

Links Between Hydrothermal Environments, Pyrophosphate, Na^+ , and Early Evolution

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Abstract The discovery that photosynthetic bacterial membrane-bound inorganic pyrophosphatase (PPase) catalyzed light-induced phosphorylation of orthophosphate (Pi) to pyrophosphate (PPi) and the capability of PPi to drive energy requiring dark reactions supported PPi as a possible early alternative to ATP. Like the proton-pumping ATPase, the corresponding membrane-bound PPase also is a H^+ -pump, and like the Na^+ -pumping ATPase, it can be a Na^+ -pump, both in archaeal and bacterial membranes. We suggest that PPi and Na^+ transport preceded ATP and H^+ transport in association with geochemistry of the Earth at the time of the origin and early evolution of life. Life may have started in connection with early plate tectonic processes coupled to alkaline hydrothermal activity. A hydrothermal environment in which Na^+ is abundant exists in sediment-starved subduction zones, like the Mariana forearc in the W Pacific Ocean. It is considered to mimic the Archean Earth. The forearc pore fluids have a pH up to 12.6, a Na^+ -concentration of 0.7 mol/kg seawater. PPi could have been formed during early subduction of oceanic lithosphere by dehydration of protonated orthophosphates. A key to PPi formation in these geological environments is a low local activity of water.

Keywords Brucite · Early evolution · Hydrothermal systems · Mariana forearc · Membrane-bound inorganic pyrophosphatase · Proton pump · Pyrophosphate · Serpentinization · Sodium pump · Subduction zones

Introduction

Lipmann (1965) assumed that, on the phosphate side, ‘the group potential might have originated with inorganic pyrophosphate (PPi) as the primitive group carrier’. The

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discovery that photosynthetic bacterial membrane-bound inorganic pyrophosphatase (PPase) catalyzed light-induced phosphorylation of orthophosphate (Pi) to pyrophosphate (Baltscheffsky et al. 1966) and the capability of PPI to drive energy requiring dark reactions (Baltscheffsky 1967) supported pyrophosphate as a possible early alternative to adenosine triphosphate (ATP), the main chemical energy currency in living cells. Like the adenosine triphosphatase (ATPase), the corresponding membrane-bound PPase is also a H⁺-pump (Moyle et al. 1974), and can be a Na⁺-pump in both archaeal and bacterial membranes (Malinen et al. 2007). Support has been obtained for an earlier transport of Na⁺ than of H⁺ through biomembranes (Mulikidjanian et al. 2008a). The hyperthermophilic bacterium *Thermotoga maritima*, found in hydrothermal environments, as well as the mesophilic *Methanosarcina mazei* contain membrane-bound PPases (Tm-PPase and Mm-PPase, respectively) that are homologous to H⁺-PPases (Belogurov et al. 2005; Malinen et al. 2008). Both Tm-PPase and Mm-PPase have an absolute requirement for Na⁺, but display maximal activity in the presence of millimolar levels of K⁺. We suggest that pyrophosphate may have preceded the ATP, and Na⁺ transport the H⁺ transport in connection with the origin and initial evolution of life on Earth. Life may have started in association with early plate tectonic processes. We agree with the concept that a molecular, or chemical, non-Darwinian evolution probably preceded the Darwinian evolution, with the genetic code as the initiator of life and biological evolution. We thus include aspects of both chemical and biological evolution at ‘the time of the origin and early evolution of life’.

