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New Insights into the Search for Life on Mars

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Abstract

The discovery by the Lander Phoenix (summer 2008) that the Mars polar soil is rich of perchloric acid salts (Na, Mg, Ca perchlorate) strongly could change the interpretation of the Martian experiment of $^{14}\text{CO}_2$ release (LR, Labeled release experiment), performed in 70's by both Viking Landers. The LR experiment gave substantially positive results but, at that time, possibility of Martian bacteria was ruled out because the CGMS instruments on board of both Vikings didn't detect any trace of complex organic molecules. But Martian organics exist and were found in fair quantities by Curiosity, landed inside the Gale crater on 2012. So it is likely that Viking CGMS, working at about 500°C , could not see any organic substances (natural or bacterial) because, at that temperature, perchlorates decompose, releasing Oxygen that destroyed organics BEFORE their detection. In any case, the discovery of keragenic compounds by Curiosity, could also be indication of a presence of archea bacteria in the distant past of Mars, when the atmosphere of the Red Planet was wetter and denser than now.

Keywords: Mars, organic substances, perchlorate, archea bacteria

1. Introduction: from Schiaparelli to Mariner 9

Before the space age, the best Mars observations were performed during the so called oppositions [1]. The distance between the orbits of Earth and Mars varies considerably, largely due to the comparatively large eccentricity of Mars's orbit. Every 780 days on average the Earth overtakes Mars and when, as seen from the Earth, Mars and the Sun are aligned, Mars is said to be in opposition. The opposition distance of Mars from the Earth varies considerably, depending on where Mars and the Earth are in their orbits at opposition. If Mars is near its closest to the Sun (perihelion) the distance is comparatively small, and the opposition is called favourable. Unfavourable oppositions are with Mars near aphelion. The opposition distance varies from 55.7–101 million km, and the corresponding angular diameter of Mars varies from 25.1–13.8 arcsec. Favourable oppositions occur roughly every 15 years.

The first person to draw a map of Mars that displayed terrain features was the Dutch astronomer Christiaan Huygens (**Figure 1**).

On November 28, 1659 he made an illustration of Mars that showed the distinct dark region now known as Syrtis Major Planum, and possibly one of the polar ice caps.

The same year, he succeeded in measuring the rotation period of the planet, giving it as approximately 24 hours.

Figure 1.
Syrtis Major, sketched by Christiaan Huygens in 1659. North is at the top.

In 1666, Cassini detected several distinct dark spots on Mars, and from observing these ascertained that the planet had a rotation on its axis in about 24 hours 40 minutes.

In the oppositions of 1777, 1779, 1781, and 1783, Sir William Herschel determined that the axis of Mars was inclined of about 25° to the plane of its orbit (so having seasons) and measured its polar and equatorial diameters. He showed also that the white spots which formed round the poles of the planet, increased with the approach of winter, and diminished with the approach of summer.

In the oppositions of 1830, 1832, and 1837, Beer and Mädler, observing with a telescope of 4 inches aperture, made a series of drawings from which they were able to construct a chart of the entire globe of Mars. The features which they then drew have been recognised at every succeeding opposition, and some of them can be identified in the rough sketches of Sir William Herschel, and even in those of the year 1666, made by Hooke and Cassini. The surface of Mars therefore possesses permanent features.

In the 1800s, observatories with larger and larger telescopes were built around the world.

A particularly favorable perihelic opposition occurred in 1877 (Mars approaching to within 56 million km on September 5, in Aquarius) [2].

On August 11, 1877 the American astronomer Asaph Hall discovered the two moons of Mars, Phobos and Deimos, using a 660 mm (26 in) telescope at the U.S. Naval Observatory.

In the fall of October 1877, Giovanni Virginio Schiaparelli (1835–1910), scrutinised Mars visually at the Brera Observatory in Milan, where he was director (**Figure 2**). He used a 8' (21.8 cm, f/14.5) aperture Mertz refractor (magnifying power of 322x), that was installed here in 1865. He named the Martian “seas” and “continents” (dark and light areas) with names from historic and mythological sources [3].

But he is best remembered for about 40 fine lines that he drew crossing the bright red areas, *canali* as he called them. Canali means channels, but it was mistranslated into “canals” implying intelligent life on Mars (**Figure 3**).

Because of the then recent completion of the Suez Canal in 1869 (the engineering wonder of the era), the misinterpretation was taken to mean that large-scale artificial structures had been discovered on Mars. The importance of canals for worldwide commerce at that time without a doubt influenced the popular interest in “canals” on Mars.

Figure 4.
Mars in 1905, drawn by Percival Lowell. Note the canals. Note also the south polar hood of cloud (at the top).

Lowell's theories influenced the young English writer H.G. Wells, who in 1898 published *The War of the Worlds*. In this novel, Wells created an invasion of Earth by deadly aliens from Mars and launched a whole new genre of alien science fiction.

On Halloween in 1938, Orson Welles and The Mercury Theater on the Air broadcast a radio version of *The War of the Worlds*. The story, presented as a series of "live" news bulletins, panicked thousands of listeners who believed that America was being attacked by hostile Martians.

In the 1953, the story of *The War of the Worlds* of H. G. Wells was adapted in a famous American science fiction film from Paramount Pictures, produced by George Pal and directed by Byron Haskin. Earth was suddenly and unexpectedly invaded by Martians. Many of the major world capitals were destroyed by the Martians, being Martians impervious to all humanity's weapons (enclosed an atomic bomb!) . But, after all that men could do had failed, the Martians were destroyed by terrestrial bacteria to which only mankind have long since become immune.

The real origin of the Mars canals was revealed by another Italian astronomer, Vincenzo Cerulli (1859–1927), founder in 1890 of the Astronomical Observatory in Teramo (in the Abruzzo region), equipped by a Cook Refractor of 40 cm. Starting from 1897, he gave a convincing explanation, still generally accepted. He suggested that the lines were a sort of optical illusion, created by the human brain that "needs" to interpret even vague and indistinct images with familiar shapes. Therefore, poor quality images, such as those that low quality telescopes would provide, would be interpreted as structured shapes, for example connecting individual roughly aligned "dots" into straight lines. This has been demonstrated by many laboratory and field experiments.

During the great opposition of 1909, on the night of September 2020, thanks to exceptional seeing conditions, Eugène M. Antoniadi (1870–1944), one of the most skilled observer of his time, using the new big 83 cm reflector of Meudon observatory, gives some exquisite drawings of Mars, in which all "canals" having some feedback in the past vanished (**Figure 5**).

