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1 **On the why's and how's of clay minerals' importance in life's emergence**

2

3 Simon Duval^{1*}, Elbert Branscomb², Fabienne Trolard³, Guilhem Bourrié³, Olivier Grauby⁴,

4 Vasile Heresanu⁴, Barbara Schoepp-Cothenet¹, Kilian Zuchan¹, Michael J. Russell^{5,6} and

5 Wolfgang Nitschke¹

6

7

8¹Aix Marseille Univ, CNRS, BIP (UMR 7281), Marseille, France

9

10²Carl R. Woese Institute for Genomic Biology, and Department of Physics, University of

11 Illinois, Urbana, Illinois, 61801, USA

12

13³EMMAH (UMR 1114), INRA, Avignon, France

14

15⁴Aix Marseille Univ., CINaM (UMR 7325), Luminy, France

16

17⁵NASA Astrobiology Institute, Ames Research Center, California, USA

18

19⁶Dipartimento di Chimica, Università degli Studi di Torino, via P. Giuria 7, 10125 Turin, Italy

20

21*Corresponding author: sduval@imm.cnrs.fr; phone: +3391164435

22

23**Abstract:**

24 A possibly prominent role for Green Rust minerals in life's emergence is inferred from a
25 comparison of their structural, mechano-dynamic and electrochemical properties and of the
26 layout of bioenergetic, i.e. free energy converting processes in extant organisms. From
27 fundamental thermodynamic considerations, the conversion of environmental free energy into
28 the decrease of entropy that defines life is an indispensable ingredient for life to emerge. A
29 specific scenario for life's emergence mediated by Green Rust minerals in the framework of
30 the alkaline hydrothermal vent hypothesis is proposed.

31

32**Keywords:**

33 Emergence of life, Green Rust, double layered Fe-oxyhydroxides, alkaline vent hypothesis,
34 bioenergetics, fougérite

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371.1. The focus on catalysis; betting on the wrong horse?

38 The potential relevance of clay minerals to origin of life research has been recognised
39 several decades ago (Bernal, 1951; Greenland et al. 1962; Cairns-Smith, 1966, 1982;
40 Solomon, 1968; Odom et al., 1979; Rao et al., 1980; Ponnampereuma et al., 1982). Due to their
41 extraordinary sorption properties, clays have been shown to accumulate monomers (mostly
42 organic molecules) from the solvent to local concentrations exceeding those of the bulk by
43 several orders of magnitude (Lailach et al., 1968; Ferris et al., 1996; Ferris, 2002; Aldersley et
44 al., 2011). The reduction in degree of orientational freedom of these monomers, brought about
45 by essentially restricting them to two dimensions, *i.e.* surfaces, adds a further intriguing
46 property to clay-type minerals. Of these, the anion-exchanging clays, hydrotalcites or layered
47 double hydroxides (LDH or DLH), are now a particular focus as organic anions (counter ions)
48 are readily absorbed as “guests” in their interior galleries (Kuma et al., 1989; Arrhenius, 2003;
49 Braterman et al., 2004). Due to such concentrating and structuring capabilities, clays in
50 general have been considered instrumental in facilitating and speeding-up fundamental
51 reactions and condensations at life’s origin. Several groups investigate their catalytic
52 properties and have already produced invaluable insights into the fine details, both with
53 respect to 3D-arrangement and to thermodynamic parameters, of clay-mediated reactions
54 (Pitsch et al., 1995; Ertem and Ferris, 1998; Hill et al., 1998; Krishnamurthy et al., 1999;
55 Meunier et al., 2010; Greenwell, 2010a; Coveney et al., 2012; Erastova et al., 2017;
56 Bernhardt, 2019; Barge et al., 2019). The fact that many clays can harbour in their interlayers
57 metal ions which mimic the catalytic sites of bioessential metalloenzymes makes them almost
58 irresistible candidates for the very earliest catalysts and promoters (Matrajt and Blanot, 2004;
59 Peretó, 2005; Rimola et al., 2009).

60 However, we suggest taking a step back and asking ourselves whether the exclusive
61 focus on catalysis is warranted. Catalysis is basically making exergonic reactions proceed
62 more readily by lowering their activation barriers and this is precisely what clays have been
63 shown to do. Catalysts thus facilitate reactions that would occur by themselves, just much
64 more slowly. This clearly is not what characterises living things. Life is all about processes
65 which would not happen spontaneously, but which are driven “uphill” by free energy –
66 (electro)chemical disequilibria as we will argue below – in the environment. The phenomenon
67 “Life” transforms rather randomly dispersed elements and molecules into highly ordered
68 structures and reaction networks. It only manages to effect this generation of order, as
69 imposed by the 2nd law of thermodynamics, by drawing upon environmental disequilibria and,
70 *in fine*, by decreasing the degree of order of the larger system encompassing both life and its

71environment (Endres, 2017; Branscomb et al. 2017; Branscomb and Russell, 2019). No
72ensemble of whatever catalysts can therefore ever bring forward life since they will only
73speed up exergonic reactions but cannot make endergonic ones proceed. What truly made life
74possible was the presence of converters of environmental disequilibria into the highly ordered
75machinery of metabolising cells. At first sight, these considerations may well appear
76appropriate but nevertheless too theoretical and utterly unhelpful when it comes to unravelling
77life's emergence. However, examining how these thermodynamic truisms play out in extant
78life on our planet turns them into extremely powerful criteria for constructing plausible
79scenarios in which emerging life actually resembles life as we know it today.

80

811.2. **Deducing the ancestral disequilibria and their converters from extant biology**

82 Let us first emphasize that modern life, no matter whether prokaryotic or eukaryotic,
83unicellular or multicellular, features an extraordinary unicity with respect to its free energy
84converting processes (Schoepp-Cothenet et al., 2013). In brief, an electrochemical gradient
85between reductants and oxidants (in photosynthetic organisms produced by photon energy) is
86collapsed by electron transfer events mediated by protein complexes which are integrated
87into, or are peripherally associated with, the cytoplasmic membrane (Fig. 1). These redox
88reactions are coupled to the transfer of protons (and occasionally sodium ions) generating an
89electrostatic (and sometimes an additional ion-concentration) disequilibrium (a “gradient”)
90over the membrane which topologically insulates the compartment from the outside world
91(Fig. 1). The simplest and most widespread strategy in extant life to achieve this coupling
92relies on combining reducing equivalents and protons into uncharged entities which readily
93diffuse through the barrier. In bioenergetic systems this task is performed by quinones and
94their functional analogs (*e.g.* methanophenazines) which take up and release 2 electrons and
95two protons and hence formally transfer a hydrogen molecule over the membrane. The
96outcome of the ensemble of these mechanisms is a (hydrogen- or sodium-) ion-motive force
97(imf) which is converted by membrane-integral systems into the first of the following two
98predominant sources of free energy that in turn drive the entropy-lowering processes of living
99cells.

100 (1) A phosphate-group transfer disequilibrium which in the majority of cases consists in
101extremely far-from-equilibrium ATP/ADP ratios but frequently also takes the simpler form of
102pyrophosphate (PP_i) to orthophosphate (P_i) disequilibria (PP_i/P_i) (Stucki, 1980; Baltscheffsky
103et al. 1999; Oster and Wang, 2000; Drozdowicz and Rea, 2001). The paramount importance
104to life of maintaining high ATP/ADP disequilibria (of approximately 10¹⁰) is for example

105 illustrated by the fact that humans transform roughly the equivalent of their own body weight
106 in ATP per day to ADP in order to maintain low entropy states, that is, to avoid decay. The
107 vast majority of biochemical reactions making up metabolic networks are indeed intrinsically
108 endergonic and are only rendered exergonic by strict coupling to ATP hydrolysis. For the case
109 of the ATP/ADP disequilibrium, the quintessential converter is the multi-subunit enzyme
110 ATP-synthase (Fig. 1, 1st from right). ATP-synthase is an intricate molecular motor which,
111 due to its very high molecular complexity, is extremely unlikely to have played a role while
112 life emerged. The protein machine which converts imf into PP_i/P_i disequilibria, by contrast, is
113 a single polypeptide membrane-transporter (Fig. 1, 2nd from right) with a comparatively
114 simple functional mechanism (Tsai et al., 2014). PP_i/P_i disequilibria are therefore often
115 stipulated as the ancestral phosphate-transfer potential (Russell et al., 2013).