Considerable geological evidence supports an initiation of plate tectonics on Earth shortly after the end of the Hadean about 4 Ga ago (Harrison 2009; Ehrenfreund et al. 2010). The salinity of the young ocean was probably high, since sodium is rapidly mobilized from rocks by hydrothermal activity (Nisbet 1991). Such processes also lead to the continuous release of Mg²⁺ and precipitation of brucite, Mg(OH)₂, during serpentinization of olivine in mafic rocks of the ocean floor (Holm et al. 2006). The serpentinization processes are now recognized as probably the most important metamorphic hydration reactions that may contribute to our understanding of the origin of life, since they are coupled to the formation of source molecules like H₂, thought to have been required for the origin of life (Müntener 2010). The transformation of olivine at relatively low temperature (50–300°C) to the serpentine mineral lizardite as the prevalent phase is particularly associated with reduction of water to hydrogen and oxidation of Fe(II) to Fe(III) (Evans 2010). During weathering of olivine and pyroxene in mafic rocks Fe(OH)₂ may be formed as an intermediate phase (in solid solution with Mg(OH)₂) during the partial oxidation of Fe (II). Fe(OH)₂ is metastable with respect to magnetite and will convert to this mineral via a spontaneous reaction (Schoonen et al. 2004; Holm and Neubeck 2009). However, the conversion also creates a small amount of native iron, which means that the ocean floor is quite reducing. The oceanic crust is hydrated to a depth of a kilometer or more and can therefore provide a substantial flux of water for serpentinization of upper mantle rocks when it is subducted (Kasting and Holm 1992). A modern hydrothermal environment in which Na⁺ and Mg²⁺ are abundant exists in sediment-starved alkaline subduction zones, like the Mariana forearc in the western Pacific Ocean (Mottl et al. 2003, 2004; Mottl 2009). It is considered to mimic the Archean Earth (Holm and Neubeck 2009). Notably, PPI could have been formed during early subduction of oceanic lithosphere by dehydration of protonated orthophosphates (Sales et al. 1993; Arrhenius et al. 1997). The key to pyrophosphate formation in these geological environments is low water to rock ratio, i.e. low local activity of water. The difference in complexity between the inorganic pyrophosphate and ATP also supports the possible role of PPI as early energy donor during the early evolution of life.

After a short description of the pH conditions of the Mariana forearc in the following section, we will proceed to the sodium abundance and to the apparent scarcity of phosphorus. These items, followed by a detailed treatment of prebiotic pyrophosphate formation, serve as background to the Discussion and Summary which include the presentation of a novel evolutionary scheme for cation transport through membranes.

The pH Conditions of the Mariana Forearc

Near the Mariana trench, i.e. at a lateral distance of 48–54 km from the maximum depth of the trench into the overriding Philippines plate (see Fig. 1), the upwelling pore waters of the Mariana forearc have pH of 10.7 and are fresher than the ambient seawater, because the waters originate by dehydration of the subducting Pacific slab at temperatures of 300–375° C (Alt and Shanks 2006; Mottl 2009). These proximal springs form chimneys on the seafloor of the secondary mineral brucite, $Mg(OH)_2$. Farther from the trench (70–90 km lateral distance) the fluid chemistry changes abruptly and the waters have pH 12.5 and are more concentrated with respect to dissolved inorganic species relative to seawater (Mottl 2009). These distal springs form chimneys of aragonite and calcite, both consisting of $CaCO_3$. The reason that the fluids close to the trench have a pH of about 10.7 is because the consumption of H^+ during serpentinization (and brucite formation) of primary silicate

