

LETTER TO THE EDITOR

Life detection experiments of the Viking Mission on Mars can be best interpreted with a Fenton oxidation reaction composed of H_2O_2 and Fe^{2+} and iron-catalysed decomposition of H_2O_2

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Abstract: The findings of the life detection experiments carried out during the Viking mission to Mars were reinterpreted with a chemical hypothesis. The labelled release (LR), pyrolytic release (PR) and gas exchange (GEx) experiments were interpreted with Fenton chemistry. Oxygen and carbon dioxide evolution from Martian soil upon wetting and nutrient addition could be attributed to competition reactions between the Fenton-type oxidation of organic nutrients with the aqueous (hydrogen peroxide + Fe(II)) combination and the iron-catalysed decomposition of hydrogen peroxide. A substantial evolution of radioactive gas upon addition of labelled organic nutrient solution to soil, whereas the ceasing of this gas with a heat treated sample in the LR experiments, was attributed to Fenton oxidation and hydrogen peroxide thermal decomposition, respectively. The peculiar kinetics of LR and PR experiments – that cannot be fully explained by other chemical or biochemical scenarios – were easily explained with this new hypothesis, i.e. limitation of the Fenton reaction may arise from the depletion of reactants, the build-up of ferric hydroxide on soil and excessive scavenging by the organic nutrients of the generated hydroxyl radicals. Reabsorption or adsorption of evolved or introduced CO_2 may involve the formation of carbonate compounds (e.g., magnesium carbonate and bicarbonate) on the surface of alkalized soil as a result of the Fenton reaction.

A critical evaluation of the recent biological hypothesis assuming the utilization of a hydrogen peroxide–water intracellular fluid by putative organisms (Houtkooper & Schulze-Makuch 2007) is also made.

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Three different types of biochemical experiments on samples of Martian surface material ('soil') were conducted during the Viking mission to Mars. In the carbon assimilation or pyrolytic release (PR) experiment, $^{14}\text{CO}_2$ and ^{14}CO were exposed to soil in the presence of light. A small amount of gas was found to be fixed by soil (interpreted to be organic material with a biological hypothesis). Heat treatment of a duplicate sample prevented this fixation (Klein *et al.* 1976). In the gas exchange experiment, soil was first humidified with water vapour, and then wetted with a complex aqueous solution of metabolites, and the gas above the soil was analysed with gas chromatography (GC). A substantial amount of O_2 was detected in the first chromatogram taken 2.8 h after humidification, while subsequent analyses revealed that significant increases in CO_2 and small changes in N_2 had also occurred. In the labelled release experiment, soil was

moistened with a solution containing several ^{14}C -labelled organic nutrients. A substantial evolution of radioactive gas was noted but this did not occur with a duplicate heat-treated sample (Klein *et al.* 1976). These experimental results were mostly interpreted with a chemical rather than a biological hypothesis.

As a recent biological hypothesis to interpret the Viking experimental results, Houtkooper & Schulze-Makuch (2007) have speculated that the putative organisms on Mars might have utilized a water–hydrogen peroxide (H_2O – H_2O_2) mixture rather than water as intracellular liquid. They reinterpret the findings of the Viking experiments in the light of their hypothesis, and reach the conclusion that the hitherto mysterious oxidant in the Martian soil, which evolved oxygen when humidified, might be H_2O_2 of biological origin.