116 (2) The second major source of free energy for driving metabolic reactions arises from the
117 maintenance of a cytoplasmic pool of strong reductants mainly in the form of NAD(P)H and
118 reduced ferredoxins (Nicholls and Ferguson, 2013). The electrochemical potentials of these
119 cytoplasmic reductants are in most organisms substantially more negative (Fig. 2) than those
120 of available environmental reducing substrates. A further type of disequilibrium converter
121 therefore increases the reducing power of environmental substrates to the level required for
122 the respective metabolic reactions to occur. Several processes (Fig. 2) have been found to
123 achieve this goal:

124 (i) So-called reverse electron transfer (Ferguson and Ingledew, 2008) taps into the free
125 energy stored in the imf to augment the reducing power of environmental substrates (Fig. 2,
126 i).

127 (ii) Certain types of photosynthesis (Schoepp-Cothenet, et al., 2013) produce reducing
128 equivalents with sufficiently low redox potentials to directly reduce ferredoxins (Fig. 2, ii).

129 (iii) The phenomenon of electron bifurcation (Fig. 2, iii) allows two-electron compounds
130 to generate a very low potential electron at the expense of the reducing power of the other one
131 (Mitchell, 1975; Nitschke and Russell, 2011; Crofts et al., 2013; Lubner et al., 2017; Buckel
132 and Thauer, 2018; Baymann et al., 2018).

133 (iv) Two specific redox cascades of substrates abundant in many environments stand out
134 by their intriguing electrochemical properties: the reduction of nitrogen oxides and oxyanions
135 as well as the oxidation of alkanes and in particular methane (Fig. 2, iv). The reduction of
136 NO_2^- to NO (occurring at a standard potential of about +400 mV with respect to the standard
137 hydrogen electrode) enables a further reduction reaction to N_2O (at +1200 mV). The product
138 of nitrite reduction is thus by about 800 mV more oxidising than nitrite itself. Nitrite is

139formed *via* two-electron redox conversion of nitrate at an ambient potential almost equal to
140that of the nitrite/NO transition. On the other end of the redox scale, the oxidation of methane
141to methanol and on through formaldehyde to eventually CO₂ (as observed in certain
142methanotrophic bacteria) generates ever more reducing products (Nitschke and Russell, 2013)
143which eventually are able to reduce NAD(P)⁺ and ferredoxin (Fig 2, iv). Coupling the
144reduction of nitrogen oxides to the oxidation of methane (as occurring in the methanotroph
145*Methylomirabilis oxyfera*) thus produces a network of redox reactions (Fig. 2, iv) which, very
146much like electron bifurcation, augments the intracellular electrochemical disequilibrium
147substantially over that prevailing in the environment.

148 To comply with the 2nd law, life throughout its existence had to rely on environmental
149disequilibria to fuel its order-generating processes. Applying Occam's razor (that is, avoiding
150scenarios more complicated than necessary), we have previously stipulated that the types of
151environmental disequilibria have likely remained constant from life's emergence to the
152present day. On the background of this hypothesis and given the intriguing and well-
153established catalytic properties of clay-type minerals, it is tempting to envisage that such
154minerals be able to perform processes similar to the above described free-energy-converting
155reaction schemes. The redox reactions of scheme (iv) (Fig. 2) and the make-up of involved
156metal centres directly lead from extant biology to double layered Fe-oxyhydroxide minerals,
157that is, Green Rusts, as we will elaborate upon below.

158

1592.1. **Green Rust, an intriguing candidate for the ancestral disequilibrium converters**

160 Structural affinities between catalytic centres in bioenergetic enzymes and certain
161minerals have been pointed out in the past (Nitschke et al., 2013). One of the presented cases
162of metalloenzyme/mineral is particularly interesting since the respective enzyme performs the
163key step in the redox-upconverting methanotrophic pathway mentioned above (Russell and
164Nitschke, 2017). Fig. 3 juxtaposes the catalytic site of soluble methane monooxygenase
165(sMMO) to the iron-containing sheet of double layered Fe-hydroxides, Green Rusts.
166Stimulated by this structural resemblance, we looked more deeply into the properties of Green
167Rusts and their naturally occurring form, fougérite (Trolard et al., 1997; Trolard and Bourrié,
1682006, 2012; Génin et al., 2006, 2008; O'Loughlin et al., 2015). The following remarkable
169properties indicate a potential role of Green Rusts in life's emergence.

170 - Mineralogists have shown that Green Rusts are able of performing the reduction of
171nitrate to ammonia (Hansen et al., 1996, 2001) as well as several of the partial reduction steps
172(Etique et al., 2014; Guérbois et al., 2014). These are precisely the redox reactions driving the

173 generation of strongly reducing compounds *via* the energetic pull from the reductive arm of
174 the anaerobic methanotrophic reaction network required for life to emerge (Schoepp-Cothenet
175 et al., 2013; Nitschke and Russell, 2013). A potential ability to also perform the oxidation of
176 methane to methanol (using intermediates of the nitrogen oxide arm as O-atom donors) has
177 not been tested so far. We are presently addressing this question in our laboratories. In
178 addition to this potential role in an ancestral methanotrophic reaction scheme, producing
179 reduced nitrogen compounds from nitrate is certainly crucial for a plethora of synthesis
180 reactions yielding organic compounds (amino acids, flavins, NAD, etc). We have recently
181 summarized intriguing reaction pathways involving intermediates and end-products of the
182 nitrate to ammonia reduction by Green Rusts (Duval et al., 2019; Duval et al. 2020).

183 - Green Rusts are redox-flexible over a very wide range of reduction levels (Poinsignon,
184 1997; Génin et al., 2006; Ruby et al., 2010a, 2010b; Mills et al., 2012) allowing facile transfer
185 of charges within the Fe-oxyhydroxide layers and likely even (much slower) electron
186 tunnelling between layers. Interestingly, high oxidation levels (resulting in so-called
187 metastable ferric Green Rust, Génin et al., 2014) have been shown to be associated with
188 deprotonation of the μ -hydroxo bridges. Transfer of charges parallel to the Fe-oxyhydroxide
189 layers therefore seem to be associated to protonation/deprotonation events reminiscent of the
190 redox behaviour of quinones.

191 - In addition to their redox softness, Green Rusts also show an extraordinary structural
192 flexibility due to their clay-like structure with interlayer spaces that can be occupied by a
193 range of different counterions (anions for the case of Green Rusts while in most clays the
194 interstitial ions are positively charged). The initial Cl^- interstitial ions have for example been
195 replaced by carbonate, sulphate and many others (Usman et al., 2018). Such anion exchanges
196 have been studied by mineralogists in the past and the heights of interstitial galleries have
197 been determined by XRD. Two main types have been reported corresponding to Green Rust 1
198 (GR1) with a monolayer of spherical or flat anions and interstitial height of about 7.5 Å and
199 Green Rust 2 (GR2) with two distinct layers of tetrahedral anions (e.g. sulphate) resulting in
200 interlayer spacings of about 11 Å (Usman et al., 2012; 2018). Swelling of interstitial spaces
201 by long linear carboxylates and alkanes of up to ~40 Å have been reported (Braterman et al.,
2022004; Ayala-Luis et al., 2010; Usman et al., 2018).

