

Expert opinion

Can potassium phosphonate be considered a naturally occurring mineral?

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Publicly appointed, sworn expert

- 4. **Viticulture**
 - 4.1 Assessments and compensation matters in viticultural businesses
 - 4.2.1 Outdoor businesses (plants, plant protection, technical and structural facilities)
 - 4.2.2 Oenology (technology, structural facilities, operating facilities etc.)
 - 4.2.4 Assessment of economic limits through use restrictions
 - 4.3 Other assessments for viticulture
- Awarding authority: Kassel Regional Council

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Table of contents

1. Reason for the expert's report
2. Request for an expert's report
3. Definitions
4. Occurrence of phosphonates and phosphorous acid in nature
 - 4.1. Mineralogical occurrence
 - 4.2 Biogenic occurrence
5. Findings
 - 5.1 Does potassium phosphonate occur in nature as an anorganic salt and if so, in what form?
 - 5.2 Can potassium phosphonate be considered a naturally occurring mineral?
 - 5.3 Should potassium phosphonate by its nature be considered in accordance with the requirements of the EU Organic Production Regulation?
6. References

Preliminary remark

Like every other expert's report, this report aims to provide an illustration of a specific situation. The task of this expert's report is outlined in more detailed in chapter 1. The expert's report may only be used for this purpose and only in full with all its pages, overviews and appendices. This also includes any colour marking or other highlighting in texts, tables, drawings and photographs. Liability for uses deviating from these requirements and towards third parties is excluded.

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1. Reason for the order

The plant protection agent

"Frutogard" plays an important role in plant protection in organic viticulture, especially in the context of the strategy to minimise the use of copper. Frutogard is an algal extract with the added potassium salt of phosphorous acid ($\text{KH}_2\text{PO}_3 + \text{K}_2\text{HPO}_3$) as well as phosphate and oligosaccharides. Since the ratification of EU Regulation 1107/2009 in national law, the situation regarding the classification of Frutogard as a plant fortifier has changed. The active agent potassium phosphite (term used in the EU notification) has been registered for inclusion in the list of approved plant protection agents (pesticides) in Annex 1. At the same time, national / zonal approval of plant protection agents containing this active substance is also being implemented. As a result of the expected inclusion of the active substance potassium phosphite in Annex 1 of Regulation 1107/2009 (replacing 91/414), the substance can no longer be used in organic viticulture in the absence of an inclusion in the list in Annex 2 of EU Regulation 889/2008 in accordance with Art. 16 of EU Regulation 834/2007.

The previous discussions at national level (between the organic farming associations, at the phosphonate conference JKI Nov. 2010) and at international level (Frick 1995; Rome 2010) regarding the use of phosphorous acid (phosphonic acid) or the potassium salt of phosphorous acid brought up a question which remains unanswered in relation to the inclusion in the list as a plant protection agent permitted for use in organic viticulture (in addition to the issue of residues):

- What is the nature of the substance potassium phosphonate (or phosphite) ($\text{KH}_2\text{PO}_3 + \text{K}_2\text{HPO}_3$), as an anorganic salt of phosphonic acid (phosphorous acid)?
- Does this substance occur in nature as an anorganic salt and if so, in what form?
- Can the substance be considered a naturally occurring mineral?

This question regarding the nature of the substance is an essential assessment criterion for recognition and inclusion in the list in Annex 2 of Regulation 889/2008 in accordance with the criteria in Art. 16 of Regulation 834/2007. As set out in Art. 16, the substances approved as plant protection agents must have a plant, animal, microbial or mineral source. In addition, it can be deduced from Art. 16 (2) c) ii) of the above Regulation that products to combat harmful organisms also have a natural character (e.g. pheromones, K-bi (hydrogen) carbonate; KHCO_3).

This expert's report aims to use secondary literature to determine - taking into account the above questions - whether the substance potassium phosphonate, as an anorganic salt and as phosphonic acid (phosphorous acid), occurs naturally as an effective substance and whether there is sufficient scientific evidence for the natural occurrence of these substances.

2. Request for an expert's report

Creation of an expert's report on the question:

- What is the nature of the substance potassium phosphonate (or potassium phosphite) ($\text{KH}_2\text{PO}_3 + \text{K}_2\text{HPO}_3$), as an anorganic salt of phosphonic acid (phosphorous acid)?
- Does this substance occur in nature as an anorganic salt and if so, in what form?
- Can the substance be considered a naturally occurring mineral?