Although Houtkooper & Schulze-Makuch (2007) have devised a plausible scenario for interpreting the Viking findings, it is hard to understand why the putative microorganisms in the Martian soil should have witnessed a hyperhydration death upon soil wetting (due to increased osmotic pressure) and that they release CO₂ and O₂ as a result of hydrogen peroxide oxidation of dead organisms, given the hypothesis of the authors that these organisms utilized a mixture of water and hydrogen peroxide as intracellular liquid. As they put it, cellular organics in an admixture with hydrogen peroxide and water (i.e. the organisms are assumed to consist of organics + H₂O₂) auto-oxidized completely at pyrolysis temperatures with no or very little organic residue (i.e. non-detectable by gas chromatography-mass spectrometry (GC-MS) at the part per million (ppm) to part per billion (ppb) range in soil heated up to 500 °C). This is improbable with intracellular H₂O₂ as the single oxidant, as it has been established in simulation experiments that the half-lives of oxidation of some organic macromolecules with H₂O₂ are of the order of years or more (McDonald *et al.* 1998). It is also not conceivable why hydrogen peroxide (of hypothetically biological origin) should release oxygen when humidified, without mentioning the presence of any transition metal salt catalysts. The moderate rise of CO₂ and the surprisingly large rise of O₂ in the gas exchange experiment (GEx) were also left uninterpreted, whereas these phenomena should actually be more attributable to a much more potent chemical oxidant than H₂O₂. Since the rise in oxygen (800 nmol of liberated oxygen) by far surpassed that in CO₂ (25 nmol of radio-carbon-labelled gases) during the gas exchange experiments and labelled release experiments, respectively, carried out with humidification (Plumb *et al.* 1989), all oxygen evolution could not be attributed to the hypothesized forms of life, and some O₂ should have been liberated from inorganic sources. Perhaps the weakest point in the argument of Houtkooper & Schulze-Makuch (2007) regarding the biological origin of H₂O₂ was the failure of oxygen evolution upon second humidification in the Viking experiment. They visualize a small absorption of CO₂ in the pyrolytic release (PR) experiment as assimilation of inorganic carbon for organic synthesis, but this may actually be re-absorption/adsorption of CO₂ rather than assimilation. They accept that their hypothesis was not able to explain the differences in amplitude of the response of the PR experiment. Moreover, although the decrease in the evolution of radiocarbon-labelled gases (in the 'Chryse and Utopia' PR experiments) could point to a presumptive biological assimilation reaction of the organic nutrients by putative organisms, such an activity also occurring – although at a diminished level – in a sterilized sample (heated at 175 °C for 3 h) should falsify the biological hypothesis. As Klein (1999) emphasized, these putative organisms must have had an extremely efficient metabolism, one capable of decomposing organic matter at a high rate without any period of adaptation to the Viking experimental conditions, and capable of selectively assimilating probably one of the nutrient organic acids among several one-, two- and three-carbon-atom containing acids. Lastly, GC-MS

testing of organic compounds in soil was negative in the Viking test, but the authors indicate the possibility of insufficient detection limits (due to analytical interference from soil minerals) at the time of the experiments. In fact, some physico-chemical simulation experiments on Earth carried out by adding hematite (Ponnamperuma *et al.* 1977) or certain clay minerals (Banin & Rishpon 1979) to labelled release (LR) constituents have almost duplicated the essential findings of the LR experiments on Mars (Klein 1999).

In summary, the results of the first six LR analyses of the Mars surface material (Levin & Straat 1976) have demonstrated the following:

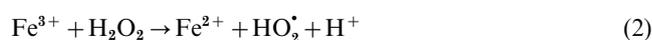
- (1) Addition of nutrient to surface material resulted in a rapid evolution of counts until a level of 10 000 to 15 000 counts per minute is achieved, possibly corresponding to utilization of only one of the seven carbon substrates offered (namely, formate, glycolate, glycine, D- and L-alanine, D- and L-lactate, uniformly labelled with ¹⁴C). On the other hand, no organic molecules were detected in the Martian soil with the use of GC-MS. The weak positive result of the PR experiment could possibly point to carbon assimilation (by putative organisms) as well as to non-biological absorption/adsorption of CO₂ by soil.
- (2) The active responses attained at both landing sites were remarkably similar in kinetics and magnitude. In particular, the evolution of oxygen gas upon wetting of soil required a strong oxidant at sufficiently high concentration.
- (3) The active response did not appear to depend on direct or recent ultraviolet (UV) activation of the surface material tested, because an optical filter to screen out the UV wavelengths below 320 nm was included in the experiment.
- (4) The active response was stable to 18 °C but was greatly reduced by heat treatment for 3 h at 50 °C, and was obliterated by 160 °C treatment. In contrast, exposure to 18 °C for two Martian days did not inhibit the reaction. The kinetics of gas evolution after the treatment at 50 °C were unaccountably peculiar and differed significantly from those after 160 °C treatment and from those of unheated samples.
- (5) Second injection in all cycles except the 50 °C cycle resulted in a sharp spike of evolved radioactivity, then an immediate 30–35 % decrease in gas level, followed by a gradual linear rise during subsequent incubation.