203 As is obvious from the general outline of bioenergetic conversion of disequilibria
204 which we have presented above, the anion most pertinent to emergence of life scenarios is
205 phosphate (Arrhenius et al., 1997; Bocher et al., 2004; Barthélémy et al., 2012; O’Loughlin et
206 al., 2015). Pyrophosphate/orthophosphate disequilibria are extremely likely candidates for

207having played the role of high ATP/ADP-ratios at life's emergence. Phosphate has a
208tetragonal geometry and, in its fully deprotonated state, is isostructural to sulphate which has
209been shown to be readily incorporated into GR's interstitial spaces and to form the di-
210interlayer structures of GR2. The steric similarities between fully deprotonated phosphate and
211sulphate render the possibility of phosphate intercalating GR's Fe-oxyhydroxide sheets in
212ways resembling the sulphate interstitial di-layers tempting. However, the empirical data with
213respect to intercalating phosphate are somewhat ambiguous so far. While Hansen and Poulson
214(1995) reported that phosphate can replace about half of the sulphate anions in GR2, in most
215other studies (Bocher et al., 2004; Ruby et al., 2006; Barthélémy et al., 2012) phosphate was
216seen as adsorbing to the edges of GR nanocrystals without entering interlayer galleries.
217Indeed, the perceived steric similarity between sulphate and phosphate may be misleading.
218Firstly, the net charge of deprotonated phosphate is 3- rather than 2- for sulphate which may
219render the charge-balancing act between Fe-oxyhydroxide layers and interlayer anions
220trickier. Secondly, phosphate features 2 pK values in the relevant pH region (that is, slightly
221acidic to strongly alkaline) in bulk water and will therefore occur in 3 distinct protonation
222states (and hence with net negative charges varying between 3- and 1-) over this pH-interval.
223This problem is likely exacerbated by the fact that water and proton activities in the interlayer
224must be expected to differ substantially from those of bulk water. The inconsistencies of
225published results therefore in our mind beg for more experimental work to arrive at a
226comprehensive understanding of phosphate sorption to GR nanocrystals.

227 A superposition of phosphates in GR2-type interstitial di-layers comparable to that of
228sulphates would obviously be particularly pertinent in the framework of emergence of life
229hypotheses since the strongly lowered water activity in the interstitial spaces would
230necessarily displace the PP_i/P_i equilibrium towards higher proportions of the condensed
231pyrophosphates. Pyrophosphates, once formed, hydrolyse only sluggishly and take in the
232range of a hundred hours to resume equilibrium proportions if transferred back into bulk
233water (von Wazer et al., 1955; Huang, 2018, 2019). Of course, to be of use as a vector of free
234energy, these pyrophosphate molecules would need to be transported to where the ancestral
235entropy-lowering processes would have occurred. We have previously developed a scenario
236in which GR nanocrystals are hypothesised as embedded in the amyloid-based walls of
237vesicles (Fig. 4) which separate an electron-rich interior (resulting from mineral-catalysed
238oxidation of reducing gases such as molecular hydrogen and/or methane) from an oxidising
239(due to the presence of nitrogen oxides and nitrogen oxyanions, NO_3^- , NO_2^- and NO) outside
240world (Duval et al., 2019). Due to this redox disequilibrium, electrons would flow through the

241oxyhydroxide layers from the vesicle interior towards the outside electron acceptors. Such a
242current of electrons is equivalent to the hopping of positive charges, *i.e.* locations of Fe^{3+} sites,
243towards those edges of the nanocrystals which face the vesicle interior (Fig. 4). Since
244interstitial anions charge-compensate Fe^{3+} sites, the inward movement of these Fe^{3+} sites is
245expected to pull the interstitial anions in the same direction. For the case of
246phosphates/pyrophosphates as interstitial anions, the higher negative charge of pyrophosphate
247(4-) as compared to that of phosphate (~50% 1-, ~50% 2- at pH 7) (and possibly also their
248differing bulkiness) will strongly favour delivery of pyrophosphate to the vesicle interior and
249thus further augment the displacement of the PP_i/P_i ratio from its equilibrium value within the
250vesicles. The analogy to the processes occurring in living cells is obviously striking. The
251details of the proposed structural picture (that is, types of environmental substrates and nature
252of the dielectric barrier) are rationalized by the fact that we consider alkaline hydrothermal
253vents (Russell et al., 2013; Branscomb and Russell, 2018a; Duval et al., 2019) as the most
254promising sites for life's emergence. The reasons for this choice are manifold, ranging from
255the stunning analogies in pH and electrochemistry between these vents and extant cells (Lane,
2562010; Schoepp-Cothenet et al., 2013) to fundamental thermodynamic considerations
257(Branscomb and Russell 2018b). We feel that spelling out these reasons exceeds the scope of
258this article and direct interested readers to the respective literature (Branscomb et al., 2017).

259 We emphasise that the mentioned experimental ambiguities with respect to phosphate
260sorption to GR don't necessarily impact our scenario for the role of GR as disequilibrium
261converter as described above. The envisaged processes do not require mass-replacement of for
262example sulphate by phosphate. Rather, a tiny fraction of interstitial anions substituted by
263phosphate would be enough for these mechanisms to proceed. The cited mineralogical
264studies, by contrast, measure bulk properties and almost certainly would fail to detect highly
265sub-stoichiometric anion replacements.

266 There are certainly still fundamental conceptual differences between the model we
267propose and the presumed functional mode of protein machines such as H^+ -translocating
268pyrophosphatases and cellular bioenergetics in general. To progress towards better defining
269the similarities and differences, we have formulated our scenario intentionally in a very
270specific manner which renders it amenable to experimental falsification of some of its parts or
271of its entirety. However, irrespective of your preferred hypothesis for life's emergence, most
272of the analogies in behaviour of Green Rust and bioenergetic systems are scenario-
273independent and suggest that an ancestral role of GRs in putting life on the road may have
274been overlooked for far too long.

2762.2. **GRs' properties relevant to life's emergence; the path from speculation to**
277**knowledge**

278 The scenarios we have developed here and previously (Nitschke and Russell, 2013;
279Russell et al., 2013, 2014; Russell, 2018; Duval et al., 2019), and which imply a crucial role
280of fougérite in life's emergence, invoke a number of redox processes and nano-structural
281properties of GR minerals. Some of these features have indeed already been found in GRs
282while others are still speculative although plausible given the ensemble of available data.
283Apart from the mentioned methane-to-methanol reaction scheme, most other speculative
284features discussed above are correlated to putative nano-structural properties of GR
285nanocrystals. To assess the validity of these features, a better understanding of these
286properties is required:

287 - The precise nanostructure of nanocrystals containing mixed populations of
288flat/spherical and tetragonal interstitial anions is unknown even if computational approaches
289on several clay-type materials are starting to provide glimpses into the range of possible
290geometries (Bernal et al., 1959; Génin et al., 2001, 2008; Braterman et al., 2004).

291 - Water activities in the interstitial galleries of diverse GRs are badly constrained.
292Again, computational methods are yielding first data.

293 - Charge conductivity parallel and normal to the layer sheets is badly defined (but see
294Poinsignon, 1997; Wander et al., 2007; Katz et al., 2012).

295 - Nanoscale redox inhomogeneities within single GR nanocrystals have not been studied
296so far.

297 - The possibility of motional coupling of layer/interlayer pairs of opposite charges
298represents an intriguing topic but has also not been studied so far.

299 - The interaction of single GR nanocrystals with barriers made up of organic molecules
300(polypeptides, lipids) as hypothesised in our scenario described above (Fig. 4) has never been
301studied.