3. Definitions

| | |
|---|--|
| phosphonic acid (phosphorous acid) ¹ | H_2HPO_3 ; $\text{P}(\text{OH})_3$ |
| Dihydroxy form (phosphonic acid) | $\text{HPO}(\text{OH})_2$ |
| Phosphonate ion (also called phosphite ion) | HPO_3^{2-} |
| Hyperphosphonate "Hydrogen phosphite" | $\text{HP}(\text{O})_2(\text{OH})^-$ |
| Phosphoric acid | H_3PO_4 |
| Orthophosphate ion | HPO_4^{3-} |

Phosphate minerals:

| | |
|-------------------|--|
| Apatite | $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$ |
| e.g. fluorapatite | $\text{Ca}_5(\text{PO}_4)_3\text{F}$ |
| Whitlockite | $\text{Ca}_9(\text{Mg}, \text{Fe})(\text{PO}_4)_6\text{PO}_3\text{OH}$ |
| Schreibersite | $(\text{Fe}, \text{Ni})_3\text{P}$ |

Anorganic salts of phosphorous acid = anorganic phosphonates (phosphites)

| | |
|--|---|
| e.g. potassium phosphonate (phosphite) | $1/3 \text{KH}_2\text{PO}_3 + 2/3 \text{K}_2\text{HPO}_3$ |
| Calcium-phosphonate (phosphite) | CaHPO_3 |

The anorganic salts of phosphorous acid are defined by the predominant **P-H bond**.

Organic phosphonates are defined by their highly stable **C-P bond** and as organic compounds of phosphorous acid². The organic compounds of this

¹ International Union of Pure and Applied Chemistry: (IUPAC Recommendations) (2005). Nomenclature of Inorganic Chemistry . Cambridge (UK):RSC-IUPAC, ISBN 0-85404-438-8.

element group (phosphoric acid ester) have the general structure $R-PO(OH)_2$ (R = alkyl group or aryl group) and are distinguished from the esters of phosphoric acid by their direct carbon-phosphorus bond (**C-P bond**). By contrast, phosphates (like sulphates and sulphones) have **C-O-P bonds**, which hydrolyse much easier compared to C-P bonds. Compounds of this type have the properties of a salt (or an acid) alongside the properties of an organic compound. There are many water-soluble compounds of this type.

Naturally occurring, organic phosphonates

In 1959³, Hortiguchi and Kandutsu identified the first natural phosphonic acid in 2-Aminoethylphosphonic acid. This occurs in plants and in many animals, predominantly in cell membranes. Phosphonates occur frequently in many different organisms, e.g. in prokaryotes, eubacteria, mushrooms, molluscs and insects.

| | |
|---|--------------------|
| e.g. 2-aminoethyl-phosphonate | $NH_3(H_2C)_2PO_3$ |
| Phosphonolipids | $R-C-PO_3$ |
| Methylphosphonate (Methylphosphonic acid) | $(CH_3)PO(OH)_2$ |

Synthetic phosphonates

Use as: Corrosion inhibitors, wastewater treatment (water softening, limescale bonding) and as peroxide stabilisers. Peroxide stabilisers are found in small quantities in laundry liquids which also contain bleach. They bind heavy metals from laundry dirt and water to ensure that the effectiveness of the bleach is not disrupted and that the textile fibres are not damaged by the uncontrolled release of oxygen⁴.

Examples:

- aminotris(methylenephosphonic acid) (ATMP or NTMP)
- ethylenediamine tetra(methylene phosphonic acid) (EDTMP)
- diethylenetriamine penta(methylene phosphonic acid) (DTPMP)
- hexamethylenediaminetetra(methylenephosphonic acid) (HDTMP)

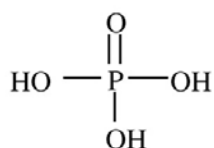
Fig. 1 shows the chemical structural formula for: phosphoric acid, phosphorous acid, and hypophosphorous acid "phosphinic acid"⁵.