On 15 July 1965 the NASA spacecraft Mariner 4 flew past Mars, at a minimum distance of only 9800 km. This first Mars flyby gave a major negative surprise: all 22 of the images sent to Earth showed a cratered landscape more akin to the Moon (**Figure 6**). The heavily cratered (and hence ancient) surfaces indicate lack of

Figure 5.
In 1909, E.M. Antoniadi got the chance to use the great 33" refracting telescope at Meudon, on the outskirts of Paris, and on the first night, Sep. 20, he saw Mars so clearly that he could not believe his eyes. It was covered with detail, but not a bit of it was geometric—there was not a canal in sight.

Figure 6.
Images sent to Earth by Mariner 4 and Marine 6 during their flyby of Mars in July1965 and July 1969.

geological activity and lack of extensive weathering by water, which would have erased these craters in a fraction of the age of Mars. Moreover, when Mariner 4 passed beyond Mars as viewed from the Earth, the changes induced by the atmosphere enabled the surface pressure of the atmosphere to be determined: the value was a mere 6 millibars, ten time less than previously believed. A pressure of 6 millibars is close to the triple pressure of water, below which water cannot exist in a

stable liquid phase at any temperature. Because all life on Earth requires liquid water, the prospect of finding life on Mars faded a lot.

The next two successful missions to Mars, were the flyby (at a distance of about 3400 km) of Mariner 6 on July 31, 1969 and the flyby of Mariner 7 a few days later on August 5, 1969, flying by over the equator and south polar regions and analyzing the Martian atmosphere and surface with remote sensors, as well as recording and relaying hundreds of pictures. The two spacecraft returned a combined total of 143 approach pictures of the planet and 55 close-up pictures (**Figure 7**).

Again the small amount of martian surface investigated was found covered by impact craters. More, the temperature of the south polar cap was measured and found to correspond to the solid-gas phase boundary of CO_2 at a pressure of a few millibars. This provided strong evidence that a polar cap of CO_2 was roughly in equilibrium with the CO_2 atmosphere.

Subsequent studies have confirmed that the seasonal cap at both poles is indeed predominantly CO_2 snow and frost, but that this overlies a permanent cap mainly composed of dusty water ice at the North Pole, and dusty CO_2 ice at the colder South Pole, perhaps underlain by dusty water ice.

The results of Mariner 4,6,7 were very disappointing. But it was soon realized that some fast flybys over no more than 20% of the martian surface, could not give a satisfactory knowledge of a complex planet as Mars. It would have been necessary to map the *whole* planet and make continuous observations for a long period of time, objectives that only an orbital mission could carry out. The Mariner 9 mission was born.

On November 14, 1971 the spacecraft Mariner 9 was placed, for the first time in the history, in orbit around Mars. But, unbelievably, Mariner 9 arrived when Mars was obscured by the largest dust storm ever observed. The surface was totally obscured for a couple of months and the imaging program did not get underway until mid-January 1972. The spacecraft was turned off on October 27, 1972, after 349 days in orbit, and 7,329 images transmitted, covering 85% of Mars' surface. With two astonishing discoveries (**Figure 8**).

Figure 7. South polar cap of Mars as seen by Mariner 7 in August 1969. The IRS spectrometer on board of Mariner 7 demonstrated the presence of CO_2 ice and, possibly, also trace of NH_3 and CH_4 [4].

Figure 8.
 The largest dust storm ever observed obscured all the surface of Mars in November 1971, when Mariner 9 entered orbit for the first time. When the storm subsides, Mariner 9 made two main discoveries: big volcanoes and hundreds of extinct riverbeds.

The first main discovery was the existence of several huge ‘young’ shield volcanoes, so high that their peaks emerged also from the dust storm. Most of these volcanoes were located in the Tharsis Regio, a vast plateau 4.000 m high, centered near the Martian equator, that formed about 2 billion years ago, giving rise to an enormous canyon system, named Mariner Valley, after Mariner 9 in honor of its achievements. The second main discovery was that of hundreds of extinct riverbeds, that seem to have been carved by the flow of liquid water early in Martian history: an indication that Mars was much warmer and wetter in the past. Certainly most exciting discoveries as far as life on Mars is concerned, that convinced NASA to plan a mission to directly search for life on Mars. The Viking program was born.

2. The intriguing results of the Vikings program

The two Viking Landers in the ‘70 years made the first direct search of traces of present or past biological life on Mars [5] (**Figures 9 and 10**).

The results were so contentious that, after more than 45 years, no unambiguous interpretation was found.

The GCMS instruments (Gas Chromatograph-Mass Spectrometer) on board both Viking Landers [6, 7] were tasked with detecting organic compounds. GC-MS heated many samples of martian soil up to 500°C, but did not detect any trace of complex organic molecules, even if detected an amount of 0,1–1% of H₂O and 50–500 ppm CO₂ respectively (**Figure 11**) and the enigmatic release of about 15 ppb of CH₃Cl (chloro-methane) and up to 20–30 ppb of CH₂Cl₂ (methylene chloride) (**Figure 12**).

At that time, the two light chloro-derivatives, being released together with some trace of a solvent of sure terrestrial origin such as Freon-E, were considered as a terrestrial contamination, ruling out the occurrence of any form of martian life [8]. In the meantime the H₂O and CO₂ release upon heating were explained as thermal decomposition of hydrous silicates and carbonates respectively.

Figure 9.
Viking 1 on the surface of Crise Planitia. The white arm in the center is a meteorological sensor; the arm that took samples is visible to the right.

Figure 10.
May 18, 1979: water frost on Mars rocks and soil near the Viking 2 lander.

The measured ratio $^{37}\text{Cl}/^{35}\text{Cl} = 0,319$ similar to that one of the terrestrial chloride supported to this interpretation. However, Z.D. Sharp [8] found that the ratio $^{37}\text{Cl}/^{35}\text{Cl}$ is quite constant all over the Solar System: actually its value is the same on the Earth, on the chloro-salts enclosed inside the carbonaceous chondrites and also on some Martian meteorites.

Moreover, a suitable inquiry proved that CH_3Cl and/or CH_2Cl_2 never were used during the Viking assembly, so any trace on board was impossible [9].

We could re-discuss the conclusion taken from the Viking GC-MS results on the basis of a couple of reasons.