302 The methods routinely applied to study clays and in particular transition-metal
303containing clay-related minerals such as GRs (e.g. XRD, Mössbauer spectroscopy) average
304over many atoms and many layers and therefore inform on bulk properties only. This lack of
305atomic scale information has over the last few years increasingly been remedied by
306computational approaches (Thyveetil et al., 2008; Greenwell, 2010b; Pérez-Villa et al., 2018;
307Martínez-Bachs and Rimola, 2019; Ugliengo, 2019). However, state-of-the-art
308nanotechnological approaches (e.g. nano-SIMS, nanoscale chemical analysis in TEM,

309Synchrotron beamlines) may well provide more solid grounds to notions obtained solely via
310computation (see Fracchia et al., 2018). The conductivity properties of nanocrystals may be
311addressed by growth on microelectrodes or incorporation into black membranes coupled to
312electrochemical techniques. Interaction of GR nanocrystals with micro-sized organic
313structures can be studied by biochemical methods in combination with SEM and TEM. We
314have recently initiated research on some of these questions in our laboratories.

315

3163. Conclusions

317 We fully share the clay community's conviction that clay-type minerals are extremely
318likely to have played a crucial role in life's emergence. In this contribution we have tried to
319raise awareness, based both on thermodynamic arguments and on the layout of extant life, that
320the common focus on clays' catalytic capacities may be too narrow. To make life emerge we
321first and foremost need processes which convert environmental disequilibria (think redox and
322possibly also pH gradients) into the entropy decrease that characterises life. The clay-type
323mineral Green Rust appears prone to perform processes which are intriguingly reminiscent of
324certain disequilibrium converters observed in life. The challenge of assaying the pertinence of
325these perceived similarities between Green Rusts (and fougérite) and pivotal processes in life
326will heavily rely on nanotechnological approaches to obtain atomic resolution information on
327the above-mentioned processes in the layered Fe-oxyhydroxide minerals. The scope of
328possible approaches seems virtually limitless and we partially conceived this contribution as
329an appeal to the community of mineralogists to join research on GRs' potential role in life's
330emergence.

331

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334

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338 **Figure Captions**

339 Figure 1: Schematic representation of cellular conversion of environmental free energy
340 (electrochemical disequilibria) into phosphate-group-transfer disequilibria in the form of far-
341 from-equilibrium ratios of ATP/ADP or PP_i/P_i . The plethora of different layouts of electron
342 transfer chains (in response to varying types of environmental substrates) is represented by a
343 dark gray box (for details, see Schoepp-Cothenet et al, 2013). The principal outcome of the
344 collapse of environmental redox gradients by these chains is the buildup of an electrostatic
345 field which, in certain cases in combination with a concentration gradient, translates into a
346 “proton-motive-force” (which may in a few organisms be converted *via* antiporters into a
347 “sodium-motive-force”). The proton-motive gradient is converted into far-from-equilibrium
348 values of ATP/ADP and PP_i/P_i by rotor-stator-type ATP synthases (1st enzyme from the right,
349 pdb-entry:5DN6) and H^+ -translocating pyrophosphatases (2nd enzyme from the right, pdb-
350 entry: 4A01), respectively.

351

352 Figure 2: Four predominant strategies exploited by extant life to maintain strongly reducing
353 conditions in their cytoplasm, required for a wide range of metabolic processes. Low redox
354 potential conditions are mediated by high reduction levels of the soluble redox compounds
355 NAD and ferredoxins. As detailed in the main text, it is in particular scheme iv which points
356 towards a potential role of Green Rust minerals as inorganic precursors of the enzymatic
357 systems employed by extant life.

358

359 Figure 3: Structural juxtaposition of a diiron unit within an Fe-oxyhydroxide layer of Green
360 Rust (top, left) and the catalytic site of the enzyme sMMO catalyzing the conversion of
361 methane to methanol in many methanotrophic organisms (top, right). The bottom schemes
362 represent two Green Rust layers (bottom, left) from which the diiron centre was extruded and
363 the parent enzyme sMMO (bottom, right, pdb-entry: 1MTY).

364

365 Figure 4: Schematic representation of a part of the barrier of a hypothetical (dielectrically
366 insulated) compartment in hydrothermal vent chimneys (Russell, 2018) spiked with a Green
367 Rust nanocrystal protruding on both sides of the barrier. The envisaged redox reactions are
368 shown in the left scheme while resulting electron transport (in the Fe-oxyhydroxy layers) and
369 condensation as well as ion-transport phenomena (in the interlayers) are depicted in the
370 blown-up representation of the right-side scheme. These processes are described in the main
371 text and in more detail in Duval et al. (2019) as well as Duval et al. (2020).

372

373

374

375References

- 376Aldersley, M.F., Joshi, P.C., Price, J.D., Ferris, J.P., 2011. The role of montmorillonite in its
377 catalysis of RNA synthesis. *Appl. Clay Sci.* 54, 1-14.
- 378Arrhenius, G.O., 2003. Crystals and Life. *Helvetica Chimica Acta* 86, 1569-1586.
- 379Arrhenius, G., Sales, B., Mojzsis, S., Lee, T., 1997. Entropy and charge in molecular
380 evolution - the case of phosphate. *J. Theoret. Biol.* 187, 503-522.
- 381Ayala-Luis, K.B., Koch, C.B., Hansen, H.C.B., 2010. Intercalation of linear C9–C16
382 carboxylates in layered FeII–FeIII-hydroxides (green rust) via ion exchange. *Appl. Clay*
383 *Sci.* 48, 334-341.
- 384Baltscheffsky, M., Schultz, A., Baltscheffsky, H., 1999. H⁺-PPases: a tightly membrane-
385 bound family. *FEBS Lett.* 457, 527-533.
- 386Barge, L.M., Flores, E., Baum, M.M., VanderVelde, D.G., Russell, M.J., 2019. Redox and pH
387 gradients drive amino acid synthesis in iron oxyhydroxide mineral systems. *Proc. Natl*
388 *Acad. Sci.* 116, 4828-4833.
- 389Barthélémy, K., Naille S., Despas, C., Ruby, C., Mallet M., 2012. Carbonated ferric green rust
390 as a new material for efficient phosphate removal. *J. Colloid. Interface Sci.* 384, 121-127.
- 391Baymann, F., Schoepp-Cothenet, B., Duval, S., Guiral, M., Brugna, M., Baffert, C., Russell,
392 M.J., Nitschke, W., 2018. On the natural history of flavin-based electron bifurcation. *Front.*
393 *Microbio.* 9, 1357.
- 394Bernal, J.D., 1951. *The Physical Basis of Life*. London: Routledge & Kegan Paul
- 395Bernal, J.D., Dasgupta, D.R., Mackay, A.L., 1959. The oxides and hydroxides of iron and their
396 structural inter-relationships. *Clay Min. Bull.* 4, 15-30.
- 397Bernhardt, H.S., 2019. Making molecules with clay: layered double hydroxides,
398 pentopyranose nucleic acids and the origin of life. *Life* 9, 19.
- 399Bocher, F., Géhin, A., Ruby, C., Ghanbaja, J., Abdelmoula, M., Génin, J.-M.R., 2004.
400 Coprecipitation of Fe(II–III) hydroxycarbonate green rust stabilised by phosphate
401 adsorption. *Solid State Sci.* 6, 117-124.
- 402Branscomb, E., Russell, M.J., 2018a. Frankenstein or a submarine alkaline vent: Who is
403 responsible for abiogenesis? Part 2: As life is now, so it must have been in the beginning.
404 *BioEssays* 40, 8, 1700182.
- 405Branscomb, E., Russell M.J., (2018b) Frankenstein or a submarine alkaline vent: Who is
406 responsible for abiogenesis? Part 1: What is life - that it might create itself? *BioEssays* 40,
407 7. 1700179.