² http://en.wikipedia.org/wiki/Phosphorous_acid

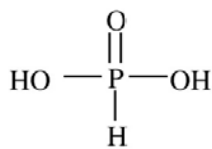
³ Hortiguchi M. and Kandutsu M (1959) Isolation of 2aminoethane-phosphonic acid from rumen protozoa. Nature **184**, 901 Cited in Hillebrand 1983

⁴ Fürhacker M et al (2005) Research project no. 1378 "Phosphonates – AMPA (Aminomethylphosphonic acid). Department for the Assessment of Sources, Environmental Concentrations and Breakdown by Photolysis Water-Atmosphere-Environment University of Natural Resources and Life Sciences Vienna

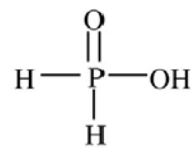
⁵ Schwartz AW (2006): Phosphorus in prebiotic chemistry Phil. Trans. R. Soc. B29 Vol. 361 no. 1474; 1743 -1749



phosphoric acid



phosphorous acid



hypophosphorous acid

Fig. 1: Structural formula of phosphoric acid, phosphorous acid and hypophosphorous acid "phosphinic acid"

Fig. 2 shows the tautomeric structures of phosphorous acid.

The preferred tautomer form of phosphorous acid is the structure with double-bonded oxygen ($\text{P}=\text{O}$), making it a dual-proton acid. Salts and esters of phosphorous acid are called phosphonates (or: phosphites). The phosphorus in these compounds has oxidation level III⁶.

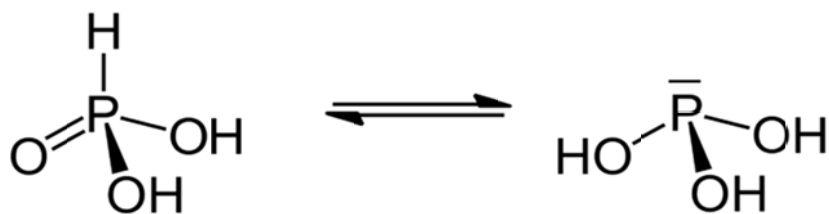


Fig. 2: Tautomeric structures: phosphonic acid $\text{HPO}(\text{OH})_2$ and phosphite $\text{P}(\text{OH})_3$ (organic only)

⁶ https://en.wikipedia.org/wiki/Phosphorous_acid

4. Occurrence of phosphonates and phosphorous acid in nature

4.1. Organic phosphonates

The occurrence of natural organic phosphonates (2-Aminoethylphosphonate, vinylphosphonate (vinyl-phosphonic acid) as well as phosphonolipids in animals and plants is described in some detail (Hilderbrand 1983).

25% of the organically bound phosphorus compounds occurring in the oceans are phosphonates and 5% of the organic P-compounds bound in the soil are also phosphonates.

Many microorganisms use phosphonates as a source of potassium in the absence of sufficient phosphate.

It has also been shown that individual organisms reduce phosphate to yield phosphonate, with the result that higher phosphonate concentrations can occur in our environment (Dymann et al (2006) cited in Pasek 2008).

Antibiotics, which are formed by different species of *Streptomyces* as secondary metabolites, represent another phosphonate group with a biogenic origin.

The clarification of enzyme crystal structures also involves the use of the inhibitory effect of substrate-analogous substances: To give an example, Herzberg *et al.* (2002) successfully used the C-P compound phosphonopyruvate, a structural analogue to phosphoenolpyruvate, to crystallise the recombinant enzyme pyruvate,phosphate dikinase from *Clostridium symbiosum* (cited in: Johnen 2005).

4.2. Occurrence as anorganic mineral

Since the 1950s, the phosphorus cycle has triggered countless discussions among scientists. How is it possible for a substance which only occurs in the Earth's crust in small quantities, which is hardly soluble and which, in contrast to N and C, does not have a gas phase, play such an important role in the creation of life (DNA, ATP, biological membranes, cell walls⁷)?

*"But one aspect has remained constant: an understanding of the P cycle is critical to our understanding of biological, chemical, and geological cycles on Earth and beyond, so it will likely continue to be an active research topic for decades to come"*⁸.