The first reason is that the Martian soil in any case should be enriched by the organic molecules (that is carbon-containing chemicals) that could be taken by comets and carbonaceous chondrites. The recent discovery of simple and polymeric organic substances inside many Martian meteorites could be an evidence in this regard [10].

Carbon-containing chemicals such as those that make up the stuff of life on Earth, had been found in rocks that were blasted off Mars millions of years ago by large asteroid impacts and fell to Earth as meteorites (at present about 300 Martian meteorites are known). But no one could be sure the organics in Martian meteorites

Figure 11.
The main analytical results of the CGMS (GasChromatograph-Mass Spectrometer) on board of the Viking landers.

Figure 12.
The GC on board of the Viking Landers detected only enigmatic presence of chloro-methane and methylene chloride, at that time deemed terrestrial pollutants.

weren't just earthly contamination. So microbiologists of the Carnegie Institution for Science's Geophysical Laboratory in Washington, D.C., looked in the most protected parts of Martian meteorites: microscopic mineral grains that had been securely locked in larger crystals for up to 4 billion years. Using a number of analytical techniques, they probed for organic matter through the encasing minerals. Organic chemicals were found in 10 of 11 once-molten meteorites examined, at an abundance of about 20 parts per million. Raman spectroscopy showed that

they include large, complex carbon compounds rich in benzene-like rings of carbon atoms, included polycyclic aromatic hydrocarbons (PAHs), typical of organic-rich meteorites such as carbonaceous chondrites. Given the way the organic matter was sealed in the rock, “it is carbon from Mars,” not terrestrial contamination.

A special case remains that of ALH 84001, (**Figure 13**) a meteorite found in 1984 in the antarctic region of Allan Hills. Ejection from Mars seems to have taken place about 16 million years ago. Arrival on Earth was about 13 000 years ago. Cracks in the rock appear to have filled with carbonate materials (implying groundwater was present) between 4 and 3.6 billion-years-ago. Evidence of polycyclic aromatic hydrocarbons (PAHs) have been identified with the levels increasing away from the surface. In the crack were also found deposits of iron as magnetite, that are claimed to be typical of bio-deposition on Earth [11].

In some SEM (Scanning Electronic Microscope) pictures taken inside the carbonate material, small ovoid and tubular structures were found [12], that might be interpreted as nanobacteria fossils (**Figure 14**), but also as sample preparation artifacts, being, at that time, unknown earthy life forms so small. The controversy has never ceased even if, some years after, living colonies of nano-organisms were found on Triassic and Jurassic sandstones from petroleum exploration wells off-shore western Australia [13]. These living forms were up to 10 times smaller in diameter (10 nm) compared to ‘normal’ cellular structures.

The other reason for which the negative response of the two GCMS onboard the Viking Landers has to be rediscussed is linked to the fact that the Viking Labeled Release (LR) experiment, made at ambient temperature (10–15°C), gave a biological result substantially positive (Levin, 1976). LR it has been the only experiment with a clearly positive response, whereas the other two ‘biological’ experiments, i.e. the Gas Exchange (GEX) experiment [14] and the Pyrolytic Release (PR) experiment (Carbon Assimilation Experiment) [15] gave dubious results, suggesting a lack of biological reactions.

Figure 13.
Inclusions of carbonates inside the Martian meteorite 84001, found in Antarctica in 1984.

Figure 14.
The tube-like forms on this highly magnified SEM image of ALH84001 could be fossils of simple Martian organisms that lived over 3.6 billion years or, simply artifacts of sample preparation.

Figure 15.
A scheme of the LR experiment (Labeled Release) on board of Viking Landers.

The LR experiment (**Figure 15**) was based on the well-known concept that all terrestrial microorganisms metabolize the organic substances releasing CO_2 .

In the Viking LR experiment, the Landers collected samples of Martian soil by means of their robotic arm, injected them with a drop of dilute nutrient solution containing alanine, formic acid, glycine, glycolic acid and lactic acid, and then monitored the air above the soil for signs of metabolic byproducts. Since the nutrients were tagged with radioactive carbon-14, if microorganisms in the soil

metabolized the nutrients, they would be expected to produce radioactive byproducts, such as radioactive carbon dioxide ($^{14}\text{CO}_2$). $^{14}\text{CO}_2$ was indeed released when an aqueous solution of ^{14}C labelled aminoacids was added, but a much lower amount (i.e by more than one order of magnitude) was released in the case of terrain samples sterilised at 160°C (**Figure 16**). To rule out the possibility that the strong ultraviolet radiation on Mars might be causing the positive results, the Landers collected also soil buried underneath a rock, which again tested positive. The control tests also worked, with the 160°C sterilization control yielding negative results [16].

In 2002 a possible circadian fashion (i.e. having the same periodicity of the Martian day) of $^{14}\text{CO}_2$ release was found, which may be a typical biological signature [17]. A complex statistical analysis [18] reached the same conclusion.

In any case, it is important underline that the same Levin [19] observed that the release of radioactive CO_2 could be due also to nonbiological reactants, a real possibility discussed also by Klein [20]. On this subject some lab tests were performed, assuming that the Fe superoxides are built up in the Martian soil by the strong UV radiation. This Fe superoxide could decompose (with the release of $^{14}\text{CO}_2$) the carbon molecules of the LR nutrient solution directly [21] or through the formation of H_2O_2 [22]. In the presence of water, the superoxide ion reacts to produce Oxygen, perhydroxyl radical, and hydroxyl radical [23]: $2\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{HO}_2^- + \text{OH}^-$.

This release of oxygen could decompose carbon molecules in the LR experiment, but could also explain the results of the Gas Exchange (GEX) esperiment. In GEX a water solution of many amino-acids and salts, was injected into a sample of martian soil, measuring by GC (Gas Cromatography) any gas emission such as the release of

Figure 16.
The Viking 1 result of Labeled Release experiment on active and sterilized Martian soil (see the text for details).

Figure 17.
 June 25, 2008: a trench, called 'Dodo-Goldilocks,' showing lumps of water ice in this picture taken by the Phoenix Lander. A big surprise was the discovery of perchlorates by the MECA instrument.

H₂, N₂, O₂, CH₄, Kr, and CO₂. Analyses showed that a 1 cm³ of Martian soil sample produced up to 700 nM of Oxygen after 50 hours, an amount far superior to any terrestrial test, and so not believed to be of biological origin.

