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MINI REVIEW

Anaerobic dissimilatory phosphite oxidation, an extremely efficient concept of microbial electron economy

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Abstract

Phosphite is a stable phosphorus compound that, together with phosphate, made up a substantial part of the total phosphorus content of the prebiotic Earth's crust. Oxidation of phosphite to phosphate releases electrons at an unusually low redox potential (690 mV at pH 7.0). Numerous aerobic and anaerobic bacteria use phosphite as a phosphorus source and oxidise it to phosphate for synthesis of nucleotides and other phosphorus-containing cell constituents. Only two pure cultures of strictly anaerobic bacteria have been isolated so far that use phosphite as an electron donor in their energy metabolism, the Gram-positive *Phosphitispora fastidiosa* and the Gram-negative *Desulfotignum phosphitoxidans*. The key enzyme of this metabolism is an NAD^+-dependent phosphite dehydrogenase enzyme that phosphorylates AMP to ADP. These phosphorylating phosphite dehydrogenases were found to be related to nucleoside diphosphate sugar epimerases. The produced NADH is channelled into autotrophic CO_2 fixation via the Wood-Ljungdahl (CO-DH) pathway, thus allowing for nearly complete assimilation of the substrate electrons into bacterial biomass. This extremely efficient type of electron flow connects energy and carbon metabolism directly through NADH and might have been important in the early evolution of life when phosphite was easily available on Earth.

INTRODUCTION

The element phosphorus exists in nature in numerous redox states, from III (PH_3, phosphine) to +V (HPO_4^{2-}, phosphate). Phosphine is highly toxic and unstable in the presence of air oxygen, and the latter is true also for elemental phosphorus (Emsley & Huxtable, 2000; Schink, 2005; Schink & Simeonova, 2015); only hypophosphite ($H_2PO_2^-$), phosphite (HPO_3^{2-}), and phosphate are stable under air. Hypophosphite and phosphite are found in minor amounts in meteorite minerals such as schreibersite (Pasek, 2008; Pasek & Lauretta, 2008), and also in recent waters and swamps (Pasek et al., 2014). They are constituents of geothermal fluids (Pasek et al., 2014; Pech et al., 2001) and are formed also by lightning strikes (Pasek & Block, 2009). Reduced phosphorus species were probably more abundant in the early Archaean ocean (Pasek et al., 2013) and may have played an essential role in the early evolution of life (Pasek et al., 2022).

Oxidation of phosphine via elemental (white) phosphorus, hypophosphite and phosphite to phosphate releases electrons at very low redox potentials (E_0' 525, 922, 913, and 690 mV, respectively) (Schink, 2005; Schink & Friedrich, 2000), a property that renders these phosphorus compounds good electron donors but very bad electron acceptors for a microbial metabolism. Nonetheless, reports on biological reduction of phosphate to phosphine appeared repeatedly in the literature (see Roels & Verstraete, 2001; Schink, 2005 for overviews). In the early papers, a 'garlic-like odour' of undefined enrichment cultures was taken as proof of

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phosphine formation; fortunately, nobody died from this dangerous qualitative product analysis! This smell was probably due to mercaptanes formed from peptone and other amino acid-rich medium additions in these cultures. The first reliable proofs of phosphine in natural sampling material were reported by Glindemann and coworkers (Glindemann et al., 1998), using up-to-date analytical gas chromatography and mass spectroscopy techniques. These authors found traces of phosphine (in the low nanomol per litre range) in harbour sediments where they were formed probably by microbially enhanced hydrolysis of phosphide-containing stainless steel scrap metals. Similar low concentrations of phosphine were found in manure samples of cattle, swine, and man (Gassmann & Glindemann, 1993) but its origin remained obscure. Perhaps the digestion of organophosphonates and organophosphinates (compounds containing C-P linkages) contributed to the formation of these trace findings. Until now, there is no reliable proof of microbial reduction of phosphate to phosphine in the literature.