Phosphate compounds in particular rarely form under prebiotic conditions, due to the lack of source materials. By far the most frequently occurring phosphorous minerals in nature, fluorapatite and hydroxapatite, are barely water soluble. As a result, they are very unsuitable as components of a prebiotic phosphorus chemistry. It therefore makes sense that phosphorus in the form in which it normally occurs on Earth, was not involved in the creation of life. For a long time,

⁷ WESTHEIMER F.H (1987) Why Nature chose Phosphates Science. **235**, 1173–1178

⁸ Filippelli G.M (2008) The global phosphorus cycle: Past, Present and Future Elements Vol 4, 89-95

there was no plausible explanation for the "non-existence" of this substance which is so important for life on Earth.

Until a solution is found, scientifically founded theories abound on the origin of phosphorus in its bioactive, available form as phosphate.

In the interplanetary zone, phosphorus occurs in forms which would be highly unusual on Earth. The interesting compounds extracted by chemists from the Murchison meteorite (Cooper et al 1992), included phosphorous acids among others, which have been mentioned as components of a prebiotic chemistry.

Schwartz (1996) confirms that the phosphonates found are the organically bound phosphonates MPA methyl-phosphonic acid and EPA ethyl-phosphonic acid. In addition, phosphite was found, which is used to create phosphorous acids. But the sheer variety of anorganic phosphorus compounds in meteorites is astonishing, since, in addition to phosphite and the more common apatites, they also included chlorapatite, whitlockite and the surprisingly reactive schreibersite $(\text{Fe,Ni})_3\text{P}$ in noteworthy concentrations (De Graaf et al 1996, Schwartz 2006, Pasek 2008).

Pasek (2008) describes how, in contrast to today's "terrestrial" conditions of oxygen-enriched air, in which orthophosphate is the most common P-compound because reduced P-compounds are instantly oxidised, the oxygen-free prebiotic conditions would have favoured reduced phosphoric compounds as the dominant substances. In the interplanetary zone of our solar system and in primeval times on our Earth, with its air enriched with H_2/CO_2 , both lithophile phosphates and siderophile⁹ phosphites predominate/d. Today, siderophile P as phosphite is rare on the Earth's surface, but many meteorites contain this, particularly in their iron core.

Fig. 3 summarises the most important P-compounds for life.

*"Inorganic compounds used in life include orthophosphate, pyrophosphate and other condensed phosphates, phosphate, hypophosphite and phosphine. These inorganic forms are either used by organisms as sources of P for the synthesis of organic P-biomolecules or are possible metabolic by products of P metabolism (PH_3)"*¹⁰.

⁹The **Goldschmidt classification**, named after Victor M. Goldschmidt, is a classification frequently used in geochemistry, which groups chemical elements based on their affinity for different host phases into **siderophile** (iron-loving), **lithophile** (silicate-loving), **chalcophile** (sulphur-loving) and **athmophile** (gas-loving). The Goldschmidt classification e.g. plays a role in the differentiation, i.e. the formation of an iron core and a mantel/crust around an initially homogeneous planet or asteroid. For example, siderophile elements can be found preferentially in the iron core and lithophile elements preferentially in the mantel or crust of a planet.

¹⁰ From: Pasek MA (2008): Rethinking early Earth phosphorous geochemistry <http://www.pnas.org/content/105/3/853.short>