A possible explanation of the intriguing results of the Viking analyses was found by the Wet Chemistry Laboratory on the Phoenix Mars Lander (**Figure 17**) that, in the summer of 2008, discovered up to 0,6% of Magnesium perchlorate - Mg (ClO₄)₂ in the North polar sands of Mars [24]. This salt is inert at low temperature, but at high temperature became a strong oxidant able to decompose all carbon compounds.

So, if we suppose that also the soil sampled by Viking were rich of perchlorates, the GCMS analysis, being performed at 500°C, possibly could results in a demolition of all organic molecules (biological or not) during the same analytical process. The assumption of the presence of perchlorates at the Viking landing sites might seem a little hasty, because perchlorate may form preferably at high latitudes [24], whereas the Viking 1 landing site was at equatorial latitudes, and the Viking 2 one at intermediate latitudes. However, we could not exclude this possibility, specially after the discovery of perchlorates inside the Gale Crater (Lat = 5,24° S), landing site of Curiosity [25] and the discovery of perchlorates also in some martian meteorites [26].

In the case of analyses performed at low temperature, perchlorates are totally inert and so a positive response, as observed by the Viking LR experiment, may really suggest the presence of organic substances.

3. Viking and perchlorates

A further support to a biological interpretation of the Viking LR experiment was given by R. Navarro-Gonzales [27]. In summary, a sample of a Mars-like soil of the driest core of the Atacama desert in Northern Chile (The Yungay Area), containing

very low organic concentration (32 ppm), was subjected to a thermal volatilization process. The released gases and volatiles have been then measured by a GCMS similar to the Viking ones. At 500°C a clear emission of organic substances such as benzene, toluene, formic acid was observed. But when the same soil was heated at 500°C after the addition of 1% of Mg perchlorate, the organic substances mentioned were no longer observed, whereas release of CO₂ and H₂O and, amazingly, also of CH₃Cl and CH₂Cl₂ was measured (**Figure 18**).

According to Navarro Gonzales [27] the release CH₃Cl and CH₂Cl₂ was ascribed to a reaction between perchlorate and organics. According to experiments on simulated Martian soil [28], the thermal action of perchlorate in the Vikings GCMS results should have substantiate by the detection of some chlorinated aromatics (such as chlorobenzene and chlorotoluene). Well, an accurate re-examination of the original, microfilm preserved, Viking GCMS data sets [29] found evidence for the presence of chlorobenzene in Viking Lander 2 (VL-2) data, at levels corresponding 0.08–1.0 ppb, in two sample heated to 350°C and 500°C. A surprising discovery that is also a demonstration of the presence of perchlorate in the Viking martian soil.

Unfortunately, the two Vikings were not able to search for perchlorates. But it is possible ‘to read’ the potential presence of these salts in some meaningful clues.

For example, the RXFS (X-Ray Fluorescence Spectrometer) on board the Viking lander was suitable to search for Cl (Chlorine) in martian soil, finding similar values: Viking 1 found 0,8% of Cl on the landing site of Cryse (22,7°N, 48,2° W) and Viking 2 found about 0,4% of Cl on the landing site of Utopia (48,3°N, 226°W) [30, 31]. Furthermore Pathfinder (1997) found up to 1% of Cl on Ares Valley (19,3°N, 33,6°W) [32], Spirit found about 0,5% of Cl inside the Gusev crater (14,6°N, 175,5°E) [33] and Opportunity found up to 1% of Cl on Meridiani Planum (1,9°S, 354,5°E) [34]. A more general investigation was made by the orbital spacecraft Odyssey 2001, between June 2002 and April 2005. Its Gamma Ray Spectrometer (GRS), measured the equatorial and mid-latitude distribution of Cl at the near-surface of Mars, finding a not homogeneously concentration, with a mean value of 0.49 wt% Cl and variation up to a factor of 4 [35]. The kind of compound containing Cl should be investigated.

After the unexpected discovery of up to about 1% of Mg-perchlorate on the Martian polar soil (68.3°N, 127.0°W) performed by Phoenix Lander [24], with only

Figure 18.

The dry soil of the Yungay Area (Northern Atacama), if heated up to 500°C with the external addition of perchlorates, shows the same behaviour of the Martian soil: disappearance of organic signals and release of light chloro-hydrocarbons.

traces (0,02%) of other salt containing Cl, the quite abundant amount of Cl found by Vikings appears as a strong indication of the presence of perchlorates. The mechanism of Martian perchlorate production is still being debated. It has been suggested that production pathways for perchlorate on Mars are similar to Earth, primarily photochemically in the upper atmosphere via oxidation of chlorine by ozone [36]. But because of the low amount of Ozone in the Martian atmosphere, mechanisms involving surface components are probable [37]. For example, perchlorates may form from the radiolysis of surface component caused by galactic cosmic rays, causing a sublimation of chlorine oxide in atmosphere, where final oxidation to perchloric acid is performed by some sources of active Oxygen (i.e. O₃ and/or CO₂ photolysis) [38]. And in the presence of a suitable catalyst such as TiO₂ the strong Martian UV illumination could oxidize chloride ions to perchlorate also in aqueous solutions [39].

The permanence of perchlorates (very soluble in water) on the martian soil is made possible by the strong ambient dryness: Mars lacks rains able to dissolve perchlorates for millions of years.

The logical interpretation of the Navarro Gonzales [27] results on the Atacama soil starts from the well known decomposition of Mg(ClO₄)₂ at temperature > 400°C [40], with release of O₂ and Cl:

O₂ and Cl react with organics compounds, releasing, on one side, H₂O and CO₂, and, on the other side, the chlorine compounds observed by the Viking GCMS.

The results of Phoenix and Atacama analyses, suggested to reconsider methods for searching carbon molecules on Mars, taking in account the significant risk arising from the thermal methods.

4. Curiosity and SAM results

The first chance for to this new approach occurred with the Curiosity mission (NASA, Mars Science Laboratory Press Kit, 2012), a rover of 900 kg that landed successfully on August 6, 2012 inside the Martian Gale crater (5.4°S 137.8°E) at a lower latitude than Viking (Cryse at 22,7°N and Utopia at 48,3°N), an ancient lake, with a layered mountain 5,000 m high in the center (the Mount Sharp). The task of Curiosity was to reach the mountain and to climb on it, in order to disclose the geological past of Mars, starting from the farther past (lower stratification) (**Figure 19**). The most interesting soils were found right at the base of Mount Sharp, where Curiosity encountered a dangerous expanse of dark sand (Bagnold Dunes), a long ridge rich of hematite (Vera Rubin Ridge), a clay-bearing unit (Glen Torridon), followed by Sulfur-rich uneven ground.