On the other hand, partly reduced phosphorus compounds were found to be used as phosphorus source by several aerobic and anaerobic bacteria. A '*Bacillus caldolyticus*' strain was reported to use hypophosphite or phosphite as a phosphorus source (Heinen & Lauwers, 1974) via a 'hypophosphite oxidase' which, unfortunately, was not characterised in detail, and the host strain is not available anymore. More detailed studies on assimilatory phosphite utilisation were performed with *Klebsiella aerogenes*, *Escherichia coli*, and *Pseudomonas stutzeri* strain WM 88 (Imazu et al., 1998; Metcalf & Wanner, 1991; Metcalf & Wolfe, 1998). The latter bacterium oxidises hypophosphite via phosphite to phosphate; genetic analysis indicates that the first step is catalysed by an oxygenase enzyme. Phosphite is oxidised to phosphate by an NAD^+-dependent phosphite dehydrogenase (Garcia Costas et al., 2001). The reaction appears to be irreversible which is not surprising, considering the huge electron potential difference between the electron donor (E_0' 690 mV) and the acceptor system (E_0' 320 mV). The enzyme is very specific for phosphite as electron donor and, according to sequence similarities, is related to D-hydroxyacid dehydrogenases. The reaction mechanism of this enzyme has been discussed on the basis of three different models which all include a hydride transfer from phosphite to NAD^+ but differ towards the nature of the primary attack on the phosphite molecule (Vrtis et al., 2001).

The low redox potential of the phosphate/phosphite redox pair renders phosphite an excellent electron donor also for a microbial energy metabolism. Nonetheless, only two pure cultures of strictly anaerobic bacteria and some enrichment cultures have been described so far which run their energy metabolism on the basis of phosphite oxidation. The Gram-negative *Desulfotignum phosphitoxidans* (Schink et al., 2002; Schink & Friedrich, 2000) is a sulphate reducer that uses phosphite, beyond other substrates, as an electron donor for a chemolithoautotrophic type of metabolism with either sulphate or CO_2 as terminal electron acceptor. A Gram-positive, spore-forming isolate, *Phosphitispora fastidiosa*, is specialised on the utilisation of phosphite as sole electron donor and CO_2 as electron acceptor (Mao et al., 2021). Dissimilatory anaerobic oxidation of phosphite to phosphate was also observed in undefined enrichment cultures (Ewens et al., 2021; Figueroa et al., 2018).

In the subsequent chapters, we will concentrate on this novel type of metabolism, showing that in our pure cultures the phosphite electrons are nearly entirely assimilated into cell material, thus documenting an extremely efficient type of chemolithoautotrophic metabolism.

FIGURE 1 Growth and stoichiometry of substrate conversion by *Phosphitispora fastidiosa* and *Desulfotignum phosphitoxidans* in anoxic mineral medium with phosphite as electron donor and carbon dioxide as electron acceptor. *P. fastidiosa* strain DYL19 (GDMCC 1.2680) and *D. phosphitoxidans* strain FiPS-3 (DSM 13687) were grown with 10 or 15 mM sodium phosphite as sole electron donor and carbon dioxide as sole electron acceptor in marine or freshwater mineral medium under strictly anoxic conditions in the dark at 30°C as described before (Mao et al., 2021; Schink et al., 2002). Shown are mean values of triplicates ± standard deviation. Some error bars are smaller than symbol size.

PHOSPHITE AS AN ENERGY SOURCE

Anaerobic enrichment cultures with phosphite as sole electron donor in bicarbonate-buffered media were

started in our lab more than 20 years ago (Schink & Friedrich, 2000). Cultures always grew rather slowly, and addition of sulphate as electron acceptor did not increase the growth rates. A first pure culture of a Gram-negative bacterial strain was obtained in 2000 (Schink et al., 2002; Schink & Friedrich, 2000), and a second culture of a Gram-positive spore-forming bacterium only recently (Mao et al., 2021). Both strains grow slowly, with doubling times of 2.5–3 days, but with comparably high molar growth yields (10–12 g cell dry mass per mol phosphite). They use phosphite as electron donor for their energy metabolism, but also for autotrophic CO_2 fixation via the CO dehydrogenase (Wood-Ljungdahl) pathway. Unnecessary to mention, they assimilate phosphorus as phosphate that is supplied with the medium and is also produced through their energy metabolism.

Time-dependent growth of *P. fastidiosa* and *D. phosphitoxidans* with documentation of substrate and products is shown in Figure 1. In these experiments, phosphite was the only electron source, together with CO_2/HCO_3^- as electron acceptor. The only major products detected were phosphate and cell material. Occasionally, traces of acetate (<0.2 mM) were detected as a side product. Cultures of *D. phosphitoxidans* produced slightly more acetate (<0.6 mM acetate). In the presence of sulphate, *D. phosphitoxidans* produced also small amounts of sulphide (<1 mM). No further organic or inorganic side products were detected by HPLC or chemical analyses.