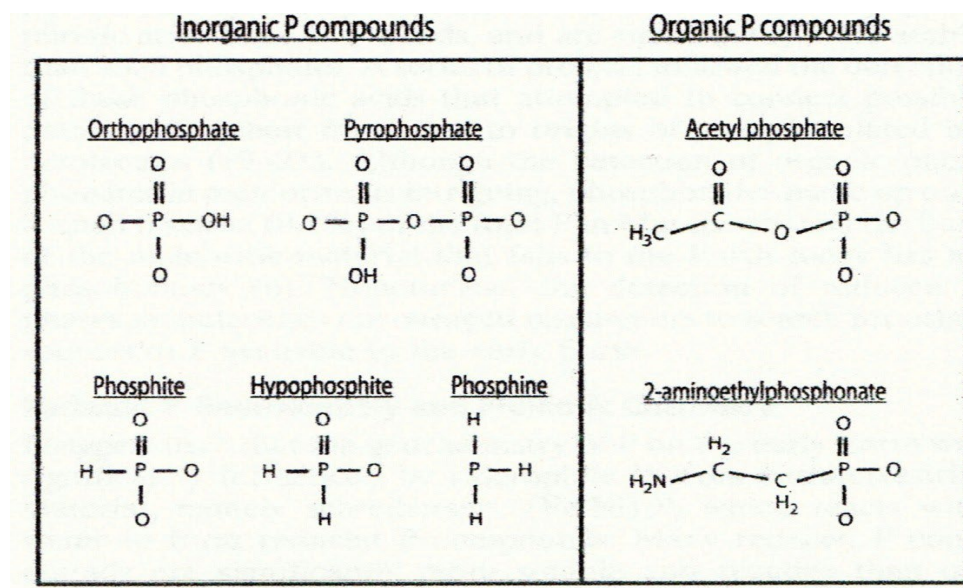


Fig. 3: Structure of the P-compounds occurring in the biological system at pH8. (on the left) Anorganic P-compounds, (on the right) Organic P-compounds).¹¹

In addition to apatites, condensed phosphates which are reactive relatives of phosphate, occur on Earth in small quantities. They are chains of two or more phosphate groups which can form naturally in the context of volcanism. Pyrophosphate, for example, which has been shown to occur in fumaroles, or phosphorus pentoxide, which rises from magma as a gas. Condensed phosphates e.g. react with sugars to yield phosphoric acid esters or with amino acids to create reactive intermediate products. These compounds already contain the key structural feature of ATP, the carrier of chemical energy in the cell. All this aligns fairly well with hypotheses which assume that life was created near hydrothermal fluids (black smokers). However, the problem with this is that the concentrations of these compounds in volcanic fluids are low – too low for prebiotic chemistry.

In theory, the naturally occurring phosphate minerals can simply be reduced to the phosphonate (phosphite) $\text{HP}_2\text{O}_4^{2-}$. This is thousands of times more water-soluble than phosphate and therefore could e.g. accumulate normally and be involved in chemical reactions. The main problem with this is that the reduction of phosphate into phosphonate (phosphite) requires a vast amount of energy, which is why it was for a long time considered unlikely.

- De Graaf et al (1996) and Schwartz (1996 and 2006) were able to demonstrate in laboratory tests that there is one spectacular way in which volcanoes may have created large volumes of phosphite during eruptions. Under conditions similar to those of the early Earth's atmosphere, electrical discharges highly effectively convert phosphates into phosphonates (phosphite). For this to happen, a lot of phosphate-containing dust must be present near lightning, as is e.g. the case in the eruption cloud of volcanoes. Since volcanism was more intense on the early Earth than it is today,

¹¹ Pasek MA (2008): Rethinking early Earth phosphorous geochemistry <http://www.pnas.org/content/105/3/853.short>

considerable amounts of phosphite may have been created in this way and have reached the oceans.

"The interest of phosphite as a possible prebiotic phosphorous source is not only due to the higher solubility of its calcium-salt compared to apatite (approx. 1000 times higher), but also to its greater reactivity as a phosphorylating agent. It has been established that ammonium phosphate for example, readily reacts with nucleosides to yield nucleoside-phosphites (nucleoside-H-phosphonates) under conditions in which ammonium phosphate is unreactive" (Schwartz 2006).

- Pasek (2008) describes another natural way for phosphorus compounds to be created in the prebiotic early earth. The mineral schreibersite (Fe,Ni)₃P found extra-terrestrially on meteorites reacts with water to yield siderophile P-compounds. These reduced P-compounds are much more soluble and reactive than orthophosphates.

"The primary product of schreibersite oxidation by water is phosphite, HPO₃²⁻, with >50% of the total aqueous P in this form. A majority of these P compounds likely originate through free radical combination reactions" (Pasek 2008).

"Phosphorous acid is considered to be the plausible prebiotic source of phosphorus due to its hydrolytic production from the mineral schreibersite." (Gulick 1955)

De Graaf et al (1996), Pasek (2008), Schwartz (2006) substantiate the occurrence of P-compounds in "ancient rocks, older than 2.5 billion years" as well as in meteorites, i.e. carbonaceous chondrites¹².

They were able to provide evidence of CaHPO₃ and NaH₂PO₃. However, phosphonates (phosphites) are highly unstable and reactive. For example, potassium phosphonate in plants very rapidly breaks down into the potassium and the HPO₃²⁻ ion, while the phosphite ion as an active agent is responsible for triggering the "systemically induced resistance" (SIR). The HPO₃²⁻ ion is highly mobile and in plants is transported both in the phloem and in the xylem.