408 Branscomb, E., Russell, M. J., 2019. Why the submarine alkaline vent is the most reasonable
409 explanation for the emergence of life. *Bioessays* 41, 1800208.

410 Branscomb, E., Biancalani, T., Goldenfeld, N., Russell, M., 2017. Escapement mechanisms
411 and the conversion of disequilibria; the engines of creation. *Phys. Rep.* 677, 1-60.

412 Braterman, P.S., Xu, Z.P., Yarberr, F., 2004. Layered double hydroxides (LDHs). *Handbook*
413 *of Layered Materials* pp. 373-474.

414 Buckel, W., Thauer, R.K., 2018. Flavin-based electron bifurcation, ferredoxin, flavodoxin,
415 and anaerobic respiration with protons (Ech) or NAD⁺ (Rnf) as electron acceptors: A
416 historical review. *Front. Microbiol.* 9, 401.

417 Cairns-Smith, A.G., 1966. The origin of life and the nature of the primitive gene. *J. Theor.*
418 *Biol.* 10, 53–88.

419 Cairns-Smith, A. G., (1982). *Genetic Takeover and the Mineral Origins of Life*. Cambridge
420 University Press.

421 Coveney, P.V., Swadling, J.B., Wattis, J.A., Greenwell, H.C., 2012. Theory, modelling and
422 simulation in origins of life studies. *Chem. Soc. Rev.* 41, 5430-5446.

423 Crofts, A. R., Hong, S., Wilson, C., Burton, R., Victoria, D., Harrison, C., Schulten, K., 2013.
424 The mechanism of ubihydroquinone oxidation at the Qo-site of the cytochrome bc1
425 complex. *Biochim. Biophys. Acta* 1827, 1362-1377.

426 Drozdowicz, Y.M., Rea, P.A., 2001. Vacuolar H⁺ pyrophosphatases: from the evolutionary
427 backwaters into the mainstream. *TiPS* 6, 206-211.

428 Duval, S., Baymann, F., Schoepp-Cothenet, B., Trolard, F., Bourrié, G., Grauby, O.,
429 Branscomb, E., Russell, M.J., Nitschke, W., 2019. Fougérite: The not so simple progenitor
430 of the first cells. *Interface Focus*, in press. DOI: 10.1098/rsfs.2019.0063.

431 Duval S., Zuchan, K., Baymann, F., Schoepp-Cothenet, B., Branscomb, E., Russell, M.J.,
432 Nitschke, W., 2020. Minerals and the emergence of life, in *Metals in Life Sciences*. Edited
433 by Kroneck, P., Sosa Torres, M.E., Chapter 5, Walter de Gruyter, Berlin.

434 Endres, R.G., 2017. Entropy production selects nonequilibrium states in multistable systems.
435 *Sci. Rep.* 7, 14437.

436 Erastova, V., Degiacomi, M.T., Fraser, D.G., Greenwell, H.C., 2017. Mineral surface
437 chemistry control for origin of prebiotic peptides. *Nature Comm.* 8, 2033.

438 Ertem, G., Ferris, J.P., 1998. Formation of RNA oligomers on montmorillonite. Site of the
439 reaction, *Orig. Life Evol. Biosph.* 28, 485-499.

440Etique, M., Jorand, F., Zegeye, A., Grégoire, B., Despas, C., Ruby, C., 2014. Abiotic Process
441 for Fe(II) oxidation and Green rust mineralization by a heterotrophic nitrate reducing
442 bacteria (*Klebsiella mobilis*). Environ. Sci. Technol. 48, 3742–3751.

443Ferguson, S.J., Ingledew, W.J., 2008. Energetic problems faced by micro-organisms growing
444 or surviving on parsimonious energy sources and at acidic pH: I. Acidithiobacillus
445 ferrooxidans as a paradigm. Biochim. Biophys. Acta 1777, 1471-1479.

446Ferris, J.P., 2002. Montmorillonite catalysis of 30–50 mer oligonucleotides: laboratory
447 demonstration of potential steps in the origin of the RNA world. Orig. Life Evol. Biosph.
448 32, 311-332.

449Ferris, J.P., Hill, A.R., Liu, R., Orgel, L.E., 1996. Synthesis of long prebiotic oligomers on
450 mineral surfaces. Nature 381, 59-61

451Fracchia, M., Visibile, A., Ahlberg, E., Vertova, A., Minguzzi, A., Ghigna, P., Rondinini, S.,
452 2018. α - and γ -FeOOH: Stability, reversibility, and nature of the active phase under
453 hydrogen evolution. ACS Appl. Energy Mat. 1, 1716-1725.

454Génin, J-MR., Refait, P., Bourrié, G., Abdelmoula, M., Trolard, F., 2001. Structure and
455 stability of the Fe (II)–Fe (III) green rust “fougerite” mineral and its potential for reducing
456 pollutants in soil solutions. Appl. Geochem. 16, 559-570.

457Génin, J.M.R., Ruby, C., Upadhyay, C., 2006. Structure and thermodynamics of ferrous,
458 stoichiometric and ferric oxyhydroxycarbonate green rusts; redox flexibility and fougerite
459 mineral. Solid State Sci. 8, 1330-1343.

460Génin, J.-M.R., Renard, A., Ruby, C., 2008. Fougérite FeII-III oxyhydroxycarbonate in
461 environmental chemistry and nitrate reduction. Hyperfine Interactions 186, 31-37.

462Génin, J.M., Mills, S.J., Christy, A.G., Guérin, O., Herbillon, A.J., Kuzmann, E., Ona-
463 Nguema, G., Ruby, C., Upadhyay, C., 2014. Mössbauerite, $\text{Fe}^{3+}_6\text{O}_4(\text{OH})_8[\text{CO}_3]\cdot 3\text{H}_2\text{O}$, the
464 fully oxidized ‘green rust’ mineral from Mont Saint-Michel Bay, France. Mineralog. Mag.
465 78, 447-465.

466Greenland, D.J., Laby, R.H., Quirk, J.P., 1962. Adsorption of glycine and its di-, tri-and
467 tetrapeptides by montmorillonite. Trans. Faraday Soc. 58, 829-841.

468Greenwell, H.C., 2010a. Layered-mineral organic interactions. In Ideas in Chemistry and
469 Molecular Sciences: Advances in Nanotechnology edited by B. Pignataro, Wiley e-book.

470Greenwell, H.C. 2010b. Modeling layered-mineral organic interactions. In Ideas in Chemistry
471 and Molecular Sciences: Advances in Nanotechnology, Materials and Devices, pp. 255-
472 279.

473Guerbois, D., Ona-Nguema, G., Morin, G. Abdelmoula, M., Laverman, A.L., Mouchel, J.-M.,
474 Barthelemy, K., Maillot, F., Brest, J., 2014. Nitrite reduction by biogenic
475 hydroxycarbonate Green Rusts: Evidence for hydroxy-nitrite Green Rust as an intermediate
476 reaction product. *Environ. Sci. Technol.* 48, 4505–4514.

477Hansen, H.C.B., Poulsen, I.F., 1999. Interaction of synthetic sulphate “Green Rust” with
478 phosphate and the crystallization of vivianite. *Clays Clay Min.* 47, 312318.

479Hansen, H.C.B., Guldborg, S., Erbs, M., Koch, C.B., 2001. Kinetics of nitrate reduction by
480 green rusts - effects of interlayer anion and Fe(II):Fe(III) ratio. *Appl. Clay Sci.* 18, 81-91.

481Hansen, H.C.B., Koch, C.B., Nancke-Krogh, H., Borggaard, O.K., Sørensen, J., 1996. Abiotic
482 nitrate reduction to ammonium: key role of green rust. *Environm. Sci. Tech.* 30, 2053-
483 2056.