On January 1, 2018 (sol 1992) near the southern edge of the Vera Ruin Ridge, the Mars Hand Lens Imager (MAHLI) camera on Curiosity movable arm, pointed out a cluster of millimetric dark, stick-shaped features whose origin is uncertain. One possibility is that they are erosion-resistant bits of dark material from mineral veins cutting through rocks in this area (**Figures 20 and 21**).

But the morphological analogy with terrestrial fossil traces of life-substrate interactions is impressive [41]. Some studies even highlight occurrence, on Martian sediments, of widespread structures like the famous microspherules discovered by the Rovers Spirit and Opportunity, often organized into some higher-order settings (**Figure 22**). Such structures also occur on terrestrial stromatolites in a great variety

Figure 19.
The path of Curiosity inside the Gale crater, to reach the base of Mount Sharp.

Figure 20.
December 13, 2017 (sol 1903): Curiosity near the Vera Rubin Ridge, a formation very rich of hematite.

of microscopic structures, such as voids, gas domes and layer deformations of microbial mats [42].

SAM (Sample Analysis at Mars) is a suite of instruments aimed at analyzing of soil samples on board of Curiosity (**Figure 23**).

It includes an improved and more sensitive (up to 100 times) version of the Viking GC MS [43] and a laser infrared spectrometer (TLS) [44] able to analyse any gaseous substance from both Martian atmosphere and GC–MS, with a sensitivity of 1 ppb (part per billion). The SAM works by accepting drilled or scooped Martian grit into a tiny cup made of quartz, that can be cooked in an oven up to 1100°C. Tiny puffs of helium gas move the gases from the sample cup into a MS (Mass Spectrometer), that sift through the resulting fumes for molecular signatures, directly (EGA, Evolved Gas Analysis) or after a previous separation inside one of 6 column GC (Gas Chromatographic) (**Figure 24**). There are 74 cups in a carousel: 59

Figure 21.
January 1, 2018 (sol 1992): these enigmatic dark, stick-shaped features taken from the MAHALI camera on board of Curiosity look alike terrestrial fossils of the Ordovician period.

Figure 22.
Examples of mesostructural parallels with occurrence of spherical bodies having similar shape and structure. On Mars, 'blueberries' could assume polycentric polispherules or concentric structures. Such parallels occur also for living colony of cyanobacteria (frame II), as polispherule and concentric structures and for stromatolites (the knot structure in the frame III).

are quartz tubes slated for “dry” chemistry, 9 are solvent cups, sealed with foil, contain solvents for ‘wet’ chemistry to tease out organic molecules, like amino acids and degraded fatty acids, that would otherwise resist vaporization; the last 6 are calibration cups (**Figure 25**).

Among other capacities, the TLS [44], detecting the IR absorption band of CH₄ at 3,27 micron, was aimed at confirming the existence and the seasonal cycle of methane discovered by terrestrial telescopes [45] and possibly confirmed by PFS

Figure 23.
The suite of instruments of SAM (Sample Analysis at Mars) laboratory on board of Curiosity.

Figure 24.
Inside the SAM lab., gases released by a sample of Martian soil heated up to 1000°C can be sent to a Mass Spectrometer (MS) directly (EGA-MS, Evolved Gas Analysis) or passing before though Gas-chromatographic column (GCMS).

Figure 25.
The Carousel of SAM, called the SMS (Sample Manipulation System). It contains 74 cups, dedicated to receiving solid samples collected by the Curiosity rover. The 74 sample cups are separated into three categories: 59 solid sample quartz cups, 9 foil topped metal cups for wet chemistry experiments (7 with MTBSTFA, 2 with TMAH), and 6 foil topped cups of reference samples.

spectrometer on board of Mars Express [46]. The task of TLS was to continue the search for methane in order to establish its source (geological or biological).

Really, TLS detected methane many times over the course of the mission, though with a very strange behaviour. Background levels of the gas seem to rise and fall seasonally (0,24–0,65 ppbv, parts per billion units by volume) [47] (**Figure 26**).

The highest methane levels do appear just after the warmest time of the year, suggesting that heat spreading downward allows more of the gas to be released.

Figure 26.
Seasonal variations of Martian methane, detected by the SAM-TLS spectrometer, during 55 months (about three Mars years from March 17 2014 to March 21, 2017). Potential methane sources include methanogenesis by microbes, ultraviolet degradation of organics, or water-rock chemistry. The methane could be later destroyed by atmospheric photochemistry or surface reactions, as examples. Seasons refer to the northern hemisphere.

Finding methane in Mars’s atmosphere is intriguing because chemical reactions should destroy the gas after about 300 years. So its presence today suggests that something on the planet is still sending the gas into the atmosphere. The source could be geological, such as reactions between certain types of rock and water (basaltic serpentinization) or could be linked to ancient methane trapped in clathrate hydrates; more intriguingly, the warmest season could ‘awaken’ buried microbes or other forms of life, taking in account that most of the methane in Earth’s atmosphere comes from living processes. But a recent statistical analysis [48] casts doubt on the hypothesis of “seasonal variability” in Mars’ surface methane, finding that it is unsupported by the Curiosity TLS data. This is because the data are too sparse over too limited timespan, to favor a seasonally cyclic explanation of the data over alternative hypotheses of stochastic variation or variation with other periods.

TLS detected also episodically increases (‘spike’) of Martian methane [49]: for example on June 16, 2013 and on early January 2014 readings averaged ten time the background level (6–8 ppbv). The largest concentration of methane detected in situ by the Curiosity reached a spike to 21 ppbv, on June 20, 2019, dropping quickly over a few days (**Figure 27**).

The PFS spectrometer of Mars Express found a possible geological origin of this n usual pattern [50]. Indeed, in a re-examination of archive data, PFS, on June 16, 2013, observed an elevated spot level (15.5 ± 2.5 ppbv) of methane, from a nearby area called Medusae Fossae, located about 500 km east of Gale crater. The Mars Express observation was made 20 hours before the methane spike of 5.78 ± 2.27 ppbv reported by TLS-SAM. Being Medusae Fossae a fractured and likely volcanic in origin, it is possible that a therein geological emission of methane has been carried by the prevailing winds towards the Gale crater (**Figure 28**).

