the best of our knowledge, temperature-induced oxidation of natural phosphides has never been considered as a route to prebiotic phosphorus. Since the discovery of aquatic oxidation of meteoritic phosphides by Bryant and Kee (2006), all research in this field has focused on that process (Pasek, 2020). Meanwhile, pyrometamorphism is not the sole natural process that can result in phosphide pyrolysis. Any cosmic body entering the atmosphere is subjected to severe ablation—the process of vaporization and high-temperature oxidation of meteoritic substances. Ablation-induced weight loss can be estimated to be as much as 85% of the incoming meteorite flux (Bhandari et al., 1980). Recent experimental studies and simulations indicate that all phosphorus that has suffered the ablation process must be present in the oxidized form (Carrillo-Sánchez et al., 2020). Mineralogical speciation of phosphorus in the ablated substance is unexplored, but it may be similar to that produced by pyrometamorphic oxidation of phosphides.

The rarity of cyclophosphates in the contemporary lithosphere does not imply that these minerals could not have been more widespread on early Earth. The geochemical environment in the Archean was substantially more reducing than that of today (Kasting, 1993; Hao et al., 2019), and phosphides—the parent compounds required for cyclophosphate formation—could be readily synthesized via reduction of orthophosphates (apatite or iron phosphates) by abiogenic methane or dihydrogen at elevated temperature (300–400 °C); i.e., at the foci of any geothermal activity (see Britvin et al., 2015, and references therein). The terrestrial phosphide assemblages discovered in the surroundings of the Dead Sea can thus be regarded as a model system that reproduces phosphorus speciation at the early stages of Earth evolution. Subsequent oxidation reactions that started upon saturation of the atmosphere with dioxygen could have led to a variety of new phosphate species different from the primary orthophosphates (see the assemblage in Fig. 2). The discovery of cyclophosphates fits this hypothesis well, opening more possibilities for modeling prebiotic phosphorylation processes that resulted in the emergence of life on our planet.

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