The phosphite-oxidising enzyme in both pure cultures in our lab turned out not to be sensitive to oxygen. The biochemical characterisation of this enzyme and its properties are being described in a separate paper (manuscript in preparation). Here, we can state that phosphite is oxidised to phosphate with NAD^+ as electron acceptor, and that through this reaction AMP is phosphorylated to ADP:

$$HPO_3^{2-} + AMP + NAD^+ \rightarrow ADP + NADH + H^+.$$

An adenylate kinase (myokinase) enzyme subsequently converts ADP to AMP and ATP. This way, the free energy change of phosphite oxidation with NAD^+ as electron acceptor ($\Delta G_0'$ 71 kJ per mol) is nearly quantitatively conserved in an energy-rich phosphoanhydride linkage (Thauer et al., 1977; Buckel, 2001), and the electrons from phosphite oxidation are available for CO_2 fixation into cell material via the CO dehydrogenase (Wood-Ljungdahl) pathway.

Comparison of gene sequences of the two dissimilatory phosphite dehydrogenases described so far with sequences available in public databases revealed only

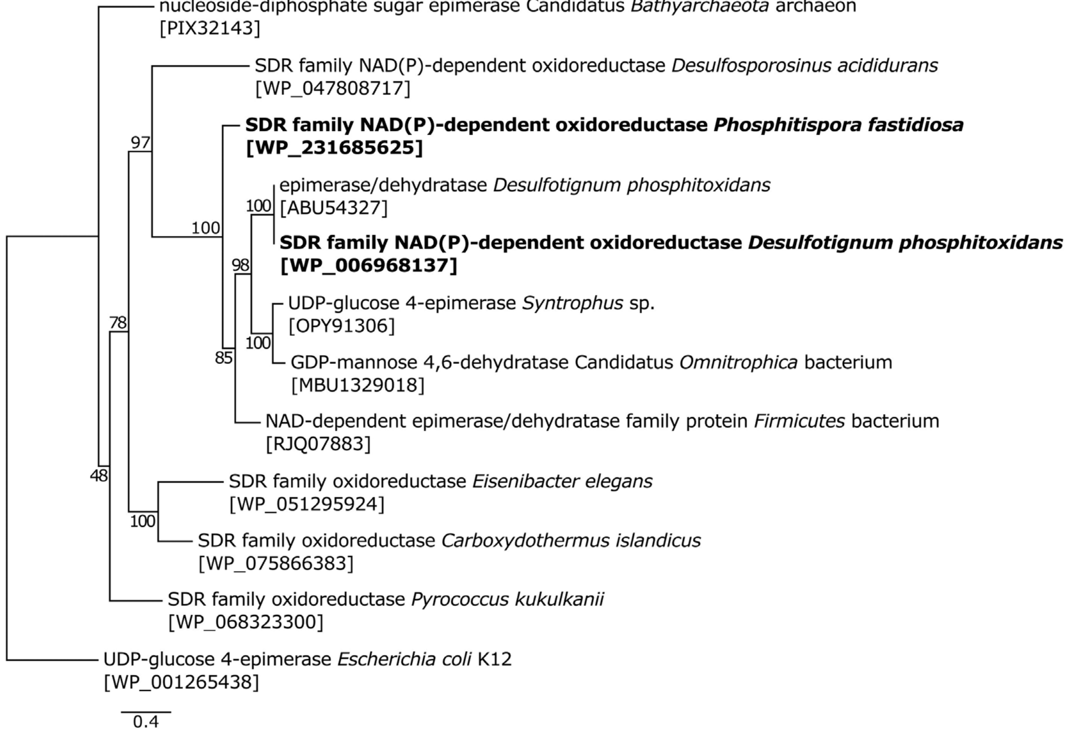


FIGURE 2 Phylogenetic distance tree of SDR family NAD(P)-dependent oxidoreductase of *Phosphitispora fastidiosa* (bold) showing the affiliation with similar sequences of other bacteria. The bar length represents 0.4 amino acid substitutions; bootstrap values and NCBI Accession numbers (squared brackets) are given. Protein alignment was calculated with Muscle v.3.8.1551 (Edgar, 2021) and used to calculate the tree with RAxML v.8.2.12 (Randomised Axelerated Maximum Likelihood) (Stamatakis, 2014) with the GAMMA model and 1000 bootstraps. The tree was rebooted with the *Escherichia coli* K12 UDP-glucose 4-epimerase in FigTree v1.4.4 (http://tree.bio.ed.ac.uk/software/figtree/).