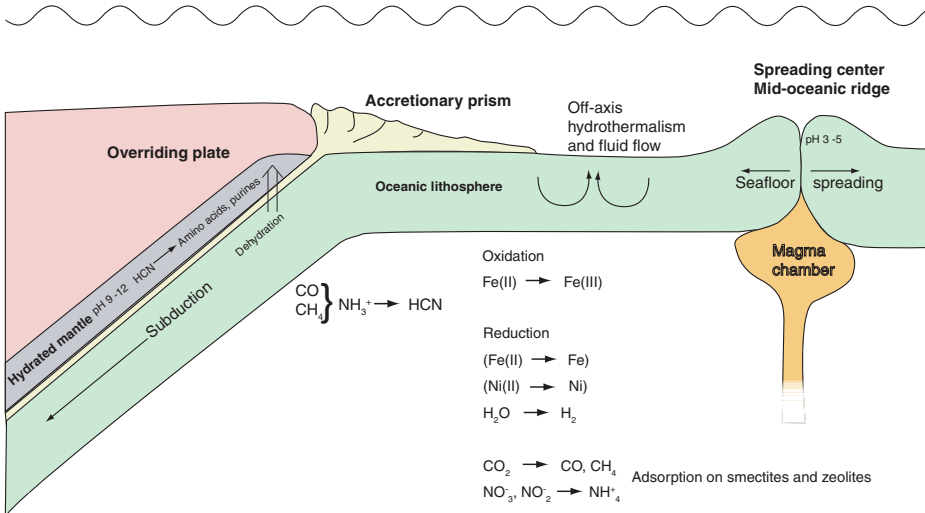


Fig. 1 Cartoon showing a cross section of oceanic lithosphere, extending from the spreading center to the subduction zone. Off-axis hydrothermal flow in the oceanic lithosphere causes partial oxidation of Fe(II) to Fe(III) and reduction of water to molecular hydrogen. Some Fe(II) and Ni(II) is reduced to native metals. CO_2 is reduced to CO and CH_4 , while NO_3^- and NO_2^- may be reduced to NH_4^+ and adsorbed on secondary minerals like smectite and zeolites. During early subduction the descending plate is heated and dehydrated. Adsorbed CO and CH_4 may react with NH_4^+ and form HCN. The released fluid carrying HCN rises from an environment of relatively low pH into hydrated mantle rock of high pH. At the high pH HCN monomers may form oligomers as well as amino acids, purine bases, nucleosides and nucleotides due to phosphorylation by pyrophosphate (from Holm and Neubeck 2009)

minerals (Holm and Neubeck 2009). $\text{Mg}(\text{OH})_2$ is, in fact, excellent at buffering pH at alkaline conditions and has been used for that purpose in prebiotic peptide synthesis experiments (Huber et al. 2003). However, the pH of 12.5 of the distal pore fluids requires an additional explanation, such as dissolution of carbonate minerals in cracks and fissures of the subducting Pacific plate (Mottl 2009). The greatest abundances of carbonate veins and highest bulk crustal carbon contents correspond with high permeability in the upper crust of the plate, where greater fluid fluxes and prolonged circulation occur (Alt and Teagle 1999).

Sodium Abundance

De Duve (1995) has remarked that the origin of the ATP-driven sodium-potassium pump is obscure and that it is conceivable that life had to defend itself very early against excessive sodium. Such an early defence would have been valid also for Na^+ -pumping by PPases. During evolution, Na^+ -driven membrane energy conversion probably preceded the proton-based one that is dominant in modern cells (Mulikidjanian et al. 2008a,b). Sodium is strongly partitioned into basaltic melts during mantle melting at oceanic spreading centers. During subsequent weathering of the basalts in the crustal (upper) part of subducting lithosphere (see Fig. 1), sodium that is liberated by breakdown of minerals like clinopyroxene (Seyfried et al. 2007) readily dissolves in the weathering solutions as Na^+ (Glassley 2001). There is an enormous variability in the relative mobility of elements in basalts during weathering. For example, the relative mobility, in decreasing order, in Icelandic basalts is: $\text{S} > \text{F} > \text{Na} > \text{K} > \text{Ca} > \text{Si} > \text{Mg} > \text{P} > \text{Sr} > \text{Mn} > \text{Al} > \text{Ti} > \text{Fe}$ (Gíslason et al. 1996). Relative to Na, close to 90% of Mg and Ca in the original rock is left behind in secondary solids. As an effect, the Mariana forearc pore fluids at some distance away from the trench have a Na^+ -concentration of 0.7 mol/kg fluid, and a Na/Cl-ratio of 1.5 compared to 0.86 in the present-day ocean (Mottl et al. 2003, 2004; Hulme et al. 2010). Simulations have shown that, above a concentration of 3 mol/kg fluid, Na^+ ions have difficulties to mobilize enough water molecules in order to fill their first hydration shell, which normally contains six H_2O (Rode et al. 2007; Bujdák et al. 2010). Due to the strong binding energy of Na^+ ions to their hydration shell, this means that Na^+ ions with lower coordination numbers can be considered as a strong dehydrating system for any reaction in which H_2O is removed, like PPi formation. This is also most likely the reason why the apparent stability constant of the MgPPi complex increases with NaCl as supporting medium (Hørder 1974). Miyakawa et al. (2006) have shown that RNA oligomer formation from monomers increases up to 10mers with concentrations of NaCl up to 1 M. Since the measured concentrations of the Mariana forearc fluids are bulk data, local niches are likely to hold concentrations of Na^+ at, or even above, 3 mol/kg fluid (Glassley 2001).