Highly sensitive measurements of the atmosphere of Mars performed by the ESA-Roscosmos ExoMars TGO (Trace Gas Orbiter) from April to August 2018 made the problem of Martian methane even more enigmatic [51]. No trace of methane was indeed found by two instrument suites onboard TGO designed to perform such measurements: ACS (the Atmospheric Chemistry Suite) and NOMAD (Nadir and Occultation for Mars Discovery) that cover the 3.3 μm spectral range,

Figure 27.
TLS-SAM methane measurements at Gale crater over an ~4.5 Earth years (~56 months) period (from 26 October 2012 to 27 May 2017), taken during the rover’s journey of 16.5 km over highly varied terrain.

Figure 28.
On June 13, 2013, the PFS spectrometer on board of Mars Express observed a methane emission over the fractured terrain of Medusae Fossae, some hours before a spike of methane detected inside the Gale crater by the TLS-SAM instrument. Geological methane carried towards the Gale crater by the prevailing winds?

which includes the strongest fundamental absorption bands for hydrocarbons such as CH₄, in particular the ν_3 asymmetric stretching band on which all the previous detections were made.

Until the end of 2020 the SAM-GCMS made more than twenty complete analyses on Gale crater soil (**Figure 29**).

Inside the Gale crater Curiosity discovered for the first time, Martian organic molecules, just after a few attempts (Rocknest, John Klein, Cumberland at Yellowknife Bay, not far from the landing site) (**Figure 30**).

Yellowknife Bay mudstone is thought to contain sediments transported by fluvial and deltaic processes from the crater rim area to the north.

Between sol 56 and 100 (October 2 to November 16, 2012) Curiosity reached the sandy terrain of Rocknest, located about 550 meters away the landing site. The APXS instrument (Alpha Particle-X rays spectrometer) [52] detected on Rocknest a little amount of S and Cl [53]. The sandy texture of the soil was suitable to be easily transferred inside the SAM. Under the heating of the sample up to 800°C, many kinds of gaseous substances were released [54]. The release of molecular Oxygen (O₂) at 300–400°C (**Figure 31**) was very important: together with the presence of

Figure 29.
A summary of all drill sites made by Curiosity at Gale Crater up the end of 2020.

Figure 30.
December 24, 2012 (sol 137): this mosaic of images from Curiosity-Mastcam shows the rocks of Yellowknife Bay formation, that record superimposed ancient lake and stream deposits that offered past environmental conditions favorable for microbial life. Rocks here were exposed about 70 million years ago by removal of overlying layers due to erosion by the wind. Yellowknife Bay mudstone is thought to contain sediments transported by fluvial and deltaic processes from the crater rim area to the north.

Figure 31.
November 2012 (sol 93–117): results from analysis of Rocknest Aeolian deposit by SAM-Curiosity. On top the EGA evolved gases, on bottom some CGMS light chloro-derivatives.

Cl, this emission is a suggestion of $\text{Ca}(\text{ClO}_4)_2$ (Calcium perchlorate), a salt that decomposes under heat just to this temperature.

Laboratory-based TGA (Thermal Gravimetric Analysis, performed by the Author with a Perkin-Elmer TGA 7 instrument) on synthetic perchlorates shows clearly that the Calcium perchlorate starts to release molecular oxygen at 350°C , leaving a main residue of Calcium chloride (CaCl_2) (**Figure 32**). Therefore, after the discovery of perchlorate at high latitude by Phoenix, SAM demonstrated an occurrence of perchlorate also at equatorial latitude: so its occurrence also at mid-latitude (i.e. Viking landing sites) comes out strengthened.

Actually, between 200 and 500°C , the soil of Rocknest released water and two peaks of CO_2 (i.e. two releases at two different temperatures). The origin of this water and Carbon dioxide is doubtful. Being released at more than 200°C , the water cannot be free, but bound to soil minerals as water of crystallization. In addition, a lab simulation shows that the two peaks of CO_2 could arise from the thermal decomposition of Mg and Fe carbonate [54].

Figure 32.
Thermal decomposition of perchlorates measured by the Author on a TGA (Thermal Gravimetric Analysis) instrument. Each perchlorate shows a specific temperature of decomposition with release of Oxygen.

But alternative hypotheses could have been given. The water and carbon dioxide seen by SAM could be breakdown products of organic substances under the action of perchlorates. This claim results from another discovery of GCMS on board SAM: the detection of simple chlorinated molecules, such as CH_3Cl and minor amount of CH_2Cl_2 and CHCl_3 [25]. At the end of February 2013 the SAM made a second series of analyses on a powdered sample of a sedimentary terrain named John Klein (**Figure 33**), located about 50 meters away from Rocknest, confirming results of first analysis, i.e. emission of CO_2 and H_2O , of O_2 over 250°C (probably generated by perchlorates dissociation), and release of $\text{CH}_3\text{Cl} + \text{CH}_3\text{Cl}_2$ [55].

Therefore, the SAM and Viking GCMS results look strikingly similar, in the sense that a sufficient amount of perchlorates could mask occurrence of organics.

Figure 33.
February 2013: results by SAM-Curiosity from a powdered material drilled into the John Klein sedimentary rock. On top the EGA evolved gases, on bottom some CGMS light chloro-derivatives.

After many months of stop due to a serious pollution problem (see later), the SAM team started again its analytical work, on a soil sample of the site of Cumberland that was taken an year before, on May 2013 not far from John Klein. The SAM results were crucial [56]: aside from the usual light Chloro-derivatives, many chlorinated aromatics were detected [57] suggesting that they could be derived from organic molecules present in the mudstone (from bacteria or from a meteoric extract): between them also an abundant release (about 250 ppb) of Chloro-benzene was detected (**Figure 34**), so reaching for an other resemblance to the Viking results, in which Chloro-benzene (as mentioned before) was found after a recent accurate re-examination of the original GCMS data [29].