"The detection of small quantities of reduced P-oxides (e.g. Phosphite and hypophosphate) or reduced C-P compounds in ancient sedimentary or metasedimentary rocks would provide strong evidence for reduced P in early Earth geochemistry" "The geochemistry of P on the early Earth is proposed to have included reduced P compounds in addition to phosphate" (Pasek 2008).

¹² Carbonaceous chondrites are grouped according to distinctive compositions thought to reflect the type of parent body from which they originated. These are named after a prominent meteorite — often the first to be discovered — in the group. Several groups of carbonaceous chondrites, notably the CM and CI groups, contain high percentages (3% to 22%) of water, as well as organic compounds. They are composed mainly of silicates, oxides and sulphides, while the minerals olivine and serpentinite are characteristic. The presence of volatile organic chemicals and water indicates that they have not undergone significant heating (>200°C) since they formed, and their compositions are considered to be close to that of the solar nebula from which the solar system condensed. Other groups of C chondrites, e.g., CO, CV, and CK chondrites, are relatively poor in volatile compounds, and some of these have experienced significant heating on their parent asteroids. http://en.wikipedia.org/wiki/Carbonaceous_chondrite

4.3. Biogenic occurrence

Biologically formed, reduced phosphorous compounds can also be found in nature. Even the most strongly reduced phosphorous compound phosphine has been shown to occur. It has been suspected for more than a century that microbes are able to reduce phosphate and that a biologically mediated phosphorus cycle actually exists.

But when considering the mineralogical role of phosphonates, phosphonic acid and phosphite, it remained unclear how they are involved in the natural cycle.

"The individual stages of phosphate reduction contain extremely low redox potential of up to -900 mV, whereas the reduction potential of a living cell is only around -500 mV to -320 mV. As a result, it seemed unlikely that phosphate respiration could be tied in with biomass oxidation. On the other hand, e.g. phosphite is an excellent electron donor for microbial respiration processes"¹³.

- When phosphite was discovered in the sediment of the Canal Grande in Venice (Friedrich 2000, Schink et al 2001, Simeonova et al 2010) as a "new", previously unknown electron donor for the development of special sulphate-reducing bacteria, this gap was successfully closed based on scientific consensus.

Scientists at the Max Planck Institute for Terrestrial Microbiology and at the University of Constance discovered a bacterium which obtains its energy from a chemical reaction that had not previously been known to occur in biological systems. In this reaction, electrons are exchanged between the anorganic phosphorous compound phosphite and a sulphur compound. This yields phosphate, which is a component of numerous important compounds such as the genetic material DNA.

The strictly anaerobic bacterium *Desulfotignum phosphitoxidans* sp. oxidises phosphite by reducing sulphate to yield phosphate or "homoacetogenically"¹⁴ reducing CO₂ to yield acetate.



Fig. 4 shows phosphonate (phosphite) oxidation.

¹³ Friedrich (2000) Phosphite oxidation by bacteria
Different energy extraction channels

Sulphate-reducing bacteria catalyse a previously unknown reaction in the biological phosphorus cycle

¹⁴ Simeonova et al (2010) Identification and heterologous expression of genes involved in anaerobic dissimilatory phosphate oxidation by *Desulfotignum phosphitoxidans* J. Bacteriol. **192**, 5237-5244