Phosphorus Scarcity

Today, phosphorus is a relatively rare element on Earth. The concentration of phosphate in the Archean ocean was, however, probably much higher compared to the present ocean, since it is more scavenged in modern oceanic environments (Konhauser et al. 2007; Planavsky et al. 2010). Phosphorus is of extreme importance for the biological transfer of energy and information in living organisms. Phosphate compounds are scavenged from sea water by ridge-flank hydrothermal activity and are accumulated

primarily in the secondary mineral brucite in the oceanic lithosphere (Wheat et al. 2003; Holm et al. 2006). In addition to binding Pi quantitatively, brucite also binds condensed phosphates like P₂i and trimetaphosphate without hydrolyzing them (Karl and Tien 1992). The uptake of phosphorus by brucite during hydrothermal circulation has led Bradley et al. (2009) to propose that the utilization of glycosyl head groups instead of phosphatidyl head groups by bacteria constitutes a strategy for conservation of scarce phosphorus. Condensed phosphates have stronger binding energies to hydroxide minerals like brucite than orthophosphate (Arrhenius et al. 1997), in the same way as polynucleotides bind stronger than mononucleotides (Holm et al. 1993). This means that the condensed phosphates have the potential to (outcompete orthophosphate and) concentrate on the mineral surfaces. Inorganic pyro- and polyphosphates are used for energy transfer and storage in many microorganisms, and it has been proposed that the chemical energy stored in this type of inorganic molecules has been used by primitive forms of life on the early Earth (Baltscheffsky and Baltscheffsky 1994). Despite the general scarcity of phosphorus on Earth, such compounds could have been produced in the prebiotic world by several possible pathways.

Prebiotic Pyrophosphate Formation

Wheat et al. (1996) have estimated that ridge-axis and ridge-flank hydrothermal processes in the ocean floor in combination today remove about 50% of the global input of dissolved phosphorus from rivers into oceanic crust. Bodeř et al. (2008) have shown that phosphate is strongly enriched as authigenic phases in the basal sedimentary layer on top of the basaltic basement, the source of phosphorus being primarily the basalts underneath. Under standard temperature conditions (25°C), apatite (Ca-orthophosphate) forms as a single phase at pH 9 or higher in a sterile seawater medium. However, in the pH range 7–9 primarily the mineral whitlockite (Ca₁₈Mg₂H₂(PO₄)₁₄) is formed under the same temperature conditions (Gedulin and Arrhenius 1994). Preformed crystals of apatite placed in a neutral or slightly alkaline sterile solution with the Mg/Ca ratio of seawater convert to whitlockite. Abbona and Franchini-Angela (1990) have also shown that amorphous calcium phosphate converts to whitlockite above the Mg/Ca molar ratio 0.8. It has long been known that hydrogen containing phosphates like whitlockite and newberyite at heating react to form pyrophosphate and water (Sales et al. 1993; Gedulin and Arrhenius 1994). Low water activity in the system promotes the pyrophosphate formation (Russell and Hall 1997). The phosphate condensation is due to the protonation of the phosphate. At heating, the hydrogen reacts with one of the oxygen ligands of the phosphorus and leaves as water. As a response, the structure of the orthophosphate rearranges to form one or more anhydride P-O-P bonds (Arrhenius et al. 1997), i.e. the backbone of condensed phosphates like pyrophosphate.

A seemingly alternative pathway for pyrophosphate formation would be oxidation of the phosphide mineral schreibersite (Fe,Ni)₃P. This mineral is normally referred to as a component of iron meteorites (Bates and Jackson 1987; Pasek 2008), but it is, actually, also known to occur in terrestrial basalts, like the Tertiary ones of the Disko Island, Greenland (Pauly 1969; Ulf-Møller 1985). Schreibersite has also been reported as an indigenous mineral in lunar basalts in association with native Fe and Ni (El Goresy et al. 1971). The schreibersite appears to be formed as a by-product to phosphoran olivine in P-rich basalt melts at fast quenching (Boesenberg and Hewins 2010), and it is possible that the occurrence of this compound is the solution to the ‘phosphate problem’ as discussed by

Schwartz (1971, 2006) and Rauchfuss (2008), i.e. solubilisation of phosphate compounds is necessary before activation can occur. Schreibersite oxidizes slowly in contact with fluid water as the surrounding mineral matrix gets weathered, and forms several phosphorus species of mixed oxidation states like orthophosphate, pyrophosphate, hypophosphate, phosphite, etc. (Pasek and Lauretta 2005; Pasek et al. 2007; Pasek 2008; Pasek et al. 2008). Since the ocean floor is reducing we would expect a similar mix of oxidation states in natural environments. In systems containing dissolved Mg^{2+} and Ca^{2+} chloride salts whitlockite is also formed (Pasek and Lauretta 2005). The presence of Na^+ in the system encourages corrosion of the metal phosphide (ibid.). In addition, de Zwart et al. (2004) have found that the presence of Fe(II) precipitates increases the stability of pyrophosphate. Nitschke and Russell (2009) have proposed that pyrophosphate is dissolved in basaltic glasses (which are formed during rapid quenching of magma) and is released upon alteration of the glass into palagonite (Staudigel et al. 1981). This is supported by the results of Bodeř et al. (2008) which reveal that phosphates in the basal sediments above basement originate from volcanic glass in the basalts. Studies have shown that partitioning of phosphorus between different solid phases preferentially favours glasses, alkaline glasses in particular (Brunet and Chazot 2001). Glass of phosphate is widely distributed in the lithospheric mantle (Zhang et al. 2007). Therefore, phosphates in the expelled fluids of a subduction zone are likely to originate from the hydrated mantle root zone of the overriding plate (see Fig. 1).