I have a much simpler non-biological (chemical) explanation which can effectively interpret the Viking results: I hypothesize that the oxygen and radioactive carbon dioxide evolution from Martian soil upon wetting and labelled nutrient addition was due to competition reactions between the Fenton-type oxidation of organic nutrients with the [hydrogen peroxide + Fe(II)] combination and the iron-catalysed decomposition of hydrogen peroxide. Thus, I propose that the mysterious oxidant on the Mars surface was a Fenton reaction system of which the iron component came into effect upon wetting of soil. The concerned reaction is as follows:



where the most potent non-specific oxidant $\cdot\text{OH}$ (hydroxyl radical) emerging at the end of the Fenton reaction can react with organic substrates with second-order rate constants (k) ranging between 10^8 and $10^{10} \text{ mol}^{-1} \text{ s}^{-1}$ (Halliwell & Gutteridge 1984; Bektasoglu *et al.* 2006). The rate constants for certain $\cdot\text{OH}$ scavenging organic compounds were recently measured by our group using a modified CUPRAC (cupric ion reducing antioxidant capacity) assay (Bektasoglu *et al.* 2006). The Fenton oxidation system does not need oxygen for its strong oxidizing action on organic nutrients (injected to soil during the Viking experiments). An optical filter was used in the experiments to filter out UV wavelengths of the electromagnetic spectrum, but Fenton reactions – although not necessitating light, and occurring even in soil slurries of insufficient light penetration (Weeks *et al.* 2000) – can also be enhanced by visible light (i.e. via photo-Fenton reactions). It is also probable that at a certain stage of Fenton oxidations the formed hydroxyl radicals may be scavenged to a certain extent by one or more of the organic nutrients (e.g., formate, known to be a potent hydroxyl radical scavenger). Both hydrogen peroxide (at an estimated concentration of 30 ppm on the surface of Mars (Clark 1979)) and ferrous iron in the basaltic minerals of Martian soil (Levin 2007) were present at the experimental site of the Viking mission, and the small amounts of Fe^{2+} required for the Fenton reaction (with respect to Eq. (1)) could pass into aqueous solution upon wetting of the soil. Thus water was the key parameter in initiating the Fenton reactions during the Viking experiments. Using the data obtained by the gas exchange experiment on Viking, and for simplicity assuming that all of the O_2 released came from H_2O_2 , the concentration range for hydrogen peroxide on the surface of Mars can be calculated to be 25–250 ppm (Mancinelli 1989). This hydrogen peroxide may possibly be in different physical forms (e.g., stabilized forms such as colloidal silica-stabilized H_2O_2 or magnesium peroxide) and concealed by soil particles that are resistant to UV degradation. The Fenton reactions requiring liquid water – assumed to have taken place during the Viking experiments – normally should not occur under Martian conditions, because the surface temperatures of the planet average between -70 and -100 $^\circ\text{C}$, and any water ice should be frozen into rock layers that melt only on geologically rare occasions (Kerr 2000).

The complete reaction sequence – in addition to Eq. (1) – of a Fenton oxidation system in accordance with a free radical mechanism (Barb *et al.* 1951; Walling & Weil 1974) can be summarized as follows:



where the second-order rate constants in acidic solution were compiled (Walling 1975; Lee *et al.* 2003) as $k_1=56\text{--}76$,

$k_2=10^{-2}\text{--}10^{-3}$, $k_3=2.7 \times 10^7$, $k_4=5.0 \times 10^5$ and $k_5=1.2 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, for reactions represented with Eqs (1)–(5).