484Hill, A.R., Böhler, C., Orgel, L.E., 1998. Polymerization on the rocks: negatively-charged α -
485 amino acids. *Orig. Life Evol. Biosph.* 28, 235-243.

486Huang, X.L., 2018. Hydrolysis of phosphate esters catalyzed by inorganic iron oxide
487 nanoparticles acting as biocatalysts. *Astrobiology* 18, 294-310.

488Huang, X.L., 2019. Iron oxide nanoparticles: an inorganic phosphatase. In *Nanocatalysts*.
489 IntechOpen, DOI: 10.5772/intechopen.82650.

490Katz, J.E. Zhang, X., Attenkofer, K., Chapman, K.W., Frandsen, C., Zarzycki, P., Rosso,
491 K.M., Falcone, R.W., Waychunas, G.A., Gilbert, B., 2012. Electron small polarons and
492 their mobility in iron (oxyhydr)oxide nanoparticles. *Science* 337, 1200-1203.

493Krishnamurthy, R., Pitsch, S., Arrhenius, G., 1999. mineral induced formation of pentose-2,
494 4-bisphosphates. *Orig. Life Evol. Biosph.* 29, 139-152.

495Kuma, K., Paplawsky, W., Gedulin, B., Arrhenius, G., 1989. Mixed-valence hydroxides as
496 bioorganic host minerals. *Orig. Life Evol. Biosph.* 19, 573-601.

497Lailach, G.E., Thompson, T.D., Brindley, G.W., 1968. Absorption of pyrimidines, purines,
498 and nucleosides by Li-, Na-, Mg-, and Ca-montmorillonite (clay-organic studies XII).
499 *Clays Clay Min.* 16, 285-293.

500Lane, N. (2010). Why are cells powered by proton gradients. *Nature Ed.* 3, 18.

501Lubner, C.E., Jennings, D.P., Mulder, D.W., Schut, G.J., Zadvornyy, O.A., Hoben, J.P.,
502 Tokmina-Lukaszewska, M., Berry, L., Nguyen, D.M., Lipscomb, G.L. Bothner, B., 2017.
503 Mechanistic insights into energy conservation by flavin-based electron bifurcation. *Nat.*
504 *Chem. Biol.* 13, 655-659.

505Matrajt, G., Blanot, D., 2004. Properties of synthetic ferrihydrite as an amino acid adsorbent
506 and a promoter of peptide bond formation. *Amino Acids*, 26, 153-158.

507Martínez-Bachs, B., Rimola, A., 2019. Prebiotic peptide bond formation through amino acid
508 phosphorylation. insights from quantum chemical simulations. *Life* 9, 75.

509Meunier, A., Petit, S., Cockell, C.S., El Albani, A., Beaufort, D., 2010. The Fe-rich clay
510 microsystems in basalt-komatiite lavas: importance of Fe-smectites for pre-biotic molecule
511 catalysis during the Hadean Eon. *Orig. Life Evol. Biosph.* 40, 253-272.

512Mills, S.J., Christy, A.G., Génin, J.M., Kameda, T., Colombo, F., 2012. Nomenclature of the
513 hydrotalcite supergroup: natural layered double hydroxides. *Mineralog. Mag.* 76, 1289-
514 1336.

515Mitchell, P., 1975. The protonmotive Q cycle: a general formulation. *FEBS Lett.* 59, 137-139.

516Nicholls, D.G., Ferguson, S.J. (Eds.) 2013. *Bioenergetics 4*. Academic Press, London/UK.

517Nitschke, W., Russell, M.J., 2011. Redox bifurcations; how they work and what they mean to
518 extant life and (potentially) to its inorganic roots. *BioEssays* 34, 106-109.

519Nitschke, W., Russell, M.J., 2013. Beating the acetyl coenzyme-A pathway to the origin of
520 life. *Phil. Trans. R. Soc. Lond. B. Biol. Sci.* 368, 20120.

521Nitschke, W., McGlynn, S.E., Milner-White, E.J., Russell, M.J., 2013. On the antiquity of
522 metalloenzymes and their substrates in bioenergetics. *Biochim. Biophys. Acta (BBA)-*
523 *Bioenergetics*, 1827, 871-881.

524Odom, D.G., Rao, M., Lawless, J.G., Oro, J., 1979. Association of nucleotides with
525 homoionic clays. *J. Mol. Evol.* 12, 365-367.

526O'Loughlin, E.J., Gorski, C.A., Scherer, M.M., 2015. Effects of phosphate on secondary
527 mineral formation during the bioreduction of akaganeite (β -FeOOH): Green rust versus
528 framboidal magnetite. *Curr. Inorg. Chem.* 5, 214-224.

529Oster, G., Wang, H., 2000. Reverse engineering a protein: the mechanochemistry of ATP
530 synthase. *Biochim. Biophys. Acta (BBA)-Bioenergetics* 1458, 482-510.

531Pérez-Villa, A., Pietrucci, F., Saitta, A.M., 2018. Prebiotic chemistry and origins of life
532 research with atomistic computer simulations. *Phys. Life Rev.*
533 <https://doi.org/10.1016/j.plrev.2018.09.004>.

534Pitsch, S., Eschenmoser, A., Gedulin, B., Hui, S., Arrhenius, G., 1995. Mineral induced
535 formation of sugar phosphates. *Orig. Life Evol. Biosph.* 25, 297-334.

536Poinsignon, C. 1997. Protonic conductivity and water dynamics in swelling clays. *Solid State*
537 *Ionics* 97, 399-407.

538Ponnamperuma, C., Shimoyama, A., Friebele, E., 1982. Clay and the origin of life. *Orig. Life*
539 12, 9-40.

540Peretó, J., 2005. Controversies on the origin of life. *Intern. Microbio.* 8, 23-31.

541Rao, M., Odom, D.G., Oro, J., 1980. Clays in prebiological chemistry, *J. Mol. Evol.* 15, 317-
542 331.

543Refait, Ph., Benali, O., Abdelmoula, M., Génin, J.-M.R. 2003. Formation of ferric green rust
544 and/or ferrihydrite by fast oxidation of iron(II-III) hydroxychloride green rust. *Corrosion*
545 *Science* 45, 2435–2449.

546Rimola, A., Ugliengo, P., Sodupe, M., 2009. Formation versus hydrolysis of the peptide bond
547 from a quantum-mechanical viewpoint: the role of mineral surfaces and implications for
548 the origin of life. *Intern. J. Mol. Sci.* 10, 746-760.

549Ruby, C., Géhin, A., Aissa, R., Ghanbaja, J., Abdelmoula, M., Génin, J-M.R., 2006. Chemical
550 stability of hydroxysulphate green rust synthesised in the presence of foreign anions:
551 carbonate, phosphate and silicate. *Hyperfine Interact.* 167, 803-807.

552Ruby, C., Abdelmoula, M., Naille, S., Renard, A., Khare, V., Ona-Nguema, G., Morin, G.,
553 Génin, J-M.R., 2010a. Oxidation modes and thermodynamics of FeII-III
554 oxyhydroxycarbonate green rust: Dissolution-precipitation versus in situ deprotonation.
555 *Geochim. Cosmochim. Acta* 74, 953-966.

556Ruby, C., Usman, M., Naille, S., Hanna, K., Carteret, C., Mullet, M., François, M.,
557 Abdelmoula, M., 2010b. Synthesis and transformation of iron-based layered double
558 hydroxides. *Appl. Clay Sci.* 48, 195-202.

559Russell, M.J., 2018. Green rust: The simple organizing ‘seed’ of all life? *Life*, 8, 35.

560Russell, M.J., Nitschke, W., 2017. Methane: Fuel or exhaust at the emergence of life.
561 *Astrobiology* 17, 1053-1066.