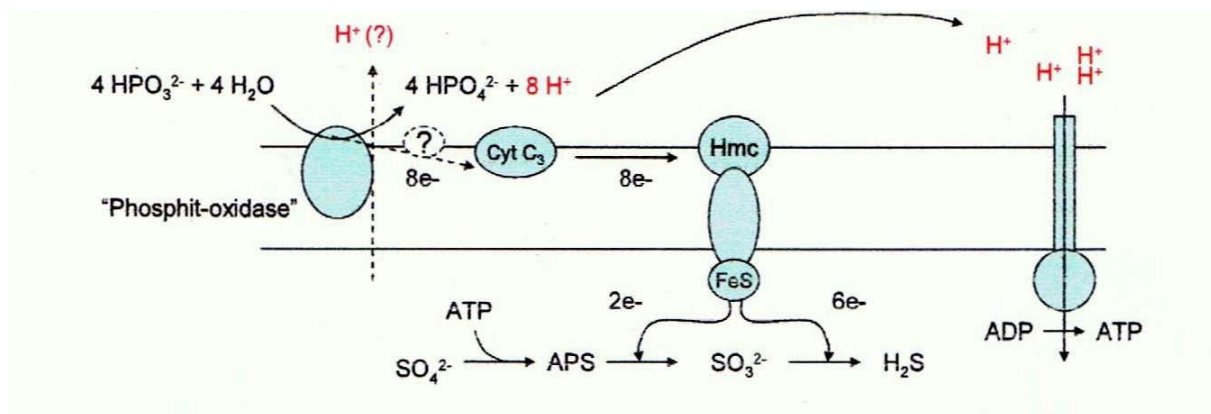


Fig. 4: Phosphonate (phosphite) oxidation

The microbial oxidation of phosphonate with the oxidation agent sulphate, which is uncommon in chemistry, is surprising because sulphate activation requires vast amounts of energy.

"The oxidative formation of phosphate from phosphonate (phosphite), as a novel substrate phosphorylation, during which an additional ATP molecular could be created for each oxidised phosphite, ... The combination of phosphite and an enzyme-bound carboxylate, and the subsequent oxidation, could yield acylphosphate whose energy-rich phosphate residue could easily be transferred to ADP alongside the formation of ATP"¹⁵.

Sulphate-reducing microorganisms normally play an important role in the decomposition of organic compounds as part of the global carbon cycle. The present findings reveal an altogether new understanding of a biologically mediated phosphorus cycle. Reduced phosphorus compounds can be converted to phosphate through microbial catalysis.

On the early Earth, when the atmosphere did not yet contain oxygen, reduced phosphorus compounds may have been important. 3.8 billion years ago, when life began on Earth, phosphites as precursors of phosphates may have played a greater role than they do today.

The oxidation of phosphite by anaerobic sulphate-reducing bacteria may thus be an evolutionary relict from the early development of life on Earth.

According to Buckel (2001), the discovery of this bacterium opens up the possibility to describe a biological phosphorus cycle which has not been done so far.

Source:

Phosphoenolpyruvate (+5) → Phosphinothricin (+1) → Phosphinate (+1) →
Phosphine (-3) / Phosphonate (phosphite) (+3) → Phosphate (+5)

Like phosphite, phosphane oxidises directly using oxygen from the air to yield phosphate.

¹⁵ BUCKEL W (2001) Anorganic chemistry in marine sediments, Applied Chemistry 113(8), 1463 - 1464

- Phosphonopyruvate, the physiological substrate of phosphonopyruvate decarboxylase, belongs to the class of substances known as phosphonates, whose characteristic is a stable, covalent carbon-phosphorus bond. This direct C-P bond, which replaces the carbon-oxygen-phosphorus bond extant in phosphate esters, is highly inert on a chemical and thermal level. As a result, organic phosphonates, compared to the more reactive oxygen, sulphur and nitrogen-phosphorus compounds, are significantly more resistant to chemical hydrolysis, thermal decomposition and photolysis. Based on the analysis of samples from a meteorite, the hypothesis was posited that phosphonates were the precursors of phosphates (Cooper *et al.*, 1992; de Graaf *et al.*, 1995) and that, with increasing oxygenation of the atmosphere, both phosphonates and C-P-bond-forming and -splitting enzymes were replaced by phosphates and corresponding enzymes (Jia *et al.*, 1999).

Von Johnen (2005) was able to corroborate the bio-synthesis path of phosphonates as a phosphonopyruvate decarboxylase enzyme reaction. Phosphonopyruvate, the physiological substrate of phosphonopyruvate decarboxylase, belongs to the class of phosphonates, whose characteristic is a stable, covalent carbon-phosphorus (C-P) bond and which as a result are resistant to chemical hydrolysis, thermal decomposition and photolysis.

Starting with phosphoenolpyruvate, their biosynthesis is normally initiated by the enzyme combination

phosphoenolpyruvate phosphomutase and phosphonopyruvate decarboxylase.

Phosphonopyruvate decarboxylase catalyses the phosphonopyruvate decarboxylation to yield phosphonoacetaldehyde, which results in the elimination of phosphonopyruvate from the Ppm-catalysed PEP/PnPyr isomerisation and hence the creation of the C-P bond.