It is known that H_2O_2 is thermodynamically unstable with respect to disproportionation according to the reaction



In practice, however, it is not very labile and survives reasonably well at moderate temperatures unless traces of transition metal catalysts are present (Shriver *et al.* 1995). Effective catalysts for its decomposition into oxygen and water should have standard potentials in the range of 1.76 V and 0.70 V, as $E^0(\text{H}_2\text{O}_2, \text{H}_2\text{O})=1.76 \text{ V}$ and $E^0(\text{O}_2, \text{H}_2\text{O}_2)=0.70 \text{ V}$. The catalysing ion should shuttle back and forth between two oxidation states as it alternatively oxidizes and reduces H_2O_2 . Since $E^0(\text{Fe}^{3+}, \text{Fe}^{2+})=0.77 \text{ V}$, this potential falls within the useful range and, therefore, iron is an effective catalyst for the decomposition of hydrogen peroxide (Shriver *et al.* 1995).

To recapitulate the major observations of the Viking landers, the mysterious oxidant on Mars caused a rapid oxygen evolution upon soil wetting in the GEx experiment (which was primarily associated with the decomposition of superoxides inferred to be present on Mars) (Oyama & Berdahl 1977). When a dilute aqueous mixture of organic acids containing one, two or three carbon atoms (all labelled with C^{14}) were added to samples of the Martian regolith in LR experiments, there was an immediate evolution of radioactive gas (presumably carbon dioxide) (Klein 1999). The rate of gas evolution was constant until approximately 10% of the added radioactivity had been released (this observation was repeatable at both of the Viking landing sites). When other samples were initially heated to approximately 160 $^\circ\text{C}$ and then incubated with the organic acid mixture, there was virtually no release of gas and, when samples were heated at about 50 $^\circ\text{C}$, the rate of gas evolution was cut to nearly 40% of that observed with unheated samples (Klein 1999). About 22% of the evolved gases were reabsorbed upon second injection, which could not be explained at that time (Plumb *et al.* 1989).

My scenario should normally explain all of the above observations of the Viking mission. The rapid evolution of oxygen upon soil wetting should have arisen from iron-catalysed decomposition of H_2O_2 . Atreya *et al.* suggested that vast quantities of the oxidant, hydrogen peroxide, could be produced in electrochemistry triggered by electrostatic fields generated in the Martian dust devils and dust storms, and in the normal saltation process to the surface (Atreya *et al.* 2007). Encrenaz *et al.* found spectral evidence in the range of $1226\text{--}1234 \text{ cm}^{-1}$ for spatial mapping of hydrogen peroxide on Mars (Encrenaz *et al.* 2004). Although H_2O_2 was proposed as a possible candidate to explain the results of the Viking biology experiments (Atreya *et al.* 2007), this compound could not duplicate the LR Mars data when placed on analogous Mars soils prepared to match the Viking inorganic analysis of the Mars surface material (Levin & Straat 1981). Therefore, H_2O_2 by itself could not have produced the