562Russell, M.J., Nitschke, W., Branscomb, E., 2013. The inevitable journey to being. *Phil.*
563 *Trans. R. Soc. Lond. B*368, 20120254.

564Russell, M.J., Barge, L.M., Bhartia, R., Bocanegra, D., Bracher, P.J., Branscomb, E., Kidd,
565 R., McGlynn, S.E., Meier, D.H., Nitschke, W., Shibuya, T., Vance, S., White, L., Kanik, I.,
566 2014. The drive to life on wet and icy worlds. *Astrobiology* 14, 308-343.

567Schoepp-Cothenet, B., Van Lis, R., Atteia, A., Baymann, F., Capowiez, L., Ducluzeau, A.L.,
568 Duval, S., Ten Brink, F., Russell, M.J., Nitschke, W., 2013. On the universal core of
569 bioenergetics. *Biochim. Biophys. Acta (BBA)-Bioenergetics* 1827, 79-93.

570Solomon, D.H., 1968. Clay minerals as electron acceptors and or electron donors in organic
571 reactions, *Clays and Clay Miner.* 16, 31–39.

572Stucki, J.W., 1980. The optimal efficiency and the economic degrees of coupling of oxidative
573 phosphorylation. *Eur. J. Biochem.* 109, 269-283.

574Thyveetil, M.A., Coveney, P.V., Greenwell, H.C., Suter, J.L., 2008. Role of host layer
575 flexibility in DNA guest intercalation revealed by computer simulation of layered
576 nanomaterials. *J. Am. Chem. Soc.* 130, 12485-12495.

577Trolard, F., Bourrié, G., 2006. Structure of fougérite and green rusts and a thermodynamic
578 model for their stabilities. *J. Geochem. Expl.* 88, 249-251.

579Trolard, F., Bourrié, G., 2012. Fougérite a natural layered double hydroxide in gley soil:
580 Habitus, structure, and some properties. In *Clay Minerals in Nature - Their*
581 *Characterization, Modification and Application* edited by M. Valášková & G.S.
582 Martynkova. InTech, 171-188.

583Trolard, F., Génin, J. M., Abdelmoula, M., Bourrié, G., Humbert, B., Herbillon, A., 1997.
584 Identification of a green rust mineral in a reductomorphic soil by Mossbauer and Raman
585 spectroscopies. *Geochim. Cosmochim. Acta* 61, 1107-1111.

586Tsai, J.Y., Kellosalo, J., Sun, Y.J., Goldman, A., 2014. Proton/sodium pumping
587 pyrophosphatases: the last of the primary ion pumps. *Curr. Op. Struct. Biol.* 27, 38-47.

588Ugliengo, P., 2019. The rise of computer modeling in prebiotic chemistry: Comment on"
589 Prebiotic chemistry and origins of life research with atomistic computer simulations" by A.
590 Pérez-Villa et al. *Phys. Life Rev.* <https://doi.org/10.1016/j.plrev.2019.03.013>.

591Usman, M., Hanna, K., Abdelmoula, M., Zegeye, A., Faure, P., Ruby, C., 2012. Formation of
592 green rust via mineralogical transformation of ferric oxides (ferrihydrite, goethite and
593 hematite). *Appl. Clay Sci.* 64, 38-43

594Usman, M., Byrne, J.M., Chaudhary, A., Orsetti, S., Hanna, K., Ruby, C., Kappler, A.,
595 Haderlein, S.B., 2018. Magnetite and green rust: synthesis, properties, and environmental
596 applications of mixed-valent iron minerals. *Chem. Rev.* 118, 3251-3304.

597vanWazer, J.R., Griffith, E.J., McCullough, J.F., 1955. Structure and properties of the
598 condensed phosphates. Hydrolytic degradation of pyro- and tripolyphosphates. *J. Amer.*
599 *Chem. Soc.* 77, 287-291.

600Wander, M.C., Rosso, K.M., Schoonen, M.A., 2007. Structure and charge hopping dynamics
601 in green rust. *J. Phys. Chem. C* 111, 11414-11423.