5. Findings

5.1. Does potassium phosphonate occur in nature as an anorganic salt and if so, in what form?

Potassium phosphonate, as an anorganic salt of phosphonic acid, is not described as occurring naturally in this form.

The literature contains references to the occurrence of calcium and sodium phosphite.

There is sufficient evidence of the occurrence of phosphonic acid and phosphite anhydride.

However, the early history of the Earth's creation and of life on Earth provides indications that, under conditions extremely hostile to life of H₂ / CO₂-saturated air and predominant volcanism, both organic phosphonates with a C-P bond and phosphonic acid / phosphite anhydride did occur.

Anorganic phosphite is significantly more reactive and water-soluble than phosphate and, as a reduced P-compound, is thus considered to be an intermediary compound in prebiotic chemistry to yield phosphate.

Particularly the solubility in water of the mineral schreibersite, which is found in large quantities in meteorites, yielding anorganic phosphite, is clear evidence for natural occurrence.

Evidence of phosphite-oxidising and sulphate-reducing bacteria in anoxic marine sediments leads to the conclusion that these bacteria contributed during the early phase of development to form phosphate, as an essential building block of the energy cycle and DNA, by oxidising phosphite.

5.2. Can potassium phosphonate be considered a naturally occurring mineral?

Based on the cited scientific works, it can be concluded that the anorganic salts of phosphonic acid are naturally occurring mineral substances which however are only intermediary products.

Potassium phosphonate, as an anorganic salt of phosphonic acid, is not mentioned in the literature.

However, the calcium salt of phosphonic acid CaHPO₃ is described as an intermediary salt of phosphonic acid during the weathering of meteorites and ancient rocks. Since water-solubility and reactivity is very high in the presence of oxygen, these substances are rare in terrestrial nature nowadays, and only occur under anoxic conditions, such as in marine sediments.

This hypothesis is corroborated by evidence of phosphite oxidation by sulphate-reducing bacteria in marine sediments.

5.3. Conclusions: What is the nature of the substance potassium phosphonate as an anorganic salt of phosphonic acid?

Scientific works on prebiotic chemistry and on the discovery of phosphite-oxidising bacteria and the reduction of sulphate to yield phosphate, do not explicitly mention potassium phosphonate (phosphite) ($\text{KH}_2\text{PO}_3 + \text{K}_2\text{HPO}_3$), as an anorganic salt of phosphonic acid. By contrast, another salt of phosphonic acid, calcium phosphonate CaHPO_3 is described as an intermediary, naturally occurring salt from the weathering of meteorites and ancient rocks. From this, it can be concluded that the potassium salt of phosphonic acid at least has a natural, mineral source.

Phosphonic acid and the phosphonate ion HPO_3^{2-} are described as naturally occurring, intermediary stages in the biological phosphorus cycle.

According to the cited scientific works, phosphonate oxidation to yield phosphate is one of the most important prebiotic reactions for the creation of life on Earth. But since these substances only occur in a stable form under anaerobic conditions extremely hostile to life, their terrestrial occurrence is hardly conceivable in air enriched with oxygen.

Anoxic marine sediments are home to specialised bacteria which oxidise anorganic phosphonate to yield phosphate through the reduction of sulphate. The discovery of these bacteria and of the reduction of sulphate used by them to form phosphate, is seen as an indication that larger quantities of anorganic phosphonate or phosphonic acid and their salts occurred in prebiotic chemistry.

It can thus be concluded from the literature research on which this expert's report is based that:

- Potassium phosphonate, as an anorganic salt of phosphonic acid, does not occur in nature directly.
- The salts of phosphorous acid, and phosphonate, might play a key role in prebiotic chemistry and the development of life on earth.
- The salts of phosphorous acid, and phosphonate as well as anhydrite HPO_3^{2-} , are highly reactive and highly water-soluble. Therefore, they are described as an intermediary carrier in prebiotic chemistry.
- The discovery of phosphite oxidation by anaerobic bacteria in marine sediments to yield phosphate with the use of sulphate as the electron donor, closed the biological phosphorus cycle. This is generally considered to be clear evidence of the prebiotic presence of phosphorous acid.

Even if potassium phosphonate cannot be said to directly occur in nature as a mineral due to its high chemical reactivity, the natural occurrence of anorganic salts of phosphonic acid (intermediary) has nevertheless been evidenced.

From this, the natural character of the substance can be deduced.