observed results of the LR experiments. To meet this criterion, a much stronger oxidant, the most potent oxidizing radical, i.e. hydroxyl radical, with extremely high rate constants, was necessary, and this radical could only be produced from a Fenton system composed of H_2O_2 and Fe^{2+} in aqueous medium supplied by the Viking experiments. The hint that H_2O_2 should have acted in conjunction with a suitable compound in the Viking experiments can be obtained from the duplication of the LR kinetics with the use of formate, an ingredient of the LR medium, exposed to H_2O_2 and $\gamma\text{-Fe}_2\text{O}_3$ (Oyama *et al.* 1978). It should be noted here that Houtkooper & Schulze-Makuch (2007) were not able to clearly explain why a combination of H_2O and H_2O_2 —claimed to be the intracellular liquid—should be more harmful to the putative organisms than H_2O_2 alone. The correct explanation comes from Fenton chemistry, which might be made feasible by water dissolution of Fe^{2+} from basalt minerals on Mars. If a H_2O_2 -utilizing organism ever existed on Mars together with liquid water, it should have undergone toxic Fenton chemistry when H_2O_2 combined with H_2O and Fe(II) salts, which would eventually kill the cell even if the hypothetical H_2O_2 – H_2O intracellular fluid was separated from its environment with a cell wall. Extending this argument further, if H_2O_2 is present in Martian soil at the estimated concentrations of several tens of ppm, it would prevent any emerging life forms when combined with liquid water and dissolved Fe(II) due to the toxicity of potential Fenton reactions. Moreover, the oxidation of organic compounds with H_2O_2 at mineral–water interfaces involves faster kinetics, e.g. it was found by He *et al.* (2005) that aromatic compounds could undergo rapid decomposition and complete mineralization in the presence of both $\alpha\text{-FeOOH}$ and H_2O_2 under UV irradiation, and the degradation rates of the organics were related to their adsorption ability at the goethite–water interface. This scenario may explain why there are no organics left in Mars soil if the planet was the host of liquid water and possible life forms in the past. In future missions to Mars, this fact should be taken into account when designing new experiments, as Fenton chemistry would be extremely toxic to putative organisms—if they ever existed.

Although the unidentified powerful oxidant of the Martian soil was suggested to be ferrate (VI) that is capable of splitting water to yield molecular oxygen and oxidizing organic carbon into CO_2 (Tsapin *et al.* 2000), recent data have shown Mars surface iron to be not completely oxidized (i.e. to the ferric or higher oxidation state) but to occur mostly in the ferrous form, which could not be expected in a highly oxidizing environment (Levin 2007). Moreover, the findings by the Viking Magnetic Properties Experiment had previously shown that the surface material on Mars contained a large magnetic component, providing evidence against highly oxidizing conditions (Levin 2007). These observations can only be reconciled by assuming that the oxidant was not originally present on the Mars surface at the time of the experiments, but could only come into power upon addition of water by combining the weak oxidant H_2O_2 and the reductant Fe^{2+} to form

one of the most powerful oxidizing mixtures ever known: the Fenton system, producing $\cdot\text{OH}$ with highest rate constants for oxidation of organic substrates.

Where did the Fe^{2+} , the reactant of the Fenton system in aqueous solution, come from? Clinopyroxene and olivine as unweathered basalt minerals—containing Fe(II) as the major iron species—on Mars were identified by evaluation of thermal emission spectroscopic data (Christensen *et al.* 2000). Even though the aqueous solubility of Fe^{2+} from these minerals may be low under normal conditions, the participation of the Fe^{2+} in the Fenton oxidation would shift solubility equilibria to the right-hand side (i.e. to the formation of Fe^{2+} in aqueous solution from basaltic minerals) increasing the Fe^{2+} yield. This is because when sparingly soluble salts take part in a redox reaction such that redox and solubility reactions are in simultaneous equilibria, the redox reaction with the much higher equilibrium constant shifts the solubility equilibrium to the right, increasing the yield of dissolved species. The solubility of both clinopyroxene and olivine decreases with temperature. These two minerals have negative enthalpy changes of dissolution; the logarithm of the dissociation constant for aqueous dissolution reaction significantly decreased (by at least seven orders of magnitude for olivine, and four orders of magnitude for clinopyroxene) as the temperature was raised from 25 to 150 °C (Stefansson 2001). This means that dissolved iron (II) upon wetting of the Martian soil during the Viking experiments significantly decreased when the temperature was raised from 18 to 160 °C, probably disabling the Fenton reaction and catalytic decomposition of hydrogen peroxide. This was observed as complete unreactivity (obliteration) of the active response principle at 160 °C. This obliteration was also coincident with the known complete decomposition of hydrogen peroxide at 160 °C within 3 h (Edwards 1962). Another parallelism can be drawn with the possible loss of surface catalytic activity of Martian soil minerals with increasing temperature, as simulation tests for the decomposition of formate and other low-molecular-weight organic acids with the use of limonite showed elimination of the organic substrate decomposition by heat treatment of this mineral (Klein 1979). On the other hand, since hydrogen peroxide was relatively stable (but nevertheless at lower stability than that at 18 °C) at 50 °C, the different kinetics of decreased gas evolution could be attributed to the deviations of olivine and related basalt minerals from ideality, and from the random distribution of Fe^{2+} and Mg^{2+} between the two types of crystallographic sites of the mineral (Stefansson 2001). At this medium temperature of 50 °C, both the amount of available iron (II) in aqueous solution and the surface properties of these basalt minerals for possible catalytic activity in H_2O_2 decomposition should be different, causing anomalies in gas evolution due to the competition between Fenton oxidation and catalytic decomposition reactions having different temperature dependencies. Moreover, the differences in amplitude of the response of the PR experiment could arise from the inhomogeneous distribution of basalt minerals on Mars that would enable the dissolution of iron silicates at different rates,