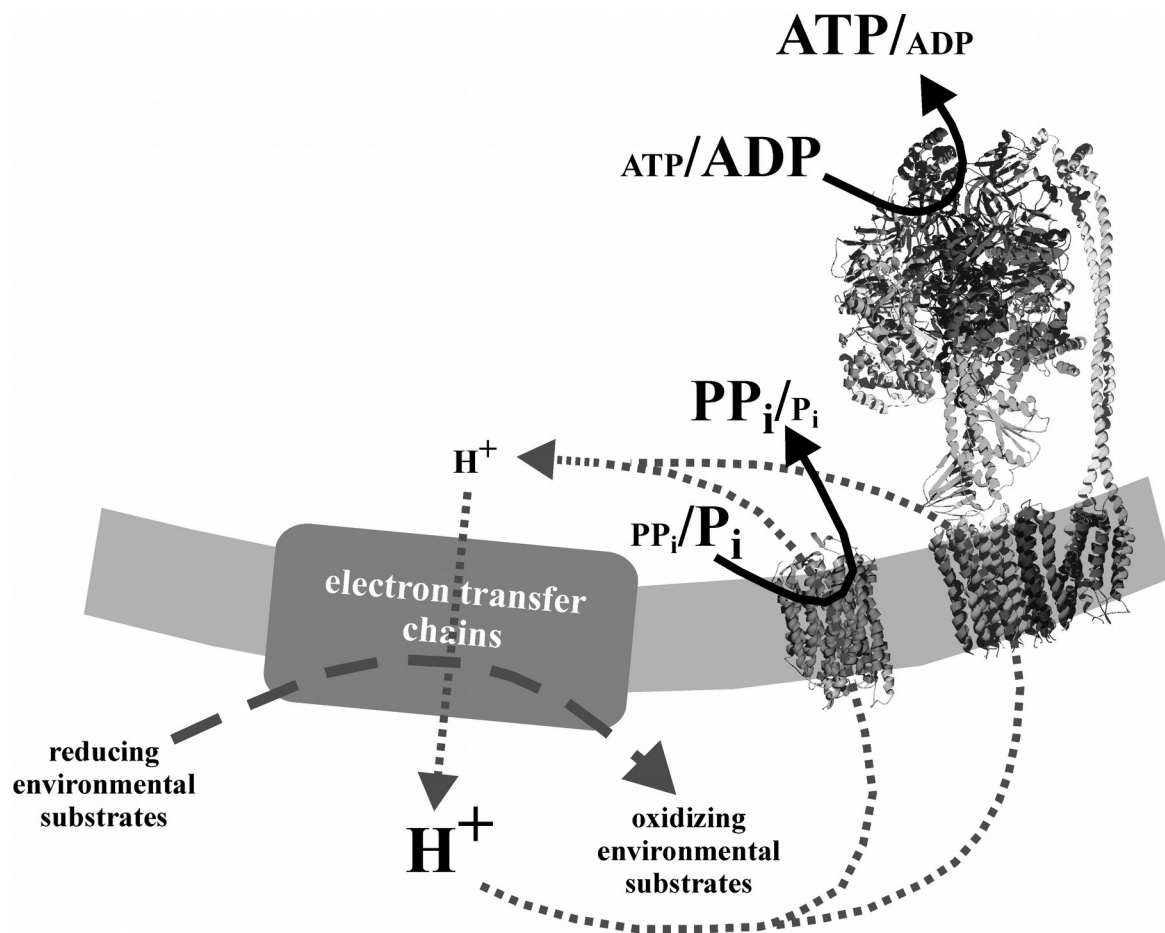
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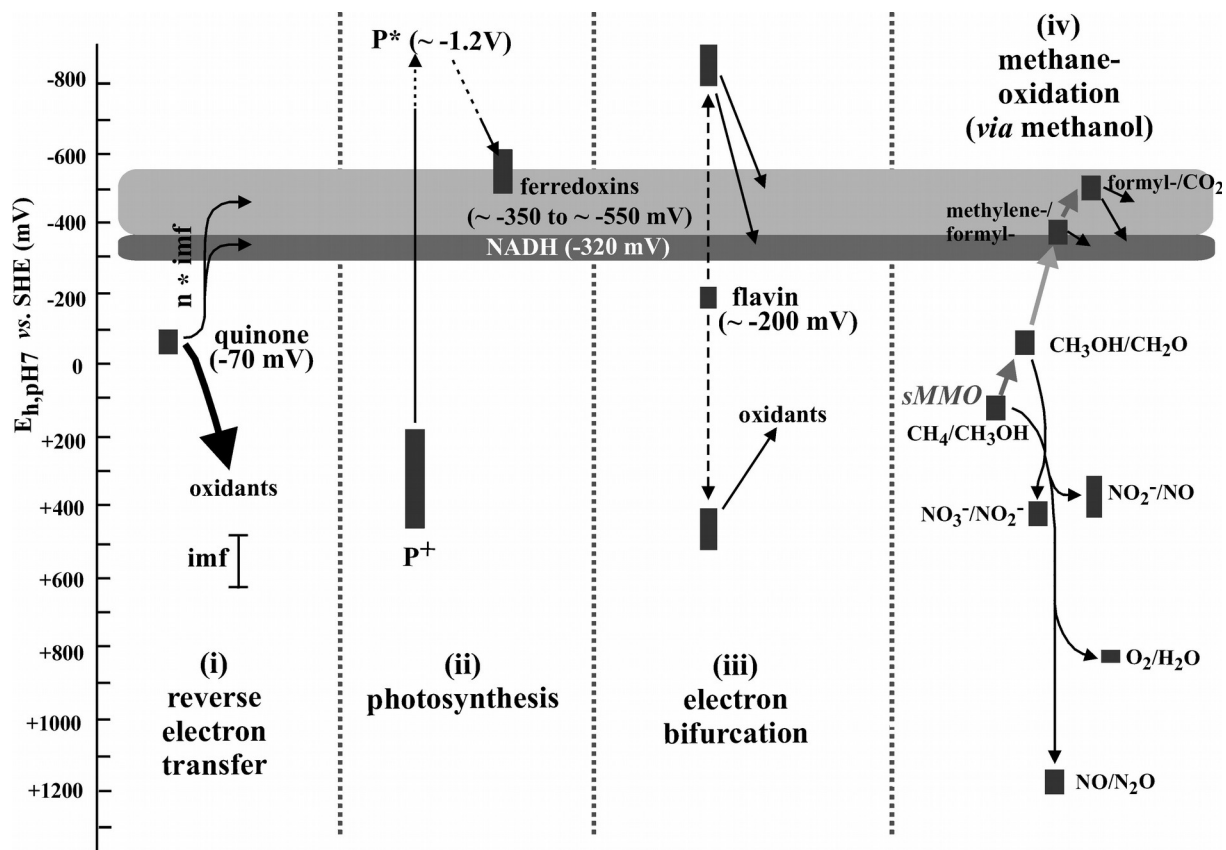
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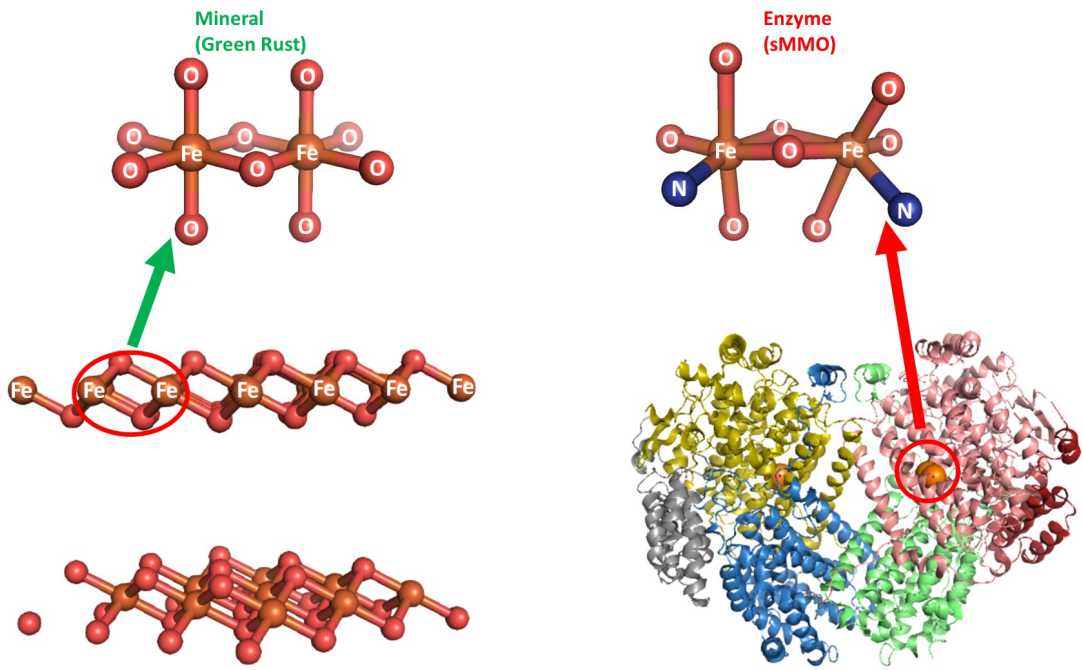
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609 **Figure 1**

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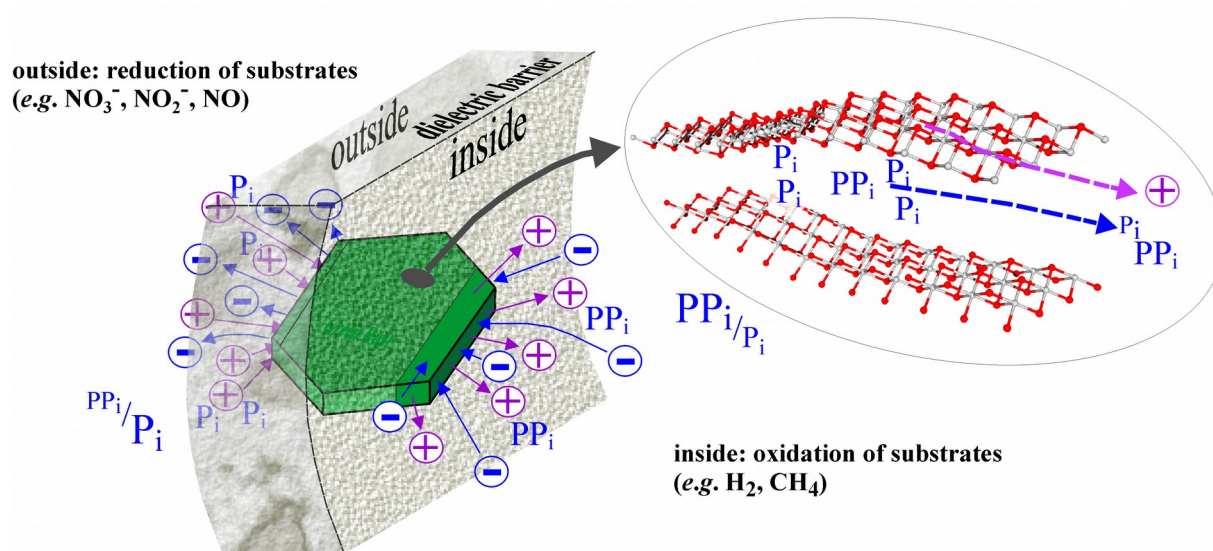


612 Figure 2



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Figure 3



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617 **Figure 4**