For a long time it has been generally stated that condensed phosphate minerals do not exist in nature (see, for instance, Byrappa 1983). However, the first occurrence of a natural pyrophosphate mineral, canaphite, was reported in the scientific literature only in 1985 (Peacor et al. 1985; Rouse et al. 1988), and the second, wooldridgeite, in 1999 (Hawthorne et al. 1999). The canaphite specimens were found on zeolite crystals (stilbite) in cavities of Triassic trap rock (basalt) from New Jersey, USA, whereas wooldridgeite was found in an unconformity between Precambrian igneous rocks and overlying Cambrian sedimentary rocks.

Magnesium pyrophosphate is easily formed under mild abiotic hydrothermal conditions (165–180°C) from magnesium salts and orthophosphate (Seel et al. 1985, 1986; Kongshaug et al. 2000). The reason may be that the size of Mg^{2+} makes it possible to simultaneously coordinate negatively charged oxygen of two adjacent phosphorus atoms (Yamagata et al. 1995). This effect has also been observed in ribosomes, in which the Mg^{2+} density with direct interaction to phosphate oxygens is greatest in the core region (Hsiao et al. 2009). The $MgPPi$ complex is stabilized by NaCl as supporting medium (Hörder 1974). Seel et al. used magnesium monohydrate phosphate dispersed in water in their syntheses, whereas Kongshaug et al. obtained low water activity by the use of phosphoric acid. As indicated by the formation and precipitation of brucite, $Mg(OH)_2$, dissolved magnesium is abundant in hydrothermal fluids of serpentinization environments.

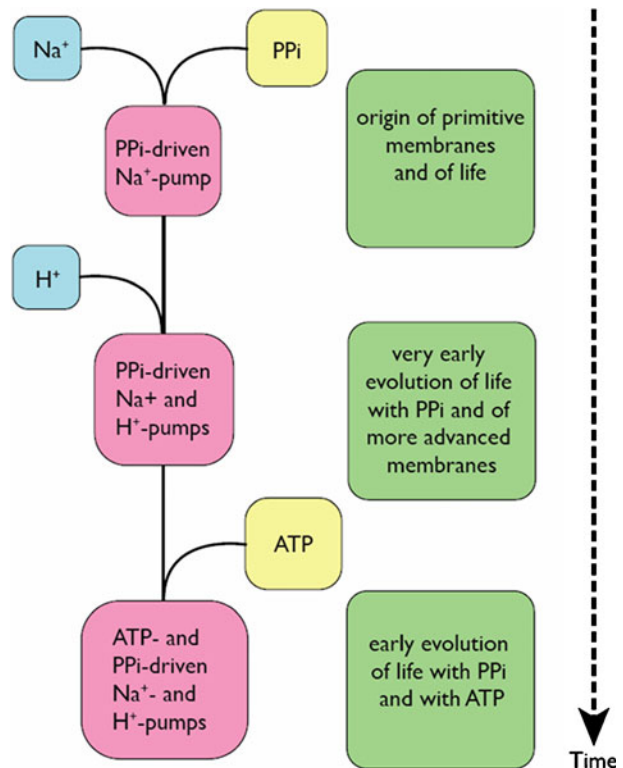
Discussion

The pH of the isoelectric point or point of zero charge (pH_{pzc}) of brucite has been found to be around 11 (Pokrovsky and Schott 2004). The pH caused by serpentinization of primary silicates (~10.7) is slightly below that value, which means that the negatively charged phosphate molecules can be adsorbed by brucite in fluids that are chemically dominated by such processes. However, if carbonate dissolution begins to dominate the fluid chemistry, pH rises above the pH_{pzc} of brucite and adsorbed negatively charged species, like orthophosphate and pyrophosphate, are desorbed and released. This effect is amplified by the concentration of