distant relationships to any other enzymes described so far: Highest similarities were found with nucleotide sugar epimerases (Figure 2). One of the most prominent members of this protein family is UDP-glucose 4-epimerase which isomerizes UDP-glucose to UDP-galactose (Beerens et al., 2015). These enzymes bind nucleosides and isomerize their sugar moieties via partly oxidised keto intermediates; NAD(P) acts as intermediary electron acceptor for these intramolecular redox reactions, which are overall redox neutral (Beerens et al., 2015). With this, they combine nucleotide binding sites with the presence of NAD(P) as a redox partner, properties that we expect to find as well with our AMP-dependent phosphite dehydrogenases. A high degree of substrate promiscuity was described and predicted for UDP-hexose 4-epimerases, and many of these enzymes might have various novel, unexpected substrates (Beerens et al., 2015). It is hence conceivable that variants of this class of enzymes might also catalyse rather unusual reactions, that is, the phosphorylation of nucleosides with phosphite.

PHYSIOLOGICAL IMPLICATIONS

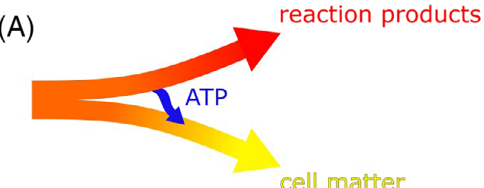
Utilisation of inorganic electron donors in microbial metabolism is a phenomenon commonly known as lithotrophy. Several reduced inorganic compounds such as CO, H_2, H_2S, SO_3^{2-}, $S_2O_3^{2-}$, S_0, NH_3, NO_2^-, Fe^{2+}, or Mn^{2+} can act as electron donors for a microbial energy metabolism either in the dark (chemolithotrophy) or in the light (photolithotrophy) (Madigan et al., 2006). Of these, only CO and H_2 can directly reduce NAD^+ and feed their electrons in at the top of the respiratory chain; all others, due to their higher redox potentials, channel their electrons in at the level of quinones or cytochromes, with consequently lower ATP yields. Quite often, microbial lithotrophy is also associated with autotrophy, that is, the synthesis of all cell components from CO_2, for which aerobic lithotrophs most often use the Calvin cycle; strict anaerobes prefer, among others, the energetically much more efficient CO dehydrogenase pathway for cell matter synthesis. Whether the often-observed coincidence of lithotrophy and autotrophy is a consequence of a certain bias in our cultivation efforts is an open question that may be a matter for future research. Depending on the energy yields in the lithotrophic energy metabolism and the energy efforts spent into cell matter synthesis, the relative amounts of electron flow through the branches for energy and carbon metabolism will vary (Figure 3): In aerobic, heterotrophic metabolism, about equal amounts of electrons flow through both branches (Figure 3A). An energetically less prolific anaerobic energy metabolism has to spend more substrate and electron flow into the ATP-yielding metabolic branch, and can therefore synthesise far less cell material than an aerobic metabolism can. This is especially true for an anaerobic chemolithoautotrophic metabolism with high energy expenditure into cell carbon synthesis (Figure 3B).

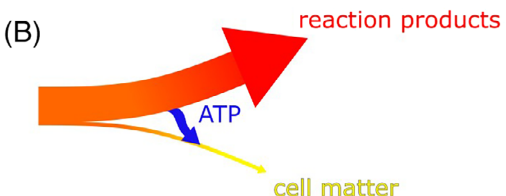
An entirely different situation arises with the metabolism of our anaerobic phosphite-oxidising bacteria. In our growth experiments illustrated in Figure 1, the phosphite electrons go nearly completely into the reduction of CO_2 to cell material, according to the formula