One of the most extraordinary SAM discovery was made at Pahrump Hills (at the base of ~3.5-billion-year-old Murray mudstone), located at the lowermost portion of the Sharp Mons (Gale Crater central mound), about 6–7 km southwest of Yellowknife Bay. This ~3.5-billion-year-old Gale lake environment is expected to have been ideal settings for concentrating and preserving organic matter [58]. Two samples were drilled: Confidence Hills on sol 759 (24 Sep 2014), and Mojave on sol 882 (29 Jan 2015) (**Figure 35**). Confidence Hills soil was rich of hematite, Mojave soil was rich of jarosite, evidence of ancient passage of water. Because ultraviolet radiation and oxidizing compounds in the Martian soil would destroy any compounds exposed at the surface, Curiosity's scientists used a robotic drill to penetrate several centimetres into the mudstone.

To unlock organic molecules from the samples, the oven baked them to temperatures of between 600°C and 860°C and fed the resulting fumes to the Mass Spectrometer, which identified a welter of closely related organic signals reflecting dozens or hundreds of types of small carbon molecules, such as aromatic rings and short aliphatic chains [59]. Abundant sulfur-bearing carbon rings called thiophenes, were also detected and identified in the GC (**Figure 36**).

Figure 34.

December 2014: results by SAM-Curiosity from a powdered material drilled into the Cumberland sedimentary rock. Very important (bottom), between the GCMS evolved chloro-derivatives, the presence of chloro-benzene, a byproduct certainly of Martian origin.

Figure 35.
Confidence Hills and Mojave drill sites, at Pahrump Hills location, were SAM made the main discovery of possible keragenic material.

Figure 36.
SAM-EGA evolved gases from Mojave drilled material: sulfur-bearing carbon rings, short aliphatic chains and aromatic rings are typical decomposition products of keragenic material.

The mass patterns looked like those generated on Earth by kerogen (aromatic rings, short aliphatic chains, sulphur containing molecules), a goopy high molecular material that is formed when geologic forces compress, during million of years, the ancient remains of algae and similar critters. Kerogen is sometimes found with sulfur, which helps preserve it across billions of years; the Curiosity scientists think the sulfur compounds in their samples also explain the longevity of the Mars compounds. At the moment, it is impossible to say whether ancient life explains the Martian organics. The signal, being found at the base of a lake 3,5 billion years old, when Mars environment was warm and wet, could be a potential catchment for the presence on Mars of archea bacteria in primordial epoch, possibly still present today

where there are sources of liquid water over the surface (superficial melting of ices rich in salts) [60] or below the surface (sub-glacial lakes identified by radar techniques) [61]. However, we must not forget that Carbon-rich meteorites and comets contain kerogenic like compounds, and constantly rain down on Mars ...

It's disappointing that we can't figure out where the carbon-rich large molecules came from. But digging a little deeper could find better-preserved molecules in Mars rocks, to determine whether these molecules came from space, from igneous rocks, from hydrothermal activity, or – the most exciting possibility – ancient Mars life. Europe's ExoMars rover, due for launch in 2022, will drill deeper than Curiosity, to soil depths better protected from radiation. But probably, detection of past life may ultimately take the precision analysis of labs on Earth, bringing samples back. Fortunately, NASA Perseverance rover, that was successful in landing inside the Jezero crater on February 18, 2021 (**Figures 37 and 38**), is set to collect some 30 rock cores for return to Earth in subsequent missions.

SAM is able to give a further usefull help to determine the nature and origin of the kerogenic materials discovered on Mars, by the so called 'wet chemistry' experiments.

In summary, if organic molecules cannot enter the GCMS because a low volatility or breaking dawn under heating, they can be "derivatized" before they're heated – meaning that they react with some chemicals in order to become more volatile – so that they can be analyzed at a lower temperature. This derivatization process uses special chemical reagents dissolved in suitable solvents, so this experiment is called "wet chemistry". As yet mentioned, SAM only has nine Inconel steel cups containing these derivatizing agents: 7 containing a derivatization-silanizing

Figure 37.
The Jezero crater, an ancient lake where the rover Perseverance landed on February 18, 2021.

Figure 38.
February 21, 2021: Perseverance sees Jezero crater rim in 360° Mars panorama.

Derivatizers used by SAM

Figure 39.
 The two derivatizing reagents for ‘wet chemistry’ on board of SAM-Curiosity.

compound named MTBSTFA (N-tert-butyldimethylsilyl- N-methyltrifluoroacetamide), 2 containing a thermochemolysis compound named TMAH (tetramethylammonium hydroxide) (**Figure 39**).

MTBSTFA is an organic compound containing Fluorine and Silicon, able to instantly replace active hydrogens on OH and NH₂ (carboxylic acid, amine, amino-acid) with a N-tert-butyldimethylsilyl group (**Figure 40**): this non-polar moiety increases the volatility of the original compound by removing its polar nature, resulting in a much lower temperature needed for a GCMS analysis [62]. Due to the limited number of cups for ‘wet chemistry’, these kinds of experiments were obviously saved for only the most interesting rock samples. But an incredible accident caused the first wet chemistry trial to be postponed for six years. During the

Figure 40.
 The MTBSTFA chemical mechanism of derivatization, called silanization.

examination of the results the SAM obtained on Rocknest and on John Klein, the SAM team discovered that a vial of MTBSTFA was broken, so polluting all the analytical system.

The problem was that MTBSTFA, being itself an organic compound, reacts under heat with perchlorates, giving the same kind of light chloro-derivatives (CH_3Cl and CH_2Cl_2) found by the SAM on the Martian samples! From here a dreadful doubt that the origin of the ‘positive’ results obtained so far by the SAM could be ‘terrestrial’ and not Martian [25]. More than a year was needed to clean the system, during which a sample from Cumberland remained stored inside SAM, waiting the right moment to be analyzed. The sample remained 1280 sols (!) in contact with MTBSTFA vapors, a situation that also provided an opportunity [63]: baking the sample up to $\sim 900^\circ\text{C}$ to verify if some reaction between MTBSTFA and Martian soil had happened. This so called ‘opportunistic derivatization’ was a success, because the GC–MS detected interesting compound such as Chlorobenzene, Thiophene, light Chloro-derivatives and many other unknown compounds (Figure 41).

Lab tests demonstrated that Chloro-benzene, an organic compound containing 6 Carbon atoms, could not be formed from the heating of MTBSTFA in presence of perchlorates [64] but only when various types of Martian organic materials are pyrolyzed (i.e. heated at high temperature) in presence of Chlorine source.

The first ‘complete’ wet chemistry experiment was made on December 19, 2017. The target was a Ogunquit Beach (OB) sand sample from the Bagnold dune field, chosen being easy to manipulate after months of trouble due recurrent problems with the drill feed mechanism (Figure 42).