cations in the fluids and their type. Barrow and Shaw (1979) have shown that desorption of phosphates from soils is faster in NaCl solutions than in either MgCl₂ or CaCl₂ solutions. This is in agreement with studies by Hagan et al. (2007) that show a linear increase in soluble phosphate with increasing NaCl concentrations. In addition, a sequence of monovalent cations desorbing phosphate from fastest to slowest of Li⁺>Na⁺>NH₄⁺>K⁺,Rb⁺>Cs⁺ has been shown (Barrow and Shaw 1979). This means that the evolution of very early organisms with pyrophosphate as energy currency (Baltscheffsky 1996) could occur at the dynamic environments that are found in subduction zones like the Mariana forearc.

Since the alkaline pH of these subduction environments may allow abiotic synthesis of amino acids, carbohydrates and heterocyclic nitrogen bases, etc. (Holm and Neubeck 2009), it also opens up the possibility both of early autotrophic as well as heterotrophic microbial communities with permeable early membranes in this setting (Deamer 2008; Mansy et al. 2008; Mulkidjanian et al. 2009). Mulkidjanian et al. (2008b, 2009) have proposed that at high temperature and/or high pH, i.e. at low concentration of protons, the sodium energetics is more advantageous than under mesophilic conditions, so that obligate anaerobes routinely exploit the sodium cycle. At high pH, the calculated proton-motive force (PMF) may drop to almost zero (Krulwich 1995). This is in line with the early suggestion of Na⁺ rather than H⁺ as a coupling ion when a proton cycle could not occur owing to low [H⁺] in the medium (Skulachev 1996). The high Na⁺ concentration in combination with the extremely high pH will also add to the ease of desorption of phosphates, including pyrophosphate, that have been adsorbed on the mineral brucite in the seafloor for tens of millions to a hundred million years (Fehn and Cathles 1986; Noel and Hounslow 1988).

Fig. 2 A novel evolutionary scheme for cation pumping through membranes



Keefe and Miller (1995) have discussed whether condensed phosphates like pyrophosphate were likely prebiotic reagents on Earth. The authors stated in the beginning of their article that they intended to show that phosphate is an unlikely reagent for the prebiotic world. A major argument was that water cannot escape from buried and heated rocks. Their study was very much focussed on the 'standard' surface conditions of Earth and omitted a number of active geological pathways that may have lead to P_{Pi}, such as that of dehydration, transformation and water to rock ratio. Surprisingly, they suggested that dihydrogen phosphate minerals are not known in nature today (cf. Nriagu and Moore 1984). Dehydration of minerals and escape of water is a normal phenomenon in geological environments both under diagenesis and metamorphism, as exemplified by the dynamics of the Mariana forearc (Mottl et al. 2003; Hulme et al. 2010).

Summary

Existing biochemical and geological information has been combined to a novel picture of the early molecular emergence and evolution of biological energy conversion, both preceding (molecular emergence) and following (early evolution) the origin of life on Earth. The evolutionary scheme for cation pumping through primitive membranes, driven by energy-rich phosphate compounds, is shown in Fig. 2. It summarizes some of the most essential points of this paper, as is seen in the sequence of evolutionary steps. This focus on the early evolution of the pumping of Na⁺ and H⁺ may be considered to be an addition to an earlier evolutionary model for photosynthetic phosphorylation linking electron and ion transport with phosphate transfer (Serrano et al. 2007)

The plausibility of prebiotic formation of P_{Pi}, a relatively simple inorganic molecule, as compared to the more complex ATP, appears to support our scheme. In addition, the energy required to form P_{Pi} from 2 Pi can be stored by non-energy requiring transphosphorylation (2 P_{Pi}→Pi+PPP_{Pi}, etc.) to higher linear inorganic oligo- and polyphosphates. Furthermore, the occurrence of Na⁺ pumping, membrane-bound pyrophosphatases in both archaea and bacteria agrees well with an early role for this kind of enzyme. Clear indications have been found for a stepwise evolution to known ion pumping pyrophosphatases from less complex polypeptide structures by gene duplication events, etc. (Au et al. 2006). Finally, we would like to emphasize that especially the recent important findings about the hydrothermal alkaline geofluids with high [Na⁺] and low [H⁺] have inspired us to the above combinations and discussions.

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