$$17\,HPO_3^{2}\ +7\,H_2O+8\,CO_2 \rightarrow 17\,HPO_4^{2}\ +2<C_4H_7O_3>.$$

Small amounts of acetate (<1 mM from 10 to 15 mM phosphite) or, with *D. phosphitoxidans* in the presence of sulphate, of sulphide were produced as side products. Thus, the entire electron flow can first be used for the synthesis of energy-rich phosphoanhydride bonds in AMP-dependent phosphite oxidation. Afterwards, the electrons deposited with NADH still are all available for cell matter synthesis (Figure 3C), and very little acetate (or sulphide) is formed as a side product of energy metabolism. Thus, all electrons provided with the substrate can be used twice, first for energy generation and subsequently for cell matter synthesis. Correspondingly, the molar cell yields of anaerobic phosphite oxidation are unusually high, with 10–12 g cell mass per mol phosphite (see Mao et al., 2021; Schink et al., 2002). For comparison, known lithoautotrophic homoacetogens or sulphate reducers growing with hydrogen or formate obtain growth yields of 0.6–2.4 g dry cell mass per mol electron pair (Cypionka & Pfennig, 1986; Eichler & Schink, 1984; Klemps et al., 1985; Tschech & Pfennig, 1984). On average, a specific ATP yield coefficient of 10.5 g dry mass per mol ATP has been experimentally obtained and has been used for such calculations (Bauchop & Elsden, 1960; Stouthamer & Bettenhaussen, 1973). Thus, the differences in cell yields between hydrogen and formate on the one and phosphite on the other hand corresponds to the equivalent of one ATP per electron pair, as deduced from the phosphite dehydrogenase reaction above. Obviously, our phosphite utilizers exploit their energy very efficiently, and the CO dehydrogenase pathway proves again to be a very efficient pathway for cell matter synthesis. To some extent, the metabolic concept of chemotrophic phosphite oxidation is comparable to that of anoxygenic phototrophic bacteria (Madigan, 1988; Pfennig, 1967): Also in their case, the entire electron freight supplied with the electron-donating substrate can be assimilated into cell matter because the metabolic energy needed for biosynthetic reactions is supplied separately, in their case externally by light.

A typical feature of lithoautotrophic types of metabolism, especially those using sulphur or nitrogen compounds as electron donors and also most hydrogen oxidisers, is the phenomenon of reversed electron transport in carbon assimilation (Aleem, 1980): Since the





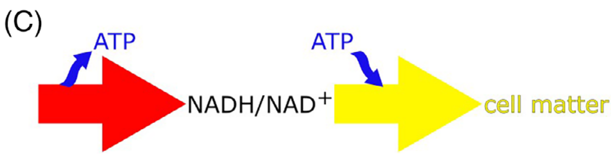


FIGURE 3 Simplified electron flow schemes in microbial metabolism. (A) Aerobic heterotrophic metabolism; (B) anaerobic metabolism, either by fermentation or by anaerobic respiration; (C) anaerobic oxidation of phosphite by *Desulfotignum phosphitoxidans* and *Phosphitispora fastidiosa*. Orange: Total electron flux; Red: Electron flux into energy metabolism; Yellow: Electron flux into cell carbon synthesis.

electrons supplied by these donors are channelled into the respiratory chain at the level of quinones or c-type cytochromes, part of these electrons have to be 'pumped' against the electrochemical potential to provide NADH that is needed for autotrophic CO_2 fixation (Figure 4). This energetic problem arises in lithoautotrophic phosphite assimilation by our bacteria only for the low-potential ferredoxin electrons needed for reduction of CO_2 to CO in the CO dehydrogenase reaction; for this step a membrane-bound Rnf complex would be helpful that shifts electrons from the NADH to the ferredoxin level. Five subunits *rnfCDGEA* of such a complex were found in the genome of *D. phosphitoxidans* (IMG-locus tags FiPS3_00252 – FiPS3_00256); one subunit, (*rnfB*), was not found but may be incorrectly annotated as a membrane domain of an aminodeoxychorismate lyase located in the direct neighbourhood of these five genes and on the same gene cluster (FiPS3_00257). In *P. fastidiosa*, we found one gene that has been annotated as a Na^{+}-translocating ferredoxin: NAD^{+} oxidoreductase RnfC subunit (IMG-locus tag Ga0451573_009_92767_94101, NCBI locus tag Ga0451573_RS10095, protein name: 4Fe-4S dicluster domain-containing protein); the other subunits are missing. Thus, for this bacterium we have to postulate an alternative way for shifting electrons from the NADH to the ferredoxin level. All other reduction steps required for this CO_2 fixation pathway can be served with NADH electrons that are supplied by phosphite oxidation.