thereby affecting the rates of the resulting Fenton reactions utilizing Fe^{2+} .

The observation in the Viking experiments that the rate of ^{14}C -labelled gas (possibly CO_2) evolution was constant until $\sim 10\%$ of the added radioactivity had been released was biologically interpreted as selective assimilation of one type of nutrient (Klein 1999) among the seven offered organic acids by putative organisms. According to my chemical explanation, this may well arise by the precipitation of ferric hydroxide ($\text{Fe}(\text{OH})_3$) from the products of the Fenton reaction (see Eq. (1)) onto the test soil, causing fouling, inefficient Fe^{2+} dissolution and ceased catalytic activity (ferric hydroxide build-up is a common problem encountered in Fenton oxidation systems applied to wastewater treatment). Furthermore, formate, known to be a potent hydroxyl radical scavenger, may limit the Fenton reaction. Thus, the powerful oxidation reaction would be expected to come to an early end after the fast initial stage, oxidizing only 10% of the added nutrient organic acids. On the other hand, the alkalinity of soil resulting from the Fenton reaction (see Eq. (1) for the liberation of hydroxide ions) or peroxide dissolution (e.g., $\text{MgO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{H}_2\text{O}_2$) may be responsible for the partial re-absorption/adsorption of CO_2 as alkaline earth metal carbonates (e.g., $\text{Mg}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{H}_2\text{O}$) and bicarbonates in the PR experiments (which was interpreted in the biological explanation as a positive result for the presence of carbon-utilizing organisms), and in LR experiments where 22% of the evolved gases were observed to be re-adsorbed upon second injection.

A primary objective of the Phoenix mission to Mars is to determine the aqueous mineralogy, chemistry and organic content – if any – of the Martian regolith (Goldstein & Shotwell 2006). To support the proposed hypothesis of this work, the following may be explored in the Phoenix or future missions: (i) showing the absence of free liquid water in topsoil; (ii) discrimination of the two valencies of iron, namely Fe(II) and Fe(III), by Mössbauer spectroscopy; (iii) showing the presence of possible clay minerals – that were envisaged by chemical models but eluded detection – in soil horizons of upward water percolation, concentrating salts and iron compounds; (iv) detection of hydrogen peroxide or other easily leachable peroxides in Martian soil by electrochemical- or bio-sensor applications, or photofragmentation laser-induced fluorescence spectroscopy, or near-infrared spectroscopy; (v) showing the increase of soil pH upon humidification as a result of the Fenton reaction, together with the X-ray spectroscopic identification of possible adsorbed carbonates/bicarbonates and the eventual build-up of ferric hydroxide on topsoil; (vi) confirming the exothermic nature of the Fenton reaction with differential scanning calorimetry thermal analysis when water and nutrients are added to soil; (vi) soil sampling with subsequent testing of soil specimens on earth to exactly identify the chemical oxidant species; (vii) GC-MS detection of any trace organics and left-handed (*laevo*-) chiral carbon molecules after chloroform extraction, i.e. without contacting soil with liquid water that would otherwise oxidize these residual compounds. The described chemical scenario is

capable of explaining all the observations and conflicting results of the Viking experiments without the need for putative organisms.

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