About 45 mg of the Ogunquit Beach sand were added to one of the MTBSTFA cups and the mixture was heated up to 900°C . Reactions clearly occurred and produced derivatized compounds. GCMS results showed the detection of derivatized benzoic acid as well as excess, unreacted MTBSTFA. However, no amino acids or fatty acids were detected [65].

During the following months engineers found a way to fix the drill problem. So the next step was to perform wet chemistry experiments on drilled clay deeper samples, as these phyllosilicate-rich minerals are known to preserve organic matter exceptionally well. A unusual Mn- and P-rich clay-bearing unit named Glen Torridon (GT) (Figure 43) was discovered in the foothills of Mount Sharp by CRISM spectrometer aboard the Mars Reconnaissance Orbiter (strong absorptions at 2.24 and 2.29 μm . EGA analyses in many locations inside Glen Torridon showed emission of free and strongly linked water and, surprisingly, absence of emission of

Figure 41.

The GCMS result of the so called ‘opportunistic derivatization’, performed on Cumberland material, that stayed in touch for months with MTBSTFA vapors accidentally leaked from a broken cup.

Figure 42.
Ogunquit Beach where SAM performed the first complete derivatization with MTBSTFA.

Figure 43.
The clay-bearing unit named Glen Torridon where SAM performed also the first derivatization with TMAH (called thermochemolysis).

O₂ from perchlorates [66]: a promising situation in order to search for organic compounds. SAM activities in Glen Torridon included an EGA/GCMS analysis, a new MTBSTFA derivatization experiment, followed by the first TMAH experiment. On Sept. 24, 2019 (sol 2536) the rover placed in the SAM the powdered drilled sample from GT- Glen Etive 2 site (**Figure 44**).

EGA/GCMS detected an abundance of S-bearing organic compounds, including aliphatic and aromatic compounds: dimethylsulfide, thiophene, and likely ethanethiol and dithiapentane. EGA also indicated results within the medium to high molecular weight ranges of masses, suggesting the presence of a complex mixture of compounds.

Figure 44.
The Glen-Etve-2 site (Glen Torridon clay unit) where SAM-EGA discovered high molecular weight carbon molecules, possibly resulting from the breakdown of keragenic material.

Figure 45.
SAM EGA + CGMS have revealed a range of organic fragments detected above 500°C, indicating the presence of recalcitrant organic matter (e.g. macromolecules). Compounds in blue were only detected via GCMS. Compound in yellow are from Glen Torridon.

The diversity of aromatics seems consistent with recalcitrant organic materials such as kerogenic-type macromolecules (remembering what was found at Cumberland and Mojeve five years before) (**Figure 45**).

MTBSTFA experiment showed the highest abundance of sulfur-bearing organics ever measured by the SAM instrument and a wide range of aromatic organic molecules including methylated polycyclic aromatic hydrocarbons (methyl-naphthalene), a potential methylated ester carboxylic acid (benzoic acid) and Benzothiophene, all detected for the first time on Mars. However, no amino acids or fatty acids have been identified [67].

Figure 46.
The TMAH chemical mechanism of derivatization, called thermochemolysis.

The possible discovery of high molecular molecules, was the long awaited reason for the first in situ TMAH wet chemistry experiment (**Figure 46**), the so called thermochemolysis, performed by heating a sample of Martian soil in contact with one of the two cups onboard of SAM, containing tetramethylammonium hydroxide (TMAH), dissolved in Methanol [68].

This strongly alkaline reagent causes hydrolysis and methylation of -OH, -O-, -NH, and -SH groups bonds and, upon heating, thermal bond breakage (of big molecules) also enuses. Volatile products of thermochemolysis were directly analyzed by the mass spectrometer (EGA) or trapped and analyzed with gas chromatography mass spectrometry (EGA-GCMS). This amazing experiment was successfully executed in September 2020 at the Mary Anning (MA) drill site (Figure 47) in the Glen Torridon region [69, 70].

‘Bands’ of masses grouped together and having mass-to-charge (m/z) 190 to 485, represent high molecular weight molecules detected by the SAM-MS. These

Figure 47.
The Mary Anning drill site (Glen Torridon clay unit) where the first TMAH derivatization was performed on September 2020.

Figure 48.

The preliminary astonishing results of the TMAH thermochemolysis on the Martian soil drilled at Mary Anning. Separation was performed using a gas-chromatographic column (GC2) able to separated molecules with more than 15 Carbon atom. The red continuous line shows the ramp of temperature (adapted from A. Williams, fall 2020 AGU meeting).

data may indicate that large, complex molecules were present. A variety of methylated, oxygen-, sulfur-, or nitrogen-bearing aromatic organics were detected in GCMS and/or EGA data. The presence of methylated single and double ring aromatics (included benzene, toluene, trimethyl- and tetramethyl-benzene, naphthalene, and methylnaphthalene) suggests that these organics might derive from a macromolecular source that was cleaved and methylated by TMAH thermochemolysis (**Figure 48**).

Examples of the organics detected in GCMS only include pentamethyl-benzene, benzoic acid methyl ester, dimethyl-, trimethyl-, and tetramethyl-benzenamine, dihydronaphthalene, 2-butyl-thio-phen, and benzothiophene. Pentamethylbenzene may be part of a multi-methylated benzene suite. The benzoic acid methyl ester reflects the reaction of TMAH methylating benzoic acid of indeterminate source. The multi-methylated benzenamine suite is also of indeterminate source. A non biological source of these organics on the surface of Mars could be the impact of meteoritic material. Several similar organics were indeed identified applying the TMAH thermochemolysis benchtop experiment to the Murchison meteorite, including toluene, trimethylbenzene, methylnaphthalene, 2-butyl-thiophene, and benzothiophene. Amines and amides are not prevalent in pyrolyzed Murchison material and benzenamines are also not generated during TMAH thermochemolysis of Murchison, so the origin of these amines remains at least problematic.

5. Conclusions

The discovery of organic molecules on Mars is a necessary but not sufficient condition for the demonstration of some present or past form of martian bacterial life. Comets and the carbonaceous chondrites are indeed copious sources of organic material. But the positive results of the 'famous' Viking LR experiment are intriguing, even because it is important taking in account that Viking LR was performed at low temperature, a condition where possible perchlorates do not show any oxidant effects.

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