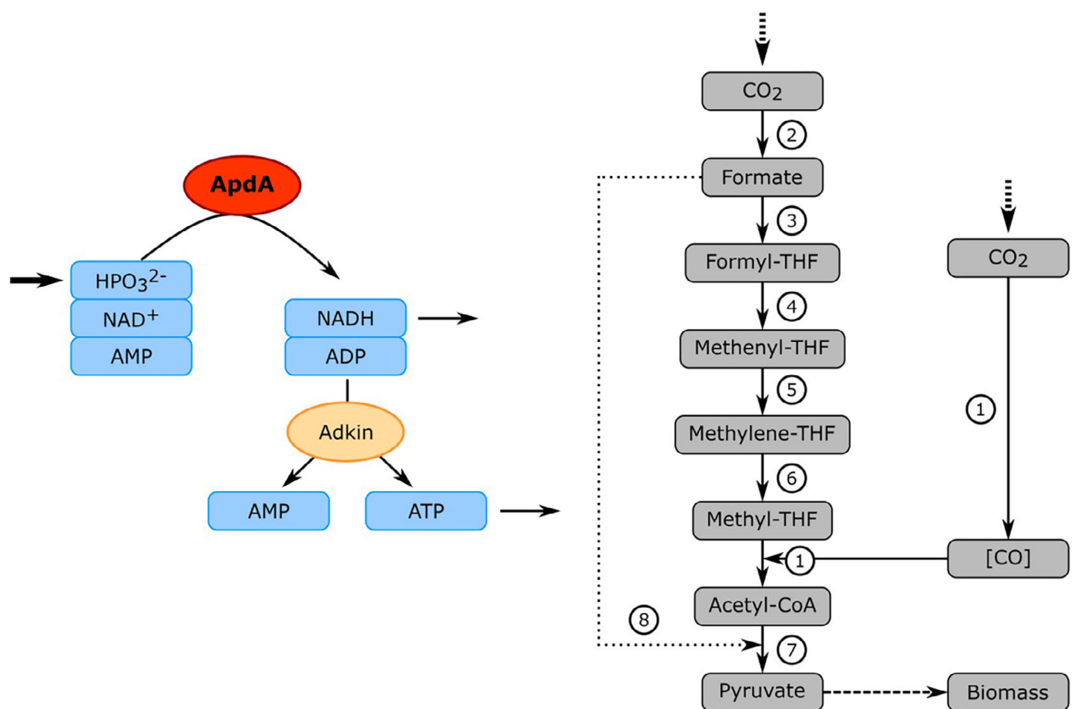


FIGURE 4 Overview of the metabolism of *Phosphitispora fastidiosa*. ApdA: AMP-dependent phosphite dehydrogenase; Adkin: Adenylate kinase (myokinase); (1) Carbon monoxide dehydrogenase (acetyl-CoA synthase); (2) Formate dehydrogenase; (3) Formyl-THF synthetase; (4) Methenyl-THF cyclohydrolase; (5) Methylene-THF dehydrogenase; (6) Methylene-THF reductase; (7) Pyruvate ferredoxin/flavodoxin oxidoreductase; (8) Pyruvate-formate lyase.

Our dissimilatory phosphite oxidisers *D. phosphitoxidans* and *P. fastidiosa* exhibit an unusually efficient concept of energy metabolism as exemplified in Figures 3C and 4. This simple concept combines energy metabolism and cell matter synthesis directly, in a way that was probably especially helpful in the early phase of bacterial evolution. At that time, phosphite was not only a valuable electron source but also a phosphorus source that was better water-soluble than phosphate, and its uptake did not require so expensive uptake systems as they are needed for phosphate uptake today (Wanner, 1993). This economic strategy combines perfectly with the assimilation of cell matter through the CO dehydrogenase (Wood-Ljungdahl) pathway which, due to its extreme efficiency, is assumed to be the oldest pathway of cell matter synthesis (Martin, 2020).

AUTHOR CONTRIBUTIONS

Zhuqing Mao: Conceptualization (equal); data curation (equal); formal analysis (equal); investigation (equal); writing – original draft (supporting). **Nicolai Mueller:** Conceptualization (equal); data curation (equal); formal analysis (equal); supervision (equal); validation (equal); writing – review and editing (equal). **Sabrina Borusak:** Data curation (equal); formal analysis (equal). **David Schleheck:** Conceptualization (equal); data curation (equal); formal analysis (equal); supervision (equal); writing – review and editing (equal). **Bernhard Schink:** Conceptualization (equal); data curation (equal); formal analysis (equal); writing – review and editing (equal).

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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